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A Comparative Analysis of Fuel Oxygenates in Soil by Dynamic and Static Headspace Utilizing the HT3™ Automatic Headspace Analyzer

Application Note   *By: Anne Jurek*

Abstract

This application note presents method development using classical headspace sample preparative techniques for the analysis of fuel oxygenates in a soil matrix. Fuel oxygenate compounds were analyzed using the HT3™ Automated Headspace Analyzer in conjunction with a Gas Chromatograph/Mass Spectrometer (GC/MS) system. Normal method validation including calibration, detection limit reporting, and reproducibility data was employed on the static and dynamic functions of the sampling system.

Introduction

Fuel oxygenates have been added to gasoline for years. These additives aid in more efficient and cleaner fuel combustion thus reducing pollution. Unfortunately, since gasoline is stored in large storage tanks that are either above or below ground, fuel oxygenates can leach into the surrounding water or soil causing contamination and possible health risks to the surrounding environment.

In this study, fuel oxygenates were evaluated by headspace analysis in both the static and dynamic modes at both a low part per billion (ppb) range and a high part per million (ppm) range on soil samples. The results were then compared to show the benefits of both modes of analysis. In particular, for analysis requiring lower levels of detection, the dynamic option is an excellent choice. Below is a brief description of the varying techniques.

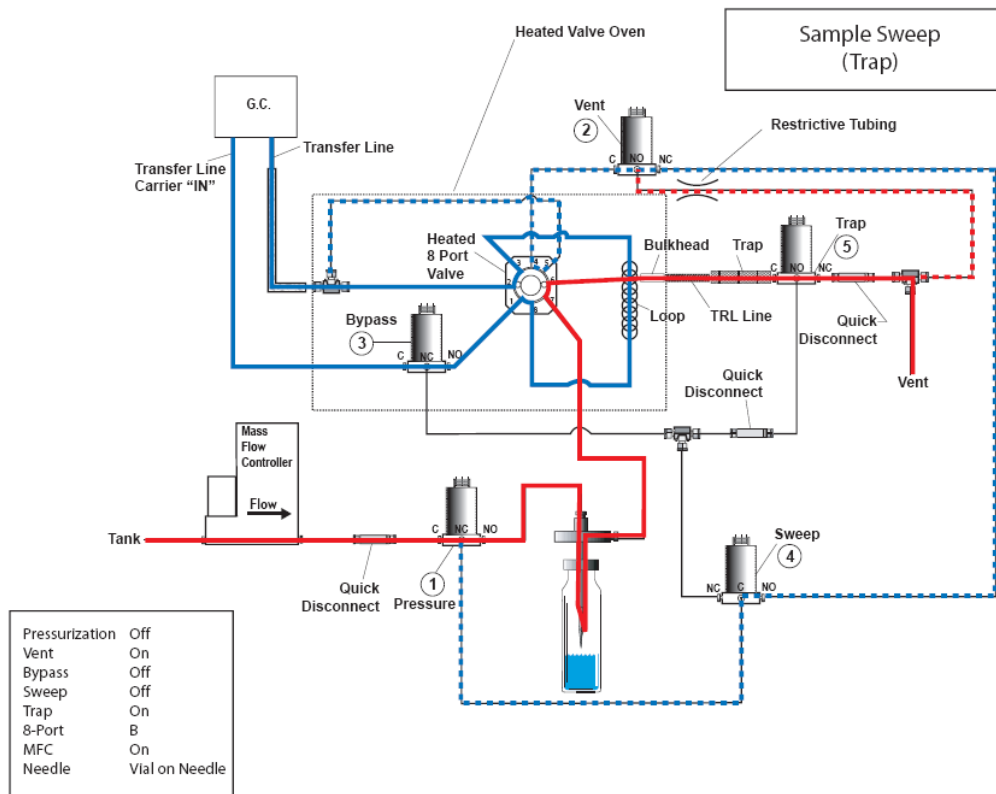Static Headspace Extraction (Illustration1)

1. A sample is placed in vial and sealed using a Teflon faced septa and metal containment cap.

2. The sample is loaded into a heating chamber with temperature control for a set amount of time. This allows for equilibration between the matrix and headspace to occur depending on the partition coefficients of the analytes under investigation.

3. At the conclusion of the heating step, the sample can be mixed using an agitation step and re-equilibrated.

4. Sample is pressurized to a predetermined set point using an inert gas source.

5. The sample is then vented to atmosphere though a fixed sample volume loop using either time or pressure feedback as the control.

6. The sample contained in the loop is then injected for a set amount of time to a GC/MS for column separation and detection.
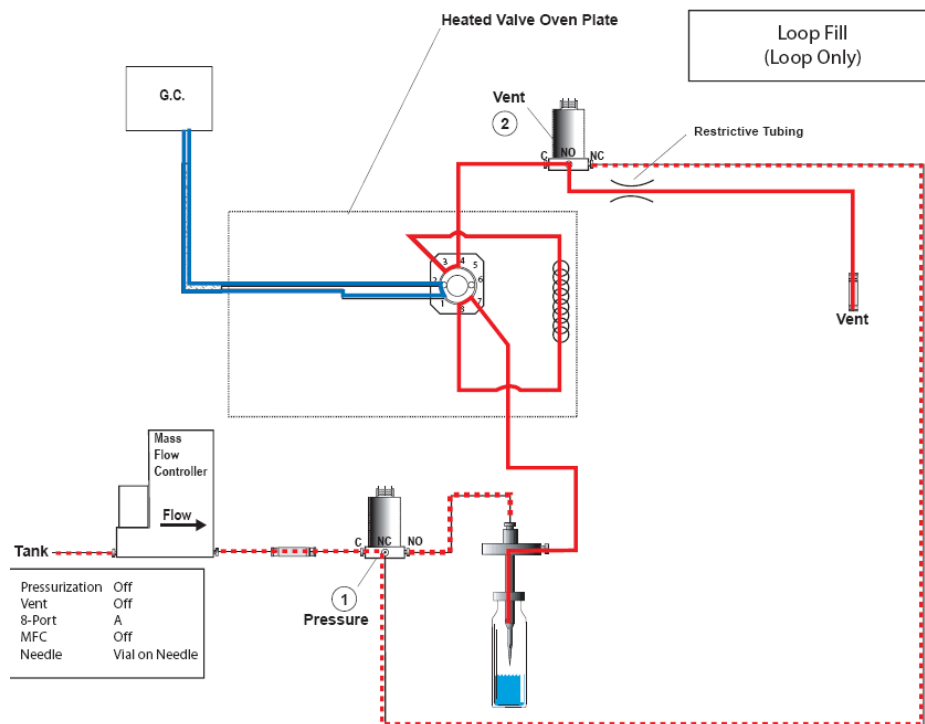
Illustration 1: Static Headspace Extraction

Dynamic Headspace Extraction (Illustration 2)

1. Steps 1 through 3 are the same as the static set-up

2. The sample headspace is swept for a set time through a sorbent concentrating trap using the inert gas source. This function allows more sample from the matrix to enter the headspace as equilibrium between the two phases cannot occur.

3. At the conclusion of the sweep step the sorbent trap is heated and back-flushed to the GC/MS system. This allows all of the analytes originally contained in the sample to be calculated in a single run.

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Illustration 2: Dynamic Headspace Extraction

Pressurization Off
Vent On
Bypass Off
Sweep Off
Trap On
8-Port B
MFC On
Needle Vial on Needle

Experimental-Instrument Conditions

The HT3[TM] Automated Headspace Analyzer, an Agilent 6890 GC and a 5973 MS were used for this analysis. A #9 adsorbent trap (Teledyne Tekmar) was used for the dynamic headspace analysis while a 1mL loop was selected for the static headspace analysis. The HT3[TM] has method development software called Method Optimization Mode (M.O.M.). This software was utilized in order to obtain the platen temperature for the dynamic and static experimental conditions and to find the optimum sweep time for the dynamic experiment. Tables 1, 2, 3 and 4 display the GC, MSD, and the static and dynamic headspace experimental conditions respectively.

GC Parameters	
GC:	Agilent 6890
Column:	Restek RTX-VMS, 20m, 0.18mm ID, 1.0 μm
Oven Program:	35°C for 3min.; 10°C/min. to 85°C for 0 min.: 40°C /min to 210°C for 2 min 13.13 min. runtime
Inlet:	150°C
Column Flow	1.2mL/min
Gas:	Helium
Split:	60:1
Pressure:	23.0 psi
Inlet:	Split/Splitless

MSD Parameters	
MSD:	5973
Source:	230°C
Quad:	150°C
Solvent Delay:	0.5 min
Scan Range:	m/z 35-350
Scans:	5.27 scans/sec
Threshold:	400
MS Transfer Line Temp:	250°C

Tables 1 & 2: GC and MSD Parameters

HT3 Static Parameters			
Variable	**Value**	**Variable**	**Value**
Constant Heat Time	On	Mixing Time	10.0 min
G.C. Cycle Time	30.00 min	Mixing Level	Level 5
Valve Oven Temp	125°C	Mixer Stabilize Time	0.50 min
Transfer Line Temp	125°C	Pressurize	10 PSIG
Standby Flow Rate	50mL/min	Pressurize Time	2.00 min
Platen/Sample Temp	60°C	Pressurize Equil. Time	0.50 min
Platen Temp Equil. Time	0.50 min	Loop Fill Pressure	5 PSIG
Sample Equil. Time	0.10 min	Loop Fill Time	2.00 min
Mixer	On	Inject Time	1.00 min

Table 3: HT3 Static Parameters

HT3 Dynamic Parameters			
Variable	**Value**	**Variable**	**Value**
Valve Oven Temp	125°C	Sweep Flow Rate	50mL/ min
Transfer Line Temp	125°C	Sweep Flow Time	8.00 min
Standby Flow Rate	50mL/min	Dry Purge Time	5.00 min
Trap Standby Temp	30°C	Dry Purge Flow	100mL/min
Trap Sweep Temp	0°C	Dry Purge Temp	25°C
Platen/Sample Temp	60°C	Desorb Preheat	245°C
Sample Preheat Time	0.10 min	Desorb Temp	250°C
Preheat Mixer	On	Desorb Time	2.00 min
Preheat Mixing Level	Level 5	Trap Bake Temp	280°C
Preheat Mixing Time	10.00 min	Trap Bake Time	5.00 min
Preheat Mixer Stabilize Time	0.50 min	Trap Bake Flow	200mL/min

Table 4: HT3 Dynamic Parameters

Calibration

A 50ppm (dynamic) and a 200ppm (static) working calibration standard were prepared in methanol. Due to solubility issues, the tert-butyl alcohol (TBA) in the calibration standard was at a higher concentration than the other compounds, thus the concentration of the TBA was 250ppm for the dynamic calibration standard and 1000ppm for the static calibration standard. 5g of baked sand and 5mL of saturated sodium chloride solution were added to each 22mL headspace vial. The vials were then spiked with the calibration standard at different concentrations in order to run both the dynamic and static curves. Refer to Tables 5 and 6 respectively.

Dynamic Mode Curve Preparation 50ppm Stock Solution							
Level	1	2	3	4	5	6	7
Stock Standard Spike Vol. (µl)	0.5	1.0	2.5	5.0	10.0	50.0	100.0
MTBE concentration (ppb)	5	10	25	50	100	500	1000
TBA concentration (ppb)	25	50	125	250	500	2500	5000
DIPE concentration (ppb)	5	10	25	50	100	500	1000
ETBE concentration (ppb)	5	10	25	50	100	500	1000
TAME concentration (ppb)	5	10	25	50	100	500	1000

Table 5: Dynamic Mode Curve Preparation

Static Mode Curve Preparation 200ppm Stock Solution					
Level	1	2	3	4	5
Stock Standard Spike Vol. (µl)	5.0	10.0	12.5	25.0	50.0
MTBE concentration (ppb)	200	400	500	1000	2000
TBA concentration (ppb)	1000	2000	2500	5000	10000
DIPE concentration (ppb)	200	400	500	1000	2000
ETBE concentration (ppb)	200	400	500	1000	2000
TAME concentration (ppb)	200	400	500	1000	2000

Table 6: Static Mode Curve Preparation

The calibration data was processed using Agilent Chemstation software. The relative response factors of all of the analytes were evaluated for %RSD. All of the analytes in the dynamic and static calibration curves had a 12.4%RSD or better, refer to Table 7.
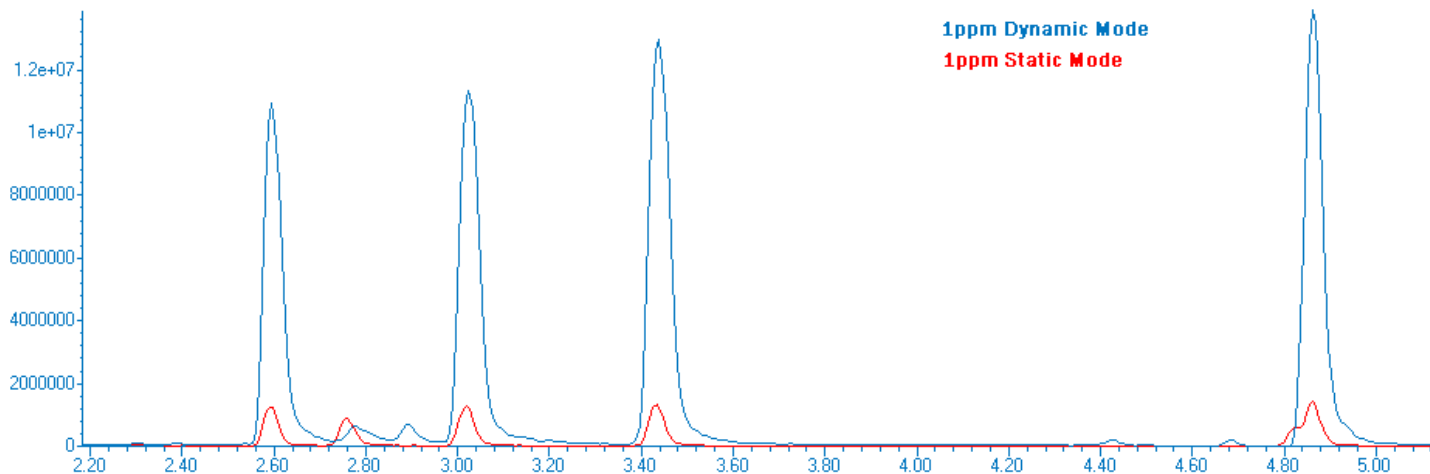
Method Detection Limit (MDL) Determination and Reproducibility Study

A statistical determination of the MDL's was established for each analyte. Seven replicate standards of the low calibration point were analyzed in order to determine the MDL's for each compound in both the static and the dynamic modes. The detection limits for the compounds in both modes are listed in Table 7.

In order to demonstrate the robustness of the experimental conditions, a reproducibility study was performed. Several replicate standards of a 100ppb concentration were run in the dynamic mode and a second set of 1000ppb standards were run in the static mode. The reproducibility data for both modes was then analyzed and these results are also presented in Table 7.

MDL according to 40 CFR 136, Appendix B, Revision 1.11								
	Dynamic Mode				Static Mode			
	Calibration %RSD	Spike Level	MDL	100ppbCCV (%RSD)	Calibration %RSD	Spike Level	MDL	500ppbCCV (%RSD)
pentafluorobenzene (IS)		100				500		
MTBE	9.17	5	1.77	3.89	6.63	200	20.65	1.09
TBA	8.87	25	17.39	7.91	9.04	1000	140.62	1.97
diisopropylether	9.48	5	1.17	5.17	6.94	200	21.28	1.82
ETBE	12.40	5	1.33	3.39	9.35	200	22.95	2.94
tert-amyl ethyl ether	6.92	5	1.29	3.89	5.72	200	21.09	3.69

Table 7: Data Summary

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Figure 1: 1ppm Fuel Oxygenate Standard in Dynamic and in Static Mode

Conclusions

The HT3^{TM} Automated Headspace Analyzer is an excellent system for the analysis of fuel oxygenates in soil. The dynamic capabilities of the HT3^{TM} allow analyte detection down to a 5ppb level while the static mode can be used for samples with higher, 200ppb, level components. Both the static and dynamic modes of the HT3^{TM} provided linear calibration curves and excellent reproducibility while providing a wide sample detection range. The versatility of the HT3^{TM} allows switching between both the static and dynamic modes of the instrument within a schedule enabling better use of instrument time, flexibility to test for both high and low level components, and less hands-on time requirements from laboratory personnel. In addition, the M.O.M. feature allows all parameters to be automatically adjusted to help users find the best conditions for their required analysis and a complete history log of how it was achieved.