Two Headspace Solutions for the Analysis of Dissolved Gases in Water by Method RSKSOP-175

Application Note

Abstract

Dissolved gas analysis has been performed using a simplified headspace method following US EPA method RSKSOP-175. This method describes the preparation and analysis of dissolved gases in water.

Recent developments in natural gas drilling from deep underground shale formations, using techniques such as hydraulic fracturing, have renewed interest in this method to determine dissolved gases in water with headspace analysis.

This application note will demonstrate the versatility of Teledyne Tekmar's HT3 and Versa Automated Headspace Analyzers for determining dissolved gases in ground water samples. Methane, ethene, ethane, and propane were evaluated.

Versa Automated
Headspace Analyzer

HT3 Automated
Headspace Analyzer

Introduction

The Ground Water and Ecosystem Restoration Division of the U.S. Environmental Protection Agency developed a Standard Operating Procedure (SOP) for sample preparation and calculations for dissolved gas analysis in water samples using a GC headspace equilibration technique, RSKSOP-175.[1] This method displaces approximately 10% of the water in the collection bottle with helium to create a headspace. The bottle is shaken for 10 minutes to allow for equilibrium to occur. An aliquot of the headspace is then sampled and injected into a GC system for the detection of the dissolved gases.

RSKSOP-175 is a manual headspace technique in which considerable labor is employed. This application note will demonstrate the capabilities of the Teledyne Tekmar HT3 and Versa Automated Headspace Analyzers to prepare samples for the quantification of methane, ethene, ethane and propane from ground water samples.

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Experimental-Instrument Conditions

The HT3 and the Versa Automated Headspace Analyzers were connected to an Agilent 6890 GC/FID for this study. A Restek Rt®-U-Bond column was used. Table 1 displays the HT3 and Versa method parameters, while Table 2 displays the GC/FID parameters.

Teledyne Tekmar HT3 and Versa Parameters		
Variable	**HT3 Values**	**Versa Values**
Constant Heat Time	On	
GC Cycle Time	21.00 min	21.00 min
Valve Oven Temp	100°C	100°C
Transfer Line Temp	100°C	100°C
Standby Flow Rate	50 mL/min	50mL/min (Factory Setting)
Platen/Sample Temp	64°C	64°C
Platen Temp Equil Time	0.50 min	0.50 min
Sample Equil Time	30.00 min	30.00 min
Mixer	Off	Off
Mixing Time	5.00 min	2.00 min
Mixing Level	Level 5	Medium
Mixer Stabilize Time	0.50 min	0.50 min
Pressurize	10 psig	10 psig
Pressurize Time	2.00 min	2.00 min
Pressurize Equil Time	0.20 min	0.25 min
Loop Fill Pressure	7 psig	7 psig
Loop Fill Time	2.00 min	2.00 min
Inject Time	0.50 min	0.50 min

Table 1: HT3 and Versa Automated Headspace Conditions for Dissolved Gases in Groundwater Samples. The gray cells indicate unused parameters.

Agilent GC / FID Parameters	
Column	Restek Rt-U-Bond, 15m, 0.53mm ID, 20µm dF
Oven Program	35°C for 4 min, 20°C/min to 190°C for 2 min, run time 13.75 min
Inlet:	Temperature 190 °C, Split Ratio 20:1 Helium Carrier Gas; Constant Pressure1.0 psi
FID	Temperature 190°C, Hydrogen 35 mL/min, Air 300 mL/min, Constant Make up 30.0 mL/min

Table 2: Agilent 6890 GC / FID Parameters

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Standard Sample Preparation

Methane, ethene, ethane and propane were obtained from local gas suppliers. Saturated stock standards for each gas were prepared by bubbling the gas through 500 mL of reagent grade water at approximately 0°C.

Calibration standards were prepared from the saturated stock gas solutions by diluting the stock standard to 10 mL of water in the headspace vials. The final volume of the solution was maintained at 10 mL. Table 3 displays the standard preparation and the associated concentration for each gas.

Seven replicates at the lowest calibration level were prepared to determine the MDL for each gas. 10 mL of chilled reagent grade water was placed into separated 22 mL headspace vials. 5 µL of the stock gas standard was added to these vials and quickly capped.

Volume of Stock Solution Used (mL)	Final Gas Concentration (mg/L)			
	Methane	Ethene	Ethane	Propane
0.005	0.020	0.141	0.066	0.074
0.01	0.040	0.281	0.132	0.147
0.05	0.198	1.405	0.958	0.735
0.25	0.990	7.025	3.292	3.675
1.0	3.959	28.100	13.168	14.700
2.5	9.898	70.250	32.920	36.750
5.0	19.795	140.500	65.840	73.500
6.0	23.754	168.600	79.008	88.200

Table 3: Gas Calibration Standard Preparation and Concentrations

Results

The peak areas were determined for all gas samples using Agilent ChemStation Software. The response factors were determined for the calibration standards by dividing the peak area by the sample concentration. Seven replicates were run at the lowest gas standard solution to determine precision and method detection limits (MDL). These results are reported in Tables 4 and 5. Figure 1 is the chromatogram of a mixed gas standard and the comparison of methane and ethane with the HT3 and the Versa.

	Range (mg/L)	Correlation Coefficient (R^2)	
		HT3	Versa
Methane	0.020 to 24	0.998	0.996
Ethene	0.141 to 169	0.998	0.997
Ethane	0.066 to 79	0.999	0.999
Propane	0.074 to 88	0.999	0.999

Table 4: Calibration Data for Methane, Ethene, Ethane, and Propane

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	Level (mg/L)	%RSD (n=7)		MDL (mg/L)	
		HT3	Versa	HT3	Versa
Methane	0.02	3.8	2.5	0.002	0.002
Ethene	0.14	5.9	3.9	0.025	0.019
Ethane	0.07	2.5	3.3	0.005	0.007
Propane	0.07	2.7	1.3	0.006	0.004

Table 5: Reproducibility Data for Methane, Ethene, Ethane, and Propane

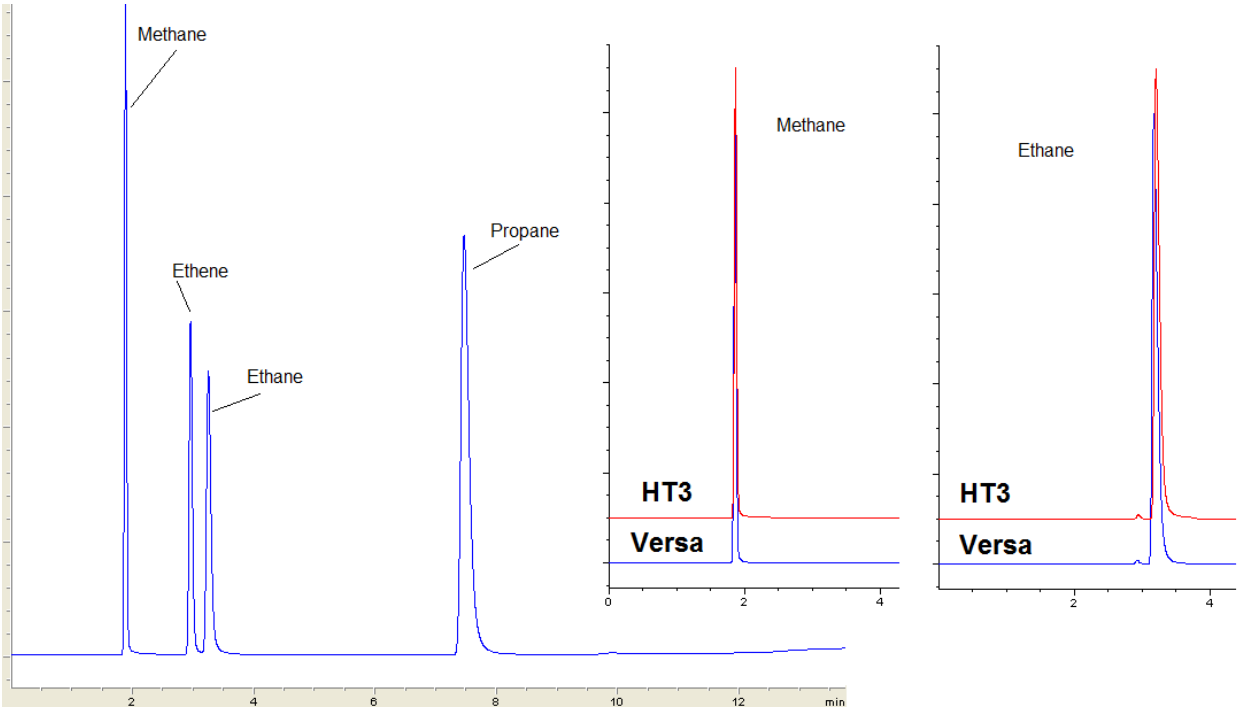

Figure 1: Gas Chromatogram Comparison of Methane and Ethane between the HT3 and the Versa and the Chromatogram of the Four Gases.

Conclusions

US EPA Method RSKSOP-175 was developed for determining dissolved gases using a manual headspace technique. The Teledyne Tekmar HT3 and Versa Automated Headspace Analyzers were utilized to demonstrate their suitability to analyze dissolved gases which are sometimes found in groundwater samples.

Calibration standards were prepared for methane, ethene, ethane and propane in water. All calibration and precision data in this study exceeded normal quality control criteria. This coupled with the automation benefits make the HT3 or the Versa Automated Headspace Analyzers excellent choices when performing RSKSOP-175.

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References

1. Hudson, F, RSKSOP-175, Rev 2, May 2004, Sample Preparation and Calculation for Dissolved Gas Analysis in Water Samples Using GC Headspace Equilibration Technique.

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