

## 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. The automation involves creating headspace in the sample vial while maintaining sample integrity and transferring the headspace to a GC-FID for analysis.

## DISCUSSION

Dissolved gas calibration can be done in assorted ways, all of which have their own positives and negatives. One method is to direct inject a known concentration of gas mix at different volumes and/or dilutions directly onto the GC column using the GC inlet. The advantage of this technique is its simplicity. There is no calibration sample preparation involved. A gas standard and several gas tight syringes are all that is required. The disadvantage is the time involved to run a curve. Since the curve is injected manually, the analyst needs to be present in order to run the calibration curve. Furthermore, as the calibration is done using a gas mix and not a saturated solution, any samples that are run would be in a different matrix than the calibration. Thus, the analyst would need to convert the results to the saturated gas concentration. This calculation is done using the Henry’s Constant which will be discussed later.

A second method would be to spike a gas mix at different volumes and/or dilutions into the headspace of a sample vial filled with a specified volume of water. Next, using a static headspace auto-sampler, the calibration curve can be injected onto the GC column for analysis and calibration. The advantage of this method is the calibration curve preparation can be done prior to analysis. The prepared curve can then be loaded onto the auto-sampler and the auto-sampler can do the work of injecting the curve. The disadvantage of this technique is the same as the direct inject calibration technique. Since the matrix of the curve and the matrix of the samples are different, the results need to be converted.

The third and final method for calibrating dissolved gases involves saturating water with the gas to be calibrated and performing a serial dilution of the saturated water. A headspace auto-sampler can then be used to inject the sample headspace onto the GC column for analysis. The benefit of this technique is that the calibration curve



matrix and the sample matrix are the same. Since both matrices are the same, there is no need to convert the sample results using the Henry’s constant. The disadvantage of this technique is the curve preparation, as every gas needs to be calibrated separately. The sample results would then be analyzed for each gas using the corresponding gas curve.

The RSK-175 standard operating procedure for dissolved gas samples involves displacing 10% of the sample volume with high purity helium, shaking the sample for 5 minutes and injecting the headspace of the sample onto the GC column for separation with detection performed by a Thermal Conductivity Detector (TCD) or Flame Ionization Detector (FID). The concentration of the dissolved gas in the sample is then determined using the following **Saturated Gas Calculation**:

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

TC = Total Gas Concentration  
 $C_{wH}$  = Aqueous Gas in Headspace after Equilibration  
 $C_A$  = Aqueous Gas in Water after Equilibration

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

MW = Molecular Weight of the gas  
 55.5 mol/L is the molar concentration of water

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

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  $\mu\text{g/L}$ .)

Using the sample temperature and the slope of the lines below, the Henry’s Constant of Methane, Ethane and Ethylene can be determined (Figure 1).

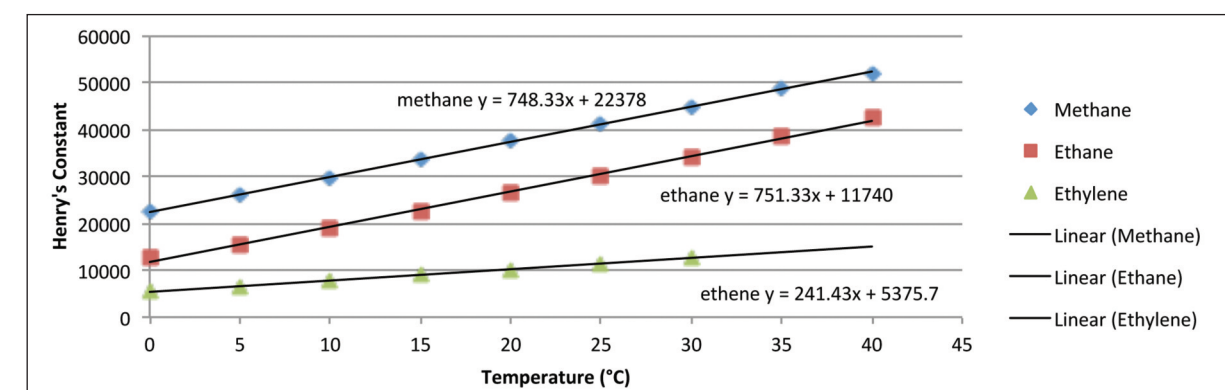


Figure 1. Henry’s Constant vs. Temperature

## LGX50 SAMPLING SYSTEM

The LGX50 sampling system was designed to accommodate individual laboratory preferences for dissolved gas calibration while adapting closely to the RSK-175 standard operating procedure for dissolved gas samples. For a gas mix calibration, a sample vial is spiked with a mixed gas and placed in the LGX50 sample tray. The LGX50 will take an aliquot of the headspace of a vial spiked with mixed gas standard and transfer the analytes to the GC (Figure 2). Therefore, the system enables automatic calibration of a mixed gas standard. However, for this type of calibration, the sample results need to be converted using the Henry’s Constant and the equations established previously.

For saturated gas calibration standards and dissolved gas samples, the LGX50 can displace a pre-programmed volume of saturated gas standard, heat and mix the standard and then take an aliquot of the headspace and transfer it to the GC/FID for separation and analysis. See Steps 1, 2 and 3 for descriptions.

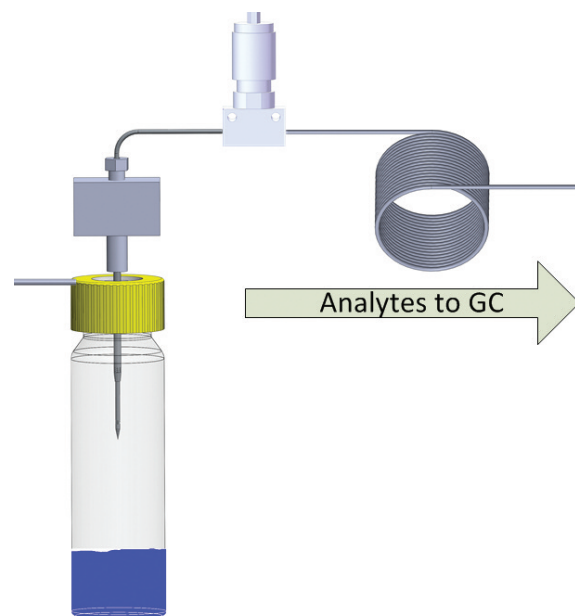
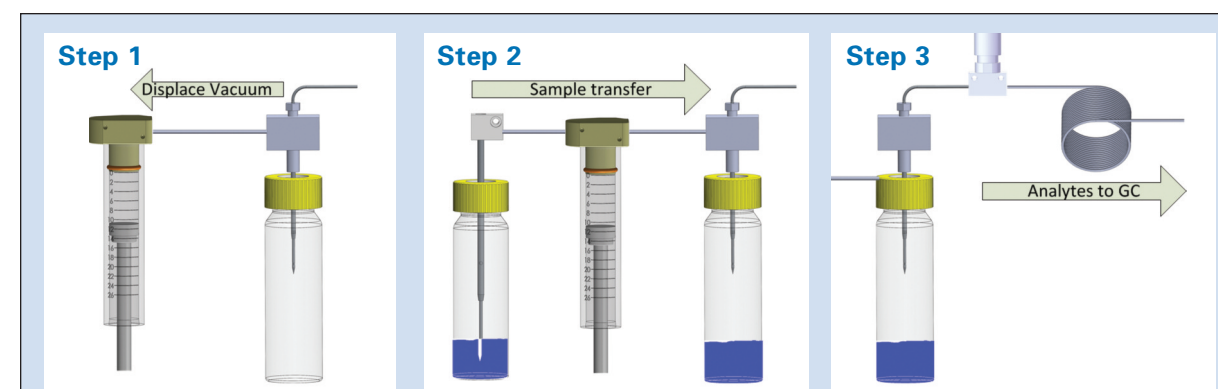


Figure 2. LGX50 Headspace Sweep of Gas Standard



**Step 1**  
Empty vials are placed in one tray while samples from the field or dissolved gas standards are placed into full vials and placed in the second tray. The system transports the empty vial, which may contain a stir bar, to the heated sampling station and it is moved onto the sample needle. The vial is swept with helium to remove any air and CO<sub>2</sub>. A vacuum is pulled by displacing the helium in the vial equal to the volume of the sample to be added.

**Step 2**  
The arm moves over to the full sample vial and the syringe removes the programmed amount of sample. Internal standard is added by injecting either a gas or a liquid into the sample as it is transported to the vial on the sampling station.

**Step 3**  
The sample may be heated and stirred for a specific period of time. Once completed, a sample loop is filled with a portion of the headspace and sent to the GC for analysis.

## 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 $\mu\text{m}$ . The LGX50 Autosampler settings and the GC/FID experimental parameters are listed in Tables 1 and 2 respectively.

Table 1. LGX50 Autosampler Settings

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

Table 2. GC/FID Parameters

GC/FID Parameters	Settings
Inlet Temperature	200°C
Inlet Pressure	8psi
Gas	Helium
Inlet	Split/Splitless
Column Flow	12ml/min
Column	Restek RT Q-bond 30m x 0.53mm x 20 $\mu\text{m}$
Oven Program	40°C hold for 2 minutes, ramp 15°C/min to 220°C hold for 1 min, 15 min total runtime
FID Temperature	250°C

For the mixed gas headspace screening calibration, 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 series of 40mL vials. The vials were capped tightly and spiked with different amounts of the gas mix in order to prepare the calibration curve.

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 3. Figure 3 displays a sample chromatogram of a 500ppm mixed gas standard.

Table 3. Mixed Gas Curve Results

Compound	Curve Range	Curve R <sup>2</sup>	Gas Mixture Results				
			MDL Spike Level (ppb)	MDL (ppm)	Precision Spike Level (ppm)	Accuracy (% Rcvry)	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

For the saturated gas calibration, high purity gases were ordered from our 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 held and monitored at a constant temperature in an ice water bath and purged with the designated gas for one hour. The saturated gas concentrations were determined using the values found in Reference 1. Using the serial dilutions the saturated gas curves were made.

The saturated gas calibration also used Deuterated methyl tert-butyl ether (MtBE-d3) as the Internal Standard (IS). For this calibration, the 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 were loaded, a sample sequence was set up and the LGX50 did all the work. Once a calibration curve was established, a series of seven low level standards were run in order to establish MDLs and a series of seven mid-level standards were run so as to ascertain the precision and accuracy of the system. The results of the calibration curves, the MDLs, the compound precision and accuracy, the IS precision, and the carryover are listed in Tables 4 through 5. Figure 4 displays a standard chromatogram overlay of the gases tested.

Table 4. Saturated Gas Curves Results

Compound	Curve Range	Curve R <sup>2</sup>	Individual Gas Results				
			MDL Spike Level (ppb)	MDL (ppb)	Precision Spike Level (ppm)	Accuracy (% Rcvry)	Accuracy (%RSD)
Methane	16ppb to 16ppm	0.998	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 5. Percent Carryover after High Gas Standard and Internal Standard Precision

Compound	High Level Standard Level	% Carryover	IS Reproducibility (%RSD)
Methane	16.0ppm	0.09	2.4
Ethane	27.5ppm	0.05	4.4
Ethene	52.5ppm	0.04	5.9

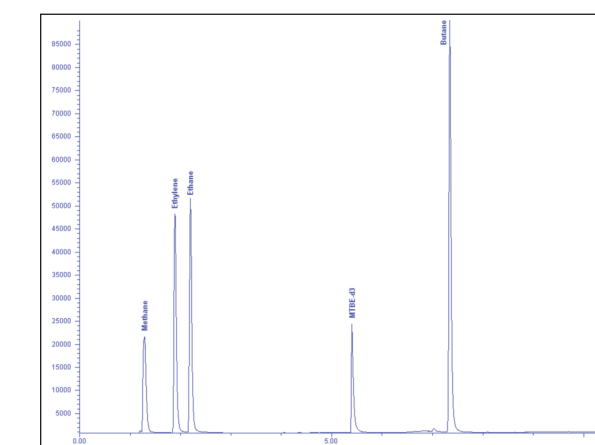


Figure 3. 500ppm Mixed Gas Standard

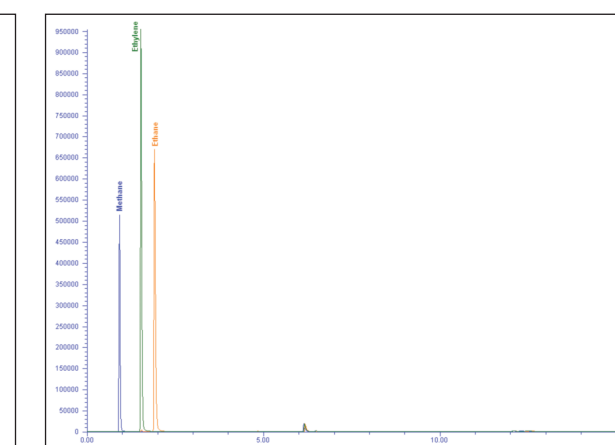


Figure 4. Gas Standard Overlay

After the mixed gas calibration and the saturated gas calibrations were 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 1. Using the gas calibration results for the mixed 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.

Table 6. Calculated Dissolved Gas Results

Compound	Standard Level	Accuracy % Recovery
Methane	1.5ppm	108
Ethane	4.4ppm	98
Ethylene	10.0ppm	114

## CONCLUSION

The LGX50 is an ideal instrument for dissolved gas analysis. The system can accommodate two different calibration techniques and add liquid or gas internal standards to the samples. The LGX50 was developed to closely mimic the established standard operating procedure of RSK-175 while still having the capability to automate the sampling process.

## REFERENCES

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