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EPA Method RSK-175 Dissolved Gasses in Water Matrices using the Teledyne Tekmar HT3 Headspace Analyzer

HT3 Application Note

Introduction ▼

The analysis of dissolved gases in ground water is important in determining whether intrinsic bioremediation is occurring in a fuel contaminated area. The gases of concern include methane, ethane, and ethylene. These compounds are used to detect biodegradation in areas of concern such as landfills and remediation sites. Presence of the compounds is used to determine if natural contaminant attenuation and destruction are occurring at a specific site. For example, fuel hydrocarbons will break down to methane and chlorinated solvents will reduce to form ethylene and chloride (1).

Previous techniques for the analysis of dissolved gases used direct injections into the gas chromatograph. The water sample would be in a sealed vial with a certain amount of headspace. The vial would be heated and/or agitated to drive the gases into the headspace. The headspace was removed with a syringe and injected into the gas chromatograph. The Teledyne Tekmar HT3 is a Static and Dynamic Headspace Autosampler for gas chromatographs. The HT3 automates the analysis, from heating and agitating the vial, to the injection of headspace into the GC. This application demonstrates the capability of the HT3 to analyze dissolved gases in water.

Experimental ▼

Gas standards were purchased from Scott Specialty Gases. One cylinder contained methane, ethane, ethylene, acetylene, propane, propylene, propyne, and n-butane all at a concentration of 15ppm. A 22mL headspace vial was filled completely with DI water and capped. 4mL of headspace was removed using high purity nitrogen. This was performed by inserting a needle through the septum as seen in figure 1.

Figure 1

4mL of nitrogen was pulled into a syringe equipped with a shutoff valve as seen in figure 2.

Figure 2

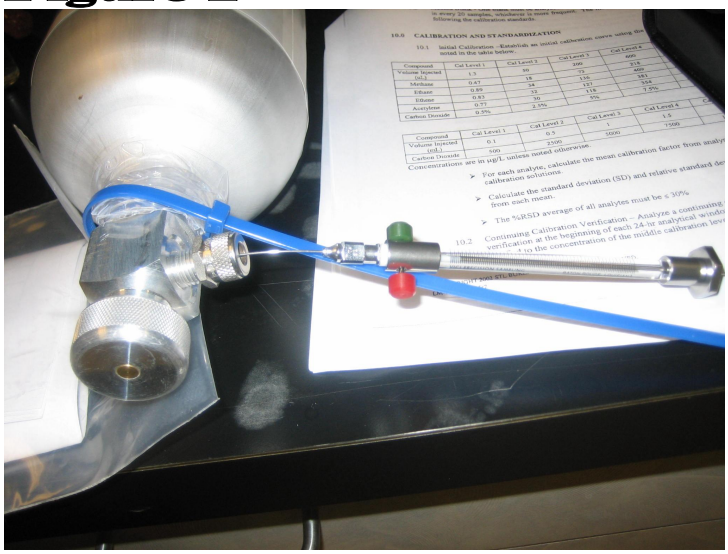
The syringe filled with nitrogen was injected into the vial, displacing 4mL of the water as seen in figure 3.

Figure 3

After the injection of nitrogen both the syringe and the needle are pulled out of the vial.

The air standard is pulled into the syringe (as seen in figure 4) and injected into the headspace vial.

Figure 4



The HT3 Headspace Autosampler was connected to an Agilent 6890 GC with an FID detector. The GC column used was a Restek PLOT column (Rt-U PLOT Catalog # 19726). The column gives excellent resolution and peak separation; however the two gases propane and propylene co-elute on the column and are integrated as one peak. A 5mL headspace loop was installed on the HT3 to inject a higher volume of mass into the GC injection port. The HT3 and GC parameters are listed below:

Figure 5 HT3 Parameters

Variable	Value	Variable	Value
Constant Heat Time	On	Mixing Time	2.00 min
GC Cycle Time	22.00 min	Mixing Level	Level 5
Valve Oven Temp	80 degrees C	Mixer Stabilize Time	1.00 min
Transfer Line Temp	80 degrees C	Pressurize	6 psig
Standby Flow Rate	50 mL/min	Pressurize Time	2.00 min
Platen/Sample Temp	40 degrees C	Pressurize Equil. Time	0.20 min
Platen Temp Equil. Time	0.00 min	Loop Fill Pressure	4 psig
Sample Equil. Time	10.00 min	Loop Fill Time	2.00 min
Mixer	On	Inject Time	1.00 min

Figure 6 GC Parameters

Variable	Value
Oven Temp.	50 degrees C to 190 degrees C @ 10/min
Inj./Det. Temp.	250 degrees C
Carrier Gas	Helium
Column Flow	5 mL/min
Split	Ratio 5:1

Results ▼

Two calibration curves were generated, one in the ppm range and one in the ppb range. The curve in the ppm range was calibrated from 0.5ppm to 4.0ppm and the curve in the ppb range was calibrated from 40ppb to 400ppb. The two curves are shown below:

Figure 7 ppm Range Curve (0.5ppm to 4.0ppm)

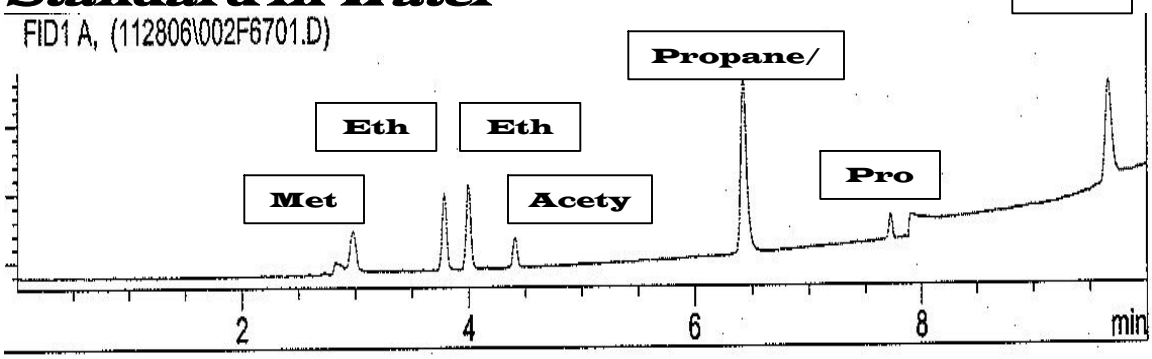
Compounds	RF 1	RF 2	RF 3	RF 4	RF 5	%RSD
Methane	0.89	1.00	0.88	0.69	0.65	17.84
Ethylene	0.85	1.00	1.03	0.99	0.94	7.22
Ethane	0.94	1.11	1.16	1.10	1.05	8.03
Acetylene	0.35	0.38	0.40	0.42	0.41	6.70
Propane/Propylene	2.45	3.02	3.16	3.04	2.89	9.51
Propyne	0.25	0.27	0.31	0.33	0.33	12.72
n-butane	1.53	1.91	2.05	2.03	1.99	11.17

Figure 8 ppb Range Curve (40ppb to 400ppb)

Compounds	RF 1	RF 2	RF 3	RF 4	%RSD
Methane	0.1182	0.1062	0.1049	0.0876	12.07
Ethylene	0.1127	0.1200	0.1187	0.1154	2.84
Ethane	0.1306	0.1410	0.1432	0.1401	4.02

Acetylene	0.0324	0.0349	0.0326	0.0324	3.68
Propane/Propylene	0.2868	0.3397	0.3676	0.3622	10.88
Propyne	0.0265	0.0230	0.0233	0.0244	6.47
n-butane	0.1577	0.2348	0.2410	0.2540	19.63

Figure 9 Chromatogram of a 200ppb Gas Standard in Water



Conclusion ▼

The analysis of dissolved gases such as methane, ethylene, ethane, acetylene, propane/propylene, propyne and n-butane proved to be a success on the HT3 Headspace analyzer. The analysis of these compounds in water would be critical for determining biodegradation of a contaminated site. This application describes the technique needed for the sample and standard preparation for Method RSK-175. Because of the HT3 electronic pressure and flow control, identical loop fill and injection into the GC produced excellent %RSD's. Preparation of samples and standards are a key factor in the method, so syringes with shut-off valves must be used for the analysis.

References ▼

1. Don H. Kampbell and Steve A. Vandegrift. Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique. *Journal of Chromatographic Science*, Vol. 36, 253-256 May 1998