Automated Determination of Dissolved Gases in Water

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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. However, 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. Since RSK-175 is an SOP and not an EPA or ASTM method; laboratories have employed different approaches in order to calibrate for the dissolved gases. This study will evaluate a standard calibration using serial dilutions of saturated gas samples. The LGX50 autosampler will do the rest of the work by creating headspace in the sample vial while maintaining sample integrity and transferring the headspace to a GC/FID for analysis. This automation provides the capability to treat calibration samples in the same manner as field samples thus reporting field sample results requires no back calculation using the Henry's Constant.

Discussion:

The LGX50 was designed to automate the time consuming process of sample preparation for dissolved gas analysis. 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, a prescribed amount of 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 set 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 calibration sample preparation and display experimental results showing the reliability and accuracy of the LGX50.

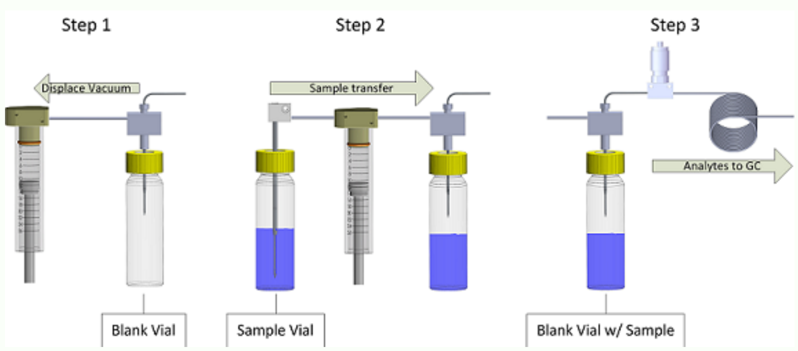

Figure 1: LGX50 Automation Graphic

Experimental:

The LGX50 Autosampler was configured with a one 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 Parameter	Setting
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	5µl

Table 1: LGX50 Autosampler Settings

GC/FID	Agilent 5890
Inlet Temperature	250°C
Inlet Pressure	9psi
Gas	Helium
Inlet	Split/Splitless
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

High purity gases were ordered from local gas suppliers. Water was purged with the designated gas for at least one hour in order to saturate the water with the gas. The water was kept in an ice water bath and allowed to cool down to 10°C before being purged with the methane, ethane or ethylene gases. The temperature of the water was monitored throughout the purging cycle in order to ensure a constant 10°C temperature. The saturated gas concentrations were determined using the values found in References 1 and 2. Next, using the serial dilutions listed in Tables 3 through 5; the saturated gas curves were made.

Saturated Methane Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	50ml	16.0ppm
Saturated Solution	25ml	8.0ppm
Saturated Solution	5ml	1.6ppm
Saturated Solution	1ml	320.0ppb
Saturated Solution	500ul	160.0ppb
Saturated Solution	100ul	32.0ppb
Saturated Solution	50ul	16.0ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 3: Methane Dissolved Gas Standard Preparation

Saturated Ethane Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	25ml	27.5ppm
Saturated Solution	10ml	11.0ppm
Saturated Solution	5ml	5.5ppm
Saturated Solution	1ml	1.1ppm
Saturated Solution	500ul	550.0ppb
Saturated Solution	100ul	110.0ppb
Saturated Solution	20ul	22.0ppb
Saturated Solution	5ul	5.5ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 4: Ethane Dissolved Gas Standard Preparation

Saturated Ethylene Gas Solution Curve Preparation		
Standard	**Amount**	**Final Concentration**
Saturated Solution	25ml	52.5ppm
Saturated Solution	10ml	21.0ppm
Saturated Solution	5ml	10.5ppm
Saturated Solution	1ml	2.1ppm
Saturated Solution	200ul	420.0ppb
Saturated Solution	50ul	105.0ppb
Saturated Solution	10ul	21.0ppb
Saturated Solution	2ul	4.2ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 5: 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. All of the experimental results are listed in Tables 6 through 8. Figures 2 through 4 display a sample chromatogram of each of the gases tested.

Individual Gas Results							
Compound	Curve Range	Curve R^2	MDL Spike Level (ppb)	MDL (ppb)	Precision Spike Level (ppm)	Accuracy (% Recovery)	Precision (%RSD)
Methane	16ppb to 16ppm	0.999	16.0	6.20	1.6	98.8	5.9
Ethane	5.5ppb to 27.5ppm	0.999	5.5	2.46	5.5	96.7	6.9
Ethylene	4.2ppb to 52.5ppm	1.000	4.2	3.17	10.5	104.9	6.0

Table 6: Saturated Gas Curves Results

Compound	IS Reproducibility (%RSD)
Methane	2.4
Ethane	4.4
Ethylene	5.9

Table 7: Internal Standard Precision

Compound	High Level Standard Level	%Carryover
Methane	16.0ppm	0.09
Ethane	27.5ppm	0.05
Ethylene	52.5ppm	0.04

Table 8: Percent Carryover after High Gas Standard

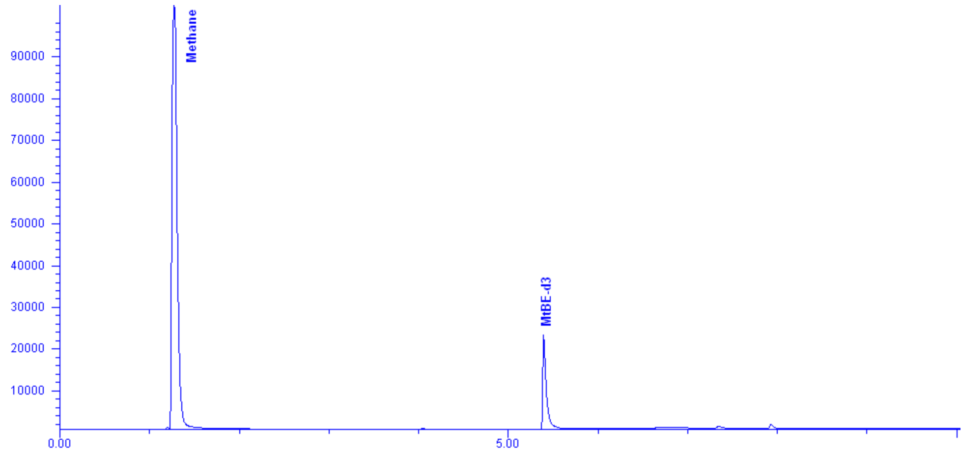

Figure 2: 1.6ppm Methane Standard Chromatogram

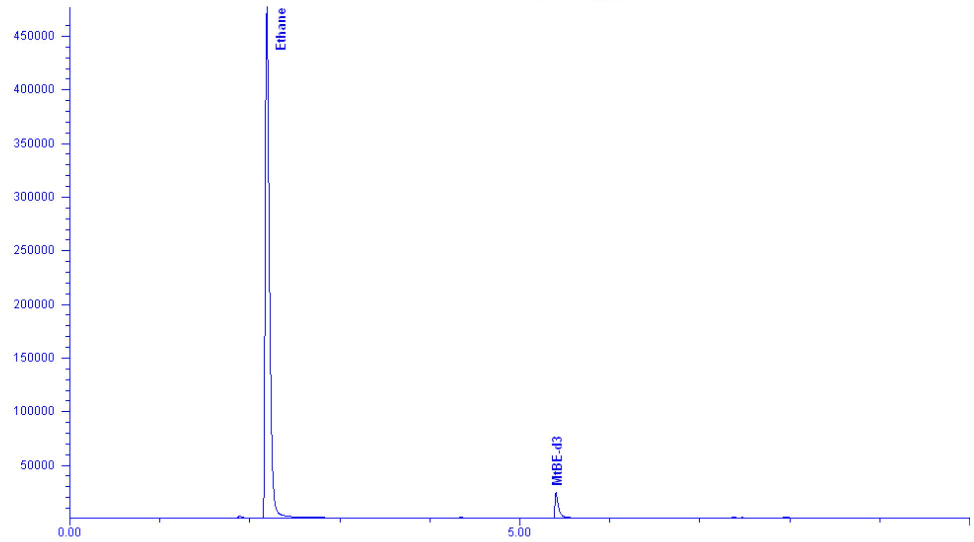

Figure 3: 5.5ppm Ethane Standard Chromatogram

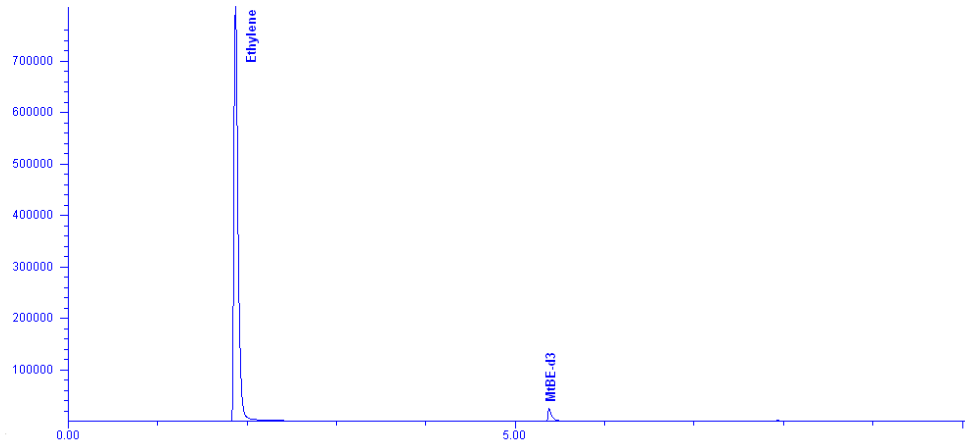

Figure 4: 10.5ppm Ethylene Standard Chromatogram

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 compound precision and accuracy and the IS precision also proved to be very good throughout the study. However, the best part is that the LGX50 is able to automate much of the sample preparation time involved for 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:

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