Automated Sampling of RSK-175 Samples

Anne Jurek

Abstract:

Tapping the natural gas reservoirs throughout the United States has long been a viable solution for energy independence; however until recently getting to these gas reservoirs was very difficult. Now, through the development of horizontal drilling in conjunction with hydraulic fracturing or “fracking”, these reservoirs have become much easier to tap for natural gas. The process of fracking involves drilling thousands of feet below the earth’s surface and injecting the ground with millions of gallons of water, sand, and chemicals. After the well is completed, the fracturing fluid or “flow back water” is captured in steel tanks or lined pits. There are some environmental concerns with the fracking process that have come to light as fracking has gained popularity. One major concern is the potential for natural gas to migrate into drinking water sources.

In order to test for dissolved gases, the RSK-175 standard operating procedure (SOP) was developed. This SOP involves some manual preparation of the water samples before the water can be analyzed. Since manual preparation is very time consuming, there has been increased interest in automated sample preparation for this analysis. This study will evaluate an automated sample preparation technique of dissolved gas in water utilizing saturated gas calibration samples. The automation involves creating headspace in the sample vial while maintaining sample integrity and transferring the headspace to a GC/FID for analysis.

Discussion:

As the analysis of dissolved gases became more prevalent in the environmental testing field, and knowing how time consuming sample preparation is, EST saw the need to automate this sample preparation. Thus, the LGX50 was designed. The automation of this analysis (patent pending) involves using two sample trays, one tray to hold empty 40ml vials with a stir bar and one tray to hold the dissolved gas samples. The LGX50 evacuates the empty vial. Next, sample is transferred from the full vial to the empty vial thus creating a headspace that retains the sample integrity by not exposing the sample or the sample pathway to the atmosphere. The system then heats and stirs the sample for a prescribed time. Finally, the sample is pressurized so as to fill a sample loop and transfer the sample to the GC/FID for analysis. See Figure 1. This application note will describe sample preparation and display experimental results showing the reliability and accuracy of the LGX50.

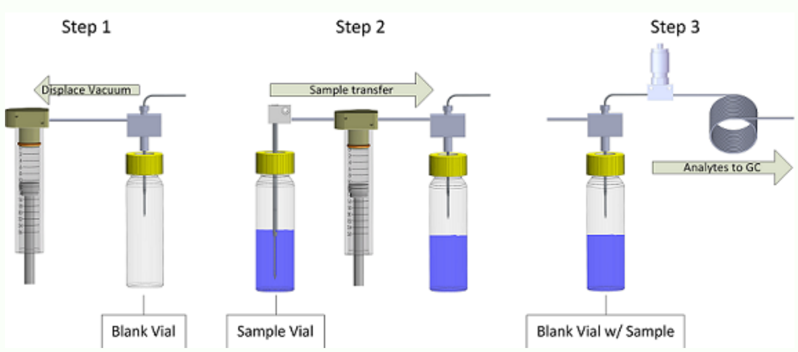

Figure 1: LGX50 Automation Graphic

Experimental:

The LGX50 Autosampler was configured with a two milliliter loop and interfaced with a GC/FID. The GC column used for this analysis was a Restek RT Q-bond 30m x 0.53mm x 20µm. The LGX50 Autosampler settings and the GC/FID experimental parameters are listed in Tables 1 and 2 respectively.

LGX50 Autosampler Parameters	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	65°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

Table 1: LGX50 Autosampler Settings

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 Parameters

Gases were ordered from our local gas suppliers. All of the gases were high purity with the exception of propane which was a standard tank used for gas grills. Water was purged with the designated gas for at least one hour in order to saturate the water with the gas. The water was held at room temperature for the propane, however for the methane, ethane and ethylene gases, the water was kept in an ice water bath. The saturated gas concentrations were determined using the values found in References 1 and 2. Using the serial dilutions listed in Tables 3 through 6; the saturated gas curves were made.

Saturated Methane Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	50ml	19.80ppm
Saturated Solution	25ml	9.90ppm
Saturated Solution	5ml	1.98ppm
Saturated Solution	1ml	400ppb
Saturated Solution	500ul	200ppb
Saturated Solution	100ul	40ppb
Saturated Solution	50ul	20ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 3: Methane Dissolved Gas Standard Preparation

Saturated Propane Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	50ml	38.36ppm
Saturated Solution	25ml	19.18ppm
Saturated Solution	5ml	3.96ppm
Saturated Solution	1ml	780ppb
Saturated Solution	500ul	396ppb
Saturated Solution	100ul	79.2ppb
Saturated Solution	20ul	15.8ppb
Saturated Solution	10ul	8ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 4: Propane Dissolved Gas Standard Preparation

Saturated Ethane Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	25ml	32.92ppm
Saturated Solution	10ml	13.08ppm
Saturated Solution	5ml	6.54ppm
Saturated Solution	1ml	1.32ppm
Saturated Solution	500ul	660ppb
Saturated Solution	100ul	132ppb
Saturated Solution	20ul	26.4ppb
Saturated Solution	5ul	6.6ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 5: Ethane Dissolved Gas Standard Preparation

Saturated Ethylene Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	25ml	70ppm
Saturated Solution	10ml	28ppm
Saturated Solution	5ml	14ppm
Saturated Solution	1ml	2.8ppm
Saturated Solution	200ul	560ppb
Saturated Solution	50ul	140ppb
Saturated Solution	10ul	28ppb
Saturated Solution	2ul	5.6ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 6: Ethylene Dissolved Gas Standard Preparation

Deuterated methyl tert-butyl ether (MtBE-d3) was chosen as the Internal Standard (IS) and added to the IS vessel on the LGX50. The saturated gas standards were poured into 40ml vials with no headspace and loaded on the second tray of the LGX50 while a series of empty vials with stir bars were placed in the first tray. After the vials and IS were loaded, a sample sequence was set up and the LGX50 did all the work. The results of the calibration curves, IS precision, and carryover are listed in Tables 7 through 9. Figures 2 through 5 display a sample chromatogram of each of the gases tested.

Compound	Curve Range	Curve %RSD	Curve R^2	Average RF
Methane	20ppb to 19.8ppm	13.27	0.999	0.588
Propane	8ppb to 38.4ppm	12.50	1.000	0.469
Ethane	6.6ppb to 32.9ppm	8.95	1.000	0.415
Ethylene	5.6ppb to 70ppm	8.23	0.999	0.451

Table 7: Saturated Gas Curves Results

Compound	IS Reproducibility through Curve Range (%RSD)
Methane	6.0
Propane	2.6
Ethane	4.4
Ethylene	4.1

Table 8: Internal Standard Precision

Compound	High Level Standard Level	%Carryover
Methane	19.8ppm	0.08
Propane	38.4ppm	0.07
Ethane	32.9ppm	0.07
Ethene	70.0ppm	0.06

Table 9: Percent Carryover after High Gas Standard

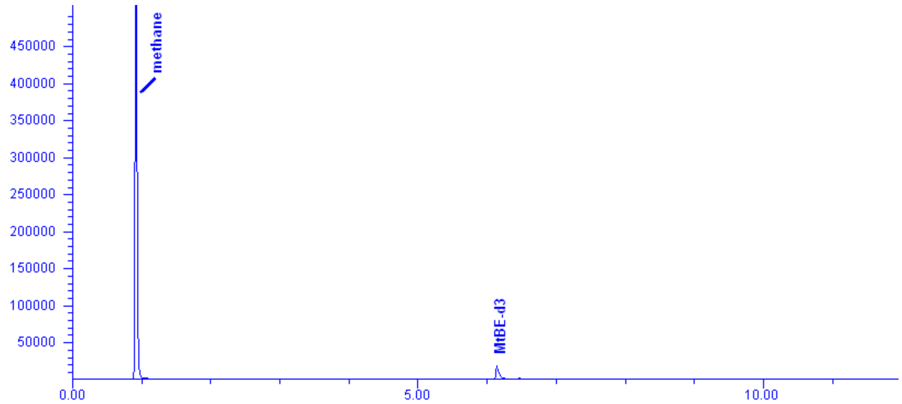

Figure 2: 9.9ppm Methane Standard Chromatogram

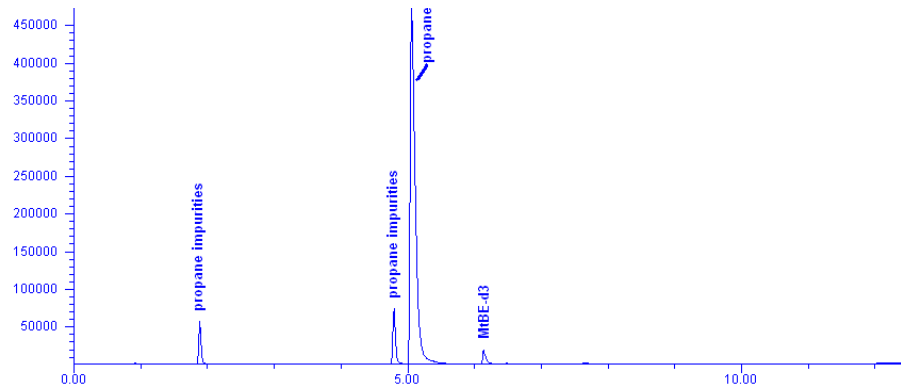

Figure 3: 19.2ppm Propane Standard Chromatogram

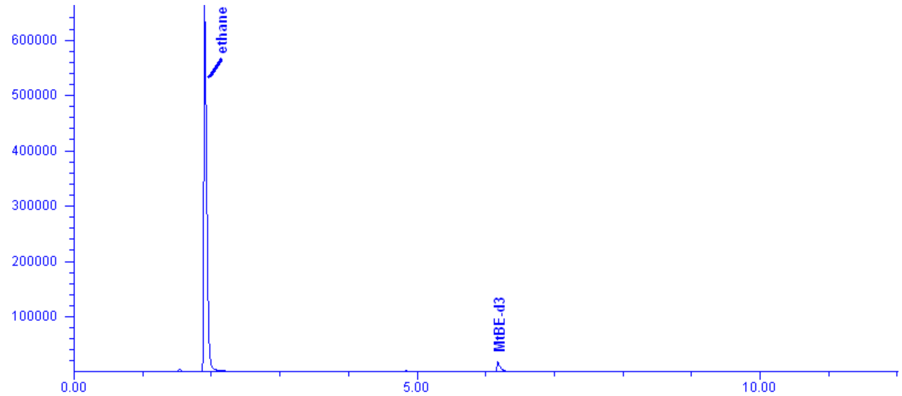

Figure 4: 13.1ppm Ethane Standard Chromatogram

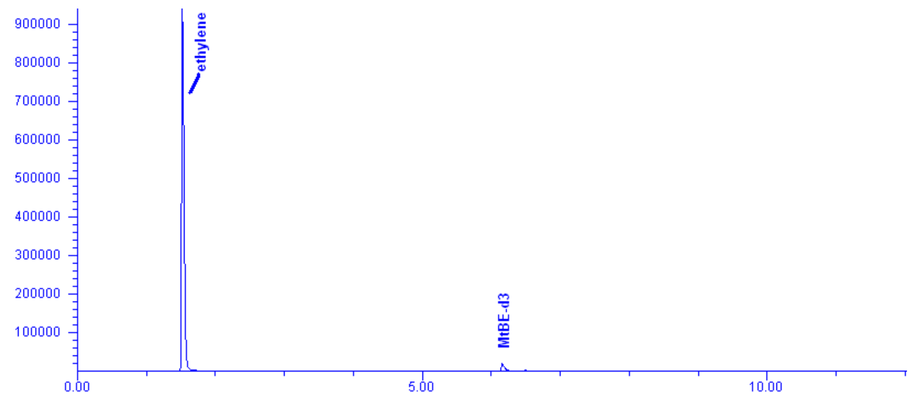

Figure 5: 14.0ppm Ethylene Standard Chromatogram

Conclusion:

The new LGX50 is both reliable and accurate for performing dissolved gas analysis. The percent carryover was very low and the linearity for each of the saturated gases tested was excellent. The IS reproducibility was outstanding throughout each of the gas curves. However, the best part is that the LGX50 is able to take the place of a person for the sample preparation of dissolved gas analysis. Since sample preparation is extremely labor intensive, this system would save both time and money for any lab performing this analysis.

For more information visit estanalytical.com or click below:

http://www.estanalytical.com/Products/Environmental/LGX50_for_RSK_Analysis

References:

1. *Solubility of Gases in Water*. Retrieved November 15, 2011, from http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html
2. *Gas Encyclopaedia*. (2009). Retrieved November 15, 2011 from http://encyclopedia.airliquide.com/Encyclopedia.asp
3. ConocoPhillips Company, *Drilling and Completion,* Retrieved January 20, 2012, from http://www.powerincooperation.com/en/pages/drilling-and-completion.html
4. Hudson, Felisa, *RSKSOP-175*, Revision No. 2, May 2004.
5. EPA New England, *Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene.* Revision 1, July, 2001.