APPLICATION NOTE

Gas Chromatography

Author

A. Tipler[1]

PerkinElmer, Inc.
Shelton, CT 06484 USA

The Determination of C_2 to C_5 Hydrocarbons in Finished Gasolines using the PerkinElmer Clarus 680 GC with Swafer Technology

Introduction

ASTM® Test Method, D2427-06, is designed to determine the C_2 to C_5 hydrocarbon content in gasolines. This method validates gasoline samples that are depentanized using ASTM® method D2001-07. These samples are intended for functional group hydrocarbon analysis by mass spectrometry according ASTM® Test Method D2789-95 (2005).

The method could be used for other sample types in which light aliphatic hydrocarbons are to be determined in samples containing significant low volatility or polar components in the matrix. The method is also suitable to determine methane content and could be extended to include higher hydrocarbons.

D2427-06 is a mature method that utilizes packed columns and mechanical valves for the backflush and foreflush techniques needed to separate the volatile hydrocarbons from the rest of the gasoline sample.

Modern gasolines contain significant concentrations of ethanol and other additives that may interfere with the existing method so there is a need to develop an alternative procedure to determine the light hydrocarbons. There have also been significant advances in column technology and chromatographic instrumentation that would improve the quality of the data and reduce the analysis time as well, so it would be appropriate to consider their use in this application.

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Analytical Approach

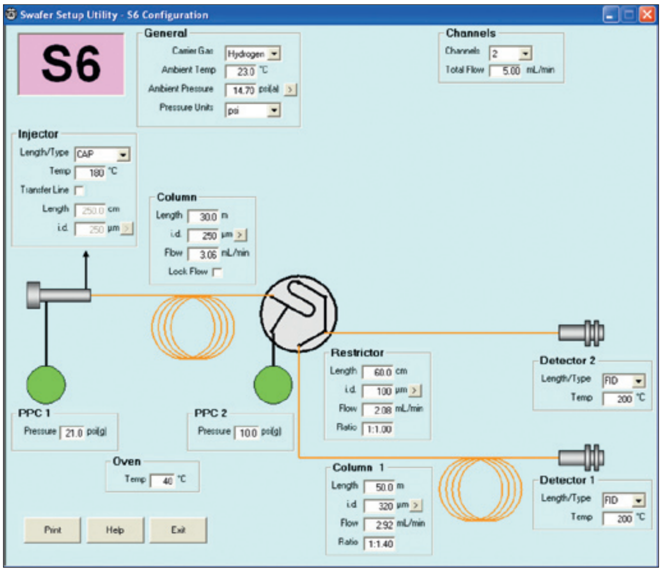
An alumina porous layer open tubular (PLOT) column with split injection and flame ionization detection is for the separation of C_2 to C_5 saturated and unsaturated hydrocarbon isomers and is an obvious choice for this application. This column however will become easily 'poisoned' if higher hydrocarbons, aromatics or ethanol are allowed to pass into it. Thus, the analytical method will need to remove these compounds from the gasoline sample vapor before it enters the PLOT column.

The removal of these 'unwanted' components is easily achieved by deploying a 2-column backflushing system. A Carbowax® precolumn was chosen to enable the C_2 to C_5 hydrocarbons to elute and pass into the PLOT column before the higher hydrocarbons, aromatics or ethanol. Reversal of the direction of carrier gas flow in the precolumn, will backflush the unwanted components back into the injector liner and out through the split vent. Chromatography of the C_2 to C_5 hydrocarbons will continue on the PLOT column during the backflush process. In this way, the backflush step does not add to the chromatographic run time.

Backflushing is a very effective technique for removing late-eluting unwanted material from a GC column.

Experimental Conditions

The Swafer™ S6 configuration is used here with a fused silica restrictor tube on one of the outlet ports to enable the chromatography on the precolumn to be directly monitored by a detector. This enables the backflush point to be easily established.



Swafer Setup Utility - S6 Configuration

S6

General
Carrier Gas: Hydrogen
Ambient Temp: 23.0 °C
Ambient Pressure: 14.70 psi(a)
Pressure Units: psi

Channels
Channels: 2
Total Flow: 5.00 mL/min

Injector
Length/Type: CAP
Temp: 180 °C
Transfer Line: ☐
Length: 250.0 cm
i.d.: 250 µm

Column
Length: 30.0 m
i.d.: 250 µm
Flow: 3.06 mL/min
Lock Flow: ☐

Restrictor
Length: 60.0 cm
i.d.: 100 µm
Flow: 2.08 mL/min
Ratio: 1:1.00

Detector 2
Length/Type: FID
Temp: 200 °C

PPC 1
Pressure: 21.0 psi(g)

PPC 2
Pressure: 10.0 psi(g)

Oven
Temp: 40 °C

Column 1
Length: 50.0 m
i.d.: 320 µm
Flow: 2.92 mL/min
Ratio: 1:1.40

Detector 1
Length/Type: FID
Temp: 200 °C

Figure 1. Swafer Utility Software showing the S6 configuration used in this method and gas pressures used for the initial work.

The Swafer Utility Software was used to establish the carrier gas pressures needed for this analysis. Figure 1 shows a screen shot taken from this software showing the configuration and suggested pressure settings used for the initial work.

Note that hydrogen is used as the carrier gas. This enables the run time to be reduced to increase sample throughput and eliminates the need for increasingly expensive helium as world stocks are depleting.

Initial Method Set Up

To set up the system and identify and calibrate the target analytes, a refinery gas standard (RGS) was used as given in Table 1. Nearly all the target analytes listed in ASTM® D2427-06 are included and indicated in this mixture. The missing analytes are two methyl-butenes.

Table 1. **Arnel Refinery Gas Calibration Blend (Lot 102-06-04137, Cylinder # 10196D).**

Component	Mol%
Hydrogen	12.4819
Carbon Dioxide	2.9971
Ethylene*	2.0025
Ethane*	4.0021
Acetylene	0.9992
Oxygen	0.9998
Nitrogen	36.1691
Methane	5.0112
Carbon Monoxide	0.9984
Propane*	6.0185
Propylene*	3.0038
Isobutane*	5.0000
Propadiene*	0.9970
n-Butane*	3.9993
1-Butene*	1.9998
Isobutylene*	1.0025
t-2-Butene*	3.0061
c-2-Butene*	1.9996
1,3-Butadiene*	3.0107
Isopentane*	1.0009
n-Pentane*	2.0002
1-Pentene*	0.4007
t-2-Pentene*	0.1996
c-2-Pentene*	0.4001
2-Methyl-2-Butene*	0.1998
n-Hexane	0.1001

* *Target analyte listed in ASTM® D2427-06*

50 µL of the RGS gas mixture were injected by gas syringe with the restrictor from the Swafer connected to the detector as shown in Figure 2.

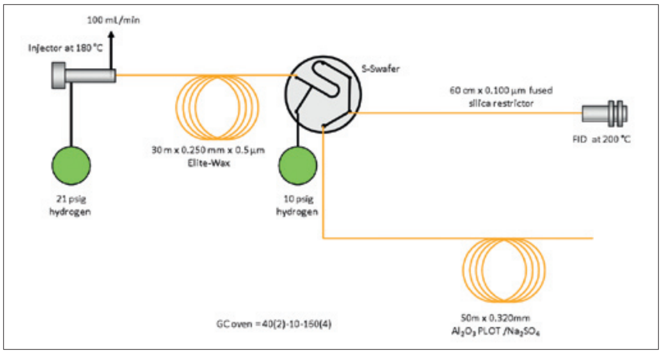


Figure 2. System configured to monitor the precolumn chromatography and establish the backflush point.

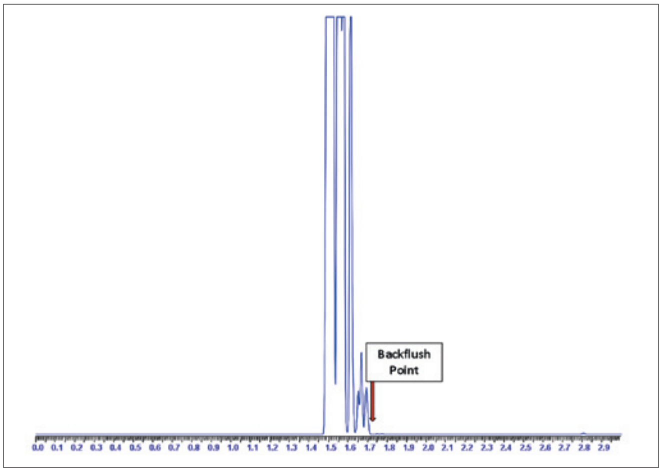


Figure 3. Precolumn chromatography of RGS mixture.

Figure 3 shows the resultant chromatography from this injection. All components have eluted from the precolumn (and into the PLOT column) within 1.7 minutes. To tolerate slight experimental variations, a backflush time of 1.72 minutes was adopted for the method.

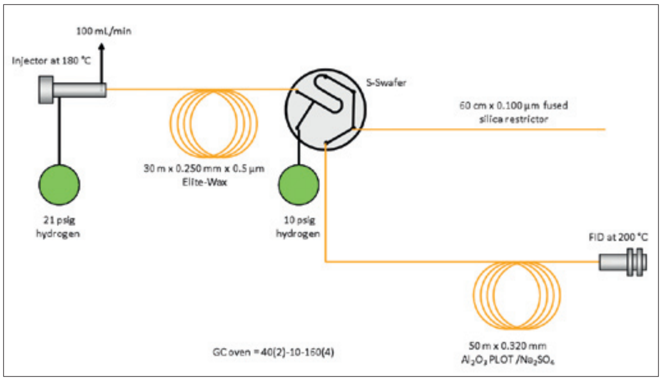


Figure 4. System configured to monitor the PLOT column chromatography to check the final chromatographic separation.

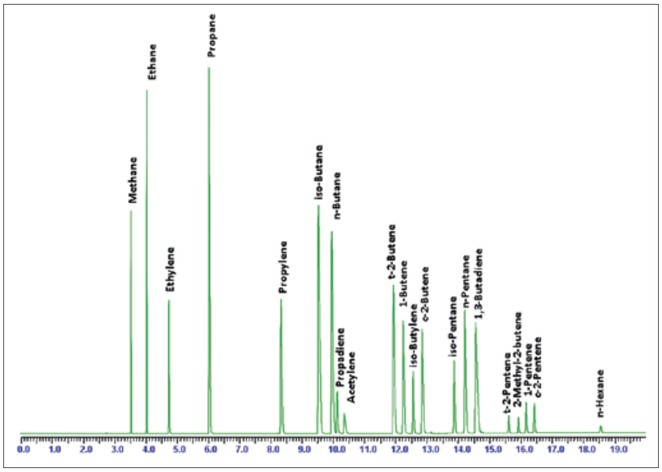


Figure 5. Chromatography of RGS mixture eluting from PLOT column.

To check the separation of the RGS mixture on the complete system, the restrictor was disconnected from the detector and the PLOT column was connected as shown in Figure 4 with a typical chromatogram given in Figure 5.

Study of Figure 3 and Figure 5 reveals that the precolumn chromatography finishes before the first peak (methane) elutes from the PLOT column. This means that both the restrictor and the PLOT column may be connected to the same detector to enable both the precolumn and PLOT column chromatography to be monitored in the same chromatogram.

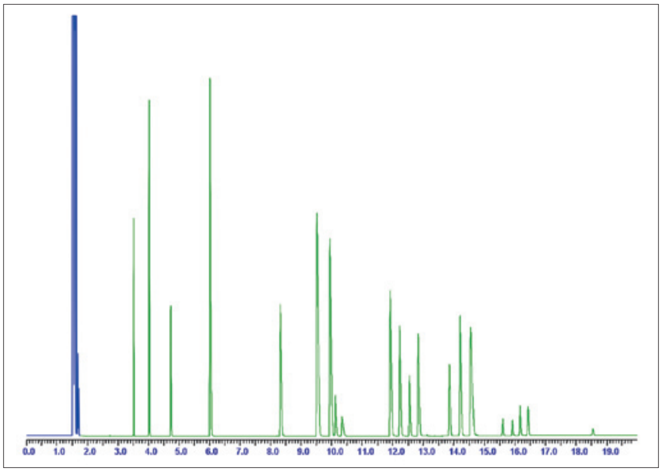
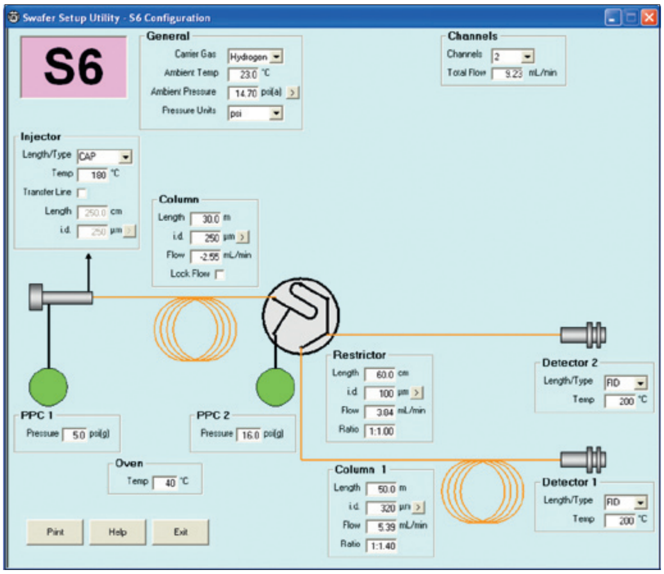


Figure 6. Combined precolumn and PLOT column chromatography of RGS mixture.

Figure 6 shows such a combined chromatogram. This approach makes set-up much easier as now there is no need to swap detector connections or buy an additional detector. The presence of both chromatograms in a single trace provides better QC as the precolumn chromatogram is now always present for checking.

When the pressure at the injector is reduced to initiate the backflush process, there is a time lag before the carrier gas starts to flow backwards into the precolumn from the Swafer. This means that sample material will continue to elute into the analytical column for several more seconds. To reduce this apparent time lag, a second timed event is added to the method to slightly raise the midpoint pressure inside the Swafer at the same time as reducing the inlet pressure.

The final method is given in Figure 7 and Table 2.



Swafer Setup Utility - S6 Configuration

S6

General
Carrier Gas Hydrogen
Ambient Temp 23.0 °C
Ambient Pressure 14.70 psi(a)
Pressure Units psi

Channels
Channels 2
Total Flow 9.23 mL/min

Injector
Length/Type CAP
Temp 180 °C
Transfer Line ☐
Length 250.0 cm
i.d. 250 µm

Column
Length 30.0 m
i.d. 250 µm
Flow -2.55 mL/min
Lock Flow ☐

Restrictor
Length 60.0 cm
i.d. 100 µm
Flow 3.04 mL/min
Ratio 1:1.00

Detector 2
Length/Type FID
Temp 200 °C

PPC 1
Pressure 5.0 psi(g)

PPC 2
Pressure 16.0 psi(g)

Oven
Temp 40 °C

Column 1
Length 50.0 m
i.d. 320 µm
Flow 5.39 mL/min
Ratio 1:1.40

Detector 1
Length/Type FID
Temp 200 °C

Figure 7. Screen shot taken from the Swafer Utility Software showing the system in backflush mode (note that in practice, a single detector is used).

***Table 2.* Full experimental conditions.**	
Gas Chromatograph	PerkinElmer® Clarus® 680
Oven	40 °C for 2 minutes, then 10 °C/minute to 180 °C and hold for 5 minutes
Injector	Split/Splitless or Programmable Split/Splitless. 100 mL/min Split at 180 °C
Detector	Flame Ionization at 200 °C Air 450 mL/min, Hydrogen 45 mL/min Range x1, Attenuation x2
Backflush Device	S-Swafer in S6 configuration
Precolumn	30 m x 0.25 mm x 0.5 µm Elite Wax
Analytical Column	50 m x 0.32 mm Al_2O_3 PLOT
Midpoint Restrictor	Fused silica, 60 cm x 0.100 mm
Carrier Gas	Hydrogen
Carrier Gas Pressure Programming	Inlet: 21 psig for 1.73 min, then 5 psig by timed event until end of run Midpoint: 10 psig for 1.72 min then 16 psig by timed event until end of run (see text)
Injection	0.3 µL by Autosampler in fast mode

Figure 8 shows a chromatogram of the RGS mixture using the final conditions. Because the midpoint pressure has been raised for most of the run, the peak retention times are much shorter. Because the PLOT column retention relies on adsorption rather than partition, increasing the carrier gas pressure and hence the linear gas velocity does not significantly degrade column efficiency. In fact, the peaks shown in Figure 8 look better than those in the chromatogram in Figure 6 which was run at a lower midpoint pressure.

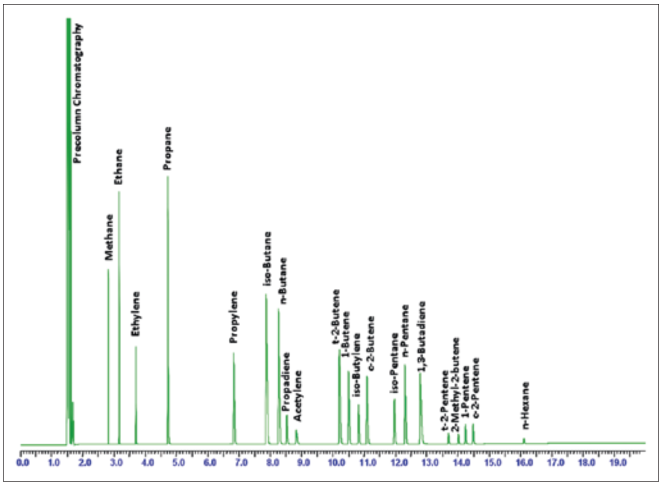


Figure 8. Chromatography of RGS mixture eluting from PLOT column with reduced inlet pressure and elevated midpoint pressure at backflush point.

Figure 9 shows a chromatogram of a gasoline sample run under these conditions.

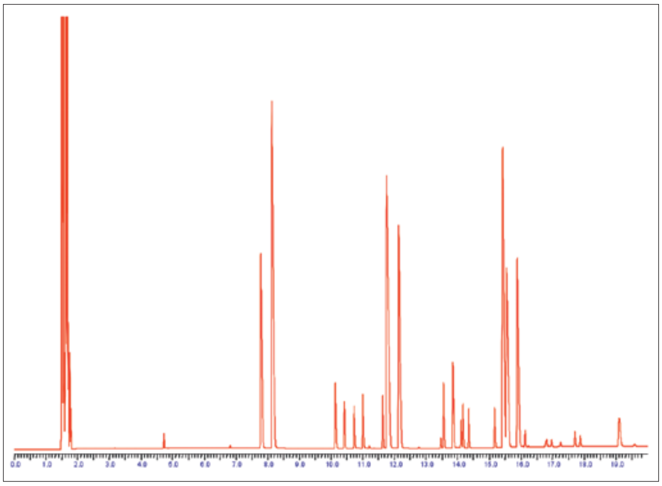


Figure 9. Combined precolumn and PLOT column chromatography with backflushing of a typical gasoline sample.

Calibration

ASTM® Test Method, D2427-06 recommends the use of an internal standard such as 2-chloropropane for the quantitative calculations. Such compounds are not compatible with the alumina PLOT column and so external standard calculations were applied.

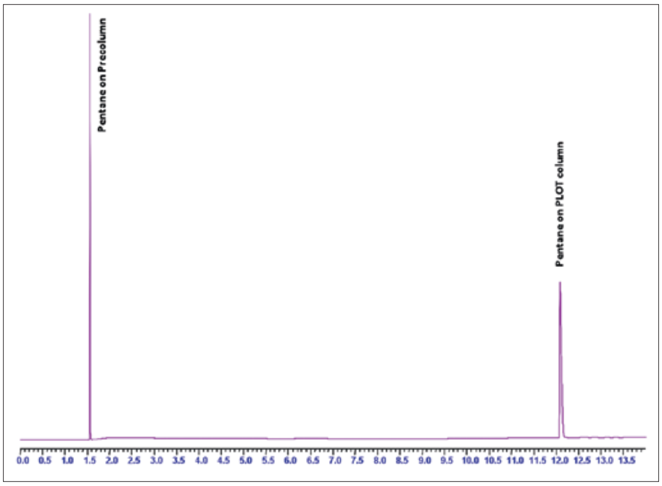


Figure 10. Chromatogram of 1.3% w/v solution of n-pentane in toluene.

The system was calibrated using a 1.3% w/v solution of n-pentane in toluene. The toluene is backflushed by the method and so only a peak for n-pentane appears as shown in Figure 10. The response factor calculation is shown in Table 3.

***Table 3.* Calculation of response factor for n-pentane.**

Weight added (g)	0.1298
Diluted volume (mL)	10.0
Concentration (% w/v)	1.298
Peak area (µV.s)	974160
Response factor (µV.s/%)	750508

Using the RGS mixture chromatography shown in Figure 8, peak areas were used to calculate relative response factors for the analytes as shown in Table 4.

These values were used to adjust the response factor of n-pentane given in Table 3 for application to each of the analytes. Note that n-pentane does not have to be in the sample for these calibrations to apply.

***Table 4.* Response Factors calculated from RGS gas mixture.**

Component	Mol%	M.W	Peak Area µV.s	Response Factor Relative to n-Pentane (Area/wt.)	Absolute Response Factors (µV.s/%)
Ethylene	2.0025	28	187178	1.14	855983
Ethane	4.0021	30	398308	1.13	850647
Propane	6.0185	44	877739	1.13	849893
Propylene	3.0038	42	421959	1.14	857610
Isobutane	5.0000	58	933182	1.10	825103
Propadiene	0.9970	38	127910	1.15	865697
n-Butane	3.9993	58	750601	1.11	829731
1-Butene	1.9998	56	368216	1.12	843078
Isobutylene	1.0025	56	175064	1.07	799586
t-2-Butene	3.0061	56	548315	1.11	835178
c-2-Butene	1.9996	56	358177	1.09	820176
1,3-Butadiene	3.0107	54	550241	1.16	867824
Isopentane	1.0009	72	219375	1.04	780557
n-Pentane	2.0002	72	421523	1.00	750508
1-Pentene	0.4007	70	82292	1.00	752283
t-2-Pentene	0.1996	70	41566	1.02	762808
c-2-Pentene	0.4001	70	82919	1.01	759151
2-Methyl-2-Butene	0.1998	70	39758	0.97	728905
3-Methyl-1-Butene	Absent	70	–	–	728905*
2-Methyl-1-Butene	Absent	70	–	–	728905*

**Response factor assumed to be equivalent to 2-Methyl-2-Butene*

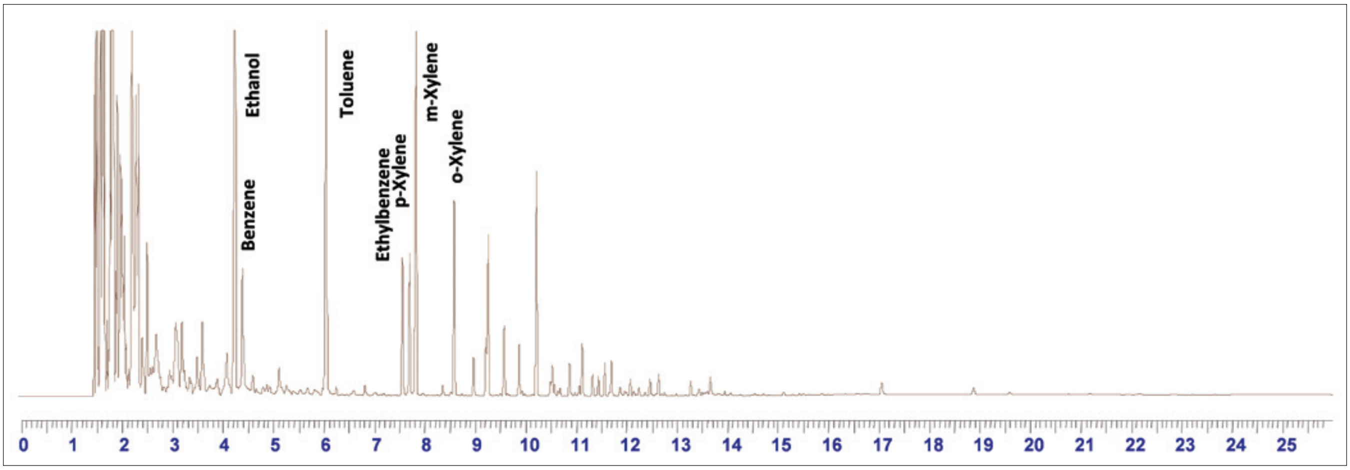


Figure 11. Example of precolumn chromatogram (no backflushing).

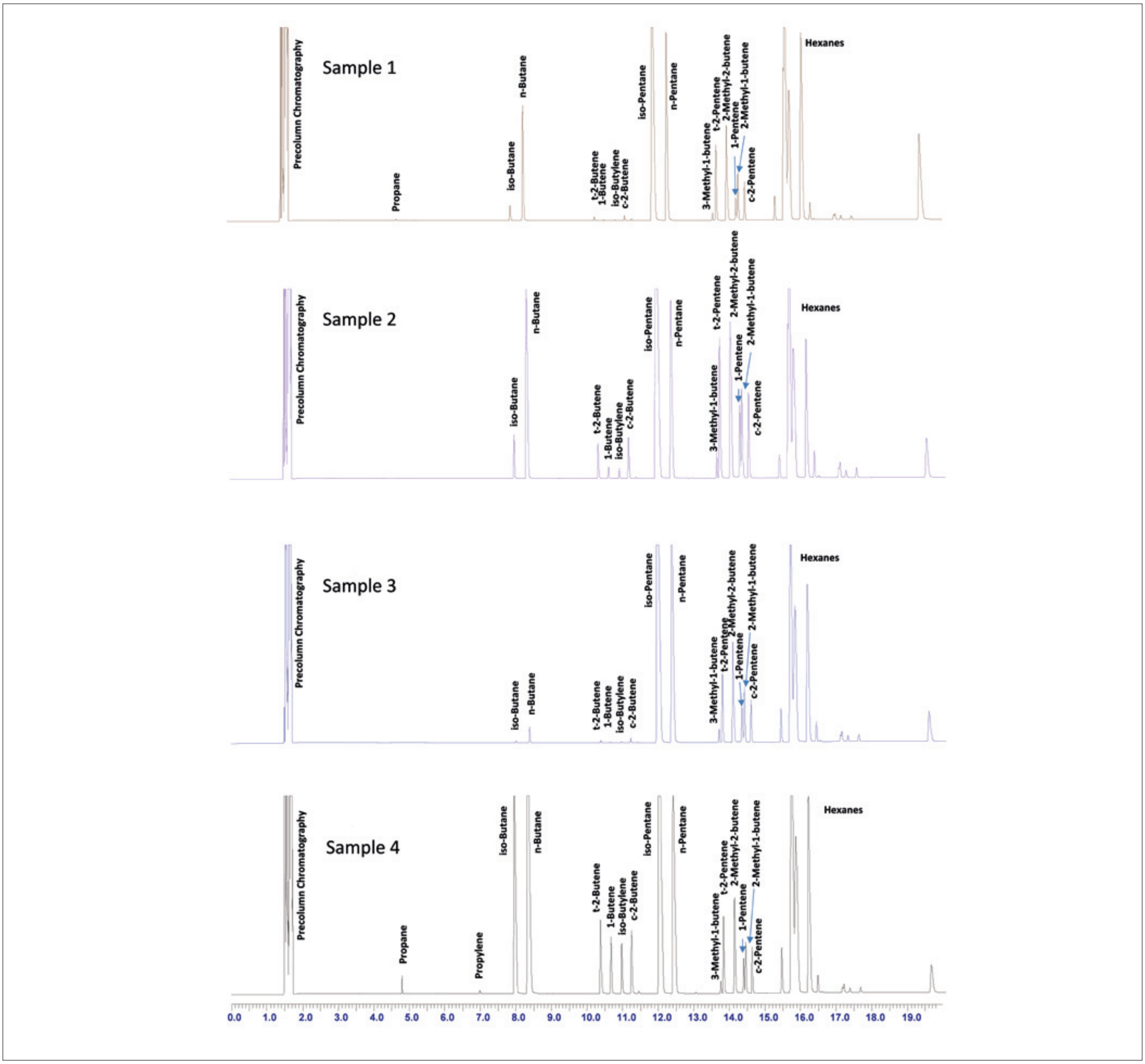


Figure 12. System chromatograms of gasoline samples (with backflushing).

Example Analyses

Four samples of gasoline were obtained as listed in Table 5. These samples were of various vintages. The recent samples were known to contain ethanol whereas the earlier samples would contain MTBE. These should provide a good test for this method.

***Table 5.* Gasoline samples analyzed.**

Sample	Description
1	2010 87-octane gasoline
2	Unleaded oxygen-free
3	1990 unleaded gasoline
4	2003 unleaded gasoline

To characterize these samples, each was chromatographed on the precolumn with no backflushing with just the precolumn connected to the detector. An example chromatogram is given in Figure 11. For the C_2 to C_5 determination, only the first 1.72 minutes of this pre-column chromatography will be sent to the PLOT column.

For the C_2 to C_5 determination, only the first 1.72 minutes of this precolumn chromatography will be sent to the PLOT column. It is clear that, with the backflushing method, all the aromatics, higher hydrocarbons and oxygenated compounds, including MTBE and ethanol, will be excluded from the PLOT column leading to a very rugged performance.

These same gasoline samples were now analyzed on the combined precolumn and PLOT column using the backflush method conditions given in Table 2. The resultant chromatograms are given in Figure 12.

The peak areas from the chromatograms shown in Figure 12 were processed using the response factors given in Table 4.

To check the quantitative precision, one of the gasoline samples was injected 10 times and the standard deviations were calculated for the quantitative results and the peak retention times, are shown in Table 7. These results far exceed the requirements of method D2427.

***Table 6.* Concentration in Sample (% w/v).**

Component	Sample 1	Sample 2	Sample 3	Sample 4
Ethylene	N.D.	N.D.	N.D.	N.D.
Ethane	N.D.	N.D.	N.D.	N.D.
Propane	N.D.	N.D.	N.D.	0.05
Propylene	N.D.	N.D.	N.D.	0.01
iso-Butane	0.06	0.19	0.01	1.66
Propadiene	N.D.	N.D.	N.D.	N.D.
n-Butane	0.61	1.36	0.06	3.68
1-Butene	N.D.	0.04	N.D.	0.26
iso-Butylene	N.D.	0.04	N.D.	0.25
t-2-Butene	0.01	0.17	0.01	0.41
c-2-Butene	0.02	0.19	0.02	0.33
1,3-Butadiene	N.D.	N.D.	N.D.	N.D.
iso-Pentane	3.33	4.54	4.18	3.64
n-Pentane	1.62	1.54	2.60	2.36
1-Pentene	0.10	0.36	0.15	0.15
t-2-Pentene	0.42	0.96	0.38	0.43
c-2-Pentene	0.19	0.53	0.22	0.23
2-Methyl-2-Butene	0.67	1.33	0.67	0.64
3-Methyl-1-Butene	0.03	0.11	0.06	0.05
2-Methyl-1-Butene	0.26	0.66	0.32	0.29

N.D.: None Detected

***Table 7.* Quantitative precision obtained from repetitive injection of a gasoline sample (n=10).**

Component	Concentration		
	Mean (% w/v)	**Std Dev (% w/v)**	**D2427-06 Req. (% w/v)**
Ethylene	N.D.	N.D.	
Ethane	N.D.	N.D.	
Propane	0.04	0.0002	0.1
Propylene	N.D.	N.D.	0.1
iso-Butane	1.62	0.0105	0.1
Propadiene	N.D.	N.D.	
n-Butane	3.59	0.0174	0.1
1-Butene	N.D.	N.D.	0.1
iso-Butylene	0.25	0.0026	0.1
t-2-Butene	0.40	0.0023	0.1
c-2-Butene	0.32	0.0019	0.1
1,3-Butadiene	0.00	0.0000	
iso-Pentane	3.58	0.0245	0.3
n-Pentane	2.33	0.0170	0.1
1-Pentene	0.15	0.0013	0.1
t-2-Pentene	0.42	0.0036	0.1
c-2-Pentene	0.23	0.0020	0.1
2-Methyl-2-Butene	0.64	0.0063	0.3
3-Methyl-1-Butene	0.05	0.0004	
2-Methyl-1-Butene	0.28	0.0027	0.2

N.D.: None Detected

Other Sample Types

Although this method was primarily designed to determine light hydrocarbons in finished gasolines, it can be applied to any sample in which there are significant levels of less volatile or more polar components in the matrix.

Figure 13 shows an example of chromatography from an injection of a light crude oil using this method. The method was modified slightly by increasing the injector temperature to 250 °C to assist in the volatilization of the heavier sample. Note that none of the heavy hydrocarbons in the crude oil were able to enter the PLOT column.

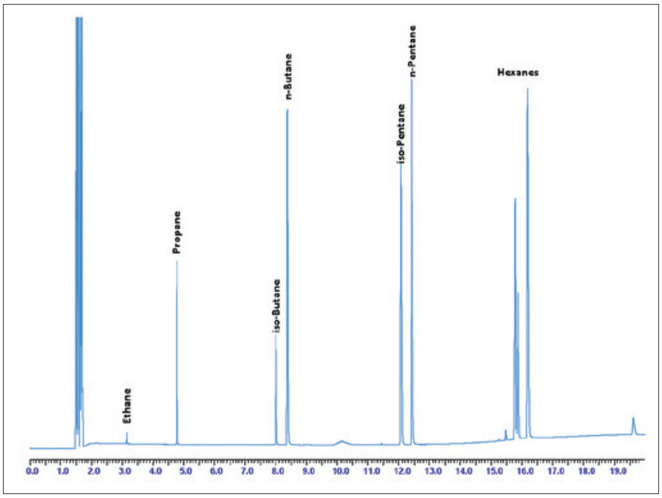


Figure 13. System chromatogram of a sample of light crude oil diluted 50:50 with toluene.

Conclusions

- The combination of modern capillary columns with the Swafer technology has taken a mature method and improved the quality of the data and reduced the run time as intended.
- Excellent separation of the C_2 to C_5 aliphatic hydrocarbons is evident with no apparent interference from higher hydrocarbons, aromatics or oxygenated compounds.
- Even though the method relies on significant carrier gas pressure and flow rate changes, the quantitative and peak retention time precisions are excellent.
- The chromatographic run time has been reduced from over 60 minutes to just 20 minutes. The total cycle time of the chromatographic analysis (including oven cool-down and equilibration) is less than 24 minutes enabling 20 samples to be analyzed during an 8-hour working shift or 60 samples a day if run continuously.
- The method will also determine levels of methane, if present (in other sample matrices).
- The method would be suitable for the analysis of other sample types in which volatile aliphatic hydrocarbons are to be monitored in a matrix containing higher hydrocarbons, aromatics and/or polar components.
- The method could be extended to allow the determination of higher hydrocarbons by increasing the time of the backflush point.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs