New ASTM Method Dissolved Gas Sampling Technique Comparison

Application Note

Environmental

Author

Anne Jurek
Applications Chemist
EST Analytical
Cincinnati, OH

Abstract

The American Society for Testing and Materials (ASTM) Method D8028 is a headspace method to determine dissolved gases in water. The method describes calibration and sampling techniques. One of the recommendations is to ensure the sample is sealed in order to safeguard the integrity of the sample. This recommendation is taken from United States Environmental Protection Agency (USEPA) Method 5030C used for the sampling of volatile organic compounds in water. Many environmental labs currently open their dissolved gas samples in order to place them in a headspace vial for sampling and analysis. This application will compare the efficacy of ensuring the sample is sealed versus opening the sample and pouring it into the sample vial for analysis.

Introduction:

Historically, the Robert S. Kerr (RSK) 175 Standard Operating Procedure (SOP) has been the primary reference for the sampling and analysis of dissolved gases. This procedure involves displacing ten percent of the sample volume, shaking the sample for five minutes and taking an aliquot of the headspace for injection onto the Gas Chromatograph (GC) column for separation and a Flame Ionization Detector (FID) for analysis. Calibration curves are performed using dilutions of a pure gas injected into the GC/FID system. The final concentration of the sample is calculated using Henry's constant.

The ASTM method calibration involves diluting a saturated gas solution in order to prepare the five point calibration curve. Since the gases are dissolved in water similarly to the samples, there is no need to use the Henry's constant. The sampling of the dissolved gases in the water is comparable to what is described in the RSK-175 procedure. Headspace is created in the sample vial and an aliquot of the headspace is sent to the GC/FID for separation and analysis.

One of the recommendations of the ASTM method is keeping the dissolved gas sample sealed during the entire sampling process. However, many laboratories currently pour the samples into headspace vials before sampling the dissolved gases in the water. By opening the sample and pouring it into a vial, the sample integrity is compromised. This application will compare calibration, precision, accuracy and method detection limits of uncompromised sealed sample handling versus poured samples.

Experimental:

The instrumentation used for this analysis was an EST Analytical Liquid Gas Extractor (LGX50) Sample Processor and an Agilent 7890 GC/FID. The LGX50 was affixed with a one milliliter headspace loop while the GC had a Restek Rt®-QS Bond 30m x 0.53mm x 20µm column installed. A 2000mg/ml standard of deuterated methyl tert-butyl ether was ordered from Restek and diluted to 500ppm for surrogate addition using the LGX50. The sampling and analysis parameters are listed in Tables 1, 2 and 3 respectively. The sealed samples were run in DGA mode of the LGX50 while the poured samples were run in Screen mode.

LGX50 Autosampler Parameter	Sealed Sample 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	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 Sealed Sample Autosampler Experimental Parameters

LGX50 Autosampler Parameter	Poured Sample Settings
Sample Type	Screen
Sample Fill Mode	Loop
Sample Volume	10ml
Syringe Prime	3 sec.
Syringe Needle Rinse	20ml
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 2: LGX50 Poured Sample Autosampler Experimental Parameters

GC/FID	Agilent 7890
Inlet Temperature	250°C
Inlet Pressure	9.97psi
Gas	Helium
Inlet	Split/Splitless
Split Ratio	20:1
Column Flow	12.0ml/min
Column	Restek RT® QS-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 3: GC/FID Experimental Parameters

High purity gases were procured from a local gas supplier. The saturated concentration of each gas was established at 20°C. Next, a 500ml volumetric flask was filled with de-ionized water and placed in a recirculating bath. The water was allowed to cool to 20°C. Once cooled, the pure gas was purged into the water for 30 minutes at a rate of 200ml/min using a flexible piece of Tygon tubing and a fritted water filter. Finally, a serial dilution of the saturated gas solution was prepared in order to make the calibration standards. These steps were repeated for each gas being tested. Tables 3 through 6 describe the calibration curve preparation.

Saturated Methane Gas Solution Curve Preparation at 20°C		
Standard	**Amount**	**Final Concentration**
Saturated Solution	50ml	11.6ppm
Saturated Solution	25ml	5.8ppm
Saturated Solution	5ml	1.16ppm
Saturated Solution	1ml	232ppb
Saturated Solution	500µl	116ppb
Saturated Solution	100µl	23ppb
Saturated Solution	40µl	9.3ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 4: Methane Curve Preparation

Saturated Ethylene Gas Solution Curve Preparation at 20°C		
Standard	**Amount**	**Final Concentration**
Saturated Solution	4ml	6.0ppm
Saturated Solution	1ml	1.5ppm
Saturated Solution	200µl	300ppb
Saturated Solution	50µl	75ppb
Saturated Solution	10µl	15ppb
Saturated Solution	4µl	6ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 5: Ethylene Curve Preparation

Saturated Ethane Gas Solution Curve Preparation at 20°C		
Standard	**Amount**	**Final Concentration**
Saturated Solution	9ml	5.6ppm
Saturated Solution	2ml	1.24ppm
Saturated Solution	500µl	312ppb
Saturated Solution	100µl	62ppb
Saturated Solution	25µl	15.5ppb
Saturated Solution	10µul	6.2ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 6: Ethane Curve Preparation

Saturated Propane Gas Solution Curve Preparation at 20°C		
Standard	**Amount**	**Final Concentration**
Saturated Solution	7ml	5.4ppm
Saturated Solution	2ml	1.5ppm
Saturated Solution	1ml	770ppb
Saturated Solution	250µl	192ppb
Saturated Solution	50µl	38.3ppb
Saturated Solution	10µl	7.7ppb

*Samples Prepared in a 100ml Volumetric Flask

Table 7: Propane Curve Preparation

For the sealed sample study, a 40ml vial was filled completely, no air bubbles, with the prepared standard. The sealed samples were run in DGA mode of the LGX50. A linear curve, Method Detection Limits (MDLs) and precision and accuracy were established for each gas in order to evaluate the limits and the precision and accuracy of the curves. The MDLs were done by preparing and sampling seven replicate low standards and calculated according to 40CFR Part 136, Appendix B. The precision and accuracy samples were done by running seven replicate standards and evaluating percent recovery and the percent relative standard deviation of the results. After the sealed sample study was finished, the poured sample study was performed. Each poured sample was prepared by decanting 10mls of the standard solution into a 40ml vial. The poured samples were run in Screen mode of the LGX50. As with the sealed samples, curves, MDLs, and precision and accuracy tests were performed for each gas. The final results were then compared.

Compound	Curve Range (µg/L)	Sealed Samples			Poured Samples		
		Curve %RSD	Curve R²	MDL	Curve %RSD	Curve R²	MDL
Methane	9.3 to 11600	17.20	0.998	1.96	22.50	0.998	4.81
Ethane	7.7 to 5400	5.45	1.000	2.02	26.09	0.999	2.88
Ethylene	6.2 to 5600	12.18	1.000	1.76	26.10	0.999	7.80
Propane	6.0 tp 6000	8.58	0.999	1.53	27.94	0.998	1.27

Table 8: Dissolved Gas Calibration Curve and MDL Results Summary

Compound	Concentration (µg.L)	Sealed Samples		Poured Samples	
		Precision	% Rec'ry	Precision	% Rec'ry
Methane	1160	5.73	94.06	3.80	88.09
Ethane	1240	6.24	98.23	2.16	86.21
Ethylene	1500	4.70	96.99	6.47	96.18
Propane	1530	3.29	93.87	2.53	91.34

Table 9: Dissolved Gas Precision and Accuracy Results Summary

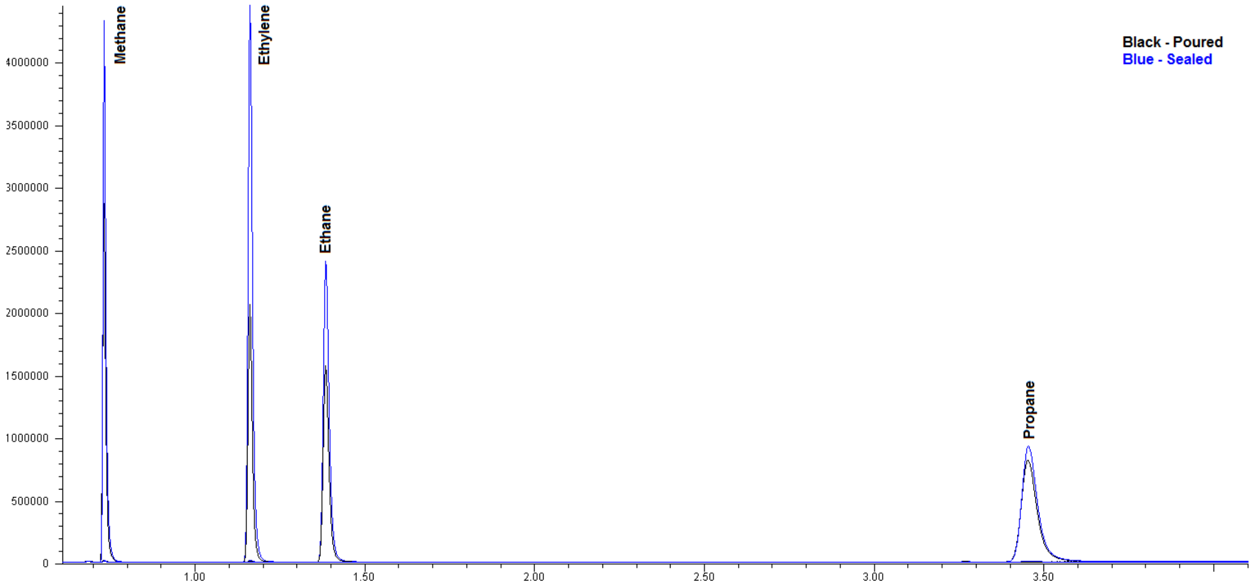

Figure 1: Overlay of Dissolve Gas Chromatograms

Conclusions:

When comparing the linearity of the sealed samples versus the poured samples, it was found that the sealed samples had a better %RSD of the compound responses than the poured samples. However, the R^2, linear regression, of each gas was comparable. The method detection limits were much better when using a sealed sample as opposed to the poured. There was also some cross contamination with the lower calibration level poured samples. Pouring the samples enabled the analytes to travel from one vial to the next. This movement caused problems with the low level calibration points which in turn affected both linearity and method detection limits. However, when examining the precision and accuracy of the higher level standards, both techniques proved to be viable. In conclusion, a sealed sample would be the preferable technique for this analysis as it prohibits the possibility of cross contamination.

References:

1. Dean, John A., Lange's Handbook of Chemistry, 14th Edition, R. R. McGraw-Hill, Inc., 1992
2. Gas Encyclopaedia, (2009), Retrieved November 15, 2011 from http://encyclopedia.airliquide.com/Encyclopedia.asp
3. Hudson, Felisa, RSKSOP-175, Revision No. 2, May 2004.
4. Light Hydrocarbons in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID), PADEP 3686, Rev. 1, October 2012.

For More Information

For more information on our products and services, visit our website www.estanalytical.com/products.