Analysis of Oxygenates and Aromatics Using ASTM Method D4815 and D5580

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1 Introduction

Gasoline samples are complex and a single column solution is not always readily available for the required analysis. As such solutions that have multiple columns, valves, backflushing and heartcutting ability have been developed to overcome these challenging separations. The resulting standardized methods can have a complex series of columns and valves that limit the flexibility of a gas chromatograph (GC) to analyze samples for other analytes. Removing and installing column sets is time consuming and causes instrument downtime with subsequent loss of productivity.
Flexibility is a key attribute in the decision to purchase capital equipment for the increase in productivity and return on investment. The PerkinElmer Model ARNEL 4004 analyzer utilizes the same column set and valving for ASTM D4815 and ASTM D5580 enabling greater sample flexibility and subsequent return on investment.

2 ASTM D4815

Test method ASTM D4815 is the standard test method for ethers and alcohols in gasoline. These additives are blended to produce a fuel that burns with acceptable performance while minimizing pollution from carbon monoxide, benzene and other exhaust emissions.
The method utilizes two columns to effect the separation. The first column is a 20% TCEP and is used to vent the lighter hydrocarbons that are present while the remaining analytes are retained. After the methylcyclopentane elutes to the vent, the valve position is changed and the TCEP column is backflushed into the Elite 1™ column, where the analytes are then separated according to boiling point. The next timed event is after TAME is eluted from the Elite 1™ column at which point the valving returns to the original position and now backflushes the Elite 1™ column for the final composite peak of heavy hydrocarbons.

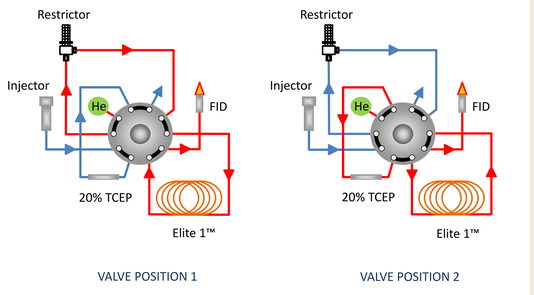

Figure 1. The valving and column set showing the two valve positions that enable the backflushing and separation of the analytes of interest.

Capillary Injector	200 °C
Flame Ionization Detector	250 °C
Oven Program	Isothermal at 60 °C hold 30* minute
Column Set	
Column 1	20% TCEP 80/100 56 cm x 1/16" Sf
Column 2	30 m x 0.53 mm x 5.0 um Elite 1™
Column Pressure	17.8 psig
Auxiliary Flow	3 mL/min
Timed Events	Switch valve on at 0.13 min
	Switch valve off at 8 min

Table 1 Method parameters for the oxygenate analysis with the timed events that are crucial to the separation. * Changing the Auxiliary flow via timed event will decrease the run time.

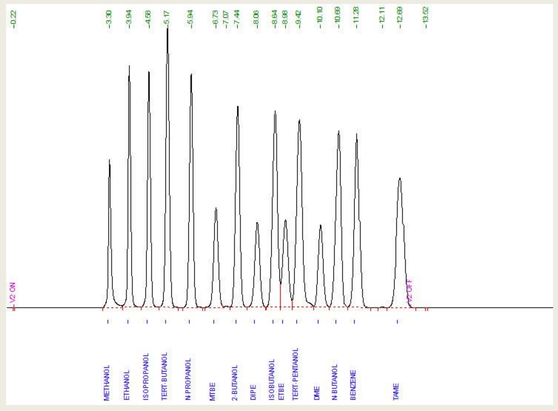

Figure 2. Separated oxygenates.

Component	Retention Time	Approximate Concentration % by Weight
Methanol	3.30	7.27
Ethanol	3.94	7.27
2-Propanol	4.58	7.26
t-Butanol	5.17	7.25
1-Propanol	5.94	7.28
MTBE	6.73	3.98
sec-Butanol	7.44	7.27
Diisopropyl ether	8.08	3.98
i-Butanol	8.64	7.27
ETBE	8.98	3.98
t-Amyl Alcohol	9.42	7.26
1,2-Dimethoxyethane	10.10	5.97
n-Butanol	10.69	7.32
TAME	12.69	3.98

Table 2. Retention times of the different oxygenates.

3 ASTM D5580

Aromatic analysis of fuels consists of two analyses that utilize the same column set. The first method is for the analysis of the aromatic compounds benzene and toluene with the second method for the analysis of ethylbenzene, o-xylene and 1,2,4-trimethylbenzene.
The first method utilizes the same two columns used for D4815 to effect the separation. The 20% TCEP column is used to vent the lighter non aromatic hydrocarbons that are present while the remaining analytes are retained. The valve position is changed so the TCEP column is backflushed before the benzene elutes to the vent and the analytes are then separated according to boiling point using the Elite 1™ column. The next timed event is after the 2-hexanone internal standard is eluted from the Elite 1™ column at which point the valving returns to the original position and now backflushes the Elite 1™ column for the final composite peak of heavy hydrocarbons.

Capillary Injector	200 °C
Flame Ionization Detector	250 °C
Oven Program	Initial 60 °C (hold 6 min) ramp at 2 °C/ min to 115 °C (hold 3 min)
Column Set	
Column 1	20% TCEP 80/100 56 cm x 1/16" Sf
Column 2	30 m x 0.53 mm x 5.0 um Elite 1™
Column Pressure	29.4 psig
Auxiliary Flow	10 mL/min
Timed Events	Switch valve on at 0.25 min
	Switch valve off at 10.00 min

Table 3. Method parameters for the analysis of benzene and toluene.

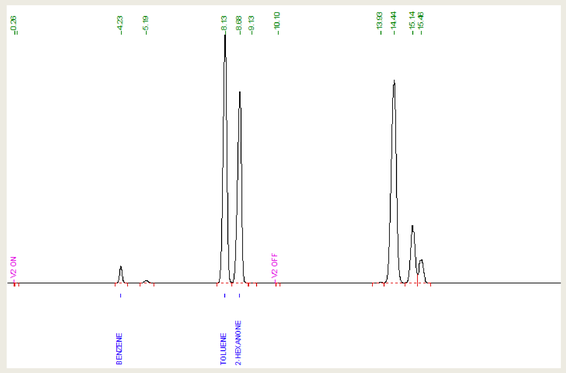

Figure 3. The benzene, toluene and 2-hexanone separation.

Component	Retention Time	Approximate Concentration % by Weight
Benzene	4.23	0.45
Toluene	8.13	9.0
2-Hexanone	8.68	10.0

Table 4. Benzene and toluene retention times.

Capillary Injector	200 °C
Flame Ionization Detector	250 °C
Oven Program	Initial 60 °C (hold 6 min) ramp at 2 °C/ min to 115 °C (hold 7 min)
Column Set	
Column 1	20% TCEP 80/100 56 cm x 1/16" Sf
Column 2	30 m x 0.53 mm x 5.0 um Elite 1™
Column Pressure	29.4 psig
Auxiliary Flow	10 mL/min
Timed Events	Switch valve on at 1.00 min
	Switch valve off at 11.70 min

Table 5. Method parameters for the analysis of the remaining aromatics.

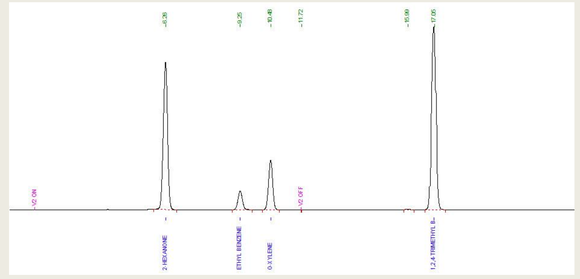

Figure 4. Separation of the aromatics.

Component	Retention Time	Approximate Concentration % by Weight
2-Hexanone	6.26	10.0
Ethylbenzene	9.25	0.9
o-Xylene	10.48	2.25
1,2,4- Trimethylbenzene	17.05	9.0

Table 6. Retention times of the aromatics.

7 Conclusion

The column set in the PerkinElmer Model ARNEL 4004 analyzer can easily be used for ASTM 4815 and ASTM 5580 by simply changing the GC oven program and the valve switching timed events. The PerkinElmer Model ARNEL 4004 analyzer offers greater flexibility, productivity and improved value over the lifetime of ownership.