Gasoline Range Organic Detection Using Headspace Sampling Techniques

Introduction:

Gasoline and/or oils spills can range from catastrophic, the Gulf Oil Spill and Exxon Valdez, to small scale spills caused by cracks in underground storage tanks or car accidents. No matter what the size or cause, the surrounding ground and water will get contaminated. To accurately determine the level of contamination, the surrounding area needs to be tested for Gasoline Range Organic (GRO) compounds. Determination of GRO compounds can be done either by Purge and Trap (P&T) concentration and GC/FID analysis or by Headspace sampling and GC/MS analysis (USEPA Method 5021). This application note will investigate Headspace injection techniques on GRO compounds in a water matrix.

Discussion:

The Markelov HS9000 headspace analyzer has several unique features that aid in headspace analysis. First, it has three distinct injection techniques: loop injection, timed injection and dynamic trapping. Second, it has electronic pressure and flow control. Finally, and most importantly, the HS9000 has the patented horizontal rotary mixing technique, Figure 1. This technique is important to GRO analysis as many GRO samples are unique in their matrix and viscosity and sampling the headspace at a horizontal angle allows for more headspace and therefore better sampling.

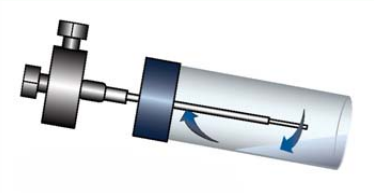

Figure 1: Horizontal Mixing Illustration

Gasoline Range Organic samples can range in contamination from extraordinarily high, ppm range, to extremely low, ppb levels. The HS9000 with its three sampling techniques is able to accommodate these diverse levels of contamination. This application note will present linearity, detection levels and precision and accuracy of all three of the sampling techniques.

Experimental:

The Markelov HS9000 was the sampling system utilized for this experiment. For the dynamic sampling technique, the headspace system was equipped with a Vocarb 3000 (K) trap. The

sweep time and sweep flow parameters were selected to displace the headspace volume by a factor of 2 in order to ensure that the entire equilibrated headspace vapor was concentrated. A volume of 30 milliliters was used for this analysis. The HS9000 dynamic sampling parameters are listed in Table 1.

For the loop injection technique, a 1ml loop was used. Both the loop and the timed injection had a 5 minute equilibration time. All sampling techniques used the rotary mixing process at a medium speed. While the samples were pressurized in order to perform the loop and timed injections. The loop and timed injection parameters are listed in Tables 2 and 3 respectively. The HS9000 was connected to an Agilent 7890GC and 5975MS for analysis. The GC was configured with an Rxi-624Sil MS 30m x 250µm x 1.4µm column. The GC/MS parameters are listed in Table 4.

Headspace	Markelov HS 9000
Trap Type	Vocarb 3000- Type “K”
Sample Vial Temperature	65°C
Sample Size	5 ml
Sample Equilibration Time	2.0 min
Mixing	Horizontal Rotary- Medium speed
Sample Mode	Adsorbent Trap
Trap Ready Temperature	35°C
Moisture Reduction Pre-Trap	Ambient
Sweep Flow Rate	15 ml/min
Sweep Time	2.0 min
Dry Sweep	1 min at 20 ml/min
Trap Inject (Desorb)	250°C for 1.0 min
Trap Bake Temperature	250°C for 8 min
Trap Bake Flow Rate	85 ml/min

Table 1: HS9000 Dynamic Sampling Parameters

Headspace	Markelov HS 9000
Loop Size	1 ml
Sample Vial Temperature	65°C
Sample Size	5 ml
Sample Equilibration Time	5.0 min
Mixing	Horizontal Rotary- Medium speed
Sample Mode	Loop Fill
Vial Pressurization	14 psi
Pressurization Equilibration Time	20 sec
Loop Fill	7 psi
Loop Equilibration Time	10 sec
Loop Injection Time	1 min
Pre-Trap Bake Temperature	200°C for 2 min

Table 2: HS9000 Loop Fill Sampling Parameters

Headspace	Markelov HS 9000
Sample Vial Temperature	65°C
Sample Size	5 ml
Sample Equilibration Time	5.0 min
Mixing	Horizontal Rotary- Medium speed
Sample Mode	Time Injection
Vial Pressurization	17 psi
Pressurization Equilibration Time	10 sec
On Column Injection Time	5 sec
Injection Solenoid Temp	100°C
Pre-Trap Bake Temperature	200°C for 2 min

Table 3: HS9000 Time Injection Sampling Parameters

GC/MS	Agilent 7890A/5975C inert XL
Inlet	Split/Splitless
Inlet Temp.	200ºC
Inlet Head Pressure	12.153 psi
Mode	Split
Split Ratio	40:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	45ºC hold for 1 min., ramp 15ºC/min to 220ºC, hold for 1.3 min.
Column Flow Rate	1.0mL/min
Gas	Helium
Total Flow	44.0mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-265
Scans	3.12 scans/sec
Solvent Delay	0.7 min

Table 4: GC/MS Experimental Parameters

The Gasoline Range Organic standard was obtained from Restek. The standard was Wisc PVOC/GRO and contained ten GRO analytes at a concentration of 100ppm each for a total concentration of 1000ppm. A six point curve was prepared and run for the dynamic headspace technique and five point curves were run for both the loop and timed injection headspace techniques. The dynamic headspace linear range was from 2ppb to 200ppb for the individual analytes (4ppb to 400ppb for p&m-Xylene) and 20ppb to 2ppm for the C6-C10 gasoline range. The loop and timed injection ranges were 100ppb to 2ppm for the individual analytes (200ppb to 4ppm for p&m-Xylene) and 1ppm to 20ppm for the C6-C10 gasoline range. Finally, seven consecutive low point calibration standards were run for each technique in order to establish MDLs and seven consecutive mid-point standards were run for each technique in order to verify

the precision and accuracy. The curve, MDL and precision and accuracy results are all listed in Table 5 while chromatograms of the various techniques are displayed in Figures 2, 3, 4, and 5.

Compound	Dynamic Headspace				Static Headspace by Loop				Static Headspace by Timed Injection			
	Curve %RSD	MDL	%RSD at 50ppb	% Rec'y at 50ppb	Curve %RSD	MDL	%RSD at 50ppb	% Rec'y at 50ppb	Curve %RSD	MDL	%RSD at 50ppb	% Rec'y at 50ppb
C6-C10	4.75	4.68	4.37	96.88	8.38	73.09	3.95	92.88	7.38	299.53	3.92	93.75
MTBE	5.84	0.45	4.40	96.45	5.31	5.27	3.16	103.70	2.73	12.33	3.34	98.15
Benzene	5.73	0.32	6.15	100.56	6.22	5.84	3.77	97.67	5.73	31.38	3.85	95.84
Toluene	4.09	0.29	5.18	99.91	8.13	8.56	3.92	95.56	6.60	31.33	3.90	95.96
Ethylbenzene	3.54	0.34	4.89	98.64	8.43	5.34	4.44	93.86	7.76	32.04	4.39	94.97
p&m-Xylene	5.43	0.84	4.63	99.85	8.91	11.79	4.52	92.88	9.08	61.58	4.47	93.90
o-Xylene	3.20	0.37	4.23	99.16	8.20	4.90	3.98	94.57	5.85	27.09	3.91	96.11
1,3,5-Trimethylbenzene	7.11	0.42	4.93	99.30	11.93	7.68	4.37	94.28	8.12	31.89	4.34	94.80
1,2,4-Trimethylbenzene	7.97	0.37	4.44	99.21	10.63	6.82	4.26	93.95	7.25	29.61	4.18	95.78
Naphthalene	6.11	0.39	2.26	90.75	9.53	4.33	2.84	98.95	9.74	32.22	2.86	98.18

Table 5: Experimental Result Summary

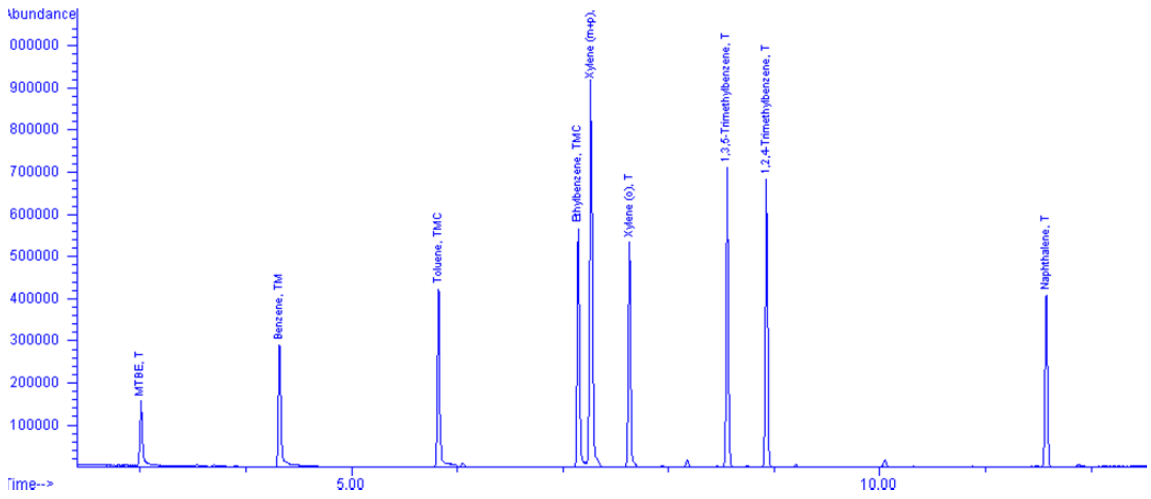

Figure 2: Chromatogram of 50ppb Standard by Dynamic Headspace

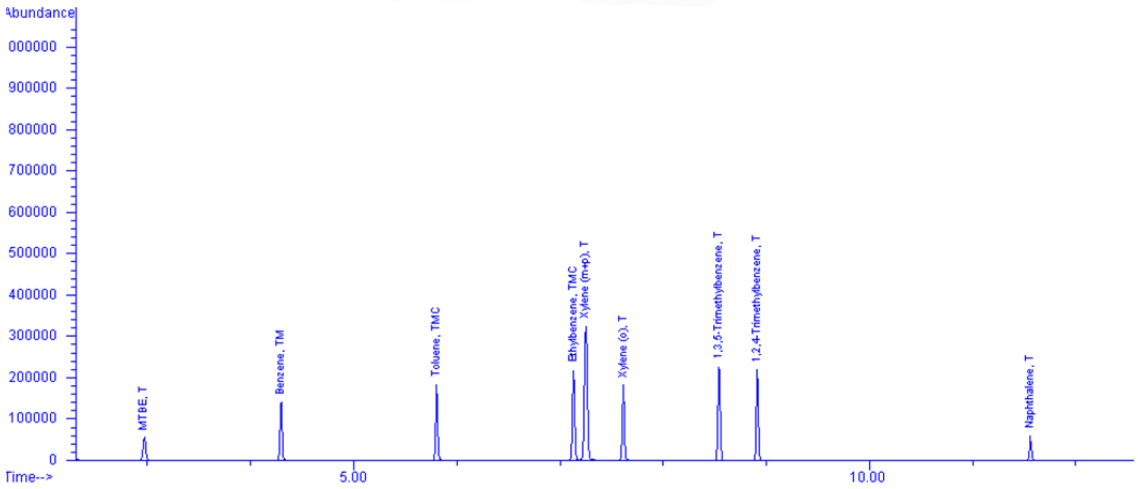

Figure 3: Chromatogram of 500ppb Standard by Static Headspace Loop Injection

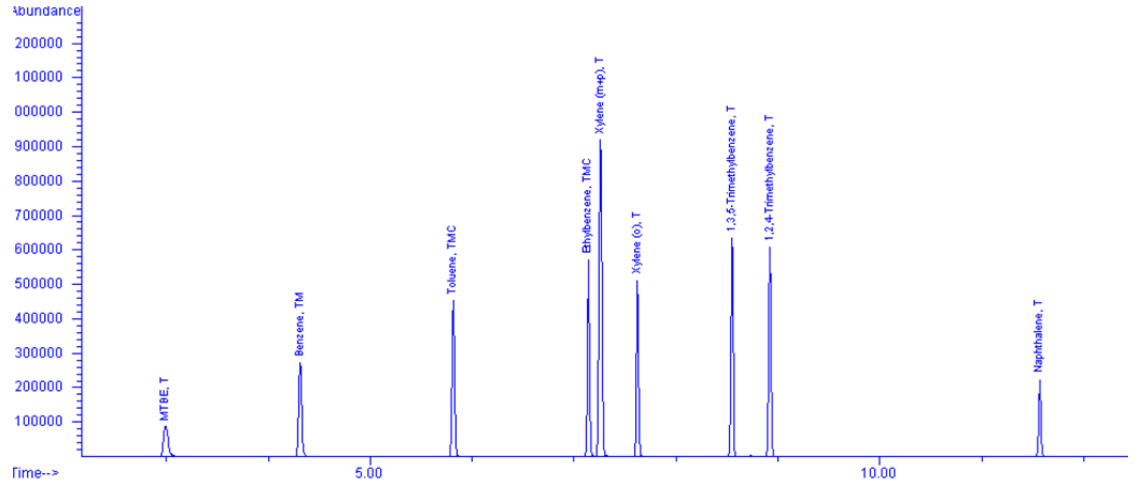

Figure 4: Chromatogram of 500ppb Standard by Static Headspace Timed Injection

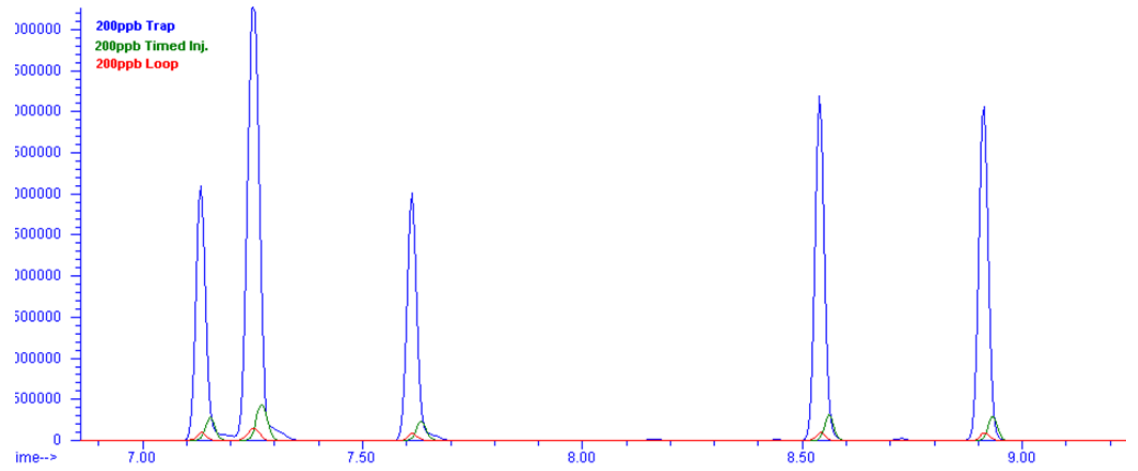

Figure 5: Overlay of 200ppb Standard by the Three Different Injection Techniques

Conclusion:

All three headspace sampling methods performed consistently and accurately. The dynamic headspace was the most sensitive with the curve linearity going down to 2ppb while the loop and timed injection techniques were similar in their respective sensitivities. Headspace sampling of Gasoline Range Organic compounds is an exceptional technique for this type of examination as dynamic headspace provides the sensitivity for low level detection while loop and timed injections enable the analysis of high levels of contamination without carryover concerns. Furthermore, the Markelov HS9000 with its horizontal sampling and three separate injection techniques proved to be an excellent system for this analysis.

References:

1. Volatile Organic Compounds in Soils and Other Solid Matrices using Equilibrium Headspace Analysis, Method 5021, Revision 0, December 1996.