APPLICATION NOTE

Gas Chromatography

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The Determination of C_1 to C_5 Hydrocarbons in Gas Streams Using the PerkinElmer Swafer Technology

Introduction

The determination of light hydrocarbons in refinery and other gases is typically performed through the use of packed columns and mechanical rotary valves. For example ASTM® Method D-2597 adopts this approach. A gas sampling valve delivers a small metered quantity of the sample gas into a non-polar packed column. The C_1 to C_5 hydrocarbons are allowed to elute from this column and into a second packed column with a polar stationary phase. At that point a rotary valve is actuated to reverse the flow of carrier gas through the precolumn and backflush any residual sample in that column to a detector to determine the total C_6+ content in the sample. In the meantime, chromatography of the C_1 to C_5 content proceeds on the second column for separation, identification and quantification. The whole analysis takes about 20 minutes and getting acceptable chromatographic separation is often a challenge because of normal variations in the columns.

In this application note, a new method is described for this analysis that uses a Swafer™ backflushing technology with capillary columns under isothermal conditions to both improve the chromatographic separation and to reduce the analysis cycle time to just over 5 minutes.

Experimental

For this analysis, an S-Swafer is used to manage the backflushing operations on the precolumn rather than a more conventional mechanical valve. The S-Swafer uses the Deans pressure balanced technique to reverse gas pressures across a GC column to initiate the backflushing process. Such systems have been widely used for 50 years – particularly for capillary columns where low thermal mass, inertness and low dead volumes are critical.

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In pressure balanced systems, the backflushed column effluent normally passes back into the injector and out of the system via a split vent. For this analysis, we need to direct the backflushed effluent into a detector to enable the total C_6+ content to be quantified.

There is also a need in a dual-column backflushing system like this to establish the backflush point – the time at which the last C_5 peak has passed from the precolumn into the second column.

Both of these requirements are addressed by configuring the S-Swafer as shown in Figure 1.

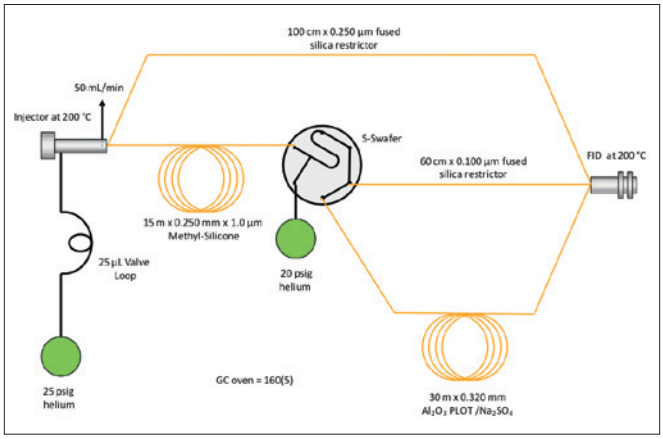

Figure 1. S-Swafer configuration to enable the backflush point to be established and the precolumn effluent to be directed to a detector.

In this system, even though there is only a single detector, it is possible to monitor the precolumn chromatography, the precolumn backflush effluent and the analytical column chromatography in a single run because these activities occur serially.

Study of Figure 1 indicates that two connections of fused silica tubing (a capillary column and a restrictor) must be made to the injector and three to the detector (a column and two restrictors). In both instances, these connections were made using soft graphite ferrules with the tubing inserted through the central hole and the nut is then tightened sufficiently to squeeze the graphite into the gaps between the tubes. This technique is surprisingly effective at making a good seal.

Another critical point is how the column and the fused silica restrictor tubing are positioned inside the injector liner. Because the precolumn backflushed effluent is going to re-enter the injector liner and then back out through the restrictor to the detector, it is important to arrange the ends of these as shown in Figure 2. The restrictor tube is inserted with its end about 5 mm downstream of the end of the column, which is inserted to the normal 40 mm depth from the base of the nut. When the column is backflushed, the carrier gas flowing through the liner will carry the backflushed effluent to the restrictor. If the positioning is incorrect, the backflushed effluent will be unable to enter the restrictor tubing.

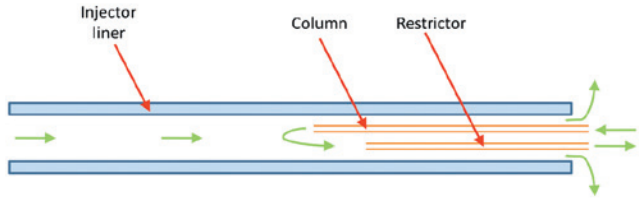

Figure 2. Positioning of the ends of the column and restrictor tube inside the injector liner.

Figure 3 shows a chromatogram of a refinery gas standard with the composition shown in Table 3 under the analytical conditions shown in Table 1.

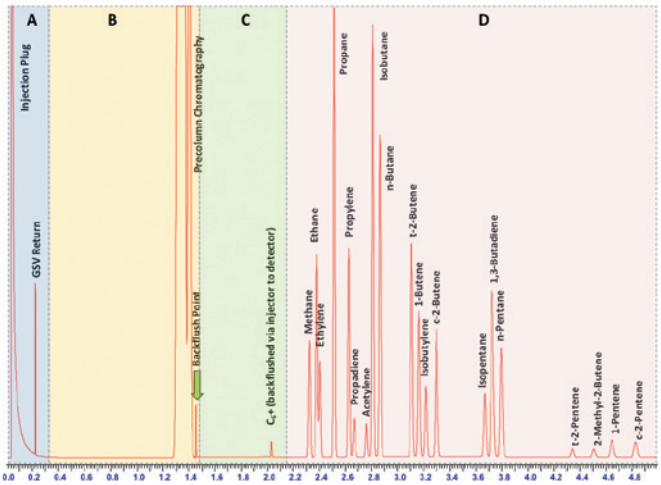

Figure 3. Chromatogram of a refinery gas standard mixture.

Table 1. **Full experimental conditions.**

Gas Chromatograph	PerkinElmer Clarus® 680
Oven	160 °C for 5 minutes
Gas Sampling Valve	Rotary valve with 25 µL loop. Pneumatic actuator. Valve connected in-line with carrier gas supply to injector. Valve loop charged prior to run with sample flowing at 3 mL/min. Actuator operated by timed event at 0.01 minutes to inject sample. Valve returned to original position by timed event at 0.20 minutes.
Injector	Split/Splitless or Programmable Split/Splitless. 50 mL/min Split at 200 °C
Detector	Flame Ionization at 200 °C Air 450 mL/min, Hydrogen 45 mL/min Range x1, Attenuation x64, Time Constant 50 ms
Backflush Device	S-Swafer in S6 configuration

Table 1. **Full experimental conditions (cont.).**	
Precolumn	15 m x 0.25 mm x 1.0 µm Elite™-1
Analytical Column	30 m x 0.32 mm Al_2O_3 PLOT
Injector Restrictor	Fused silica 100 cm x 0.250 mm
Midpoint Restrictor	Fused silica, 60 cm x 0.100 mm
Carrier Gas	Helium
Carrier Gas Programming	Inlet: 25 psig for 1.44 minutes, then 10 psig by timed event until end of run Midpoint: 20 psig for 1.43 minutes then 24 psig by timed event until end of run (see text) Split flow rate 50 mL/min for 1.80 minutes then 10 mL/min until end of run
It is recommended that an experienced chromatographer be involved during the system and method set up.	

The carrier gas programming in Table 1 requires some further explanation. To initiate backflushing of the pre-column, the inlet pressure is reduced and the pressure at the S-Swafer is increased. This combination ensures that back-flushing starts quickly after the timed events are applied. The split flow rate is reduced a little later to allow time for the pressure inside the injector to dissipate. Pressure reduction is much slower with low split flow rates so this timed event is delayed.

For clarity, the chromatogram in Figure 3 has been divided up into 4 zones: A to D.

To make an injection, the gas sampling valve loop is charged with sample vapor and the pressure is equilibrated to that of ambient. The GSV is operated and a fixed volume of the sample vapor is transferred to the split/splitless injector. Some of this vapor enters the precolumn but most is vented through the split vent. Some of the vapor enters the fused silica tubing connected to the detector. In this way, the detector will record the injection profile of the injected sample plug as seen in Zone A in Figure 3. Twelve seconds later, the GSV is returned to its original position and a small spike in the detector signal is seen at this point.

The sample is now chromatographed by the precolumn and monitored at the detector via the fused silica tubing connected between the Swafer and the detector as seen in Zone B of Figure 3.

Once the last C_5 peak has eluted, the pressure at the Swafer is increased and the pressure at the injector is decreased to initiate backflushing of the precolumn. The backflushed C_6+ components elute during Zone C in Figure 3.

Chromatography of the C_1 through C_5 components in the analytical column (which is connected directly to the detector) occurs in parallel with the precolumn backflushing but, because these components are sufficiently retained in the analytical column, the peaks do not start eluting from the analytical column until after the backflushing is complete as shown in Zone D in Figure 3.

This approach enables all four signals to be monitored with the single detector without interference between them and still have the analysis completed in just 5 minutes. After each analysis, an equilibration time of 0.4 min is applied to enable the pressures to re-stabilize before the next sample is injected, thus the total cycle time for this analysis is just 5.4 minutes.

Figure 4 shows an expansion of the chromatography from Figure 3 showing just the analyte peaks.

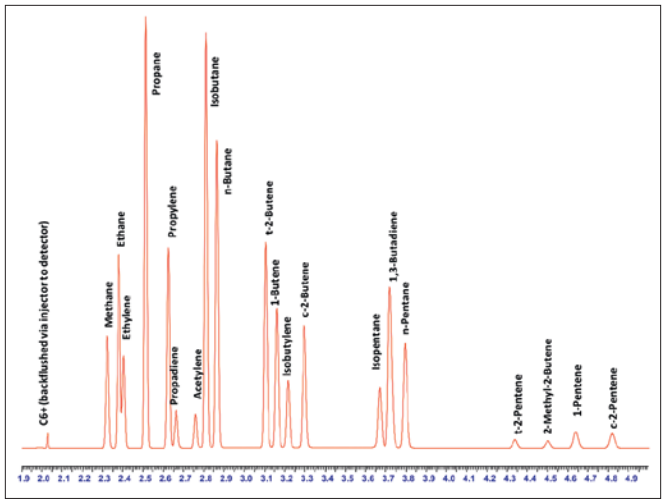

Figure 4. Expansion of a section taken from Figure 3 showing the analyte peaks.

A series of 100 repetitive injections of the same refinery gas sample were made. Table 2 shows the timing of raw data files collected for these analyses. These runs took just 9 hours and 2 minutes.

***Table 2.* Data file collection times at the start and end of a 100-run sequence.**

File Name	Time	Date
RGA_std_001.raw	18:59	1/5/2011
RGA_std_002.raw	19:05	1/5/2011
RGA_std_003.raw	19:10	1/5/2011
"	"	"
RGA_std_098.raw	03:46	1/6/2011
RGA_std_099.raw	03:52	1/6/2011
RGA_std_100.raw	03:57	1/6/2011

The data from these files were processed to establish the quantitative precision of this method. The relative standard deviations for raw peak areas of all components for all 100 runs are given in Table 3.

Table 3. **Peak Area Precision from 100 injections of Arnel Refinery Gas Calibration Blend (Lot 102-06-04137, Cylinder # 10196D).**

Component	Mol Fraction (%)	Mean Peak Area (µV.s)	Peak Area Relative Standard Deviation (%)
n-Hexane (C_6+)	0.1001	397	0.72
Methane	5.0112	6227	0.21
Ethylene	2.0025	9358	0.21
Ethane	4.0021	4569	0.27
Propane	6.0185	19897	0.20
Propylene	3.0038	9905	0.24
Propadiene	0.9970	2206	0.44
Acetylene	0.9992	1815	3.35
Isobutane	5.0000	20169	0.21
n-Butane	3.9993	15807	0.20
t-2-Butene	3.0061	11662	0.30
1-Butene	1.9998	8022	0.29
Isobutylene	1.0025	3667	0.39
c-2-Butene	1.9996	7583	0.35
Isopentane	1.0009	4016	1.19
1,3-Butadiene	3.0107	11745	0.32
n-Pentane	2.0002	7426	0.26
t-2-Pentene	0.1996	736	0.76
2-Methyl-2-Butene	0.1998	681	1.10
1-Pentene	0.4007	1556	0.59
c-2-Pentene	0.4001	1448	0.75

In most instances, the precision is significantly less than 0.5%. This is an excellent result for a system that is switching components between two columns and manipulating pressures and flow rates over just a 5-minute period.

This system may be used for samples using refinery gas. An example of this is illustrated by the chromatogram of liquid petroleum gas shown in Figure 5.

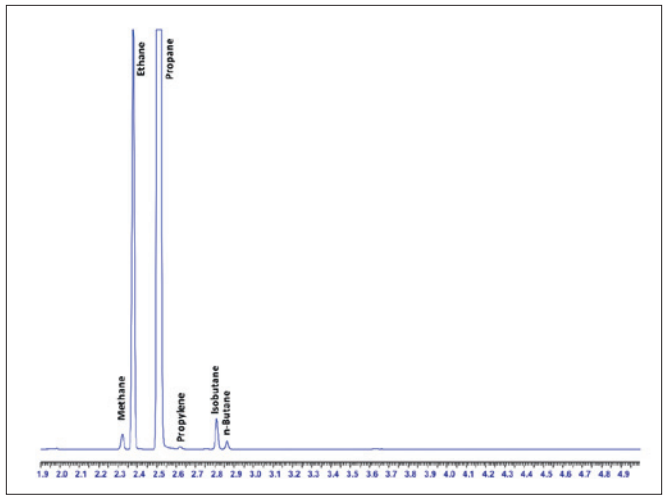

Figure 5. Chromatogram of liquid petroleum gas.

Conclusions

This application note has shown how a pressure-balanced backflushing capillary column system based on the PerkinElmer® Swafer technology may be used to determine C_1 through C_5 hydrocarbons in refinery and other gas streams.

The approach is novel in that the precolumn backflushed effluent is able to be directed to a detector for quantification of the total hydrocarbons that contain six or more carbon atoms.

The system described monitors the sample injection plug, the precolumn chromatography, the precolumn backflushed effluent and the chromatography of the C_1 through C_5 analytes all in a single run using a single detector.

The chromatography occurs at an isothermal temperature and so no oven cooldown is required and the repetitive analytical cycle time is only 5.4 minutes.

Quantitative precision is excellent and relative standard deviations below 0.5% are seen for most components.

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