APPLICATION NOTE

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

AN106 SCION Instruments

Introduction

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 SCION Instruments HT3 and Versa Automated Headspace Analyzers for determining dissolved gases in ground water samples. Methane, ethene, ethane, and propane were evaluated.

Figure 1. SCION HT3 Headspace Sampler together with the SCION Instruments 8300 GC platform in combination with to 8700 SQ-MS equipped with 8400PRO autosampler.

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 labour is employed. This application note will demonstrate the capabilities of the SCION HT3 and Versa Automated Headspace Analyzers to prepare samples for the quantification of methane, ethene, ethane and propane from ground water samples. Table 1 displays the HT3, Versa method parameters and GC/FID parameters.

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.

Table 1. Instrumentation operating conditions

Injector	Split 20:1, 190 °C
Column	SCION-PLOT U
Oven Program	35°C (4 min), 20°C/min to 190°C (2 min)
Carrier	Helium
Pressure	Constant pressure 1.0 psi
Detector	FID with ceramic jet, 190°C Air: 300 ml/min, Fuel gas (H_2): 30 ml/min, Make up (N_2): 29 ml/min
Software	Compass CDS /HT3 Teklink
	HT3
Oven temperature	100°C
Transfer line temperature	100°C
Sample temperature	64°C
Sample equilibrium	30 min
	VERSA
Oven temperature	100°C
Transfer line temperature	100°C
Sample temperature	64°C
Sample equilibrium time	30 min

Table 2. Gas calibration standard preparations and concentrations

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

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 2 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.

Results

The peak areas were determined for all gas samples using Compass 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 3 and 4. Figure 1 is the chromatogram of a mixed gas standard and the comparison of methane and ethane with the HT3 and the Versa.

Table 3. Calibration data from Methane, Ethene, Ethane, and Propane

	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. Reproducibility Data for Methane, Ethene, Ethane, and Propane

	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

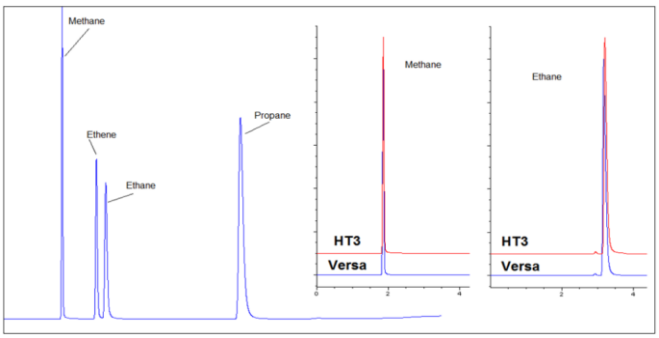

Figure 2. Gas Chromatogram Comparison of Methane and Ethane between the HT3 and the Versa and the Chromatogram of the Four Gases.

Conclusion

US EPA Method RSKSOP-175 was developed for determining dissolved gases using a manual headspace technique. The SCION Instruments 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.

Ordering Information

Part Number	SCION Ht3 Headspace
SC149300000	**HT3 Headspace Autosampler 110 V.** This static headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 115V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC149300100	**HT3 Headspace Autosampler 230 V.** This static headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 230V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC14930000S	**HT3 Dynamic Headspace Autosampler 110V.** This dynamic headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system, including trap, can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. Dynamic mode includes 12" x 1/8" Tenax/Silica Gel and Charcoal (#3) trap and Vocarb 3000 (K) trap. Static and Dynamic modes

	may be used interchangeably throughout the same schedule. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 115V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC14930010S	**HT3 Dynamic Headspace Autosampler 230V.** This dynamic headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system, including trap, can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. Dynamic mode includes 12" x 1/8" Tenax/Silica Gel and Charcoal (#3) trap and Vocarb 3000 (K) trap. Static and Dynamic modes may be used interchangeably throughout the same schedule. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 230V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC150800100	**Versa Static Headspace Vial Sampler 110V.** This analyzer comes with a 20 position autosampler, single-position platen heater, integrated mixing system, and completely heated inert sample pathway. Entire system can be heated from ambient up to 200 degrees C in increments of 1 degree C. Valve and loop configuration includes 1mL standard loop. Built-in pressure control assures consistent volume regardless of external conditions. Windows XP or higher is required to operate and includes the Versa TekLink 2G software. Power requirements are 115V, 50/60 Hz, 5A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC150800200	**Versa Static Headspace Vial Sampler 230V**. This analyzer comes with a 20 position autosampler, single-position platen heater, integrated mixing system, and completely heated inert sample pathway. Entire system can be heated from ambient up to 200 degrees C in increments of 1 degree C. Valve and loop configuration includes 1mL standard loop. Built-in pressure control assures consistent volume regardless of external conditions. Windows XP or higher is required to operate and includes the Versa TekLink 2G software. Power requirements are 230V, 50/60 Hz, 5A. Make sure to order the appropriate GC interface cable to ensure proper installation.

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