

Automated Determination of Dissolved Gases in Water By Headspace Calibration of Mixed Gases

Anne Jurek

Abstract:

Due to the expansion of natural gas drilling through horizontal fracturing, there has been increased interest in the RSK-175 Standard Operating Procedure (SOP) for the determination of dissolved gases in water. Since RSK-175 is an SOP and not a formal EPA method; laboratories have employed different approaches in order to calibrate for the dissolved gases. This paper will discuss calibration by using static headspace sampling of vials spiked with different volumes of mixed gases. Furthermore, the precision and accuracy of the calibration will be established by headspace screening of mixed gas standards and also by examining known concentrations of dissolved gases and back calculating experimental results using the Henry's Constant and the saturated gas calculation.

Discussion:

The LGX50 was designed to accommodate both automated sample displacement and headspace sampling of dissolved gas samples and headspace screening of water samples. Therefore, the system can provide automation of different calibration techniques. For mixed gas calibration, a sample vial is spiked with a volume of mixed gas and placed in the sample tray of the LGX50. The sample is then moved from the tray into a sampling station where it can be heated and stirred and IS can be added (optional). Next, after a prescribed amount of time, an aliquot of the headspace of the sample vial can be taken and transferred over to the GC/FID for analysis. See Figure 1. However, it needs to be noted that for this type of calibration the dissolved gas sample results need to be converted using the Henry's Constant and the saturated gas calculation as the sample matrix and the calibration matrix are different.

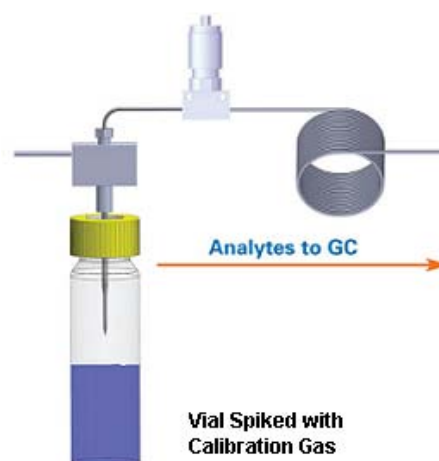


Figure 1: Headspace Sweep Graphic

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 20 μ m. The LGX50 Autosampler settings and the GC/FID experimental parameters are listed in Tables 1 and 2 respectively.

LGX50 Autosampler Parameter	Setting
Sample Type	Screen
Sample Fill Mode	Loop
Sample Volume	10ml
Syringe Prime	3 sec.
Syringe Needle Rinse	5ml
Rinse Cycles	Off
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 Screen 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

A high purity gas mix was ordered from a local gas supplier. The gas mix was dispensed into a Tedlar bag for ease of use. Ten milliliters of water was poured into a 40mL vial. The vial was capped tightly and spiked with the gas mix in order to prepare the calibration curve. See Table 3.

Gas Mixture Curve Preparation in 40ml VOA with 20ml Water		
Standard	Amount	Final Concentration
1% Gas Mix	1000µl	1000ppm
1% Gas Mix	500µl	500ppm
1% Gas Mix	200µl	200ppm
1% Gas Mix	100µl	100ppm
1% Gas Mix	50µl	50ppm
1% Gas Mix	20µl	20ppm
1% Gas Mix	10µl	10ppm

Table 3: 1% Gas Mix 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 mixed gas standards were loaded in the sample tray of the LGX50. Ten milliliters of DI water was then transferred to the sample vial along with the IS in order to make a total water volume of 20mls. After a curve was established a series of seven replicate 10ppm mixed gas standards were run in order to establish method detection limits for the method. Next, a series seven of 500ppm standards were run in order to determine the precision and accuracy of the method. The mixed gas experimental results are listed in Table 4. Figure 2 displays a sample chromatogram of a 500ppm mixed gas standard.

Gas Mixture Results							
Compound	Curve Range	Curve R ²	MDL Spike Level (ppm)	MDL (ppm)	Precision Spike Level (ppm)	Accuracy (% Recovery)	Precision (%RSD)
Methane	10ppm to 1000ppm	0.998	10.00	5.18	500	96.29	8.93
Ethane	10ppm to 1000ppm	0.998	10.00	2.47	500	95.65	8.08
Ethylene	10ppm to 1000ppm	0.998	10.00	2.37	500	94.68	8.39

Table 4: Saturated Gas Curves Results

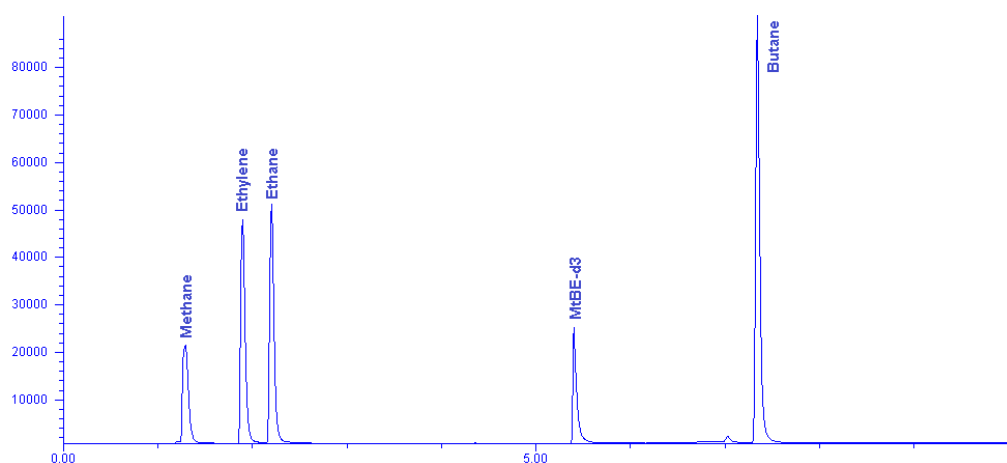


Figure 2: 500ppm Mixed Gas Standard Chromatogram

After the mixed gas calibration was established, seven replicate dissolved gas samples were prepared for each of the gases calibrated. The dissolved gas samples were placed on the LGX50 and run using the dissolved gas parameters listed in Table 5. Please refer to application note “Automated Determination of Dissolved Gases in Water” at www.estanalytical.com for an explanation on dissolved gas sample preparation and LGX50 automated sampling.

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 5: LGX50 Dissolved Gas Autosampler Settings

The experimental results were back calculated using the Henry's Constant and the saturated gas calculation in order to account for the matrix differences. The saturated gas calculation¹ is:

$$TC = C_{AH} + C_A$$

Where: TC = Total Gas Concentration

C_{AH} = Aqueous Gas in Headspace after Equilibration

C_A = Aqueous Gas in Water after Equilibration

$$C_A = (55.5 \text{ mol/L}) * ((\text{Experimental Results} / \text{Henry's Constant}) * \text{MW}) * 10^3 \text{ mg/g} = \text{Conc. gas in mg/L Water}$$

Where: MW = Molecular Weight of the gas

55.5 mol/L is the molar concentration of water

$$C_{AH} = (\text{HS vol.} / (\text{total vol.} - \text{HS vol.})) * \text{Experimental Results} * (\text{MW} / 22.4 \text{ L/mol}) * ((273 \text{K} / (\text{Sample Temp.} + 273 \text{K})) * 10^3 \text{ mg/g}) = \text{Conc. Gas in mg/L Water}$$

Where: MW = Molecular Weight of the gas

22.4 L/mol is the vol. of 1 mol gas at Standard Temperature and Pressure

(Note: multiply TC by 1000 to get the final answer in µg/L)

Using the sample temperature and the slope of the lines below, the Henry's Constant of Methane, Ethane and Ethylene can be determined².

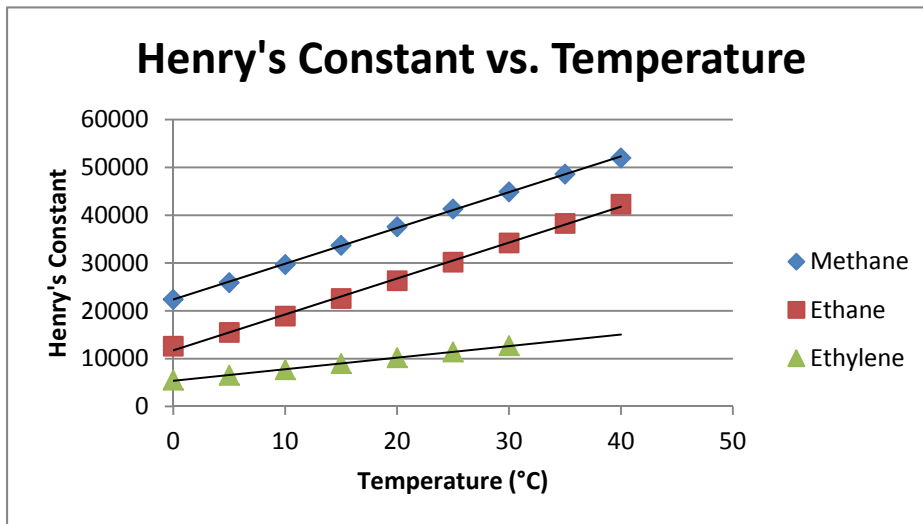


Figure 3: Henry's Constant versus Temperature

The Henry's Constant for the gases was determined to be:

$$\text{Methane} = 748.33(\text{Temp.}) + 22738$$

$$\text{Ethane} = 751.33(\text{Temp.}) + 11740$$

$$\text{Ethylene} = 241.43(\text{Temp.}) + 5375.7$$

Finally, using the gas calibration results for the saturated gas samples, the Henry's Constant and the saturated gas calculation established above, the amount of dissolved gas in the samples could be established. The calculated amount of gas was then compared to the known amount of dissolved gas in the sample. The results are listed in Table 6 below.

Compound	Standard Level	Accuracy % Recovery
Methane	1.6ppm	108
Ethane	5.5ppm	98
Ethylene	10.5ppm	114

Table 6: Calculated Dissolved Gas Results

Conclusion:

The new LGX50 is both reliable and accurate for performing dissolved gas analysis. The system is able to calibrate a mixture of gases by headspace screening and produce linear results. This calibration can then be used in conjunction with the saturated gas calculation to analyze dissolved gas samples thus enabling laboratories to have an easy way to calibrate the system with accurate results for the dissolved gas samples. However, the best part is that the LGX50 is able to drastically reduce labor costs 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.
6. *Light Hydrocarbons in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID)*, PADEP 3686, Rev. 0, April 2012.

Headquarters

JSB International
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 251 47 53
F +31 (0) 40 251 47 58

Zoex Europe
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 257 39 72
F +31 (0) 40 251 47 58

Sales and Service

Netherlands
Apolloweg 2B
8239 DA Lelystad
T +31 (0) 320 87 00 18
F +31 (0) 320 87 00 19

Belgium
Grensstraat 7
Box 3 1831 Diegem
T +32 (0) 2 721 92 11
F +32 (0) 2 720 76 22

Germany
Max-Planck-Strasse 4
D-47475 Kamp-Lintfort
T +49 (0) 28 42 9280 799
F +49 (0) 28 42 9732 638

UK & Ireland
Cedar Court,
Grove Park Business Est.
White Waltham, Maidenhead
Berks, SL6 3LW
T +44 (0) 16 288 220 48
F +44 (0) 70 394 006 78

info@go-jsb.com
www.go-jsb.com

With courtesy of

