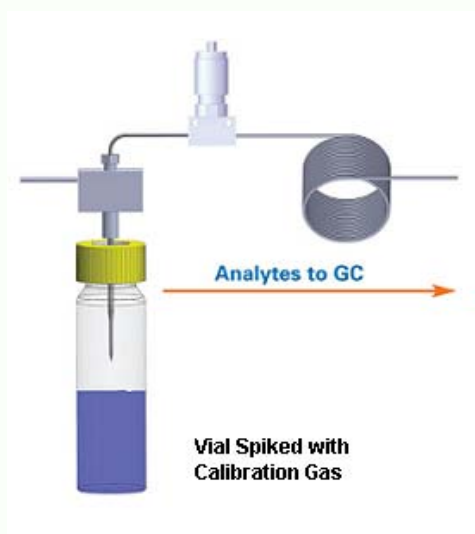


**Abstract:**

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 $\mu$ 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.

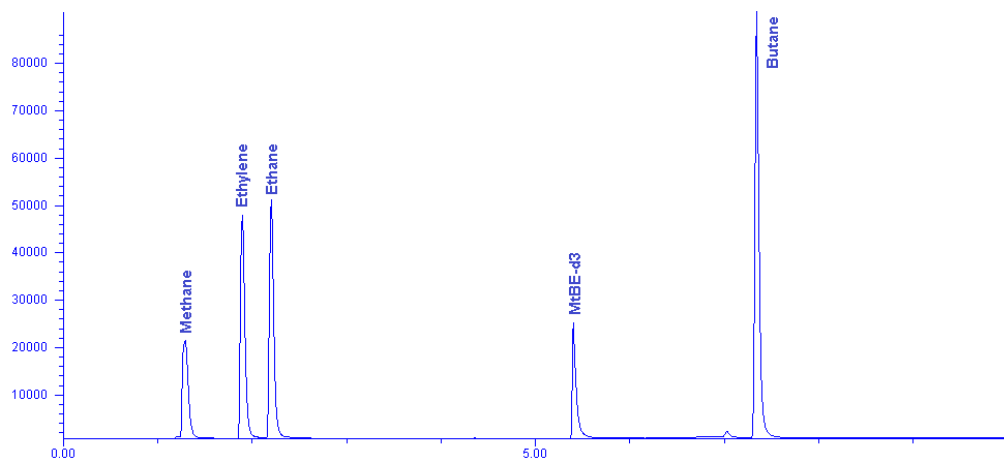
Gas Mixture Curve Preparation in 40ml VOA with 20ml Water		
Standard	Amount	Final Concentration
1% Gas Mix	1000µl	1000ppm
1% Gas Mix	500µl	500ppm
1% Gas Mix	200µl	200ppm
1% Gas Mix	100µl	100ppm
1% Gas Mix	50µl	50ppm
1% Gas Mix	20µl	20ppm
1% Gas Mix	10µl	10ppm

**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 <sup>2</sup>	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](http://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 calculation<sup>1</sup> 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

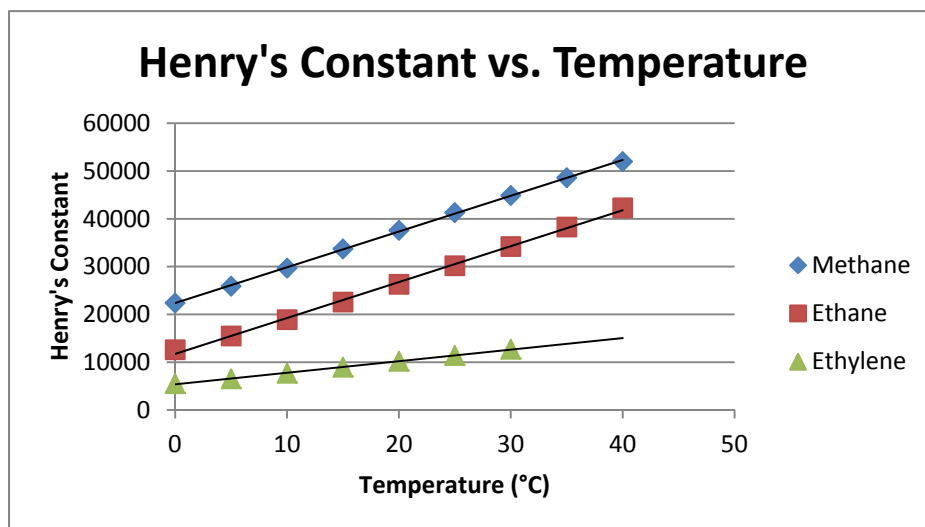
$$C_{AH} = (\text{HS vol.} / (\text{total vol.} - \text{HS vol.})) * \text{Experimental Results} * (\text{MW} / 22.4 \text{ L/mol}) * ((273\text{K} / (\text{Sample Temp.} + 273\text{K})) * 10^3 \text{ mg/g}) = \text{Conc. Gas in mg/L Water}$$

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 determined<sup>2</sup>.



**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](http://estanalytical.com) or click below:

[http://www.estanalytical.com/Products/Environmental/LGX50\\_for\\_RSK\\_Analysis](http://www.estanalytical.com/Products/Environmental/LGX50_for_RSK_Analysis)

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