

## Gas Chromatography

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## Analysis of Oxygenates and Aromatics Using ASTM Method D4815 and D5580

### 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.

## 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. Regulatory compliance is also a factor in accurately determining the concentrations of the additives present as several U.S. states have prohibited the use of MTBE.

## Method

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, and 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.

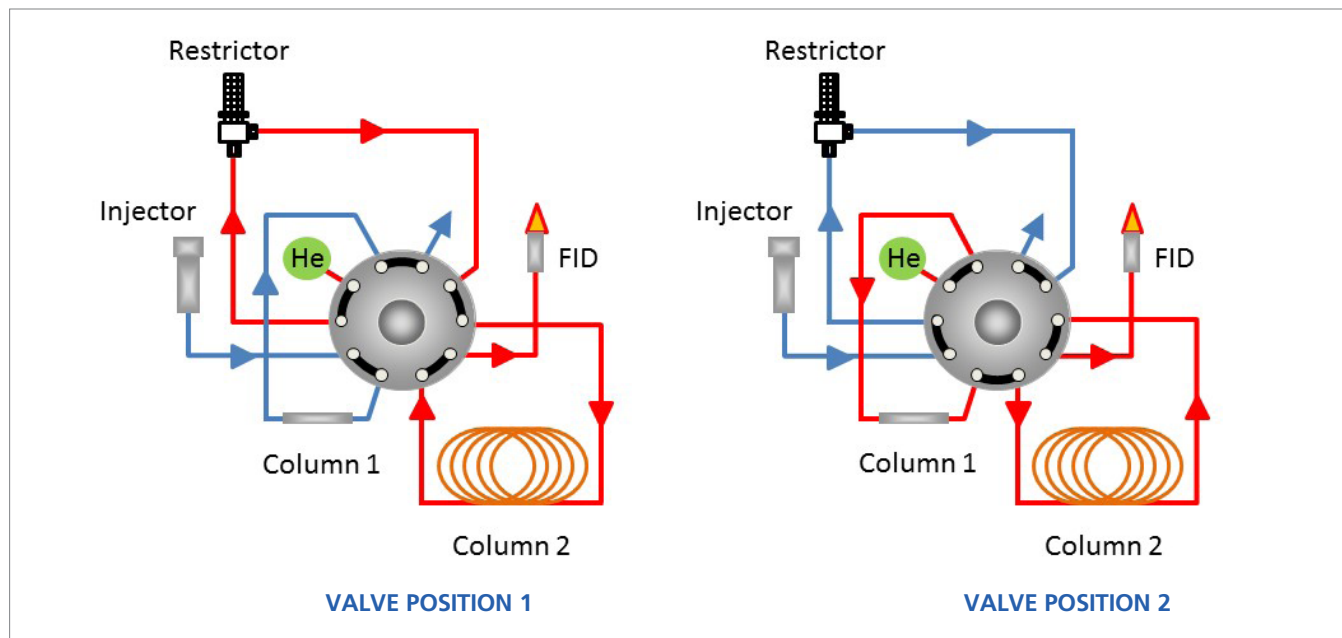


Figure 1. The column set and valve operation for ASTM D4815.

## Experimental

The Clarus® 690 gas chromatograph is operated with the conditions given in Table 1.

Table 1. GC parameters.

Capillary Injector	200 °C
Flame Ionization Detector	250 °C
Oven Program	Isothermal at 60 °C hold 30* minutes
<b>Column Set</b>	
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

Note. \* changing the auxiliary flow via instrument timed event can decrease the run time.

## Results

Table 2. Standard components with retention time and concentration.

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

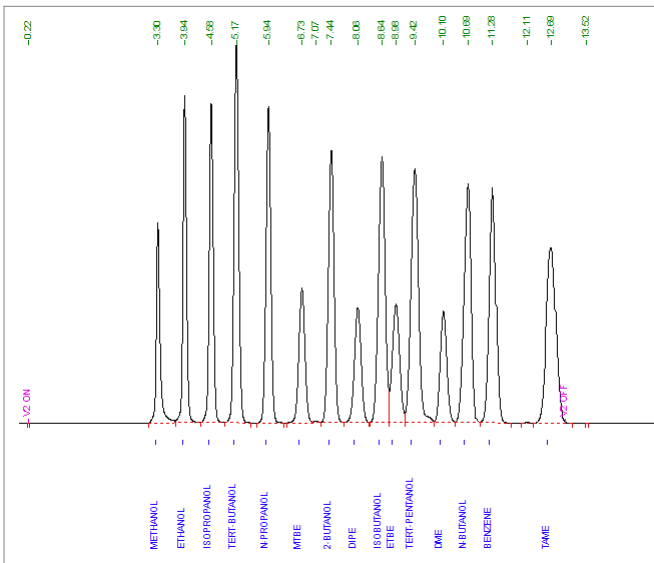


Figure 2. Separation of the oxygenates.

The oxygenates are quickly separated using the isothermal method for effective quantitation with the new wide range flame ionization detector. The wide dynamic range ensures that there is no loss of sensitivity while accurately measuring the % concentrations of the analytes without detector saturation that would require dilution and reanalysis.

The isothermal method requires no cool down and minimizes injection to injection time for increased productivity with high sample throughput.

## Conclusion

The Clarus 690 GC with wide range FID is an excellent solution for the analysis of oxygenates by ASTM D4815-15. The two column approach with backflushing efficiently separates the oxygenates of interest from the light and heavy hydrocarbons present using a robust method with preset valve switch timings.

## 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.

## Method 1 Aromatics

The 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.

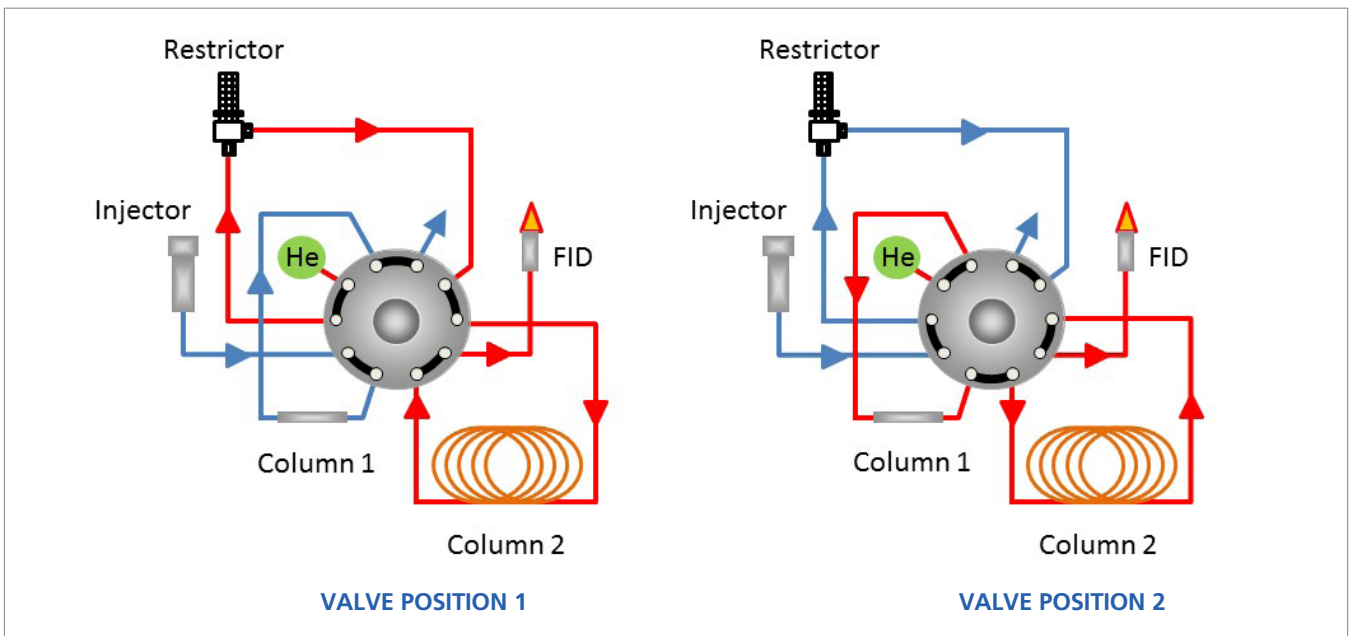


Figure 3. The column set and valve operation for ASTM D5580.

## Experimental

### Method 1 Aromatics

The Clarus 690 gas chromatograph is operated in the conditions given in Table 3.

Table 3. GC parameters.

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)
<b>Column Set</b>	
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

## Results

Table 4. Standard components with retention time and concentration.

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

## Conclusion

The Clarus 690 GC with the wide range FID is an excellent solution for the analysis of aromatics by ASTM D5580. The two column approach with backflushing efficiently separates the aromatics of interest from the other hydrocarbons present using a robust method with preset valve switch timings. Benzene and

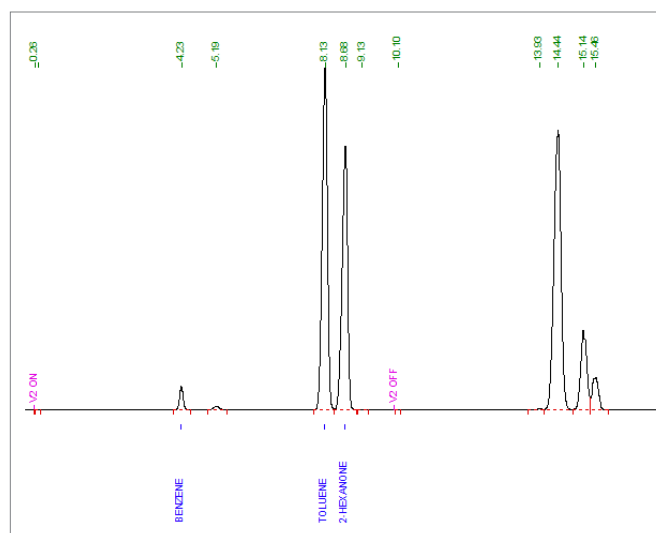


Figure 4. Separation of the aromatics with the backflushed components beginning at 13.33 minutes.

toluene are quickly separated with baseline resolution of toluene and the internal standard 2-hexanone clearly achieved.

### Method 2 Ethylbenzene, Xylenes , C9 and Heavier Aromatics and Total Aromatics

The 20% TCEP column is used to vent the lighter hydrocarbons of C12 and below as well as benzene and toluene that are present while the remaining analytes are retained. The valve position is changed and the TCEP column is backflushed before the ethylbenzene elutes to the vent with the remaining analytes then separated according to boiling point using the Elite 1™ column. The next timed event is after the o-xylene 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 aromatics and heavy hydrocarbons.

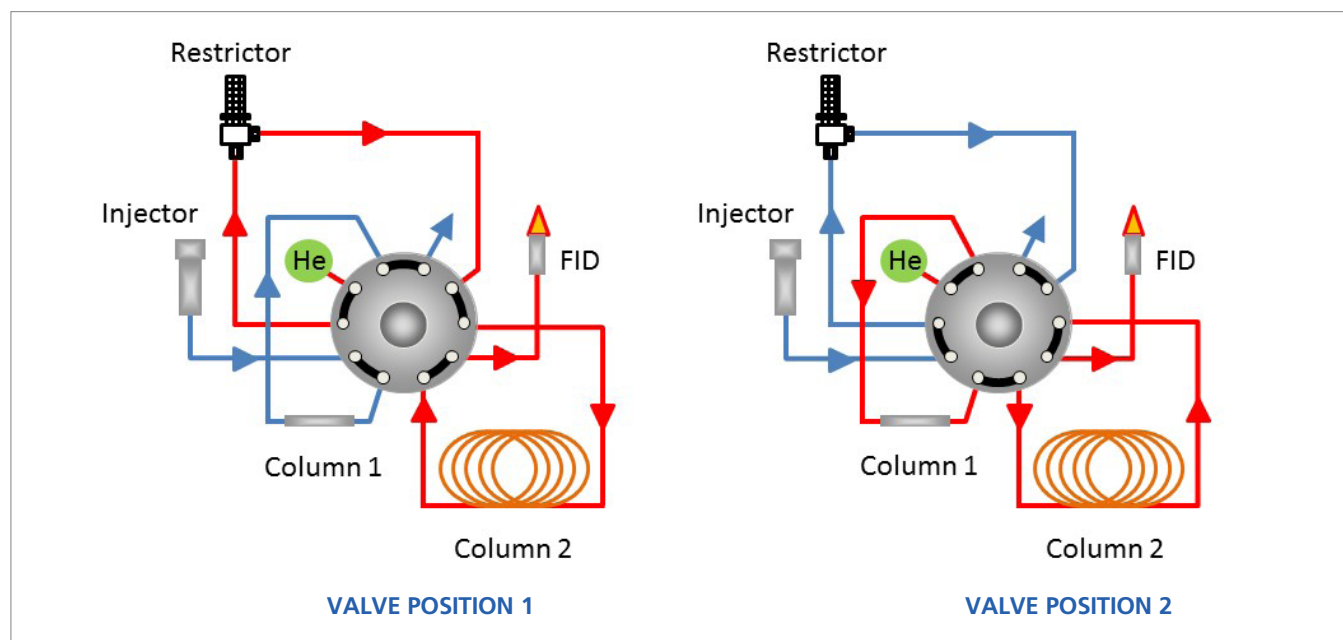


Figure 5. The column set and valve operation for ASTM D5580.

## Experimental

### Method 2 Ethylbenzene

The Clarus 690 gas chromatograph is operated in the conditions given in Table 5.

Table 5. GC parameters.

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

## Results

Table 6. Standard components with retention time and concentration.

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

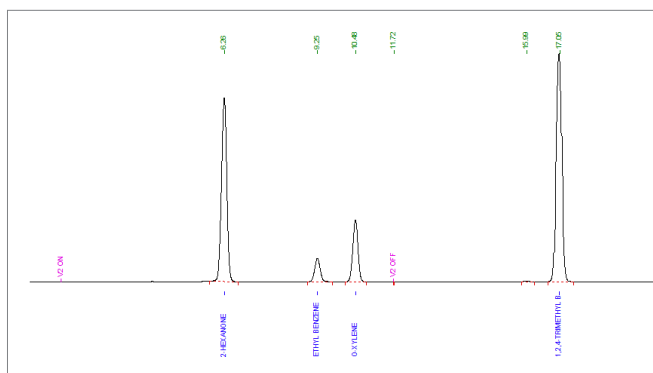


Figure 6. Ethylbenzene, O-xylene and 1,2,4-trimethylbenzene are all baseline separated.

The Clarus 690 GC with wide range FID is an excellent solution for the analysis of aromatics by ASTM D5580. The two column approach with backflushing efficiently separates the ethylbenzene, xylenes, C9 and heavier aromatics and total aromatics of interest from the other hydrocarbons present using a robust method with preset valve switch timings. As can be seen in Figure 6 the ethylbenzene, o-xylene and 1,2,4-trimethylbenzene are all baseline separated with excellent peak shape for consistent integration and quantitation.

## 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.