TELEDYNE INSTRUMENTS
Tekmar
A Teledyne Technologies Company

New Method for Fuel Oxygenates by Headspace Sampling

HT3 Application Note

Introduction ▼

Oxygenated compound have been added to gasoline for years. The benefits include better combustibility characteristics of the gasoline, resulting in a cleaner burning fuel. However, if or when these oxygenates leak into the environment, they easily dissolve into water. These compounds can render groundwater unsuitable for humans or animals. To ensure that the groundwater is clean from these unwanted compounds, the EPA has mandated testing.

Headspace analysis of volatile compounds offers many benefits. Some examples are a cleaner analysis, potentially quicker run times, and elimination of possible system contamination from high concentrated samples. Classical Headspace methods have been challenged with oxygenated compounds. Typically, headspace samplers cannot achieve the needed low-end detection required by the testing laboratory.

A new headspace sampler has been developed for the testing of oxygenates and is capable of unprecedented low-end detection. By incorporating EPA approved trapping techniques, the HT3 Headspace sampler is now capable of offering purge & trap analytic performance. This poster will describe the methodology and present sub ppb MDLs for most of the Method 8260 compound list.

Experimental ▼

The fuel oxygenates were analyzed via the Dynamic Headspace option from the HT3 which provides significantly lower detection limits. The Dynamic option continually sweeps the headspace of the vial, depositing and concentrating the volatile compounds onto an analytical trap. A five-point calibration curve was used to determine the capabilities of Dynamic Headspace, which ranged from 250 ppb to 5 ppm for Ethanol, 50 ppb to 1 ppm for *tert*-Butyl alcohol (TBA), and 2 ppb to 200 ppb for Diisopropyl ether (DIPE), Ethyl-*tert*-butyl ether (ETBE), Methyl-*tert*-butyl ether (MTBE), and *tert*-Amylmethyl ether (TAME). These compounds were analyzed via the Teledyne Tekmar HT3 coupled to a GC/MS unit. The parameters for the HT3 Headspace autosampler and GC/MS are listed in the following tables. NOTE: The standard circular mixer was replaced with the Teflon triangular mixer for a more vigorous agitation. Also, the concentration of TBA and Ethanol are typically five times higher than that of the other fuel oxygenates, so keep this in mind when making up your samples.

Table 1: HT3 Dynamic Headspace Parameters

Variable	Value
Headspace Vials	22 mL, PTFE Silicone Septa
GC Cycle Time	35.00 min.
Valve Oven Temp.	110 °C
Transfer Line Temp.	110 °C
Standby Flow Rate	50 mL/min.
Trap Standby Temp.	30 °C
Platen/Sample	75 °C for 0.10 min.
Preheat Mixing	Level 5, 10.00 min.
Preheat Mixer Stabilize Time	0.50 min.
Sweep Flow	50 mL/min. for 8.00 min.
Trap Sweep Temp.	0 °C
Dry Purge	50 mL/min. for 1.00 min.
Dry Purge Temp.	25 °C
Desorb Preheat	220 °C
Desorb	250 °C for 2.00 min.
Trap Bake Temp.	270 °C
Trap Bake	400 mL/min. for 4.00 min.

Table 2: GC/MS Parameters

Variable	Value
Column Type	60 m x 0.25 mm x 1.4 µm film
Column Oven and Injection Temp.	40 °C; 220 °C
Pressure and Split Ratio	19.6 psi; 60:1
Total Flow of Carrier Gas	He @ 75.6 mL/min.
Oven Temperature Program	40 °C (2.0 min.) → 180 °C @ 12 °C/min. → 225 °C @ 45 °C/min. (5.0 min.)
Ion Source Temperature	220 °C
Scan Time and Speed	0.50 - 26.40 min.; 1000
Detector Gain and Mass Range	1.0 kV; 35 - 350

Results ▼

The RSDs were calculated from the response factors of the calibration curve and the compounds were all below 16% and the majority of the compounds provided MDLs at and below 1 ppb, with the exception of the notoriously difficult TBA and Ethanol. This data is shown in the table below. The GC time is done in less than 11 minutes with excellent peak separation as the graph following the table shows.

Table 3: Dynamic Curves along with Calculated MDL Levels

Compounds	Dynamic %RSDs	Dynamic MDLs (ppb)
DIPE	9.8	0.462
Ethanol	15.5	67.9
ETBE	11.5	0.437
MTBE	13.7	1.01
TAME	11.6	0.344
TBA	11.8	12.6

Figure 1: Ethanol Calibration Curve

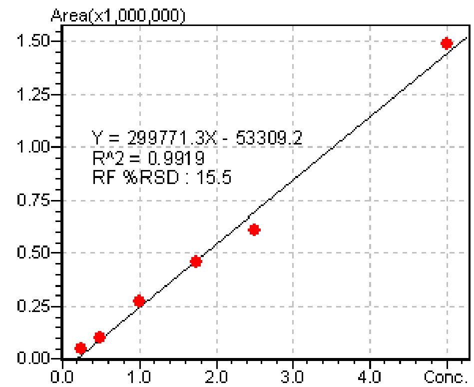
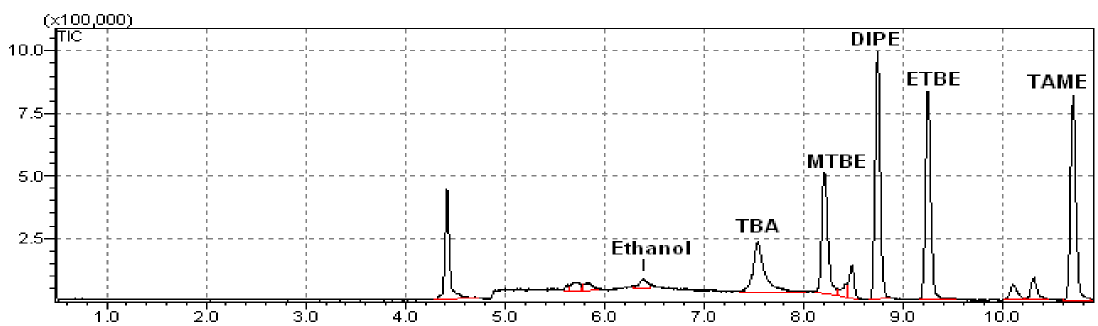


Figure 2: Example Chromatogram of a 10/50 ppb Standard Run.



Conclusion ▼

The critical conditions that have been optimized for this method are temperature, mixing method and flow. All three of these criteria are controlled, regulated, and modified with extreme precision. The increased sensitivity is due to the trapping technology once only used by classic purge and trap techniques. With all of these improvements, the method developed on the HT3 achieved unprecedented sub ppb MDLs for headspace analysis. By combining a Mass Flow Controller, Pressure Transducer, Temperature Control and Trapping System, the HT3 is capable of analyzing very difficult samples with ease.