Running ASTM Methods D4815 and D5580 on a Single Agilent 6890N Gas Chromatograph with Nitrogen Carrier Gas

Application

Petrochemical

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Abstract

An Agilent 6890N GC system is described that allows both ASTM methods D4815 and D5580 to run on single hardware configuration for the analysis of oxygenates and aromatics in gasoline. Additionally, the methods were implemented with nitrogen as the carrier gas instead of helium. Nitrogen is sometimes preferred because it is cheaper and easier to obtain in chromatographic grades in some locations. The 6890N based system offers a significant improvement in laboratory efficiency and a reduction in laboratory operating expenses. This application note outlines the details of the GC hardware, including columns and instrument conditions for performing these analyses. Setup and optimization of the methods are described in detail. The system was extensively tested with several gasoline samples and was shown to give excellent analytical precision for both retention time and detector response.

Introduction

Chromatographic separation of oxygenated and aromatic compounds from the complex hydrocarbon matrix in gasoline is difficult to achieve with a single capillary column; therefore, ASTM methods D4815 and D5580 use a two-column configuration with a 10-port column-switching valve [1,2]. At the time of sample introduction, the valve is in the "Off" position, and the sample is injected onto a polar TCEP pre-column where oxygenates, aromatics, and heavy hydrocarbons are retained while the light hydrocarbons are eluted to a thermal conductivity detector (TCD) (Figure 1). After the elution of light hydrocarbons, the valve is switched to the "On" position and oxygenates, aromatics, and heavy hydrocarbons are backflushed onto the methyl silicone capillary column for a boiling point separation (Figure 2). Once the compounds of interest are eluted from the capillary column, the valve is reset to the "Off" position so those heavier compounds remaining on the capillary column are backflushed to the flame ionization detector (FID) (Figure 3). While backflushing, the capillary column pressure is automatically increased using the electronic pneumatics control of the 6890N GC. The increased column flow will speed the elution of the heavy compounds, thus reducing the run time for the method.

Two separate gas chromatographs are usually needed to run ASTM methods D4815 and D5890 for the analysis of oxygenated and aromatic compounds in gasoline. Although these two methods use the same GC hardware configuration, the column configurations differ slightly. Each method uses the same TCEP [1,2,3-*tris*-(2-cyanoethoxy) propane] micro-packed column to remove matrix interference, however, the analytical capillary columns are somewhat different for each method. D4815 uses a methyl silicone column (HP-1 or DB-1)

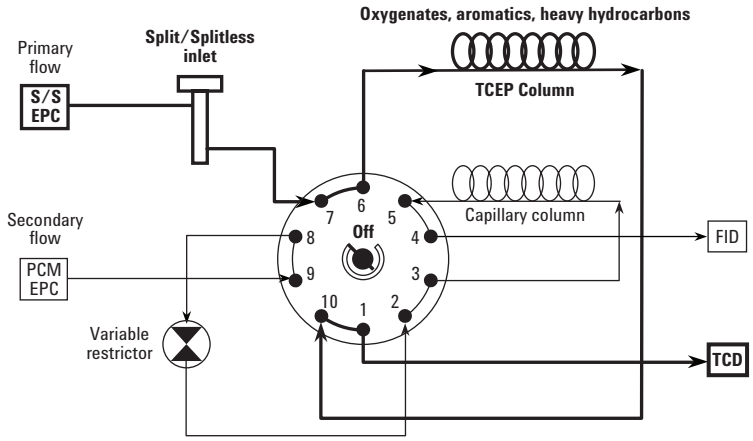

Figure 1. **The valve is in the "off" position at the time of injection. The sample flow path is shown in bold. The polar TCEP pre-column retains the oxygenates, aromatics and heavier hydrocarbons. The lighter hydrocarbons are not retained and are eluted to vent.**

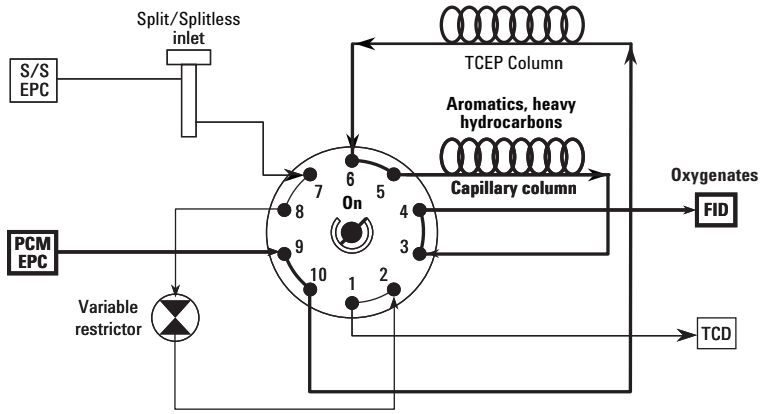

Figure 2. **After the light hydrocarbons have eluted from the TCEP column the valve is switched to the "on" position. The reversed carrier gas flow through the TCEP column is supplied by the pneumatics control module (PCM). The oxygenates, aromatics and heavy hydrocarbons are backflushed from the TCEP column to the capillary column for boiling point separation and detection by the flame ionization detector (FID).**

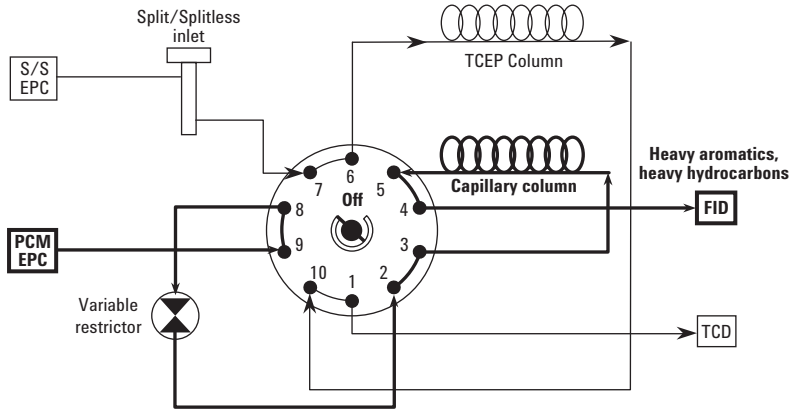

Figure 3. **The valve is in the "off" position after detection of the oxygenates. The sample flow path is shown in bold. The capillary column flow is reversed and the heavy hydrocarbons are backflushed to the FID. At this time, the capillary column pressure is increased using the PCM electronic pneumatics control. The increase column flow elutes these compounds faster.**

that is 30 meters long, 530 microns internal diameter, and a 2.65-micron film thickness. The D5580 method uses a methyl silicone column with the same column dimensions, but with a film thickness of 5 microns.

This application note describes a 6890N GC configuration along with optimized methods that allow the analysis of both oxygenated and aromatic compounds in gasoline using a single instrument equipped with a single pair of columns. Additionally, these methods use nitrogen as the carrier gas instead of helium. In some regions, chromatographic grade helium is difficult and expensive to acquire for use as a carrier gas, whereas nitrogen is much easier and less expensive to obtain as a carrier gas choice.

Experimental

The GC hardware configuration used for this work is outlined in Table 1. The capillary column used for the combined system was the 5 µm film HP-1 because this column could supply the necessary separation for all of the oxygenated additives, as well as the aromatics found in gasoline.

Table 1. Agilent 6890 Hardware Configuration for the Combined D4815/D5580 Method

Standard 6890 GC hardware	
G1540N	6890N Series GC
Option 112	Capillary split/splitless inlet with EPC control
Option 210	FID with EPC control
Option 220	TCD with EPC controls
Option 309	PCM module with EPC controls
Option 751	Temperature controlled valve box for one valve
Option 800	10-Port valve
Option 872 (2 of each)	Zero dead volume bulkhead unions
G2613A	Agilent 7683 Autoinjector
Columns	
Polar pre-column	Micro-packed 20% TCEP on chromosorb PAW 80/100, stainless steel 560 mm × 0.38 mm id
Capillary column	5 µm film HP-1, 30 m × 0.53 mm id (Agilent part number. 19095Z-623)
Data system	
G2070A	Agilent multi-technique ChemStation
Optional consumables	
5181-8809	10 µL fixed straight needle autoinjector syringe for Merlin Microseal
5183-4647	Inlet liner optimized for split operation
Standards and samples	
D-4815-VT*	AccuStandard valve timing mixture
D-4815/IS-SET*	AccuStandard quantitative calibration mixture
M-GRO-EPA-CC/IS-5ML*	AccuStandard quantitative check standard
SRM 2294**	Reformulated gasoline with 11%(w/w) MTBE

*Available from Accustandard, 125 Market St., New Haven, CT 06513, USA

**Available from NIST Standard Reference Material Program

100 Bureau Dr., Room 204, Build. 202, Gaithersburg, MD 20899-2322, USA

D4815 - Oxygenates TCEP Column Backflush Time Setting

Table 2 lists the method conditions used for the analysis of oxygenated compounds in gasoline. Since the capillary column used for this work has a thicker film than the standard D4815 column, the oven temperature was set to 80 °C instead of 60 °C. This higher temperature gave run times that were approximately the same as those in the original D4815 method. The pressure and flow settings in Table 2 were typical for this analysis, but they must be checked and adjusted for each individual instrument.

A valve timing mixture was prepared to optimize the backflush time in this system. This mixture contains 10% w/w each of MtBE, EtBE, DIPE and methylcyclopentane (MCP) in hexane. The MCP served as a marker to indicate the complete elution of light hydrocarbons from the TCEP pre-column. The valve timing mixture was run at 0.02-minute intervals between backflush times of 0.16 minutes to 0.30 minutes. At each interval the data was evaluated to determine the optimal backflush time for that particular system.

D5580 Aromatics TCEP Column Backflush Time Setting

Table 3 lists the GC instrument conditions used for the analysis of aromatics in gasoline. The pressure and flow settings in Table 3 were typical for this analysis, but they must be checked and adjusted for each individual instrument.

Table 2. Instrument Conditions for D4815 Oxygenate Analysis

Split/Splitless injection port	
Temperature	200 °C
Pressure	9 psi Nitrogen (constant pressure mode)
Split vent flow	70 mL/min
Split ratio	15:1
TCEP Pre-column flow	5 mL/min
Pneumatics control module	13 psi Nitrogen (ramped pressure mode)
Pressure program	13 psi for 14 min 99 psi/min to 40 psi
HP-1 Capillary column flow	3 mL/min
FID Temperature	250 °C
Valve temperature	60 °C
Oven temperature	80 °C Isothermal

Table 3. Instrument Conditions for D5580 Oxygenate Analysis

Split/Splitless injection port	
Temperature	200 °C
Pressure	25 psi Nitrogen (constant pressure mode)
Split vent flow	100 mL/min
Split ratio	100:1
TCEP Pre-column flow	10 mL/min
Pneumatics control module	23 psi Nitrogen (ramped pressure mode)
Pressure program (benzene/toluene)	23 psi for 12.1 min 99 psi/min to 40 psi
Pressure program (C8/C9 Plus)	23 psi for 22 min 99 psi/min to 40 psi
HP-1 Capillary column flow	10 mL/min
FID Temperature	250 °C
Valve temperature	60 °C
Oven temperature	60 °C for 6 min, 2 °C/min to 115 °C, hold at 115 °C for 1.5 min

For a complete aromatic analysis, ASTM method D5580 must be run two times with two different TCEP column backflush times. The first backflush time, T1, was used for the analysis of benzene and toluene. The second backflush time, T2, was used for the analysis of C8 and C9 plus aromatics. Each of these times was determined by running a valve timing test mixture that contains 5% w/w each of benzene, toluene, ethylbenzene, o-xylene, and 2-hexanone in isooctane (2,2,4-trimethylpentane). A 1 µL volume of this mixture was injected into the GC with the valve set to the "Off" position for the entire run so that the sample was separated on the TCEP column and detected with the TCD. This chromatogram was used to select backflush times, T1 and T2.

Evaluation of System Precision when Performing Sequential Oxygenate and Aromatic Analyses

After determining the backflush and reset times for D4815 and D5580, the system was evaluated by running two separate gasoline samples. These samples were a pump gasoline and a Renewable Fuels Association (RFA) gasoline, each one containing MtBE. These samples were run in a sequence so that the 6890N GC would have to perform an oxygenate analysis followed by a complete aromatics analysis. This sequence was repeated five consecutive times in order to evaluate the robustness and precision of the system when switching between the different setpoints (flow, pressure, temperature, valve timing) required by each method.

Results and Discussion

D4815 - Oxygenates TCEP Column Backflush Time Setting

The data obtained from the backflush time setting experiment appears in Figure 4. Inspection of this data shows that the hydrocarbons, represented by MCP, were completely eluted from the TCEP column after 0.20 minutes. This data is graphically represented in Figure 5. For this system, a backflush time of 0.22 minutes was used for the analysis of MtBE and ethanol. This backflush time was specific to the system used for this work and must be optimized for each individual GC system. This method was saved as "D4815" on the Agilent ChemStation.

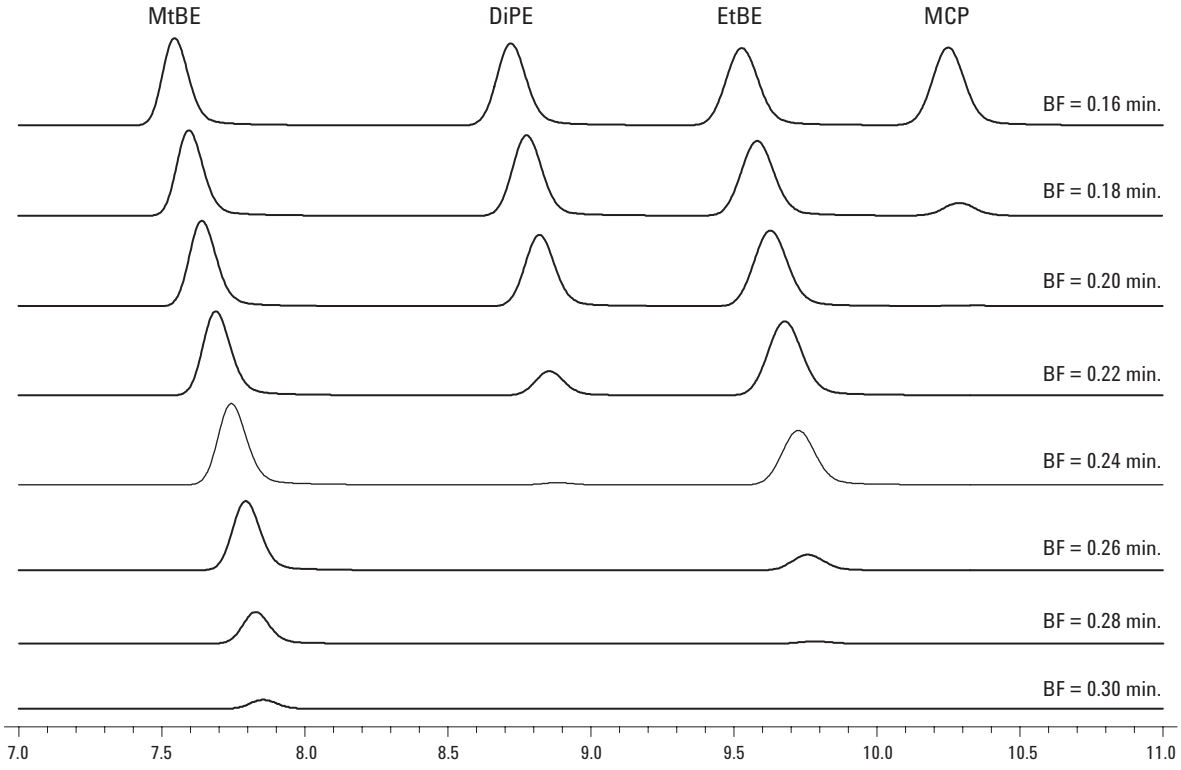

Figure 4. Chromatographic data from backflush time optimization experiment for D4815 analysis of oxygenates. In this example, the MCP is completely vented from the TCEP column after a backflush time of 0.20 minutes.

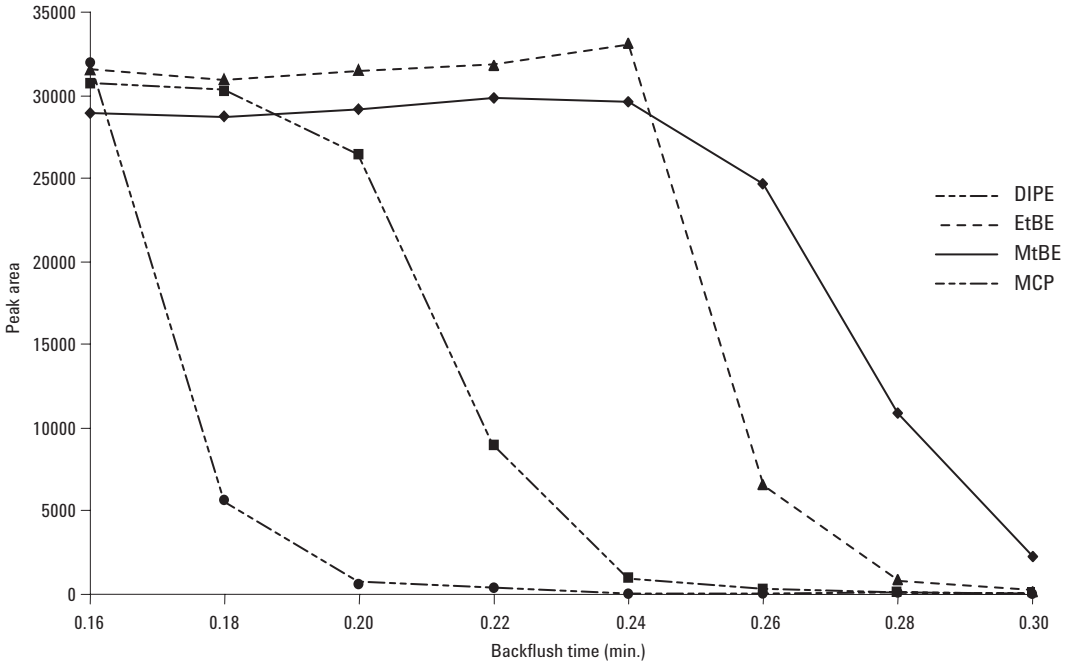

Figure 5. This shows a graphic presentation of the data from Figure 4. After 0.20 minutes the hydrocarbons represented by MCP are vented from the TCEP column, while the MtBE and EtBE are completely retained. The DIPE response is reduced indicating some loss from the column.

Using the GC conditions listed in Table 2 and with a backflush time of 0.22 minutes, a gasoline sample containing 11 wt% MtBE and another containing 8 wt% ethanol were run on this system to evaluate the chromatography. Figure 6 shows the results of these analyses. After the elution of the benzene from the capillary column, the valve was reset to the "Off" position and the PCM pressure increased to 40 psi to quickly elute any aromatic and heavy nonaromatic hydrocarbons from the capillary column.

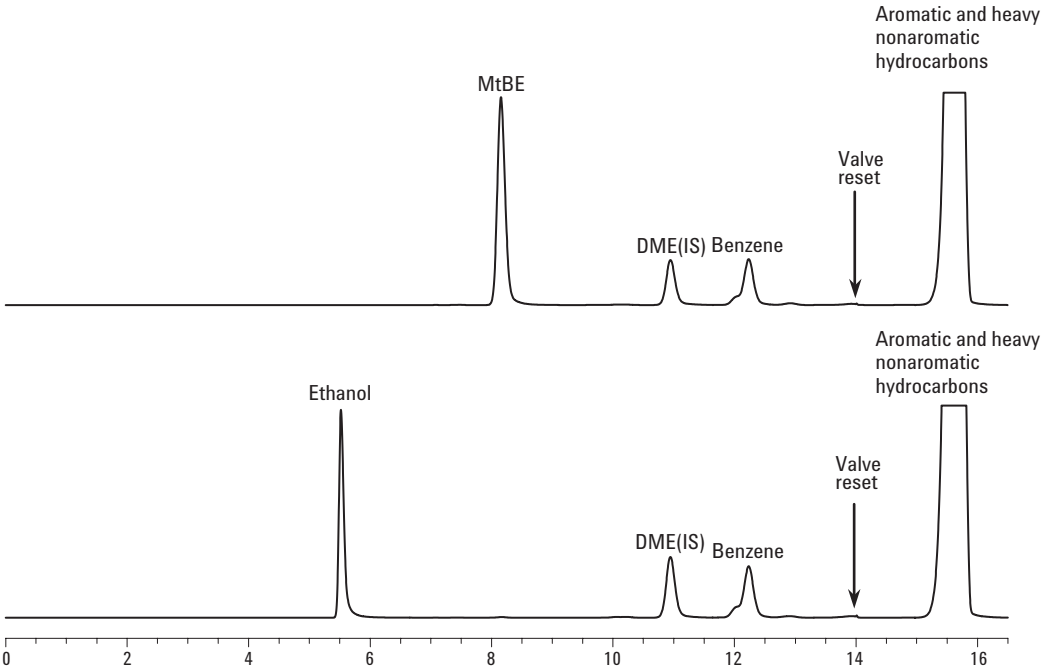

Figure 6. Analysis of two gasoline samples containing 11 wt% MtBE (top) and 8 wt% ethanol (bottom) using a backflush time of 0.22 minutes. Each sample contains 5 wt% of the internal standard, dimethoxyethanol (DME). At 14 minutes, the valve was reset to the "Off" position and the PCM module pressure increased to quickly elute any aromatic and nonaromatic hydrocarbons still on the capillary column.

D5580 Aromatics TCEP Column Backflush Time Setting

Setting the correct backflush times for the aromatics analysis was more complicated because D5580 requires two different times for a complete aromatics analysis. Figure 7 shows the chromatogram of the D5580 valve timing mix separated on the TCEP column and detected by the TCD. From this chromatogram, the benzene/toluene backflush time (T1) was determined by subtracting 6 seconds from the start of the benzene peak. For this system, 0.58 minutes was used for T1. The second backflush time (T2), for C8 and C9 plus aromatics, was determined by subtracting 6 seconds from the start of the ethylbenzene peak. For this system a value of 1.68 minutes was used for T2. The benzene/toluene method was saved on the ChemStation as "D5580A" and the C8/C9 plus aromatics method was saved as "D5580B".

With these two backflush times and the GC instrument conditions listed in Table 3, the chromatography of the system was evaluated by running a sample of pump gasoline (89 octane) that contained 10 wt% of the internal standard, 2-hexanone. Figure 8 shows the two chromatograms obtained with this method. This data was also used to determine the valve reset times for backflushing the capillary column after the last peak of interest has eluted. For the benzene/toluene analysis, 12.1 minutes was used for the valve reset time (T3). For the C8/C9 plus aromatics, the valve rest time (T4) was set to 22 minutes. After each reset time, the PCM pressure was increased to 40 psi so that any aromatic and nonaromatic hydrocarbons remaining on the capillary column will be quickly eluted to the FID for detection.

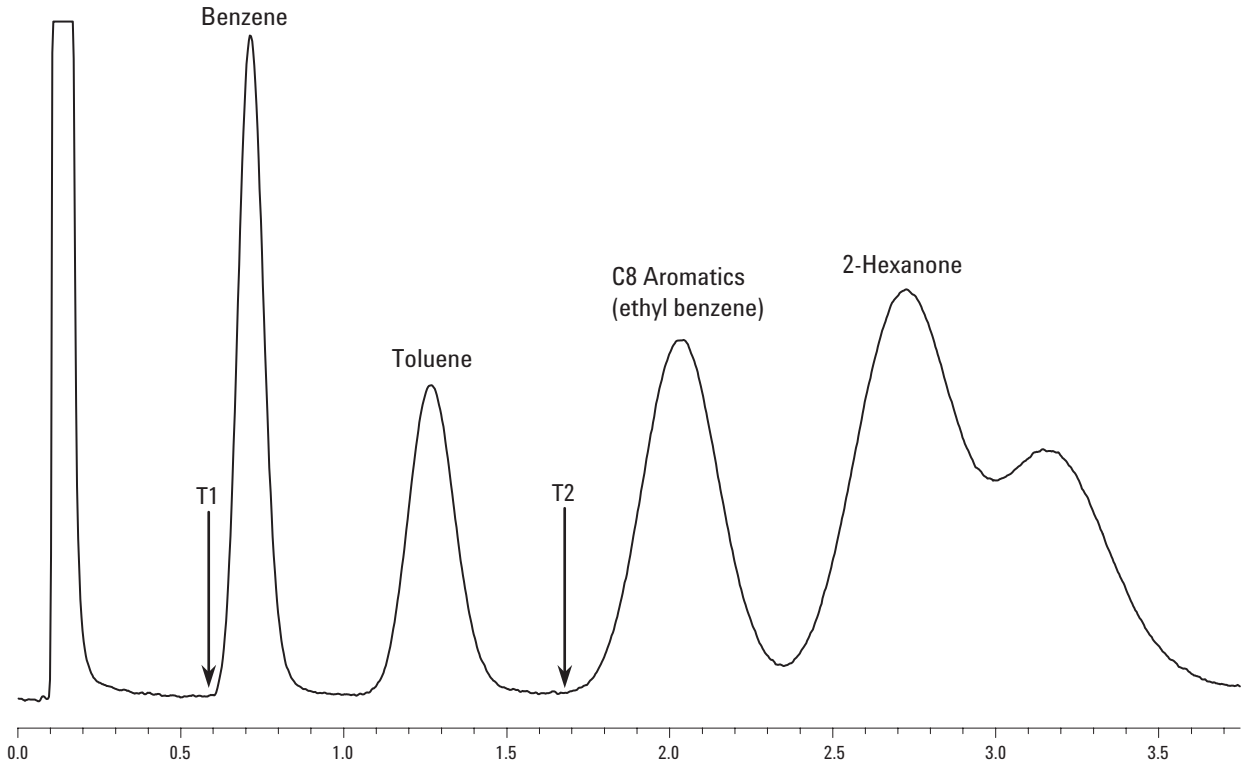

Figure 7. D5580 valve timing mix showing the two backflush times for this system. Backflush time T1 (0.58 min.) is set just before the elution of benzene from the TCEP column. This time is used for the analysis of benzene and toluene. Backflush time T2 (1.68 min.) is set just before the elution of ethylbenzene and is used for the analysis of C8 and C9 plus aromatic compounds.

Evaluation of System Precision when Performing Sequential Oxygenate and Aromatic Analyses

Although this application note describes a common 6890N GC configuration for both oxygenate and aromatic analysis, the three methods that perform these measurements used different instrument conditions such as oven temperature, column pressures, column flows, and valve timing. Many analysts using this system will want to perform a complete analysis, (oxygenate, benzene/toluene, and C8/C9 plus) for each gasoline sample before going on to the next sample. This means that these three different methods will run consecutively, and the GC system must be stable enough to ensure retention time and quantitative precision as the methods change between analyses. To test the system, a ChemStation sequence was created so that a sample was run by the D4815 method followed by the D5580A method (benzene/toluene) and the D5580B method (C8 and C9 plus aromatic). This sequence of three analyses was repeated five times for each sample.

Operating parameters (such as pneumatics stability, oven stability, and valve timing) combine to affect the overall retention time precision of this system, especially when changing methods between sample runs. Tables 4 and 5 show the retention time precision of this system for a pump gasoline sample and an RFA gasoline sample, both containing MtBE. From this data one can see that the retention time precision remains high for all compounds, even while alternating GC conditions for each sample.

Tables 6 and 7 show the detector response precision for these two samples as the three methods are alternated. The system provides excellent detector precision for all compounds analyzed by these methods.

Table 4. Retention Time Precision for Sequential Analysis of a Pump Gasoline Sample

		Retention Time (minutes)					
Run no.	**Method**	**MtBE**	**Benzene**	**Toluene**	**Ethylbenzene**	**m, p-Xylene**	**o-Xylene**
1	D4815	8.119					
2	D5580A		6.527	11.147			
3	D5580B				18.251	18.794	20.285
4	D4815	8.148					
5	D5580A		6.528	11.145			
6	D5580B				18.242	18.787	20.277
7	D4815	8.155					
8	D5580A		6.534	11.153			
9	D5580B				18.235	18.776	20.272
10	D4815	8.157					
11	D5580A		6.539	11.156			
12	D5580B				18.230	18.771	20.269
13	D4815	8.156					
14	D5580A		6.539	11.158			
15	D5580B				18.235	18.772	20.270
	Average	8.147	6.533	11.152	18.238	18.780	20.275
	Std Dev	0.016	0.005	0.006	0.008	0.010	0.007
	%RSD	0.195	0.083	0.050	0.045	0.053	0.033

Table 5. Retention Time Precision for Sequential Analysis of a RFA Gasoline Sample

		Retention Time (minutes)					
Run no.	**Method**	**MtBE**	**Benzene**	**Toluene**	**Ethylbenzene**	**m, p-Xylene**	**o-Xylene**
16	D4815	8.156					
17	D5580A		6.539	11.160			
18	D5580B				18.241	18.786	20.281
19	D4815	8.154					
20	D5580A		6.540	11.160			
21	D5580B				18.243	18.791	20.281
22	D4815	8.154					
23	D5580A		6.542	11.162			
24	D5580B				18.242	18.788	20.280
25	D4815	8.153					
26	D5580A		6.541	11.162			
27	D5580B				18.242	18.788	20.283
28	D4815	8.151					
29	D5580A		6.539	11.160			
30	D5580B				18.244	18.790	20.282
	Average	8.154	6.540	11.161	18.242	18.788	20.281
	Std Dev	0.002	0.001	0.001	0.001	0.002	0.001
	%RSD	0.025	0.017	0.010	0.006	0.010	0.005

Table 6. Detector Response Precision for Sequential Analysis of a Pump Gasoline Sample

		FID Response (area counts)					
Run no.	**Method**	**MtBE**	**Benzene**	**Toluene**	**Ethylbenzene**	**m, p-Xylene**	**o-Xylene**
1	D4815	24077					
2	D5580A		3306	19427			
3	D5580B				5402	21825	8069
4	D4815	23384					
5	D5580A		3244	19436			
6	D5580B				5402	21956	8105
7	D4815	22807					
8	D5580A		3178	19580			
9	D5580B				5422	22342	8232
10	D4815	22915					
11	D5580A		3048	19344			
12	D5580B				5432	22263	8201
13	D4815	23053					
14	D5580A		3099	19529			
15	D5580B				5422	22253	8199
	Average	23247	3175	19463	5416	22128	8161
	Std Dev	512	105	92	14	224	70
	%RSD	2.2	3.3	0.5	0.2	1.0	0.9

Table 7. Detector Response Precision for Sequential Analysis of a RGA Gasoline Sample

		FID Response (area counts)					
Run no.	**Method**	**MtBE**	**Benzene**	**Toluene**	**Ethylbenzene**	**m, p-Xylene**	**o-Xylene**
16	D4815	32456					
17	D5580A		8384	39783			
18	D5580B				11860	35424	12723
19	D4815	32762					
20	D5580A		8393	40300			
21	D5580B				11925	35583	35583
22	D4815	32998					
23	D5580A		8383	40107			
24	D5580B				11833	35272	35272
25	D4815	32715					
26	D5580A		8464	40387			
27	D5580B				11780	35205	35205
28	D4815	33339					
29	D5580A		8566	40068			
30	D5580B				11998	35841	35841
	Average	32854	8438	40129	11879	35465	12738
	Std Dev	332	79	234	84	256	93
	%RSD	1.0	0.9	0.6	0.7	0.7	0.7

Optimizing Chromatographic Resolution for Ethylbenzene and m, p-Xylene

In Figure 8, the resolution between the ethylbenzene peak and the m, p-xylene peak is not baseline, but it is acceptable for good quantitative analysis. This is due to the nitrogen carrier gas used at higher than optimum linear velocity in the capillary column. This high-linear velocity was used to give the same run times as shown in the original ASTM method, which uses helium as the carrier gas. Occasionally, some combinations of TCEP precolumns and HP-1 capillary columns will provide less retention with nitrogen carrier gas due to variations in the preparation of the TCEP column.

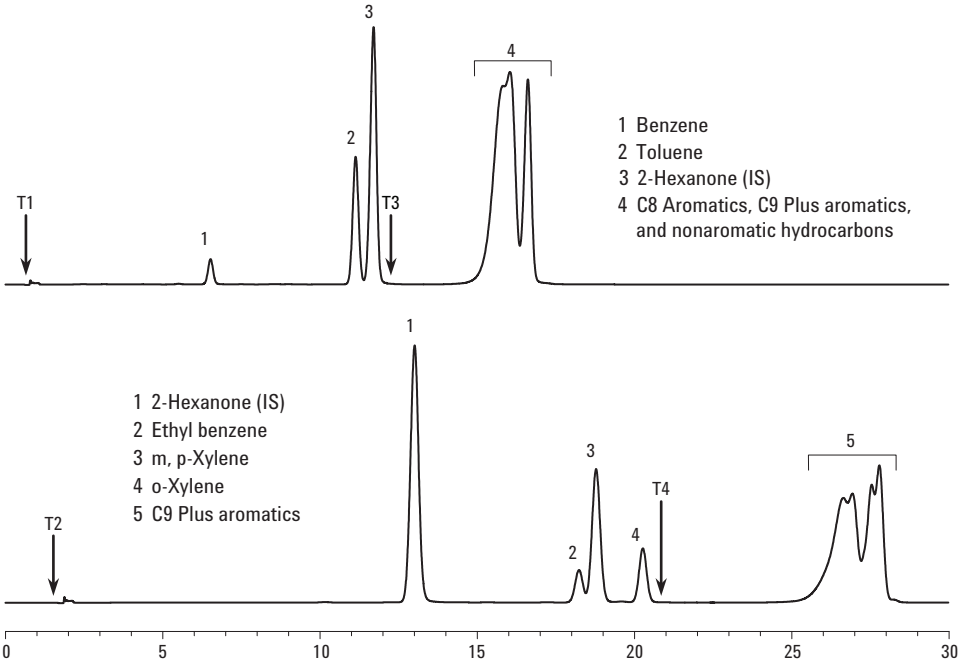

Figure 8. D5580 valve timing mix showing the analysis of aromatic compounds in gasoline. The top chromatogram uses backflush time T1 (0.58 min.) for the analysis of benzene and toluene. After elution of 2-hexanone, the valve is reset at 12.1 minutes (T3) to quickly elute the C8/C9 aromatics and any heavy hydrocarbons from the capillary column. The bottom chromatogram measures C8 and C9 plus aromatics using backflush time T2 (1.68 min.). The valve is reset at 22 minutes (T4) to elute the C9 plus aromatics.

In Figure 9 (upper chromatogram), one GC system was found to have less peak retention and resolution due to these column conditions. One can also see that the overall retention times were about 25% faster. Potential solutions to this problem include: replacing the TCEP column, lowering column flows, or using helium as the carrier gas. However, the quickest and easiest solution is to slightly change the GC oven temperature program. In Figure 9, after the initial oven temperature was lowered to 50 °C, the peak retention and resolution were returned to the levels shown in Figure 8.

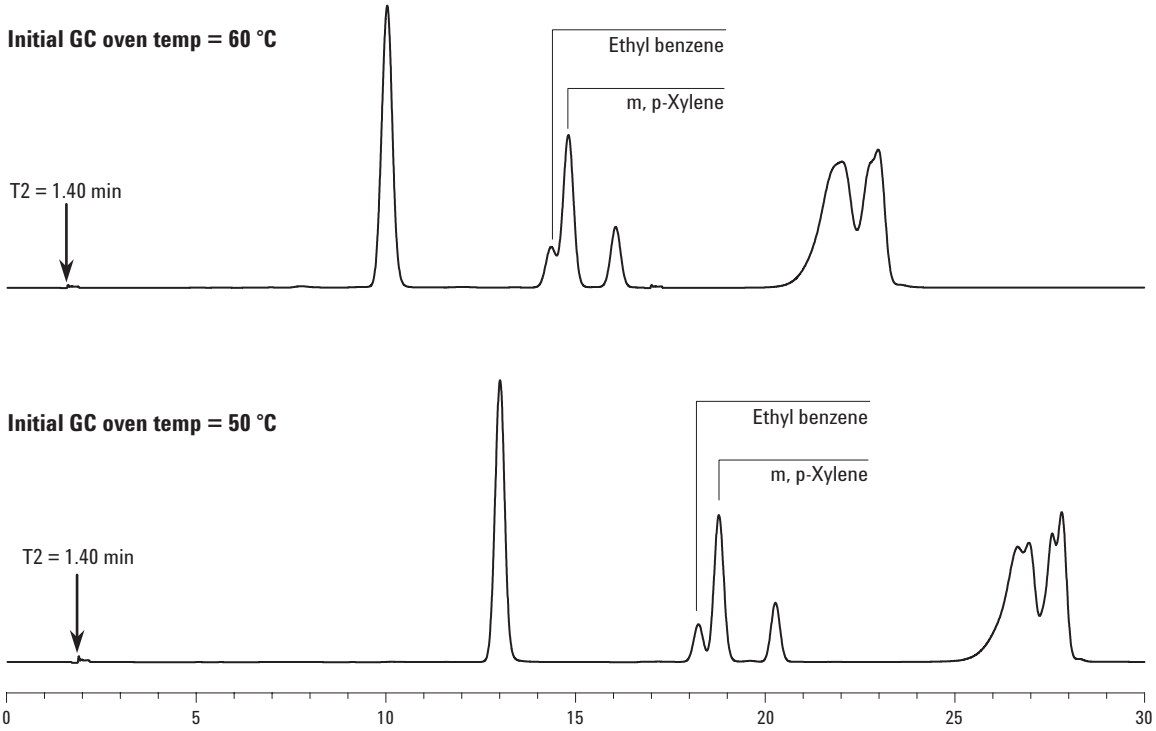

Figure 9. The upper chromatogram shows the analysis of C8/C9 plus aromatics in gasoline where the overall peak retention is faster and the ethylbenzene/m, p-xylene resolution is reduced. This is due to a variation in the TCEP micropacked column prepration. This can be corrected by simply lowering the initial GC oven temperature until the desired retention and resolution is obtained (lower chromatogram).

Conclusions

A GC hardware configuration was developed that can run ASTM methods D4815 and D5580 on a single instrument for the analysis of oxygenated and aromatic compounds in gasoline. These methods were also used with nitrogen (instead of helium) as the carrier gas, with no changes in column-flow settings and minimal loss of chromatographic resolution. Using both a single instrument and nitrogen carrier gas offers a significant improvement in laboratory efficiency and laboratory operating expenses. Real gasoline samples were used to demonstrate that this system could also provide exceptionally good performance for the analysis of these important components in modern fuels.

References

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Printed in the USA
March 17, 2003
5988-9153EN