

RSK-175 Calibration and Analysis Comparison

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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

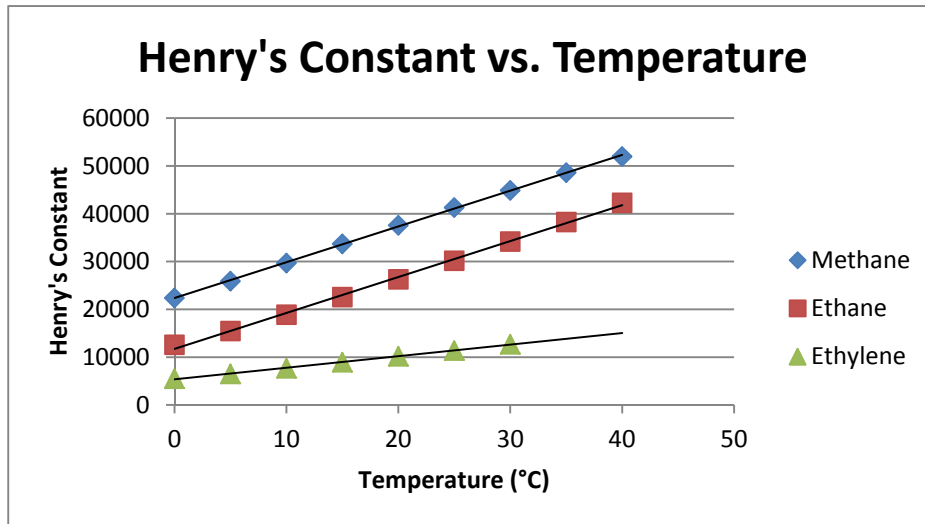
$$C_{AH} = (\text{HS vol.} / (\text{total vol.} - \text{HS vol.})) * \text{Experimental Results} * (\text{MW} / 22.4 \text{ L/mol}) * ((273 \text{K} / (\text{Sample Temp.} + 273 \text{K})) * 10^3 \text{ mg/g}) = \text{Conc. Gas in mg/L Water}$$

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.



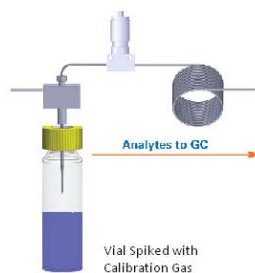
Methane Henry's Constant = $748.33(\text{Temp.})+22738$

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

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.



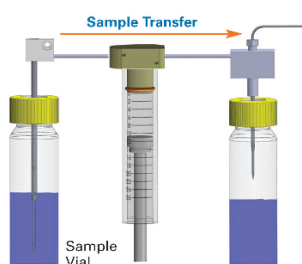
Step 1:

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.

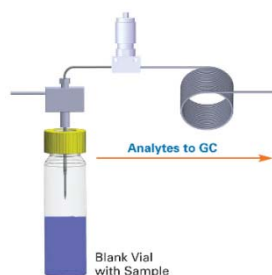
A Vacuum is pulled by displacing the helium in the vial equal to the volume of the sample to be added.



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.

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 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.

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