Gasoline Range Organics (GRO) by Headspace/GC/FID

Application Note

Abstract

Recent oil spills in the Gulf of Mexico and the Great Barrier Reef have renewed interest in the rapid analysis of crude oil byproducts in aqueous and solid samples including sand and commercial fishing products. One of the crude oil constituents, gasoline range organics (GRO) is currently determined by either EPA Method 8015C[1] or Wisconsin's modified GRO[2].

A Teledyne Tekmar HT3™ Headspace Analyzer was used in both the static and dynamic modes to determine GRO in water using an Agilent GC/FID system. The static method was linear from 50 to 1000ppb and the dynamic from 2 to 200ppb. This calibration data meets the requirements for both EPA Method 8015C and Wisconsin's modified GRO.[2]

Figure 1: HT3™ Headspace Analzyer

Experimental-Instrument Conditions

The HT3™ was connected to an Agilent 6890A GC with FID for this study. The column used was a Restek Rtx®-VMS 30m x 0.32mm x 1.8µm (Restek Catalog No 19919). A constant flow of 5mL/min with a 20:1 spilt was used to assist the oven program perform adequate separation of the GRO standards in under 9 minutes. The total GC cycle time was less than 16 minutes. A 1mm ID inlet split liner was chosen to provide better performance for use with the headspace analysis.

The analytical trap used during the dynamic analysis was a #9 adsorbent trap (Teledyne Tekmar Catalog No 14-9908-003). This trap was chosen to meet the higher system pressure from an increased vial sweep flow of 200mL/min. This higher sweep flow was used to shorten the headspace cycle time to less than the GC cycle time of 16 minutes.

Table 1 displays the static and dynamic HT3™ conditions while Table 2 displays the GC/FID parameters.

Static (Loop)		Dynamic (Trap)	
Variable	**Value**	**Variable**	**Value**
Platen/Sample Temp	75°C	Platen/Sample Temp	75°C
Valve Oven Temp	150°C	Valve Oven Temp	150°C
Transfer Line Temp	150°C	Transfer Line Temp	150°C
Standby Flow Rate	50mL/min	Standby Flow Rate	50mL/min
Sample Equil Time	10.00 min	Sample Preheat Time	0.00 min
Pressurize	10 psig	Sweep Flow Rate	200mL/min
Pressurize Time	2.00 min	Sweep Flow Time	5.00 min
Pressurize Equil Time	0.20 min	Dry Purge Time	0.00 min
Loop Fill pressure	5 psig	Dry Purge Flow	0mL/min
Loop Fill Time	2.00 min	Dry Purge Temp	25°C
Inject Time	1.00 min	Desorb Preheat	245°C
Mixer	On	Desorb Temp	250°C
Mixing Time	2.00 min	Desorb Time	1.00 min
Mixer Level	Level 10	Trap Bake Temp	260°C
Mixer Stabilize Time	0.50 min	Trap Bake Time	2.00 min
Constant Heat Time	On	Trap Bake Flow	200mL/min
GC Cycle Time	16 min	Trap Type	#9

Table 1: Static and Dynamic HT3™ Parameters

Agilent GC/FID Parameters	
Column:	Restek® Rtx-VMS, 30m, 0.32mm ID, 1.8µm; Constant Flow 5.0mL/min
Oven Program:	35°C for 2.0 min; 36°C/min to 180°C, hold for 0 min: 20°C/min to 225°C, hold for 0.1 min, run time 8.38 min
Inlet:	Split Ratio 20:1, temperature 200 °C, Helium Carrier Gas
FID	320°C, Hydrogen Flow 35.0mL/min, Air Flow -400.0mL/min, Constant Column and Makeup Flow – 30mL/min

Table 2: GC/FID Parameters

Calibration

To evaluate the system's linearity, calibration standards were analyzed from 2-200ppb for the dynamic mode and 50-1000ppb for the static mode. These standards were prepared from a Restek PVOC/GRO mix containing methyl tert-butyl ether (MtBE), benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene.

MDLs and percent recoveries were determined by using 2ppb and 20ppb standards respectively in the dynamic mode. Since the static mode is used for higher concentrations these determinations were not employed as they are below the static calibration range.

The dynamic headspace method was performed with 5mL of the standard solution in a sealed 22mL headspace vial. The static headspace method was performed with 10mL of the standard solution in a sealed 22mL headspace vial.

Dynamic Calibration

The dynamic calibration data was processed using Agilent Chemstation software for the method analyte range of 2ppb to 200ppb.

EPA Method 8015C[1] allows the use of average calibration factors when the percent relative standard deviation (%RSD) is less than 20%. When the %RSD is greater than 20%, linearity through the origin cannot be assumed and other calibration options may be used, such as linear not through the origin. To be used for quantitative purposes EPA Method 8000.[3] requires the correlation coefficient to be greater than 0.99.

The Wisconsin modified GRO[2] method uses the external standard method of the sum of the total response within the range of methyl tert-butyl ether to naphthalene. The analytes are calculated from the linear regression. The correlation coefficient must be greater than 0.99.

Table 3 displays the %RSD and linear correlation using the external standard method for the 2ppb to 200ppb standards.

Analyte	%RSD	Linear Correlation
MtBE	15.1	0.99601
Benzene	11.4	0.99886
Toluene	11.7	0.99888
Ethylbenzene	11.6	0.99890
m-, p-Xylene	12.0	0.99882
o-Xylene	14.2	0.99851
1,3,5-Trimethylbenzene	12.2	0.99874
1,2,4-Trimethylbenzene	11.1	0.99860
Naphthalene	16.8	0.99745
Sum of All Compounds	13.5	0.99882

Table 3: %RSD and Linear Correlation Coefficient for the 2ppb to 200ppb Calibration Curve by the External Standard Calibration

Dynamic MDL and Recovery

The MDL was calculated from 8 replicates of a 2ppb standard. The percent recovery was calculated from 8 replicates of a 20ppb standard. Table 4 presents these values calculated as an external standard method by both the average response factor and from the linear curve.

	Average Response Factor		Linear Curve	
Compound	2ppb MDL	20ppb Recovery	2ppb MDL	20ppb Recovery
MtBE	1.25	94.4	1.53	95.1
Benzene	0.53	94.3	0.51	92.9
Toluene	0.51	96.3	0.46	93.5
Ethylbenzene	0.48	96.6	0.44	94.1
m-. p-Xylene	0.53	96.4	0.48	94.0
o-Xylene	0.62	96.3	0.59	94.0
1,3,5-Trimethylbenzene	0.46	98.8	0.41	95.6
1,2,4-Trimethylbenzene	0.89	97.5	0.84	96.1
Naphthalene	0.44	89.6	0.71	92.8

Table 4: MDL and 20ppb Recovery Data Calculated by External Standard

Static Calibration

The static calibration data was processed using Agilent Chemstation software for the method analyte range of 50ppb to 1000ppb.

EPA Method 8015C[1] allows the use of average calibration factors when the percent relative standard deviation (%RSD) is less than 20%. When the %RSD is greater than 20%, linearity through the origin cannot be assumed and other calibration options may be used, such as linear not through the origin. To be used for quantitative purposes EPA Method 8000 requires the correlation coefficient to be greater than 0.99.[3]

The Wisconsin modified GRO[2] method uses the external standard method of the sum of the total response within the range of methyl tert-butyl ether to naphthalene. The samples are calculated from the linear regression. The correlation coefficient must be greater than 0.99.

Table 6 displays the %RSD and linear correlation using both the external standard method for the 50ppb to 1000ppb standards.

	External Standard	
Compound	%RSD	Linear Correlation
MtBE	3.5	0.99880
Benzene	2.0	0.99960
Toluene	2.0	0.99966
Ethylbenzene	2.1	0.99965
m-, p-Xylene	2.3	0.99958
o-Xylene	2.8	0.99917
1,3,5-Trimethylbenzene	3.3	0.99888
1,2,4-Trimethylbenzene	4.7	0.99856
Naphthalene	7.8	0.99388
Sum of All Compounds	2.8	0.99924

Table 6: %RSD and Linear Correlation Coefficient for the 50ppb to 1000ppb Calibration Curve by External Standard Calibration

The chromatogram of the 50ppb standard from both the static and the dynamic methods were compared in Figure 1. This indicates the increased sensitivity that the dynamic headspace method offers versus the static method.

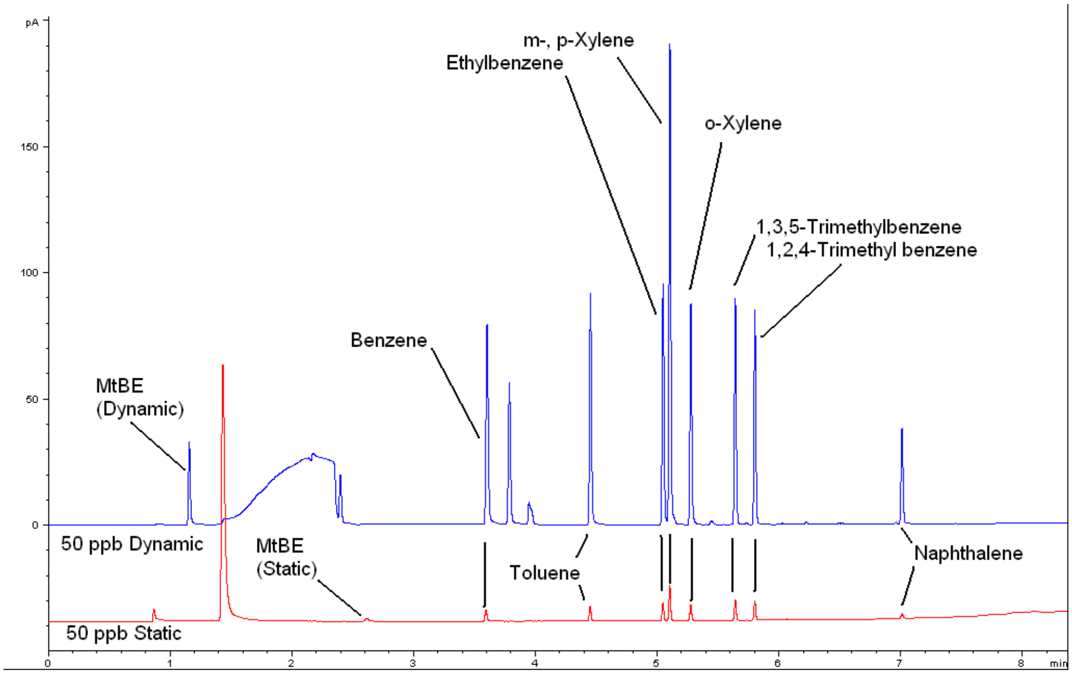

Figure 1: Same Scale Comparison of a 50ppb Standard with the Static Headspace Method (Bottom) to a 50ppb Standard with the Dynamic Headspace Method (Top)

Conclusions

The HT3™ Headspace Analyzer provides the environmental laboratories performing GRO analysis the ability to detect GRO analytes from 2ppb to 1000ppb and greater with a single headspace instrument when used in conjunction with a GC with a FID detector. The analysis can be completed in less than 16 minutes per sample increasing sample throughput for GRO analysis.

The headspace GC/FID methods fall within the linearity requirements of EPA Method 8015C[1] and Wisconsin GRO method[2].

References

1. USEPA Method 8015C, Nonhalgenated Organics by Gas Chromatography, Revision 3, February 2007.
2. PUBL-SW-140 Modified GRO Method for Determining Gasoline Range Organics, Wisconsin DNR, September 1995.
3. USEPA Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996