Application Note 10342

Automated Determination of Gasoline Range Organics (GRO) in Water Via Valve-and-Loop Headspace GC

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Key Words
Petroleum, hydrocarbons, water, flame ionization detector, headspace, EPA Method 5021A, EPA Method 8015D

Goal
The purpose of this application note is to optimize the analytical set-up for the determination of gasoline range organics in water.

Introduction
Oil spills of varying magnitudes can be a serious source of contamination of the surrounding environment, in particular for bodies of water. Water pollution can pose a serious threat to the affected ecosystem and the encircling area habitability. For this reason, it is important to have an accurate and effective system for screening and evaluating possible contaminations.

Markers of possible water contaminations are gasoline range organics (GRO) which correspond to the range of alkanes from C_6 to C_{10} and covering a boiling point range of approximately 60 °C – 170 °C[1]. EPA method 5021A[2] is applicable to a wide range of organic compounds, including GRO, that have sufficiently high volatility to be effectively removed from soil/sediment, solid waste, aqueous, and water-miscible liquid samples using an equilibrium headspace procedure.

Similar to EPA method 8015D[3], a simple and reliable GC/FID system could then be used for the quantification of volatile organics or as a screening technique prior to headspace GC/MS quantitative analysis.

The headspace analysis can be performed with a chromatographic system composed of a Thermo Scientific™ TriPlus™ 300 Headspace autosampler and a Thermo Scientific™ TRACE™ 1310 GC controlled by the Thermo Scientific™ Dionex™ Chromeleon™ 7.2 Chromatography Data System (CDS) software. This system allows sample analysis and data processing to occur in an automated, reproducible, and reliable manner.

Equipment
A TriPlus 300 Headspace autosampler and the TRACE 1310 GC are used for the analysis. The data are collected and processed with Chromeleon 7.2 CDS. The system is equipped with one Instant Connect Split/Splitless (SSL) injector with a dedicated headspace liner (P/N 453A1335) and an Instant Connect Flame Ionization Detector (FID).

A Thermo Scientific™ TRACE™ TR-1 column was used with the following dimensions: 30 m × 0.32 mm × 3 µm (PN 260A395P).

The standards used for calibration are acquired from Restek™ (PVOC/GRO mix (Wisconsin) PN 30095). The calibration curves are made with seven levels at the following concentrations for each analyte: 10 ppb, 50 ppb, 100 ppb, 1 ppm, 5 ppm, 10 ppm, and 100 ppm.

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Analysis

The sample analyzed is 5 mL of water placed into a 20 mL vial. Vials are tightly closed with magnetic caps (Thermo Scientific™ La-Pha-Pack™ Aluminum Crimp Seals, PN 18091307). The TriPlus 300 Headspace sampling system parameters are configured as follows:

- Equilibration time of the sample is 25 min with vial shaking set to high
- Oven temperature set to 85 °C
- Manifold temperature set to 95 °C
- Transfer line temperature set to 95 °C
- Pressurization mode is set to **Pressure**; pressure is set to 1 bar and the pressure equilibration time to 0.2 min
- Loop filling mode is set to **Pressure**; pressure is set to 0.5 bar with an equilibration time of 0.1 min
- Loop size is 1 mL
- Injection mode is **Standard**, and injection time is set to 0.5 min
- Sample line is purged after injection for 1 min at 100 mL/min
- Vial venting is set to **On**

The TRACE 1310 GC parameters are configured as follows:

- Starting temperature at 50 °C, hold 1 min, then raise at 15 °C/min up to 220 °C, hold 2 min.
- SSL inlet temperature is set to 150 °C, split mode with split flow 60 mL/min with a split ratio of 20:1
- Carrier used is helium, with a constant flow of 3 mL/min
- FID temperature is set to 300 °C

Results and Discussion

Table 1 reports the calibration results for all the compounds tested. All the calibration curves show outstanding linearity in the tested range.

Table 1. Calibration results for all compounds.

Peak Name	Number of Points	Coeff. of Determination
MTBE	7	0.99999
Benzene	7	0.99975
Toluene	7	0.99980
Ethylbenzene	7	0.99986
m-Xylene/p-Xylene	7	0.99989
o-Xylene	7	0.99992
1,3,5-Trimethylbenzene	7	0.99997
1,2,4-Trimethylbenzene	7	0.99998
Naphthalene	7	0.99987

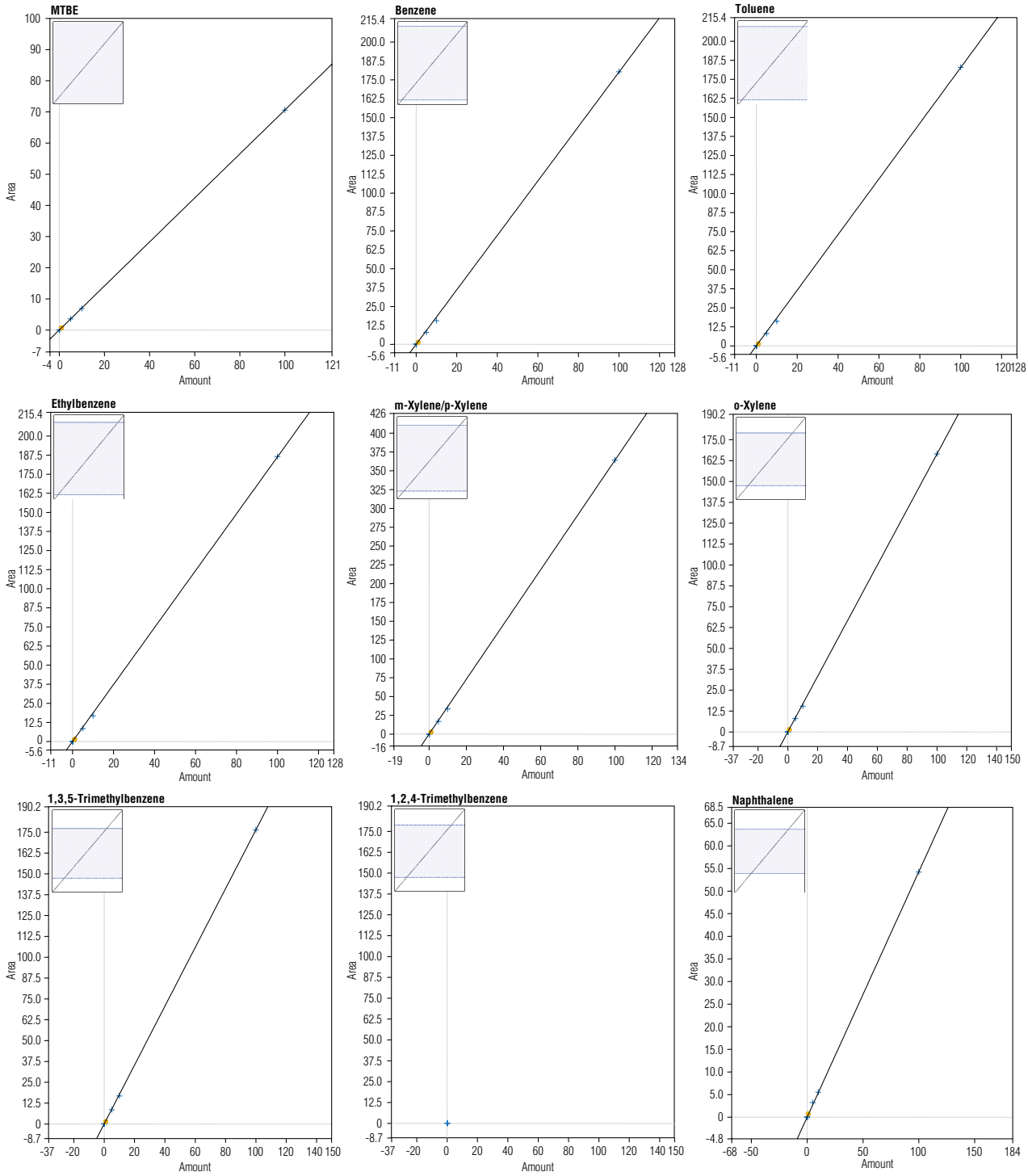

Figure 1. Calibration curves of some of the target analytes.

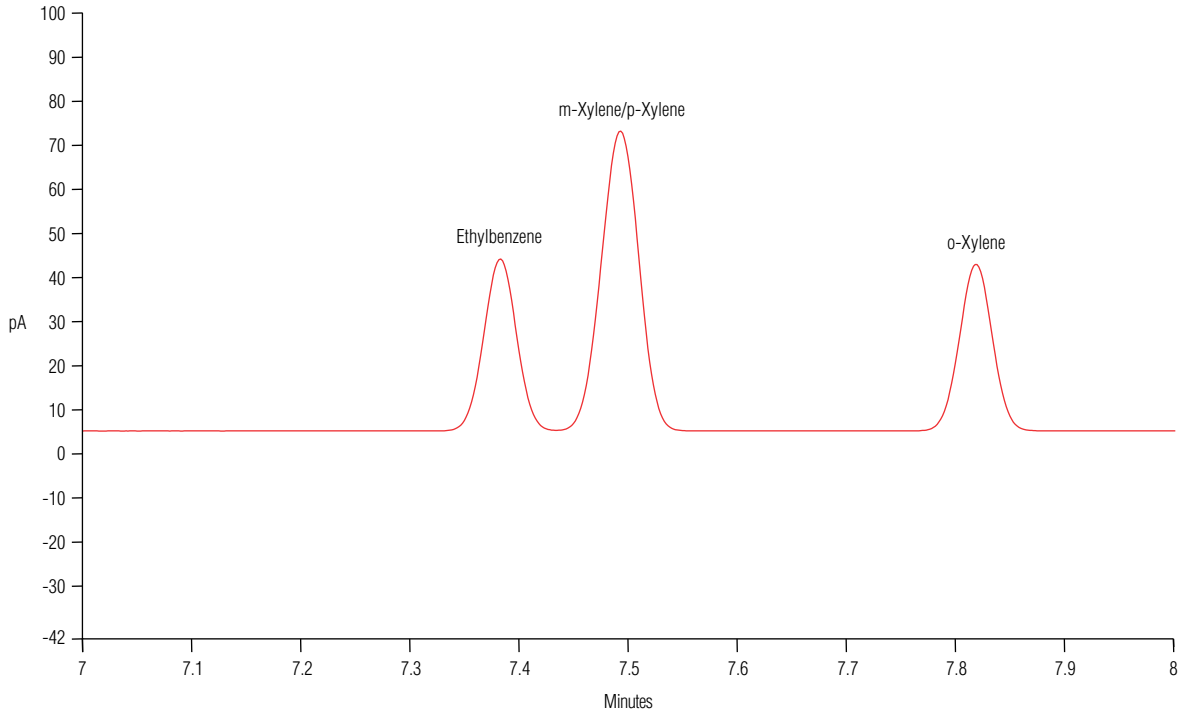

Figure 2. Separation of the couple ethylbenzene m/p-xylene at a resolution of 1.83.

Table 2. Repeatability results of each GRO compound at 1 ppm in water. Peak Area is expressed in pA*sec.

	MTBE	Benzene	Toluene	Ethylbenzene	m/p-Xylene	o-Xylene	1,3,5-Trimethylbenzene	1,2,4-Trimethylbenzene	Naphthalene
1	57.3628	55.8949	59.9575	59.6926	126.4131	74.4254	66.2386	77.0404	56.238
2	57.0797	55.4711	59.4999	59.3961	125.7007	74.0777	65.9278	76.7329	56.1561
3	57.5383	56.4514	60.8489	60.9327	128.8599	75.7043	67.8679	78.6368	56.355
4	57.6155	56.1589	60.3285	60.3256	127.5803	75.0778	67.0354	77.8603	56.5539
5	57.102	55.7743	59.9651	59.9814	126.7492	74.5956	66.5793	77.2604	55.9639
6	57.4345	56.2741	60.466	60.4806	127.7841	75.1562	67.2012	77.7268	56.0468
7	58.2604	57.1632	61.5558	61.641	130.1047	76.5622	68.5266	79.4365	56.7669
8	58.7969	57.4769	61.8347	61.8393	130.5417	76.8693	68.6879	79.5756	57.3098
9	57.3306	57.3574	61.3496	61.0969	128.8684	75.6615	67.4593	78.0111	55.9104
Standard Deviation	0.5641	0.7267	0.8032	0.8457	1.6559	0.9457	0.9607	1.0069	0.4498
Relative Standard Deviation	0.98%	1.29%	1.32%	1.40%	1.29%	1.26%	1.43%	1.29%	0.80%

Figure 2 shows good separation of the couple ethylbenzene m/p-xylene, whose resolution is 1.83.

Repeatability has been evaluated for each compound and the results are reported in Table 2.

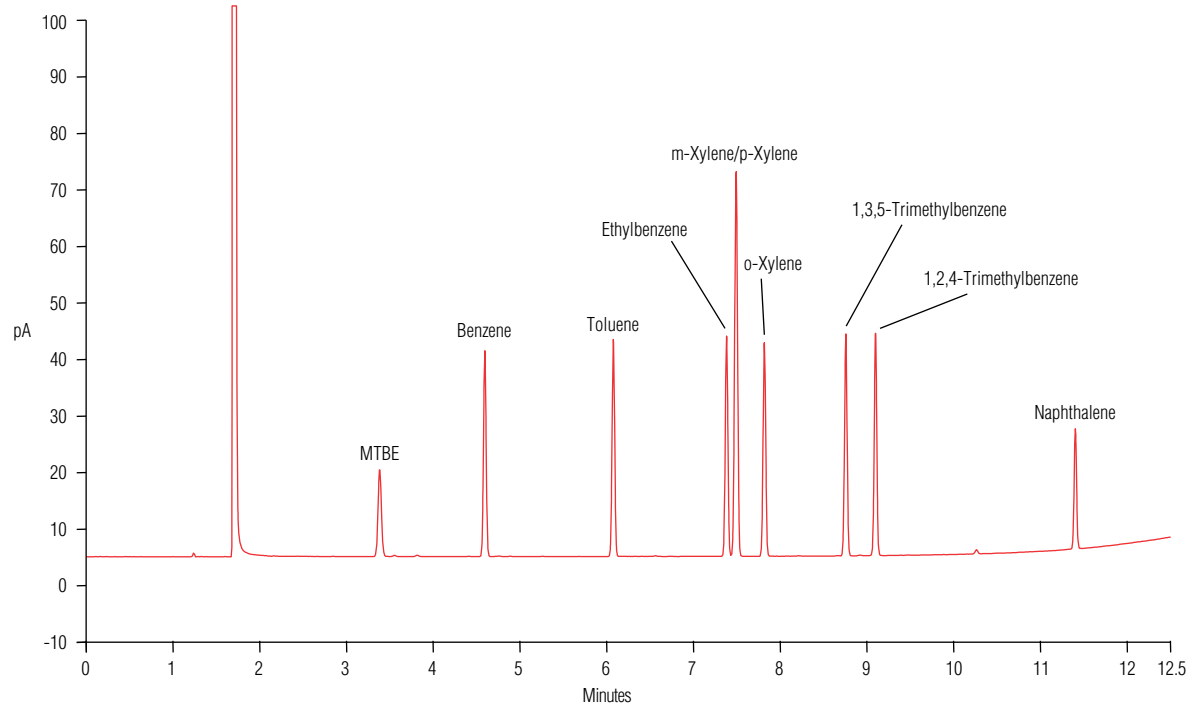

Figure 3. PVOC/GRO mix (Wisconsin) standard in water at 1 ppm.

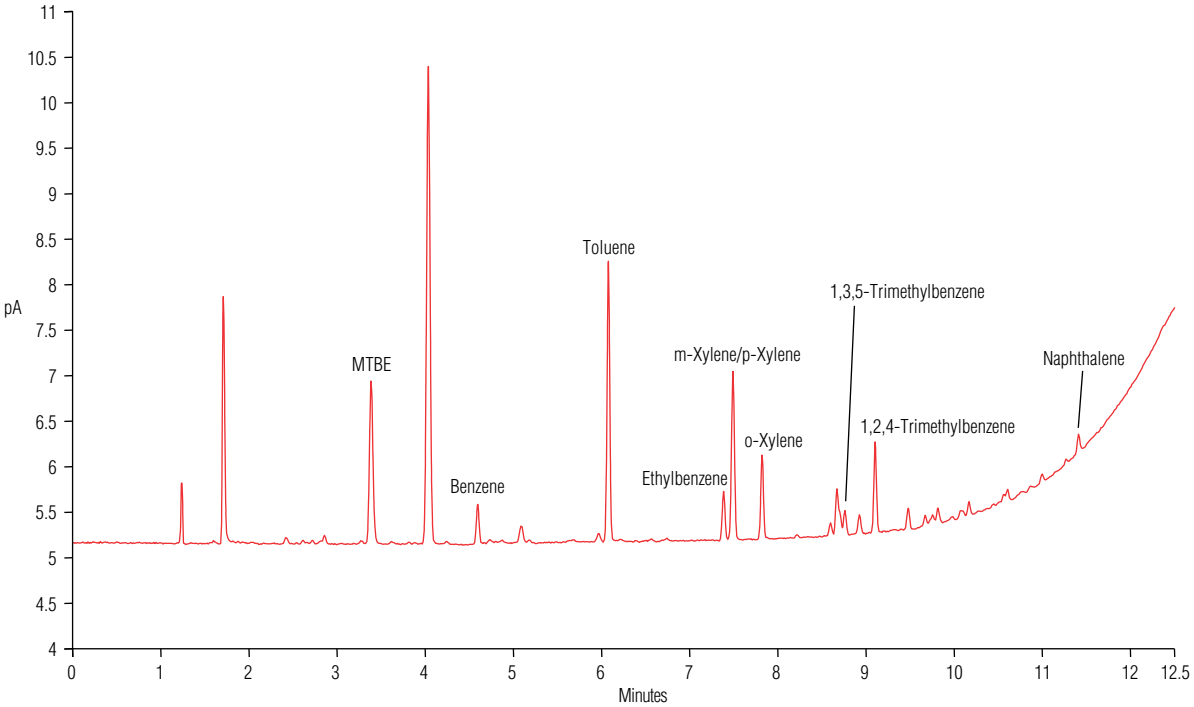

Figure 4. Chromatogram of tap water spiked with gasoline.

Blank samples have been analyzed after each sequence of at least 10 samples, and they showed a clear baseline. Figure 3 shows a chromatogram of the Wisconsin standard mix at the 1 ppm calibration point, and Figure 4 shows the chromatogram of a tap water sample spiked with gasoline.

Conclusion

As the results confirm, the system comprised of the TriPlus 300 Headspace autosampler, the TRACE 1310 GC, and Chromeleon CDS is a reliable and automated solution for Gasoline Range Organics in water. With its 120-vial sample tray and the large 18-vial incubation oven overlap capacity, the system guarantees excellent throughput. The inertness of the entire sample path and high temperature capability eliminate any carryover effect, ensuring the highest sample integrity and results consistency. The optional barcode capabilities of the autosampler and the accurate auditing capabilities of Chromeleon CDS also ensure the highest data quality and traceability.

References

1. "Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils," API. Publication Number 4599, *American Petroleum Institute*, March 1994.
2. EPA Method 5021A.
3. EPA Method 8015D.

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