Agilent 6850 Sub-Ambient Oven Performance for ASTM D3710 Simulated Distillation of Gasoline

Application

Gas Chromatography

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Abstract

The Agilent 6850 gas chromatograph is now offered with sub-ambient column oven capabilities using liquid carbon dioxide as the cryogenic gas. This extends the 6850 oven temperature from -20 °C to 350 °C. The sub-ambient oven performance of the 6850 was tested using the ASTM D3710 method for simulated distillation of gasoline range materials. This method requires starting oven temperatures of -20 °C followed by programming to 180 °C. Four chromatogaphic performance tests required by the ASTM method were used to evaluate 6850 system performance. The same tests were also run on the Agilent 6890 GC to offer a comparison with an industry standard system. Both the 6850 and the 6890 results exceeded the specifications for peak shape, resolution, and retention time repeatability and area percent repeatability. In most cases both GCs showed performance that was 10 times better than the ASTM requirements. The 6850 and the 6890 also showed nearly identical performance when compared to each other. Additionally, the 6850 used about one-half of the CO_2 cryogenic gas compared to the 6890 when running this method.

Introduction

Most gas chromatographic separations can be performed with GC oven temperatures starting above ambient conditions. However, there are some instances that require GC oven temperatures that are below ambient. For example, separation of gases, low boiling components, and solvent focusing are all examples where the chromatographer needs to use cold oven temperatures. For modern instruments, sub-ambient temperatures are achieved by controlled introduction of a cryogenic gas into the oven. Typically, liquid carbon dioxide (CO_2) or liquid nitrogen are used as the cryogenic gas.

The Agilent 6850 gas chromatograph is a rugged, easy-to-use, single channel instrument especially suited for production laboratories where space is a premium. The 6850 occupies 50% of the linear bench space compared to the Agilent 6890, while still providing the same chromatographic performance. For applications requiring sub-ambient oven temperatures down to -20 °C, the 6850 now offers a CO_2 cryogenic cooling option.

The 6850 cryogenic oven performance was evaluated using the ASTM D3710 Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography[1]. This simulated distillation method was slightly modified by using a fused silica capillary column in place of a packed column. Instrument conditions for this method are listed in table 1. The sample run on these instruments was a D3710 Qualitative Calibration Mix (part # 506427, Supelco, Bellefonte, PA, USA) which contains the nineteen compounds required for system performance evaluation. Five consecutive runs of this mix were made on each GC. The quantity of CO_2 cryogenic gas used for each run was also measured to compare consumption differences between the 6850 and 6890.

Table 1. Instrument conditions for ASTM D3710 Simulated Distillation

Autoinjector	Agilent 7683 ALS 10 µL Teflon-tipped plunger syringe
Inlet	Split/splitless operated in split mode Temperature: 200 °C Liner part # 5183-4647
Column	HP-1, 3.0 µm film thickness, 15 m × 530 µm (part # 19095Z-421E)
Oven	-20 °C for 2 min, 20 °C/min to 180 °C, hold 2 min
Detector	Flame ionization detector (FID) Temperature: 300 °C FID hydrogen flow rate: 40 mL/min FID air flow rate: 450 mL/min FID make-up flow rate: 45 mL/min nitrogen Data acquisition rate: 10 Hz
Data system	Agilent Chemstation

This ASTM D3710 method is useful for evaluating GC cryogenic oven performance. It is a widely used application and is familiar to many GC analysts. D3710 also has stringent chromatographic performance specifications that can be used to assess the sub-ambient oven performance. These requirements are listed below:

1. *Resolution* - compounds lighter than isopentane must be separated such that the valley above the baseline is less than 5% of the height of the smaller peak.
2. *Peak Shape* (Skew) - peak skew must be not less than 0.5 and not more than 2.0.
3. *Retention Time Repeatability* - the retention time difference between consecutive runs must not be not more than 3 seconds for isopentane and lighter compounds. For compounds heavier than n-pentane, the maximum difference in retention time between successive runs must not be greater than the time equivalent of 3 °C. Additionally, the minimum retention time of the propane must be greater than 15 seconds.
4. *Area Percent Repeatability* - duplicate area percent results for each compound from consecutive runs must not differ by more than 0.1 area percent.

Results

Resolution. Figure 1 shows the chromatograms of the D3710 qualitative calibration sample run on both the 6850 and 6890 GCs. The nineteen compounds in this sample are baseline resolved on both GCs in approximately 12 minutes. Figure 2 shows the resolution of the compounds that are lighter than isopentane. For all four peaks, the valley above the baseline is much less than 5% of the height of the smaller peak.

Peak Shape. Table 2 lists the symmetry of each peak in the chromatograms shown in figure 1. A skew value of 1.0 would indicate perfectly symmetrical peaks. Skews of less than 0.5 would indicate tailing, and values greater than 2.0 would indicate fronting (overload). Both the 6850 and 6890 show peaks that are almost all perfectly symmetrical.

Retention Time Repeatability. Both the 6850 and 6890 show excellent retention time repeatability as shown in table 3. For isopentane and lighter compounds, the retention time repeatability on both GCs is about ten times better than the ASTM specification. For compounds heavier than n-pentane, the ASTM specification calls for repeatability of less than the time equivalent of 3 °C. For this method, that translates into a value of ≤ 2.0 seconds. Both the 6850 and the 6890 show retention time repeatability that is 20 times better. Additionally, the retention time of the propane on each GC is greater than 15 seconds (figure 2).

Area Percent Repeatability. Table 4 shows the area percent repeatability of the 6850 and 6890. Both instruments show 5-10 times better performance than what is required by the ASTM specification.

CO_2 Cryogenic Gas Usage. The 6850 required about 1.5 lbs. of CO_2 cryogen for each run of D3710. The 6890 GC used about 3 lbs. of carbon dioxide. The smaller oven design of the 6850 makes it easier to cool below ambient conditions and hold that temperature. Oven cycle times after temperature programming were approximately the same for both instruments (10 minutes).

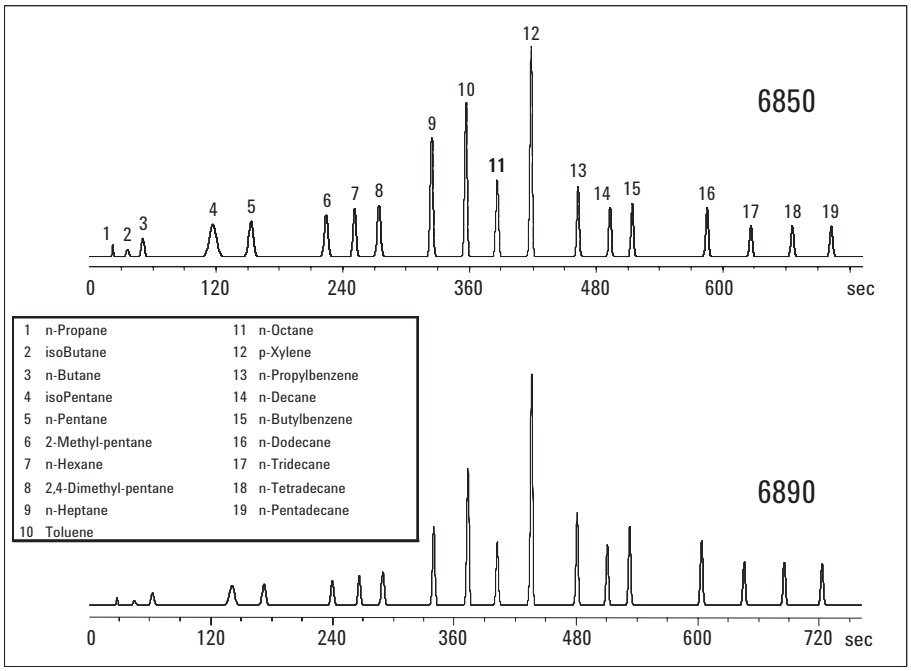

Figure 1. Separation of nineteen compounds used to evaluate GC system performance of the ASTM D3710 method for the simulated distillation of gasoline. Each run was made using CO_2 as the cryogenic gas for sub-ambient oven temperatures on both the 6850 and 6890.

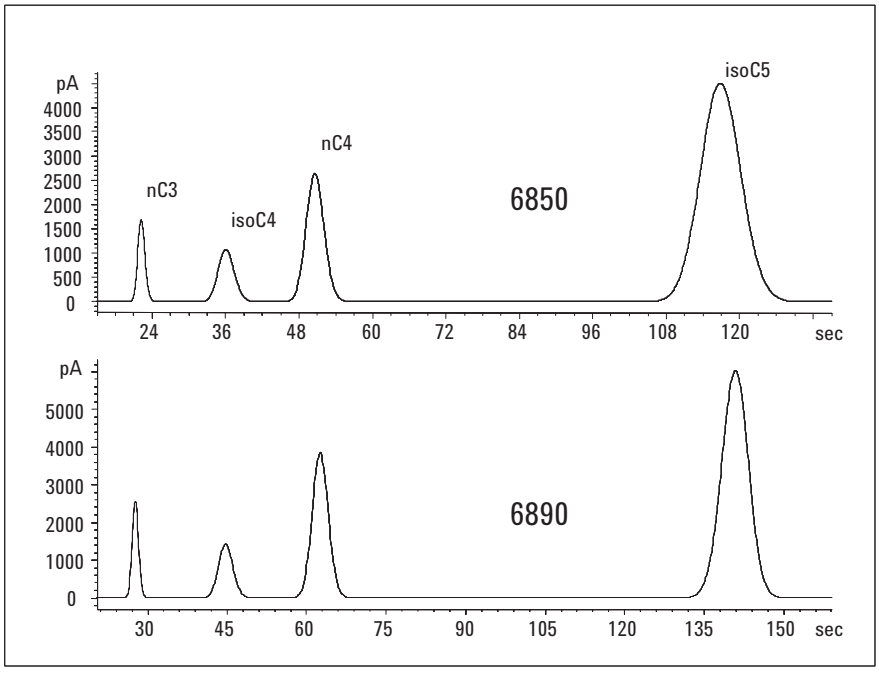

Figure 2. Baseline resolution is achieved for isopentane and lighter compounds on both the 6850 and 6890.

Table 2. ASTM D3710 Peak Symmetry Test (Skew)

Compound	ASTM Specification	Observed* 6890	Observed* 6850
n-Propane	0.5-2.0	0.9	0.9
IsoButane	0.5-2.0	0.9	0.9
n-Butane	0.5-2.0	1.0	0.9
isoPentane	0.5-2.0	1.0	1.0
n-Pentane	0.5-2.0	1.0	1.0
2-Methyl-pentane	0.5-2.0	1.0	1.0
n-Hexane	0.5-2.0	1.0	1.0
2,4-Dimethyl-pentane	0.5-2.0	1.0	1.0
n-Heptane	0.5-2.0	1.1	1.1
Toluene	0.5-2.0	1.2	1.1
n-Octane	0.5-2.0	1.1	1.1
p-Xylene	0.5-2.0	1.5	1.2
n-Propylbenzene	0.5-2.0	1.2	1.1
n-Decane	0.5-2.0	1.1	1.0
n-Butylbenzene	0.5-2.0	1.2	1.1
n-Dodecane	0.5-2.0	1.2	1.1
n-Tridecane	0.5-2.0	1.1	1.0
n-Tetradecane	0.5-2.0	1.1	1.0
n-Pentadecane	0.5-2.0	1.1	1.0

*Average from 5 consecutive runs

Table 3. ASTM D3710 Retention Time Repeatability Test

Compound	ASTM Specification	Observed (sec)* 6890	Observed (sec)* 6850
n-Propane	≤ 3.0s	0.1	0.1
isoButane	≤ 3.0s	0.1	0.1
n-Butane	≤ 3.0s	0.1	0.0
isoPentane	≤ 3.0s	0.2	0.3
n-Pentane	≤ 2.0s	0.2	0.2
2-Methyl-pentane	≤ 2.0s	0.2	0.1
n-Hexane	≤ 2.0s	0.2	0.1
2,4-Dimethyl-pentane	≤ 2.0s	0.1	0.1
n-Heptane	≤ 2.0s	0.1	0.1
Toluene	≤ 2.0s	0.1	0.1
n-Octane	≤ 2.0s	0.1	0.1
p-Xylene	≤ 2.0s	0.1	0.1
n-Propylbenzene	≤ 2.0s	0.1	0.1
n-Decane	≤ 2.0s	0.1	0.1
n-Butylbenzene	≤ 2.0s	0.1	0.1
n-Dodecane	≤ 2.0s	0.1	0.1
n-Tridecane	≤ 2.0s	0.1	0.1
n-Tetradecane	≤ 2.0s	0.1	0.1
n- Pentadecane	≤ 2.0s	0.1	0.1

*Average from 5 consecutive runs

Table 4. ASTM D3710 Area Percent Repeatability Test

Compound	ASTM Specification	Observed (area%)* 6890	6850
n-Propane	≤ 0.10%	<0.01	<0.01
isoButane	≤ 0.10%	<0.01	<0.01
n-Butane	≤ 0.10%	0.01	<0.01
isoPentane	≤ 0.10%	0.02	<0.01
n-Pentane	≤ 0.10%	0.01	<0.01
2-Methyl-pentane	≤ 0.10%	0.01	<0.01
n-Hexane	≤ 0.10%	0.01	<0.01
2,4-Dimethyl-pentane	≤ 0.10%	0.01	<0.01
n-Heptane	≤ 0.10%	0.02	<0.01
Toluene	≤ 0.10%	<0.01	0.01
n-Octane	≤ 0.10%	<0.01	<0.01
p-Xylene	≤ 0.10%	0.03	0.01
n-Propylbenzene	≤ 0.10%	0.02	<0.01
n-Decane	≤ 0.10%	0.01	<0.01
n-Butylbenzene	≤ 0.10%	0.02	<0.01
n-Dodecane	≤ 0.10%	0.02	<0.01
n-Tridecane	≤ 0.10%	0.01	<0.01
n-Tetradecane	≤ 0.10%	0.02	<0.01
n- Pentadecane	≤ 0.10%	0.02	<0.01

*Average from 5 consecutive runs

Summary

The Agilent 6850 gas chromatograph can now use liquid carbon dioxide to achieve sub-ambient column oven temperatures down to -20 °C. The CO_2 cryogenic performance characteristics of the 6850 were tested using the ASTM D3710 method for simulated distillation of gasoline. The 6850 showed ten-times better chromatographic performance. These results were also identical to the Agilent 6890 equipped with CO_2 cryogenic oven cooling. The 6850 also used 50% less CO_2 for each run of D3710 when compared to the 6890.

References

1. ASTM Method D3710, "Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography", ASTM Book of Standards, Volume 5.02, ASTM, 500 Barr Harbor Drive, West Conshohocken, PA 19428, USA.

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