

Abstract:

The RSK-175 standard operating procedure was developed in order to determine the amount of dissolved gas in water. Due to the expansion of natural gas drilling through horizontal drilling and hydraulic fracturing, there has been increased interest in this procedure. However, since the Environmental Protection Agency (EPA) does not have a method for this analysis and the RSK-175 procedure is a standard operating procedure and not a formal method, there have been many interpretations and modifications of RSK-175 in order to determine the amount of gas dissolved in the water. This paper will consider three different approaches for dissolved gas calibration and analysis and the respective pros and cons.

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.

Once a calibration curve is established, the RSK-175 SOP specifies samples to be run by static headspace. As the compounds that are being analyzed are light gases and go into headspace easily, there is no need to concentrate the compounds by purge and trap. Thus, static headspace is the sampling technique of choice for this analysis.

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 Henry's Constant, the headspace volume versus the sample vial volume, and the temperature of the sample¹.

Saturated Gas Calculation¹:

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

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

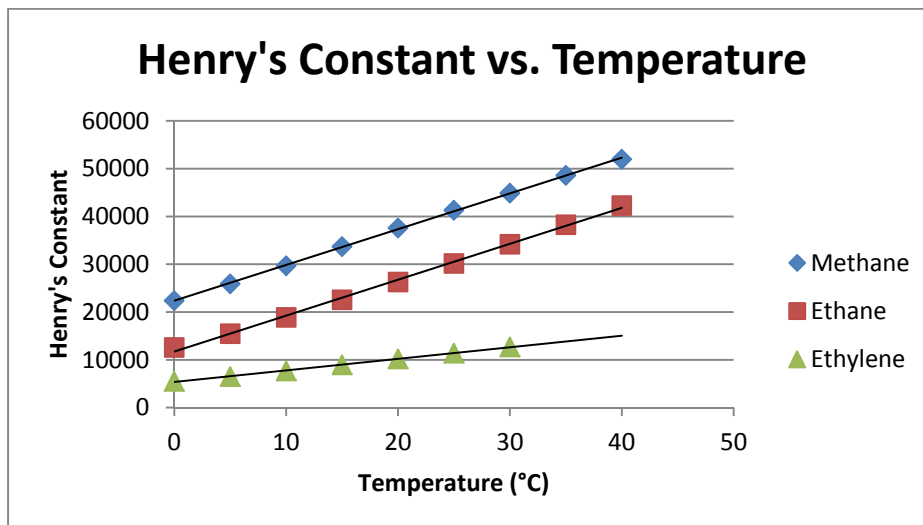
$$C_{AH} = (\text{HS vol.} / (\text{total vol.} - \text{HS vol.})) * \text{Experimental Results} * (\text{MW} / 22.4 \text{ L/mol}) * ((273 \text{K} / (\text{Sample Temp.} + 273 \text{K})) * 10^3 \text{ mg/g}) = \text{Conc. Gas in mg/L Water}$$

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

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



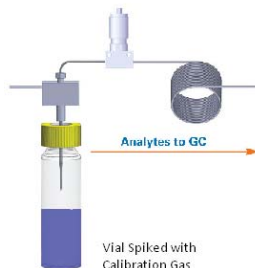
$$\text{Methane Henry's Constant} = 748.33(\text{Temp.}) + 22738$$

$$\text{Ethane Henry's Constant} = 751.33(\text{Temp.}) + 11740$$

$$\text{Ethylene Henry's Constant} = 241.43(\text{Temp.}) + 5375.7$$

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 gas mix calibration, a sample vial can be 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. See figure below. 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.



LGX50 Headspace Sweep of Gas Standard

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.

Step 1:



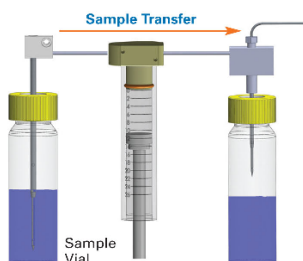
Empty vials are placed in one tray while samples from the field or dissolved gas standards are placed into full vials and placed in the second tray.

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 CO₂.

A Vacuum is pulled by displacing the helium in the vial equal to the volume of the sample to be added.

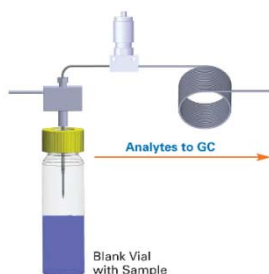
Step 2:



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 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 20 μ m. 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 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

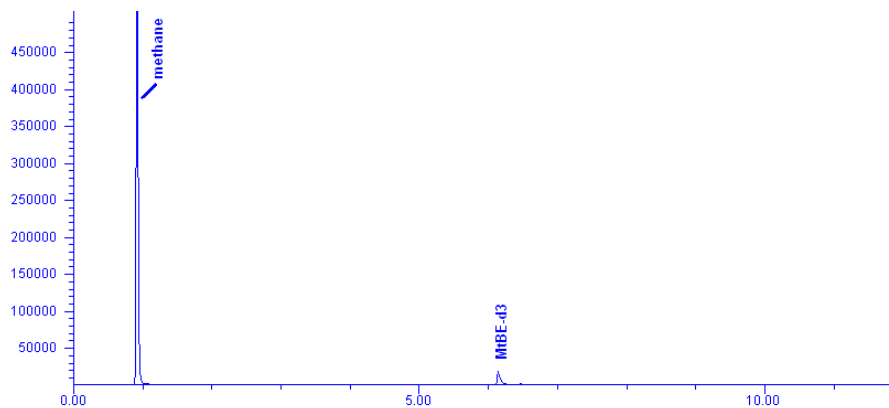


Figure 2: 9.9ppm Methane Standard Chromatogram

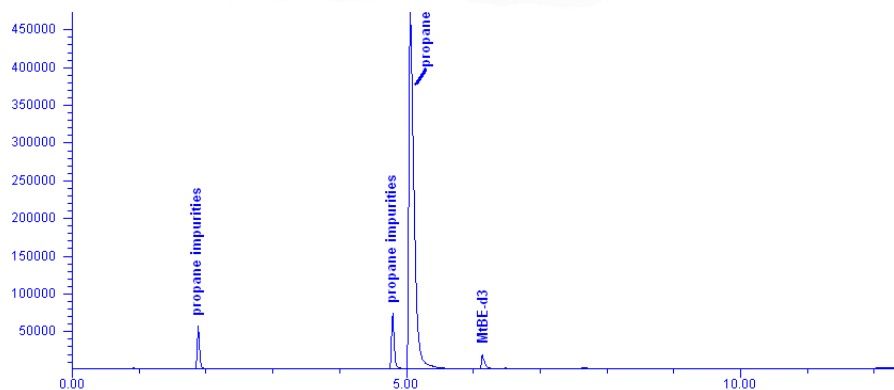


Figure 3: 19.2ppm Propane Standard Chromatogram

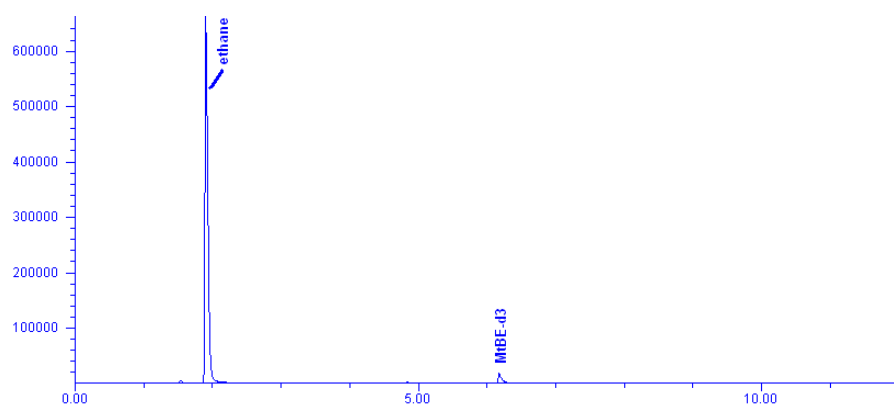


Figure 4: 13.1ppm Ethane Standard Chromatogram

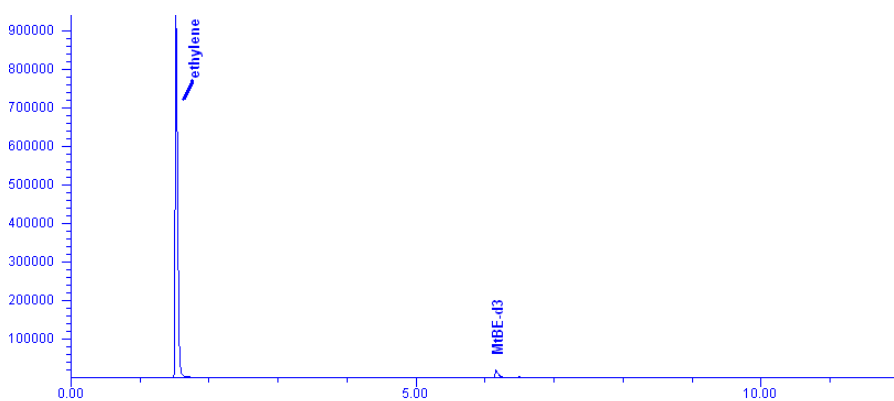


Figure 5: 14.0ppm Ethylene Standard Chromatogram

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
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

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

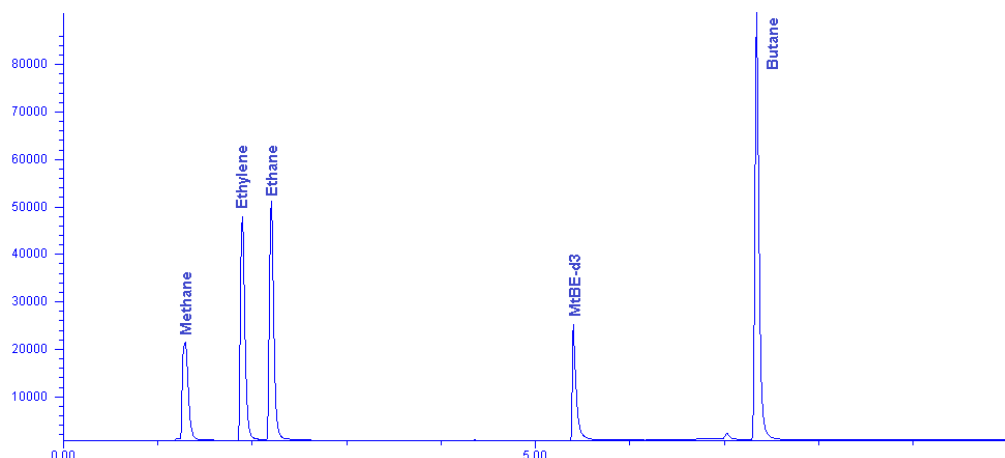


Figure 2: 500ppm Mixed Gas Standard Chromatogram

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.

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	1.5ppm	108
Ethane	4.4ppm	98
Ethylene	10.0ppm	114

Table 6: Calculated Dissolved Gas Results

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.

For more information on the LGX50 visit [estanalytical.com](http://www.estanalytical.com) or click below:

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

References:

1. Hudson, Felisa, *RSKSOP-175*, Revision No. 2, May 2004.
2. EPA New England, *Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene*. Revision 1, July, 2001.
3. *Light Hydrocarbons in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID)*, PADEP 3686, Rev. 0, April 2012.