Optimized Analysis of Gasoline (BTEX) in Water and Soil Using GC/FID with Purge and Trap

Application Note
228-324

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Abstract

Gas chromatography with purge and trap analysis using their HP-1 capillary column and the Agilent 5890 Series II gas chromatograph/flame ionization detector was done to determine gasoline components in contaminated water and soil in accordance with modified EPA Methods 8015/8020. Purge and trap and gas chromatograph parameters were optimized for accurate quantitation of gasoline range organics (aliphatics, aromatics, and oxygenates) and to increase analysis speed.

Key Words

- EPA Methods 8015/8020
- Gasoline
- BTEX
- Purge and Trap
- GROs
- GC/FID analysis
- LUST

Introduction

Modified EPA Methods 8015/8020 are used to determine gasoline and gasoline components in water and soil by capillary gas chromatography (GC) with a flame ionization detector (FID) or photoionization detector (PID). The hydrocarbons in gasoline encompass a wide range, from butane to decane and benzene to naphthalene, and cover a boiling point range of 50°C to 281°C. For such complex mixtures, an efficient purge and trap (P and T) system is required to concentrate samples for high-resolution gas chromatography. Detection is achieved using an FID, and quantitation is based on FID response to a gasoline standard. Other light petroleum products that can be determined in the same manner include paint stripper, Stoddard solvent, mineral spirits, petroleum naphtha, and aviation jet fuels using the pattern recognition technique.

The analysis of gasoline components, e.g., gasoline range organics (GROs), and benzene, toluene, ethylbenzene, and xylenes (BTEX) in particular is of great importance because BTEX is frequently used as a marker in the identification of gasoline-type products. Subsequently, the analysis of BTEX is often used to determine the composition and the origin of such products including weathered fuels leaking from underground storage tanks (LUST), spills in pipe lines, and run-off from surface transportation.

For the analysis of gasoline with BTEX, the sample is introduced into a sparge tube on the P and T autosampler or purge vessel or the P and T unit. The P and T concentrates the volatiles in the sample and transfers them onto the capillary column.

Parameters affecting the efficiency of P and T sample concentration include time and temperature for sample purge, dry purge, desorption of trapped volatile organics and trap baking. Most P and T system manufacturers recommend 11 minutes of purge or a total of 440 ml purge gas through the sample. Many laboratories use the manufacturer's set purge flow of 40 ml/min which corresponds to 11 minutes of purge time, to achieve a minimum of 440 ml purge gas through the sample. In this study a Vocarb-3000 trap was used because it can provide higher trapping efficiency and allow for higher desorption and baking temperature.

A typical analysis can usually be completed in 35 to 40 minutes. In this application both P and T parameters and GC conditions were optimized for accurate quantitation and analysis speed.

Experimental

Samples were concentrated using an Agilent 7695A P and T system with a Vocarb-3000 trap (part no. 5182-0775) and a 5-ml frit sparger (part no. 5182-0852). Using an HP-1 column (30 m x 0.53 mm x 5.0 µm, (part no. 19095Z-623), hydrocarbons were analyzed on an Agilent 5890 Series II GC with EPC and FID. Instrument requirements and optimal GC and P and T conditions are listed in **Table 1**.

Working solutions were prepared from diluting commercial gasoline, LUST-modified GROs (part no. 5182-0860), and internal standard and surrogate (part no. 8500-6007) with GC-grade methanol (Burdick and Jackson). Concentrations of GROs, gasoline, and jet fuel standards are listed in **Table 2**.

Samples were prepared from spiking 5 ml of organic-free reagent water using a 5-ml sample syringe with a luer connector (part no. 9301-1185) with standard solutions using 5-µl to 100-µl fixed needle syringes (HP part nos. 9301-0810, 9301-0818, 9301-0059, 9301-0063, respectively).

Results and Discussion

To obtain accurate and reproducible results, complete sample purging, managing water adequately from the P and T system, and preventing carry-over from the trap are essential. Many environmental laboratories analyze gasoline with BTEX using long sample purge (11 to 15 minutes), dry purge (2 to 4 minutes), trap desorb (2 to 4 minutes), and trap bake (10 to 20 minutes) times. Therefore, a typical run usually takes 40 to 48 minutes including 3 to 5 minutes for trap cool-down.

Figure 1 shows a GC/FID analysis of a gasoline standard and a GC/PID chromatogram of a GROs standard using an OI 4460A P and T system with a BTX trap and DB-1 column (30 m x 0.53 mm x 5 µm). GC and P and T conditions are listed in **Table 3**. Although the GC runs were completed in 27 minutes, the actual cycle time for each run was 37 to 40 minutes.

Table 1. Instrument Requirements and Optimized Conditions

A. Recommended Instrumentation			
Gas chromatograph:	5890 Series II		
Injection port:	Split/splitless inlet		
Column:	HP-1, 30 m x 0.53 mm x 5.0 µm (Part no. 19095Z-623)		
Detector:	FID		
Injection technique:	7695A P and T		
Data system:	3365 ChemStation and HP Vectra 486/100MX		
B. Experimental Conditions			
GC Parameters			
Inlet:	220°C, split injection (split ratio 5:1)		
Carrier:	Helium, 10 ml/min, constant flow (6.5 psi at 40°C)		
Oven parameters:	40°C (3 min) at 7°C/min to 125°C to 250°C (3 min) at 35°C/min		
Detector:	FID, 300°C; nitrogen makeup gas, 25 ml/min; H_2, 30 ml/min; and air, 350 ml/min PID, 250°C		
P and T Parameters			
Line temperature:	200°C	Purge time:	11 min
Valve temperature:	200°C	Dry purge time:	1 min
Mount temperature:	40°C	Desorb time:	2 min
MCS line temperature:	100°C	Bake time:	5 min
Purge ready temperature:	30°C	BGB time:	2 min
MCS desorb temperature	40°C		
Desorb preheat temperature:	245°C		
Desorb temperature:	250°C		
Bake temperature:	265°C		
MCS bake temperature:	300°C		

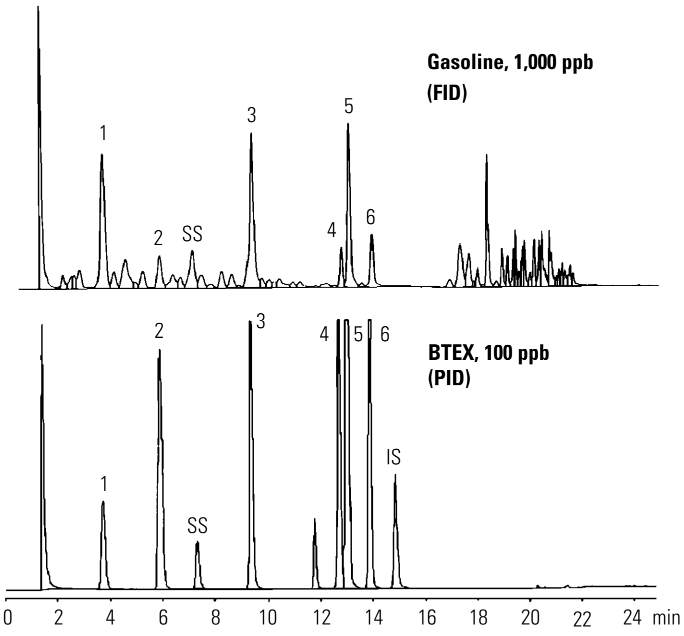


Figure 1. Typical chromatograms of gasoline and GROs standards using a DB-1 column under the GC and P and T conditions (Table 3) used in environmental testing laboratories (see Table 2 for peak identification).

Optimized GC Run Time

With the HP-1 column (30 m x 0.53 mm id x 5 µm) and a faster oven temperature, the GC run time was initially reduced to 21 minutes for GROs and gasoline (see **Figure 2**). Good baseline separations and sharp symmetric peaks **(Figure 2B)** were obtained for all GROs, including surrogate (α,α,α-trifluorotoluene) and internal (4-bromofluorobenzene) standard. The oven temperature program used was 40°C (3 min) at 7°C/min to 125°C to 250°C (3 min) at 35°C/min and a constant carrier flow of 10 ml/min. Under these conditions (**Table 1**), both pentane and MtBE were clearly separated from the large solvent peak (menthanol).

Even though the last GROs component (naphthalene) eluted below 200°C at 17.8 minutes, the oven temperature was increased to 250°C to bake out the high-boiling material purged from the sample. As a result, no carryovers were found even with repeated injections of gasoline standard in the 23,000-ppb level.

GC run times were further lowered by using a thinner-film HP-1 column and/or faster oven temperature programs. **Table 4** shows the benefits of using various column thicknesses, temperature ramps, and carrier flows to achieve the optimal GC run time of 17 minutes. Analytes generally elute faster from a thin-film column (**Figure 4**). In **Figure 3**, the thick-film column retained hydrocarbons longer initially until the faster oven temperature ramp (15°C/min) sped up the elution of all GROs components from the column. To avoid potential coelution (peaks 4 and 5), a comparative smaller carrier flow (4.5 ml/min) was used instead of the optimal 10 ml/min carrier flow. Reducing the GC run time, however, would be counterproductive because the total run time is dependent on the P and T cycle.

Table 2. Analytes in Working Standards

Standards	Peak No.	Components	Concentration
GROS mix	1	MtBE	100 ppm each
	2	Benzene	
	3	Toluene	
	4	Ethylbenzene	
	5	m-/p-Xylene	
	6	o-Xylene	
	7	1,2,4-Trimethylbenzene	
	8	1,3,5-Trimethylbenzene	
	9	Naphthalene	
	10	α,α,α-Trifluorotoluene (SS)	
	11	4-Bromofluorobenzene (IS)	
Gasoline standard		Gasoline	500 ppm
Gasoline		Gasoline	2,500 ppm
Jet fuel		Aviation jet fuel	1,000 ppm

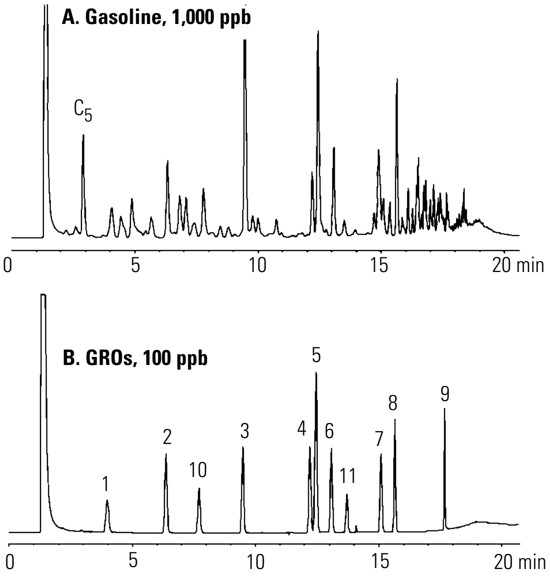


Figure 2. Chromatograms for gasoline and GROs standards using an HP-1 column under the optimal GC and P and T conditions listed in Table 1. (See Table 2 for peak identification.)

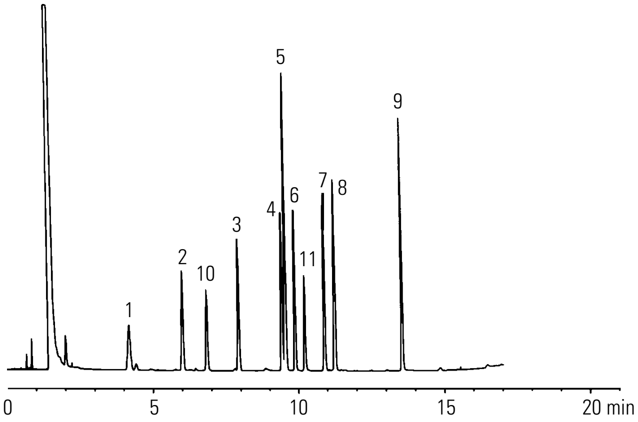
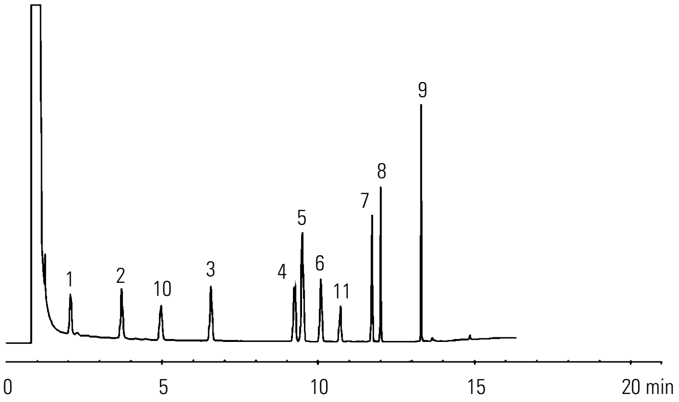


Figure 3. Chromatogram of GROs standards using a thick-film HP-1 (30 m x 0.53 mm x 5 µm) column. (See Table 2 for peak identification and Table 4 for GC conditions.)

Table 3. Typical GC and P and T Conditions for Gasoline and BTEX Analysis

GC Parameters			
Injection:	Direct injection		
Carrier flow:	Initially 10 ml/min, constant pressure mode		
Oven temperature:	50°C (hold 3 min) to 125°C at 5°C/min to 240°C (5 min) at 45°C/min		
Detector:	PID (250°C) in series with FID (300°C)		
P and T Parameters			
Trap:	BTX trap		
Purge temperature:	Ambient	Purge time:	11 min
Dry purge temperature	22°C	Dry purge time:	2 min
Desorb preheat temperature	150°C	Desorb time:	4 min
Desorb temperature	180°C	Bake time:	15 min
Bake temperature:	200°C		

Figure 4. Chromatogram of GROs standards using a thin-film HP-1 (30 m x 0.53 mm x 3 µm) column. (See Table 2 for peak identification and Table 4 for GC conditions.)



Optimized P and T Cycle Time

Further optimization of the run was dependent on obtaining the most efficient parameters for the P and T cycle. Each aspect of the cycle was optimized as follows.

Sample Purge

Experimentation showed 11 minutes of purge time, or 440 ml of helium purge gas, to be the most efficient time for analyses of gasoline and GROs because shorter purge times (8 minutes or 320 ml of purge gas) were not sufficient to purge all GROs from the sample solution. **Figure 5** shows a comparative analysis of the same GROs standard shown in **Figure 2B** using 8 minutes of purge time instead of 11 minutes of purge time. The conditions for both analyses were the same and are shown in **Table 1**. By comparison, hydrocarbon recoveries (including aromatics) for the GC runs with 8 minutes of sample purge were not as good particularly for the high-boiling fractions, such as trimethylbenzenes and naphthalene (compare peaks 7, 8, and 9 in **Figure 5** and **Figure 2B**). The naphthalene peak in **Figure 5** (8 minutes of purge) was remarkably small, and area counts were lower than 1% of that recovered in **Figure 2B**. Based on this finding, 11 minutes is the optimal sample purge time for the determination of gasoline with BTEX.

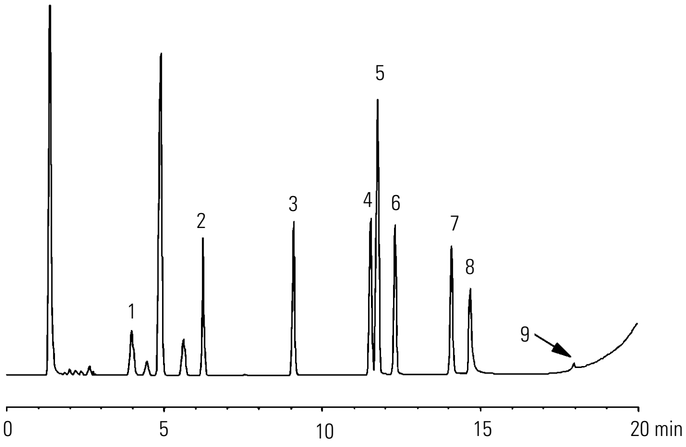
Dry Purge

During sample purge, a larger amount of water is purged along with the volatile organics and is collected on the trap sorbent. Sorbent material in the Vocarb-3000 trap is designed to minimize water trapping and reduce the release of excessive water onto the GC column during the thermal desorption process. A 1-minute dry purge of the Vocarb trap was selected because the early-eluting peaks (such as pentane, MtBE, and benzene in **Figure 2**) were not skewed by water released from the trap onto the column.

Desorption

According to Klee[1], a fast and reproducible desorption temperature is the key to good chromatography using the P and T concentration technique. The higher the desorption temperature and desorption rate, the faster the volatile analytes can be moved to the GC column, and the narrower the peak widths of the early-eluting analytes. Therefore, a short desorption time is preferred. In addition,

Figure 5. Chromatogram of GROs standard using an 8-minute sample purge. (See Table 2 for peak identification and Table 1 for GC and P and T conditions.)



Doherty[2] reported that peak heights and peak areas of volatile organics, including those in the GROs mix, were virtually unchanged when the desorb time changed from 4 minutes to 1 minute. Several manufacturers of P and T systems also recommend a 1-minute desorb time for the routine analysis of volatile organics. However, experimentation (**Figure 2**) using a 2-minute desorb time at 250°C accommodated sharp initial peaks as well as good separation. This study applied a 2-minute desorption time at 250°C to all analyses.

Trap Baking

Three different bake times were evaluated for the Vocarb-3000 trap (used a bake temperature of 265°C, recommended for the Vocarb-3000 trap): 10, 8, and 5 minutes. At each bake time, the gasoline sample (1000-ppb concentration) was run using an 11-minute purge time followed by a run of reagent water with no sample purge. Chromatograms of these two runs were evaluated for carryover. In all three cases (bake times of 5, 8, and 10 minutes), no carryover was observed for any gasoline component. Therefore, a 5-minute bake time at 265°C was selected as an optimal bake time for the analysis of gasoline and GROs aromatics.

For samples containing 46,000 ppb of gasoline, no carry over from the trapped analytes was observed at the 5-minute bake time. This is based on the comparison of chromatograms of reagent water (0-minute purge) run immediately after each sample. However, carry over from the purge vessel was found. Repeated rinsing of the purge vessel with reagent water reduced the amount of carry over but did not eliminate it. Therefore, after a high level sample is run, it is advisable to remove and clean the purge vessel prior to the next run.

Heavier petroleum products, such as diesel and jet fuel (**Figure 6**), that often contain volatile components are also detectable by this method. Again, carry over is a problem. Carry over was observed in the reagent water (used an 11-minute purge) run immediately after the jet fuel sample.

Carry over ranged from 10 ppb to 60 ppb jet fuel and was high enough to cause a false-positive identification in subsequent runs.

As demonstrated by **Figure 7B** (a chromatogram of reagent water, 0-minute purge, run immediately after a jet fuel sample), carry over from the Vocarb trap was found to be negiligible. Clearly the carry over was the result of contamination from the purge vessel (see **Figure 7A**). Although repeated rinsing reduced the amount of carry over, it did not eliminate it completely. Purge vessel carry over was eliminated completely when the purge vessel and the purge needle were removed and cleaned (see **Figure 7C**).

Table 4. GC Run Time of 17 Minutes

HP-1 Column Thickness	Oven Ramp	Carrier Flow Time
30 m x 0.53 mm x 5 µm	40°C (3 min) at 15°C/min to 250°C	4.5 ml/min (see **Figure 3**)
30 m x 0.53 mm x 3 µm	40°C (3 min) at 7°C/min to 95°C to 250°C (2 min) at 45°C/min	10 ml/min (see **Figure 4**)

Figure 6. Chromatogram of 1,000-ppb aviation jet fuel standard. (See Table 1 for GC and P and T conditions.)

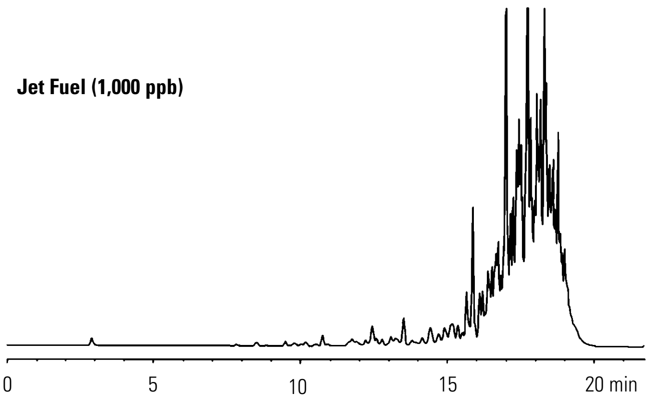
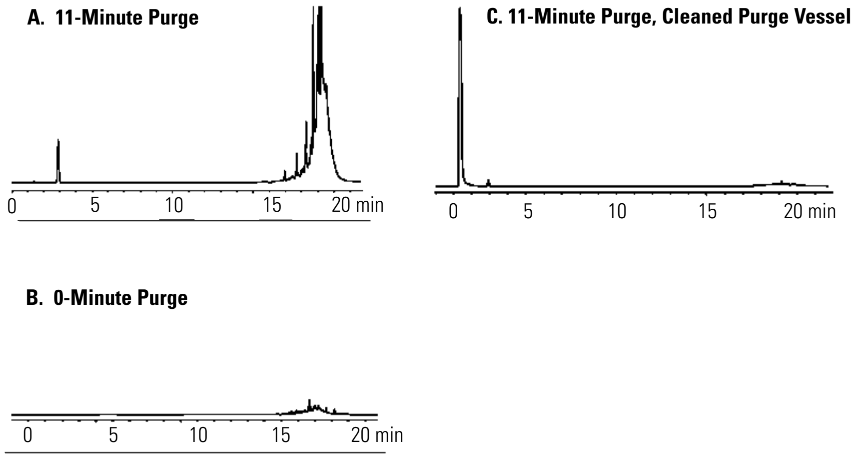


Figure 7. Chromatograms of reagent water following the analysis of the 1,000-ppb aviation jet fuel sample. (See Table 1 for GC and P and T conditions.) Note: The chromatograms were plotted on the same FID response scale.


A. 11-Minute Purge

B. 0-Minute Purge

C. 11-Minute Purge, Cleaned Purge Vessel

Conclusion

Determination of optimized P and T parameters is critical in establishing optimized run times for the analysis of gasoline/BTEX. By reducing the P and T bake time to 5 minutes and selecting shorter dry purge (1 minute) and desorption times (2 minutes), the overall P and T cycle was shortened to 25-26 minutes. This is compatible with the run time of 21-22 minutes established for optimized GC conditions. When carry over from the purge vessel is controlled, this same application can be used successfully for the analysis of samples containing in excess of 46,000 ppb of gasoline and other volatile organics in light petroleum products.

Acknowledgment

The authors wish to than Mr. Robert Remlinger at the Pace Laboratory in Petaluma, California for providing his GC/FID and GC/PID chromatograms.

Reference

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Printed in USA 04/00

Printed on recycled paper
Publication Number 5963-9968E

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