

Analysis of Fuel Oxygenates by U.S. EPA Method 8260B Using Headspace Trap with GC/MS

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Introduction

The Clean Air Act amendments of 1990 require that oxygenated compounds be added to gasoline to produce fuel with increased oxygen content. Oxygenated fuel is desirable because it burns more completely, thereby reducing tailpipe emissions. The most commonly used fuel oxygenate additive is methyl tertiary butyl ether (MTBE).

The transportation, transfer and especially storage of oxygenated fuel in underground tanks present a risk to the environment. Leaks and spillage can contaminate ground, surface and waste waters, representing a significant threat to drinking-water supplies. Consequently, there is an increasing need for the analysis of MTBE in water by many state and federal agencies. In addition,

there are new regulations requiring that MTBE be phased out, so the detection and quantification of other fuel oxygenates must also be considered.¹

This field application report describes the use of a PerkinElmer® TurboMatrix™ HS-110 Trap and Clarus® 500 GC/MS optimized for low-level determination of fuel oxygenates by U.S. Environmental Protection Agency (EPA) Method 8260B. The headspace trap uses heat to extract (partition) the compounds out of the water into an equilibrium headspace, instead of purging. This transports a significant and highly reproducible fraction of the analytes from the sample onto a thermal desorption trap, where they are retained and focused on a multi-bed adsorbent packing before injection onto the GC column. The headspace trap offers operators low detection limits, excellent linearity and high throughput for fast sample turnaround.

Experimental

Table 1. Instrument Setup Parameters.

Headspace Trap:	PerkinElmer TurboMatrix HS-110 Trap
Needle Temperature:	90 °C
Transfer Line Temperature:	120 °C
Oven Temperature:	80 °C
Trap Low Temperature:	40 °C
Trap High Temperature:	280 °C
Dry Purge Time:	5 min
Trap Hold Time:	6 min
Desorb Time:	0.5 min
Thermostat Time:	10 min
GC Cycle Time:	40 min
Pressurization Time:	1 min
Decay Time:	2 min
Outlet Split Flow:	20 mL/min
Column Pressure:	25 psi
Vial Pressure:	35 psi
Desorb Pressure:	10 psi
Transfer Line Column:	Deactivated Fused Silica 20 m x 320 µ (PerkinElmer part number N9301357)
Gas Chromatograph:	PerkinElmer Clarus 500
Headspace Connector:	Universal Connector (PerkinElmer part number N302149)
Oven Program:	40 °C hold 0 min, 10 °C/min to 100 °C, then 30 °C/min to 240 °C
Column:	Elite Volatiles* - 30 m x 250 µ x 1.4 µ (PerkinElmer part number N9316388)
Mass Spectrometer:	PerkinElmer Clarus 500 MS
Mass Range:	35-300 u
Transfer Line Temperature:	200 °C
Source Temperature:	200 °C
Multiplier:	350
Software:	TurboMass™ 5.2 with Environmental Reporting

Results

The heated headspace-trap transfer line is connected to the GC injector port with an injector adapter (PerkinElmer part number B0505266). The headspace-trap fused-silica transfer line (PerkinElmer part number N9301357) is connected through the injector port so approximately 20 cm resides in the oven. This is connected to the GC column by using a universal capillary-column connector (PerkinElmer part number N9302149). The rest of the method setup parameters are found in Table 1.

Following U.S. EPA 8260B method requirements, the system was tuned using 25 µg/L (ppb) of BFB (4-bromofluorobenzene). There are nine EPA BFB ion ratios that were checked for compliance (Figure 1).

19 compounds were analyzed and examined for detection limits, linearity and throughput. Linearity was checked using a five-level calibration curve in DI water. The range was 0.5-100 µg/L. Ethanol and tert-butyl alcohol were calibrated from 5-200 µg/L. Table 2 displays the list of components analyzed, demonstrates the quantitative precision and linearity of the method. The %RSD (based on relative response factors) for all analytes was within the 15% U.S. EPA 8260B method requirement mandated in environmental labs.

All 19 compounds were identified at all 5 calibration levels and a chromatogram of the 25 µg/L (mid-level calibration) standard is shown in Figure 2. All standards were prepared with appropriate Method 8260B internal

standards and surrogates. Inserted into Figure 2 is an extracted ion chromatogram of 5 µg/L of ethanol (the lowest level standard), which demonstrates excellent signal to noise at this concentration. Ethanol is challenging at low concentration levels, when using traditional purge-and-trap technology. Fuel oxygenates such as ethanol are highly soluble in water and difficult to purge. This application illustrates the low detection limits achieved for these difficult components using the new headspace-trap technology.

The TurboMatrix Headspace Trap system offers a standard 12-position thermostatted chamber. This allows multiple samples to be heating at the same time so, as soon as the GC becomes ready, the next sample can be injected. The instrument automatically calculates PII (period from injection to injection) time, making this 12-position overlapped thermostating the most efficient use of valuable time while running multiple samples.

The TurboMatrix Headspace Trap system uses elevated temperatures to partition the analytes of interest into the vapor phase for analysis. This offers a unique advantage over traditional purge-and-trap concentrators. The headspace trap only transfers the volatile analytes – not the solid or liquid phase – to the GC. In addition, the system automatically bakes out the flow path between injections. This results in very low carryover and minimum downtime, increasing laboratory productivity and eliminating the contamination problems that many environmental laboratories contend with when using purge-and-trap concentrators. Figure 3 is a demonstration of a typical environmental sample analyzed using a TurboMatrix Headspace Trap. This concentration level would typically cause significant carryover problems with purge-and-trap concentrators. The TurboMatrix Headspace Trap demonstrated less than 0.2% carryover on the next injection.

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Test: BFB 624/8260 TEST Result: Test Passed OK

Mass	Reference Mass	Relative Abundance	Criterion	Pass/Fail
			COMBINE(2893.2900)(2841.2876)	Pass
50	95	15.9%	>= 15% and <= 40%	Pass
75	95	45.4%	>= 30% and <= 60%	Pass
95	BPI	100%	= 100%	Pass
96	95	5.9%	>= 5% and <= 9%	Pass
173	174	0.2%	< 2%	Pass
174	95	60.7%	> 50% and < 100%	Pass
175	174	5.9%	>= 5% and <= 9%	Pass
176	174	96.7%	>= 95% and < 101%	Pass
177	176	5.6%	>= 5% and <= 9%	Pass

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Figure 1. EPA instrument-tuning criteria.

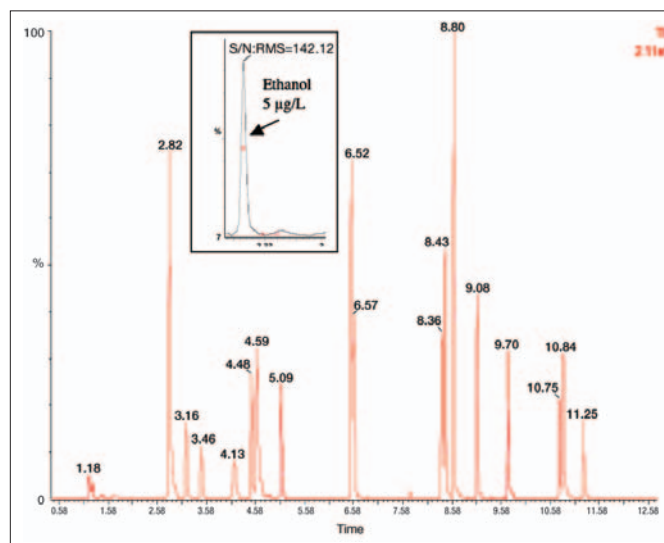


Figure 2. Fuel oxygenate chromatogram – 25 µg/L.

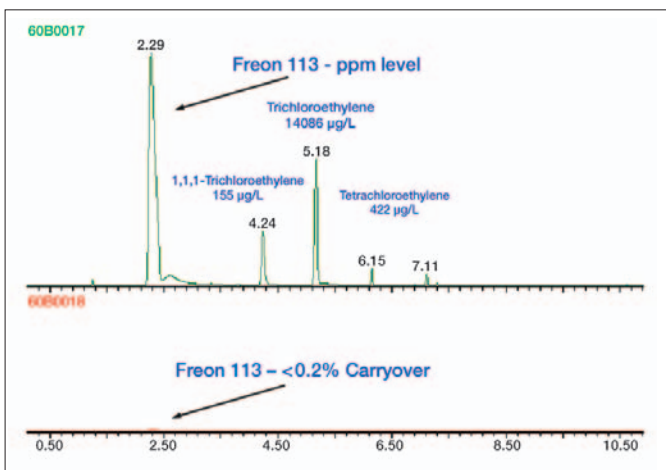


Figure 3. Carryover demonstration of the TurboMatrix Headspace Trap for a typical, undiluted, unknown sample.

Conclusions

U.S. EPA 8260B is a challenging method used in the majority of U.S. and many international environmental laboratories for the analysis of VOCs. It is a complex method that requires multiple quality criteria be passed throughout the analysis. Fuel oxygenates have traditionally been difficult to analyze using purge-and-trap concentrators. As demonstrated here, the PerkinElmer Clarus 500 GC/MS configured with a TurboMatrix HS-110 Trap meets all the 8260B method requirements for the analysis of fuel oxygenates. In addition, the TurboMatrix HS Trap offers the following advantages over a conventional purge-and-trap concentrator:

- Easy and convenient sample preparation
- Good response with poor purging compounds
- Increased sample throughput by overlapped thermostating
- Eliminates many of the carryover contamination problems seen with the purge-and-trap concentrators
- No cross-contamination of samples from using the same purge vessel

References

1. <http://www.arb.ca.gov/fuels/gasoline/cbgmtbe.htm>
2. *Test Methods for Evaluating Solid Waste*; U.S. Environmental Protection Agency, National Technical Information Service: Washington, DC, Rev. 2, Vol. B. (1996).

Table 2. Linearity and Relative Standard Deviation (RSD) Calculations.

Number	Name	%RSD*	Linearity
1	Ethanol	11.82	0.99977
2	TBA (tert-Butyl alcohol)	3.73	0.99906
3	Hexane	10.10	0.99929
4	MTBE	11.82	0.99887
5	DIPE	3.73	0.99953
6	ETBE	10.10	0.99906
7	1,2-Dichloroethane	3.73	0.99885
8	tert-Amyl alcohol	9.01	0.99679
9	Benzene	6.57	0.99022
10	TAME	6.17	0.99921
11	Toluene	9.53	0.99994
12	1,2-Dibromomethane	4.96	0.99937
13	Chlorobenzene	6.60	0.99989
14	Ethylbenzene	13.30	0.99966
15	m,p-Xylene	3.77	0.99987
16	o-Xylene	3.54	0.99923
17	1,3-Dichlorobenzene	3.50	0.99901
18	1,4-Dichlorobenzene	5.08	0.99918
19	1,2-Dichlorobenzene	5.82	0.99991

Initial Calibration Curve 0.5-100 µg/L Ethanol, and TBA 5-200 µg/L

*Traditional U.S. EPA internal standard calibration method.

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The data presented in this Field Application Report are not guaranteed. Actual performance and results are dependent upon the exact methodology used and laboratory conditions. This data should only be used to demonstrate the applicability of an instrument for a particular analysis and is not intended to serve as a guarantee of performance.