

## Gas Chromatography

## Author

A. Tipler

PerkinElmer, Inc.  
Shelton, CT 06484 USA

## The Determination of Benzene and Toluene in Finished Gasolines Containing Ethanol Using the PerkinElmer Clarus 680 GC with Swafer Technology

to improve combustion efficiency. Significant quantities of this additive may be present – for instance 10% in the USA (E10) and 25% (E25) in Brazil. The presence of large amounts of ethanol in samples caused problems with chromatographic co-elution with benzene when using the D-3606 method. The method was revised (D-3606-07) to include an alternative column set designed to handle the presence of the ethanol but there are still reports of problems with co-elution and further column sets are under consideration.

This application note describes a method that is based on the original ASTM® D-3606 method with the main difference being that capillary columns are used. This approach completely eliminated all chromatographic interference from the ethanol (even solutions made up in pure ethanol could be run), improved the quality of the chromatography in general and reduced the analysis time significantly (by 50% or 75% depending on the column set).

### Introduction

ASTM® Test Method, D-3606, is designed to determine the benzene and toluene content in gasolines using packed columns in a 2-column backflush configuration. This is an established method that was originally developed to analyze gasoline that did not contain ethanol. Ethanol is a biofuel that is added to modern gasolines

## Analytical approach

The traditional D-3606 packed column method uses a 2-column backflush configuration. The first column (precolumn) was packed with 10% polydimethylsiloxane (PDMS) on a Chromosorb®-W support. The second column (analytical column) contained a packing of 20% 1,2,3-tris(cyanoethoxy) propane (TCEP) on a Chromosorb®-P support.

In this application, these columns were replaced with narrow-bore capillary columns containing the same stationary phases as used in the packed columns. A split/splitless injector was used to introduce the sample into the precolumn. A Swafer™ system was used to manage the backflush process. Although D-3606 specifies the use of a thermal conductivity detector (TCD), in this work a flame ionization detector (FID) was used as it was more suited to high-resolution capillary chromatography and did not give baseline drift as column pressures were changed during the backflushing process.

## Experimental conditions

A PerkinElmer® Clarus® 680 gas chromatograph with a programmable split/splitless injector (PSS), flame ionization detection (FID) and Swafer system was used to perform this analysis. Further details on the Swafer technology may be found on the PerkinElmer website ([www.PerkinElmer.com/Swafer.com](http://www.PerkinElmer.com/Swafer.com)). In this instance, the Swafer S6 configuration was used 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 and accurately established.

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.

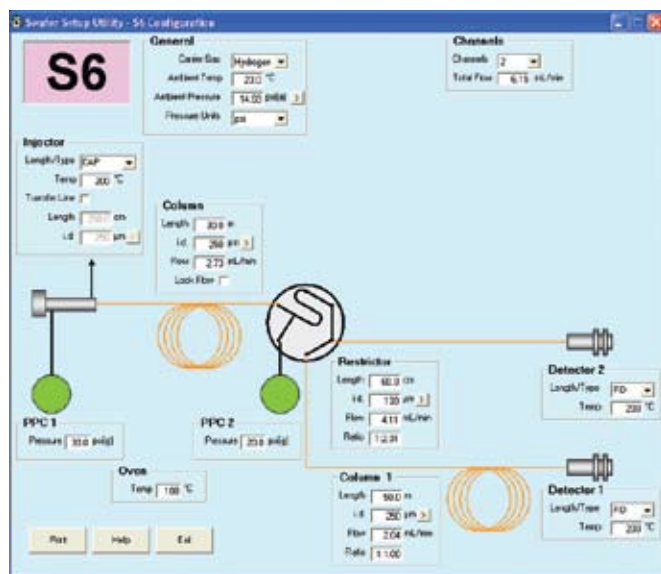


Figure 1. Screen shot taken from the Swafer Utility Software showing the S6 configuration used in this method and gas pressures used for the initial work.

## Initial Setup Procedure

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.

To begin, 0.3 µL of a solution of ethanol, benzene and toluene in iso-octane was injected into the system using the conditions shown in Figure 2. Figure 3 shows the resultant chromatography from this injection. All components have eluted from the precolumn (and into the TCEP column) within 1.61 minutes and so this time was adopted as the backflush point.

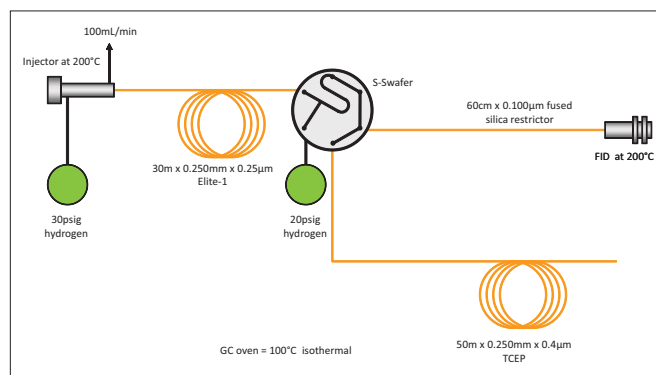


Figure 2. System configured to monitor the precolumn chromatography to establish the backflush point.

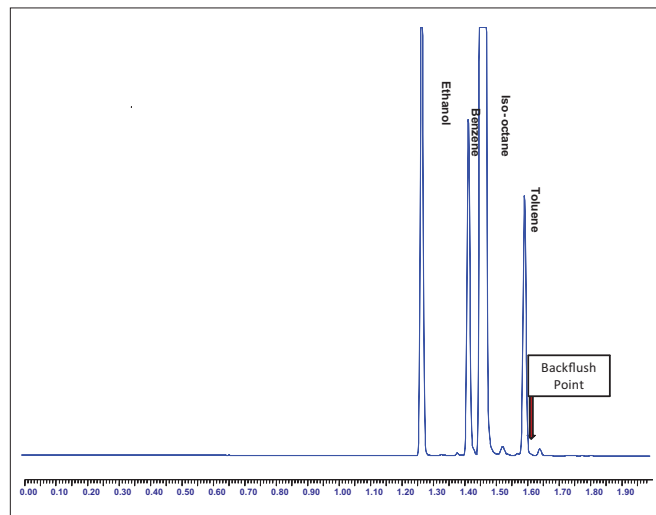


Figure 3. Precolumn chromatography of mixture of ethanol, benzene and toluene in iso-octane.

To check the separation of the mixture on the complete system, the restrictor is then disconnected from the FID detector and the TCEP column connected to this detector, as shown in Figure 4.

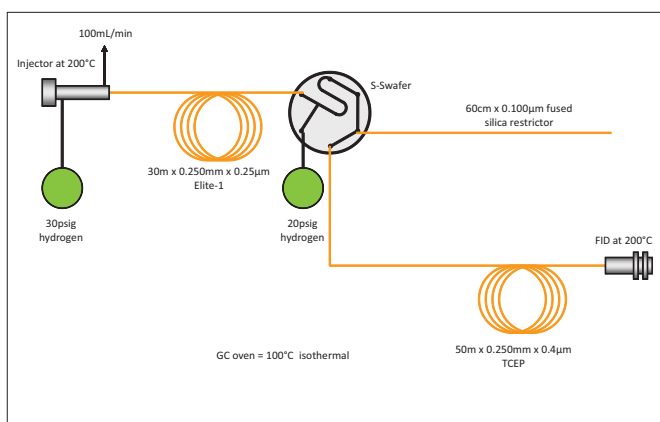


Figure 4. System configured to monitor the TCEP column chromatography to check the final chromatographic separation.

The resultant chromatogram is shown in Figure 5. Good separation of all of the components is evident.

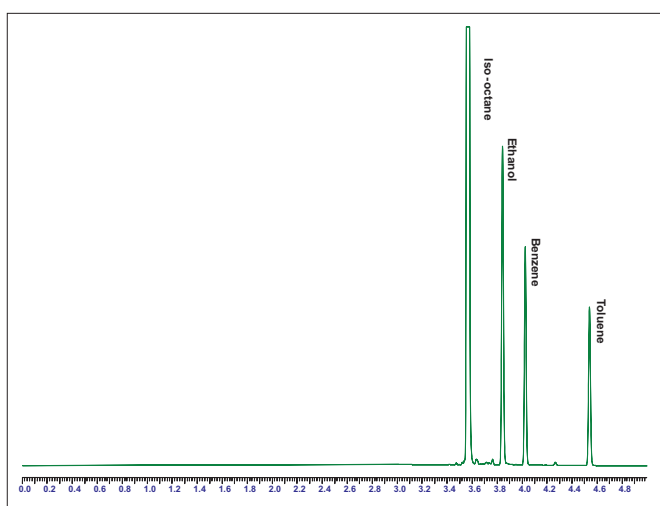


Figure 5. Chromatography of mixture eluting from TCEP column.

Because the precolumn chromatography is completed before the TCEP column chromatography starts, the restrictor and TCEP column can be connected simultaneously to the same detector. This means that both chromatograms may be monitored in the same run as shown in Figure 6. This approach makes it very easy to establish and maintain the backflush point and it provides a visible record of the chromatography on the precolumn for QC purposes. This information is not available from the original ASTM D-3606 method.

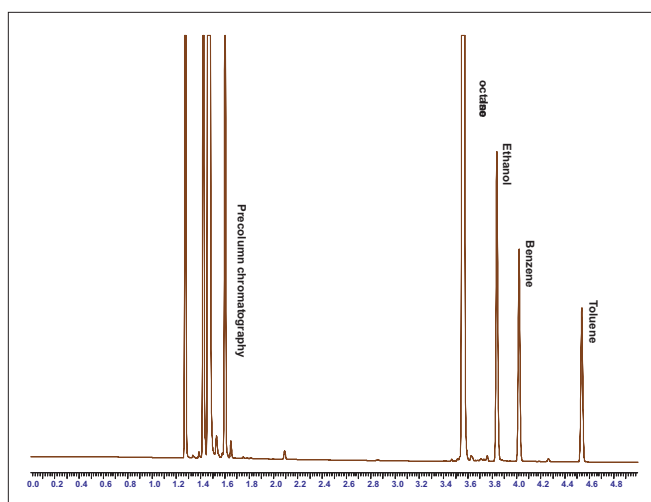


Figure 6. Combined precolumn and TCEP column chromatography of mixture.

The next step was to check the chromatography of a gasoline sample. For these samples, backflushing of the precolumn was important to keep the bulk out of the gasoline material off the sensitive TCEP column. To perform the backflush technique, the inlet pressure was reduced and simultaneously, the midpoint pressure at the S-Swafer was increased slightly.

The effect of both lowering the inlet pressure and raising the midpoint pressure to initiate backflushing provides a cleaner separation between the ethanol and benzene peaks on the TCEP column chromatography as shown in Figure 7. This approach also shortens the chromatographic run time – the full separation is complete within just 4 minutes!

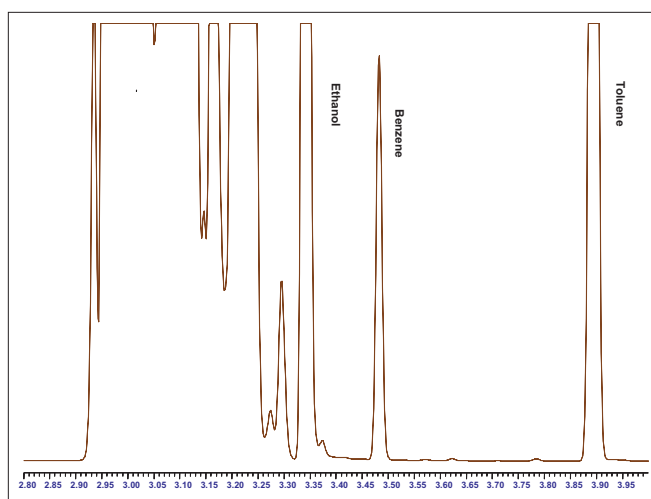


Figure 7. Chromatography eluting from the TCEP column for a typical gasoline sample with a timed event to reduce the injector pressure and increase the midpoint pressure at 1.61 minutes.

The Swafer Utility Software was further used to model backflush conditions as shown in Figure 8.

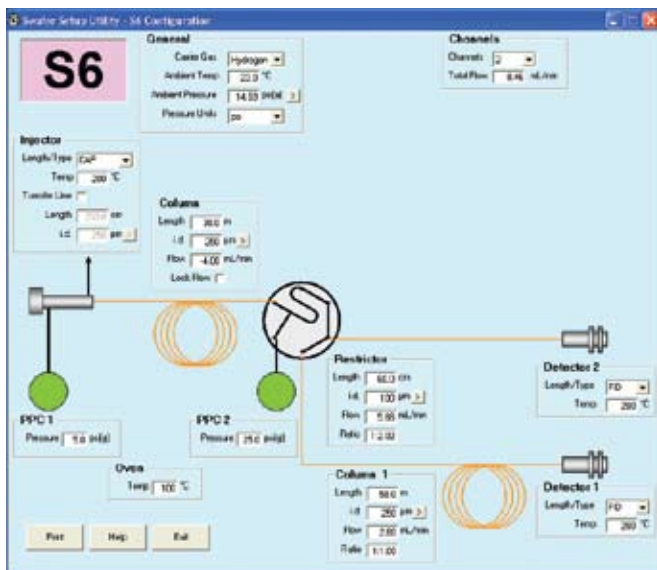


Figure 8. Screen shot taken from the Swafer Utility Software showing the system in backflush mode (note that in practice, a single detector is used).

ASTM® method D-3606 specifies the use of an internal standard. In the original method this was 2-butanol and in the updated method for gasoline samples that may contain ethanol, methyl ethyl ketone (MEK) was specified.

On this system, it was found that MEK eluted after toluene and so would extend the run time. 2-Butanol eluted between benzene and toluene as shown in Figure 9 so this compound was chosen as the internal standard to keep the chromatography to 4 minutes.

The final method for the determination of benzene and toluene in finished gasoline containing ethanol, as used to produce the chromatography in Figure 9, is listed in Table 1.

Under these conditions, the chromatography took just 4 minutes to complete. A short equilibration time is added to stabilize the carrier gas pressures before the start of each run. The total cycle time for each analysis is just 5.4 minutes which enables 11 samples to be run each hour or 88 samples over an 8-hour shift.

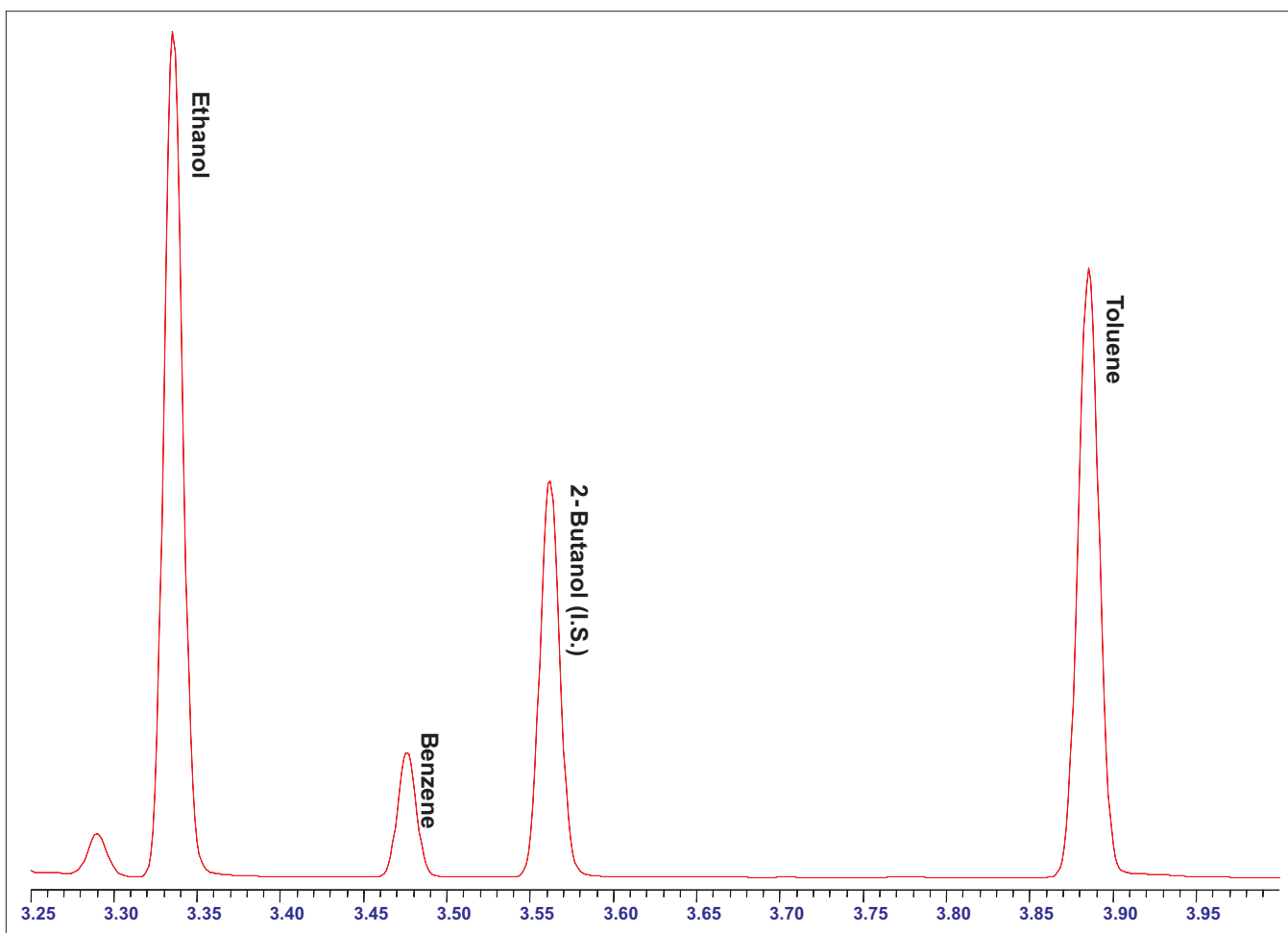


Figure 9. Chromatography of a typical gasoline sample with 2-butanol added as an internal standard.

**Table 1. Full Experimental Conditions.**

Gas Chromatograph:	PerkinElmer Clarus 680
Oven:	100 °C isothermal for 4 min. 0.5-min equilibration time
Injector:	Programmable Split/Splitless Injector (PSS) 100 mL/min. split at 200 °C Quartz Liner Part No. N6121001 A Split/Splitless (capillary) injector may also be used.
Detector:	Flame Ionization at 200 °C Air 450 mL/min. hydrogen 45 mL/min. range x1, attenuation x8
Backflush Device:	S-Swafer in S6 configuration S-Swafer Kit part no. N6520272 Swafer Kit part no. N6520270 and N9306262 for existing Clarus GCs with PPC
Precolumn:	30 m x 0.25 mm x 0.25 µm Elite-1 Part No. N9316010
Analytical Column:	50 m x 0.25 mm x 0.4 µm TCEP Part No. NR210048
Midpoint Restrictor:	Fused silica, 60 cm x 0.100 mm Part No. N9316601
Carrier Gas:	Hydrogen
Carrier Gas Pressure Inlet:	30 psig for 1.62 min., then 5 psig programming by timed event until end of run
Midpoint:	20 psig for 1.61 min. then 25 psig by timed event until end of run
Injection:	0.3 µL by autosampler in fast mode 4 solvent washes following injection
Sample Preparation:	1 mL 2-butanol (I.S.) added to 25-mL volumetric flask and then gasoline sample added to bring total volume to 25 mL.

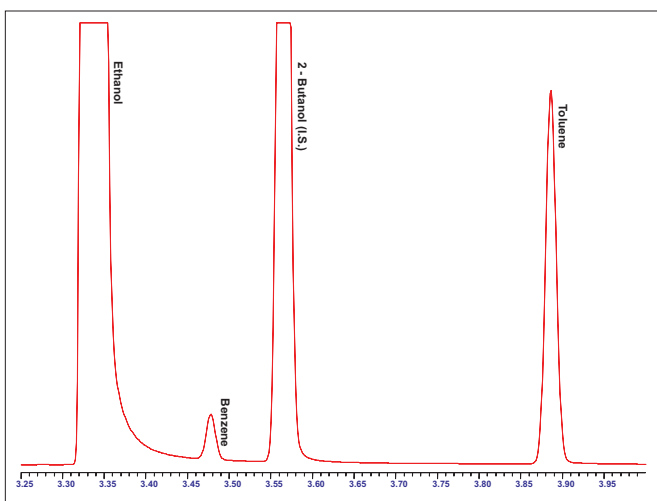


Figure 10. Chromatogram of standard mixture containing 0.05% v/v benzene and 0.5% v/v toluene in pure ethanol with added internal standard.

## Tolerance to ethanol

Since there were concerns with the original ASTM® D-3606 method when used with gasoline samples containing significant quantities of ethanol, a solution containing a low concentration of benzene in ethanol was injected. The result is shown in Figure 10. This clearly shows that this method has good tolerance to ethanol even when present at ~100% levels when determining low levels of benzene.

## Linearity

ASTM® Method, D-3606 specifies that the system should be calibrated using 7 standard solutions as listed in Table 2.

**Table 2. Calibration Solutions for ASTM® D-3606.**

Solution	Concentration (%v/v)*	
	Benzene	Toluene
1	5	20
2	2.5	15
3	1.25	10
4	0.67	5
5	0.33	2.5
6	0.12	1
7	0.06	0.5

\*Prior to addition of internal standard

A set of standard solutions was used to check linearity and calibrate the system being used for this application work. Some examples of the chromatography are given in Figure 11.

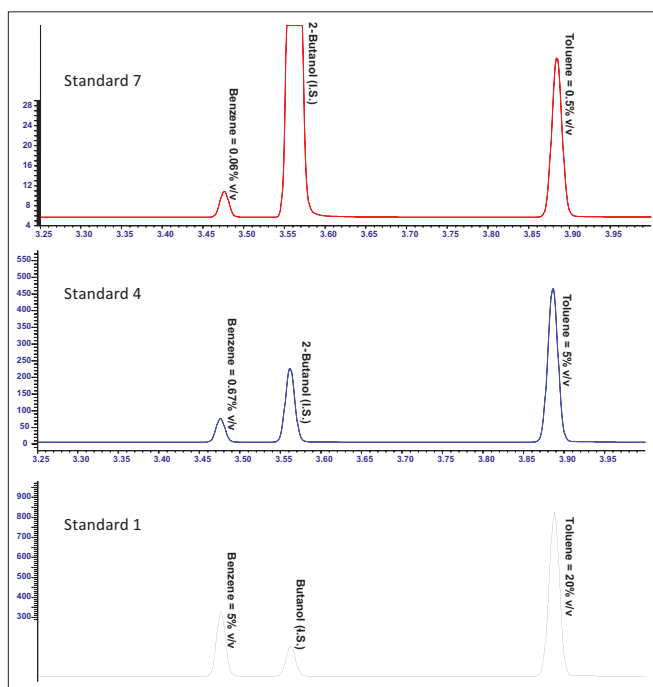


Figure 11. Example calibration solution chromatograms.

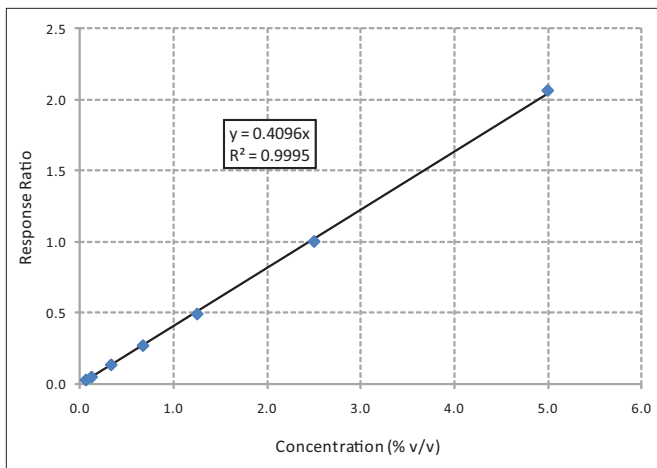


Figure 12. Calibration plot for benzene.

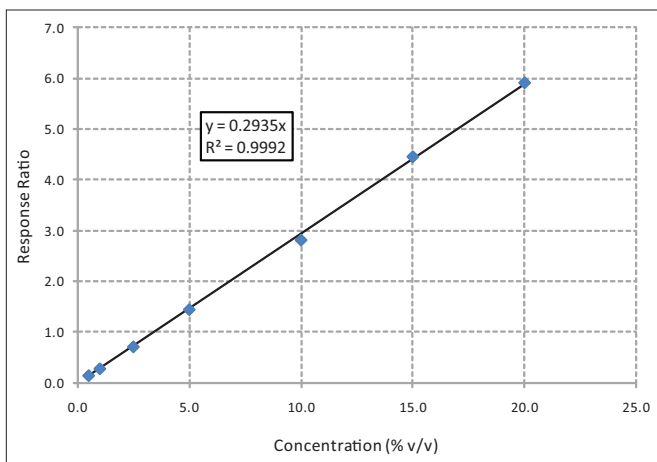


Figure 13. Calibration plot for toluene.

### Quantitative precision

To check the quantitative precision, a gasoline sample was run 100 times and the standard deviations were calculated for the quantitative results. These data are shown in Table 3. For each analyte, the quantitative repeatability requirements of D-3606 are easily met.

Component	Concentration (% v/v)		
	Mean	Std Dev	D-3606-07 Requirement
Benzene	0.723	0.003	0.032
Toluene	5.713	0.092	0.191

### Retention time precision

Retention time precision is a good indicator of a robust method. Table 4 shows excellent relative standard deviations obtained for the three components from the 100 gasoline sample runs.

Component	Retention Time	
	Mean (min)	RSD (%)
Benzene	3.478	0.020
2-Butanol (I.S.)	3.563	0.021
Toluene	3.887	0.019

### Analyte carry-over

This method is designed to monitor levels of benzene and toluene over a wide range of concentrations and so it is important that cross-contamination between successive sample injections is minimized. To check the levels of carry-over from one injection to the next, Calibration Solution 1 (see Table 2) was run and then immediately followed by an injection of iso-octane solvent. Figure 14 shows the chromatograms. The carry-over value of 0.013% from an injection of toluene at a 20% v/v concentration represents a potential interference of 0.0026% v/v in the determined concentration which is far below the 0.5% v/v minimum calibration level.

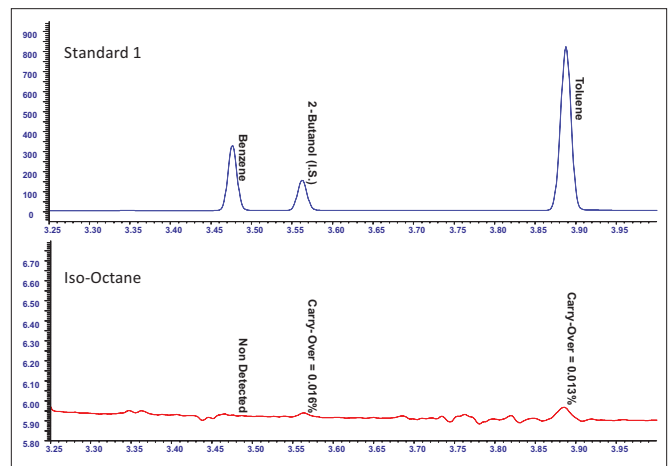


Figure 14. Carry-over study showing chromatogram of high concentration standard mixture followed by injection of solvent.

## 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.
- Baseline separation of ethanol, benzene, toluene and the 2-butanol internal standard has been demonstrated.
- 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 about 8 minutes for the original method (or 16 minutes for some revised column sets) to just 4 minutes. The total cycle time of the chromatographic analysis (including pressure equilibration) is 5.4 minutes enabling 88 samples to be analyzed during an 8-hour working shift.
- The method is able to analyze samples with low levels of benzene in the presence of high levels of ethanol.