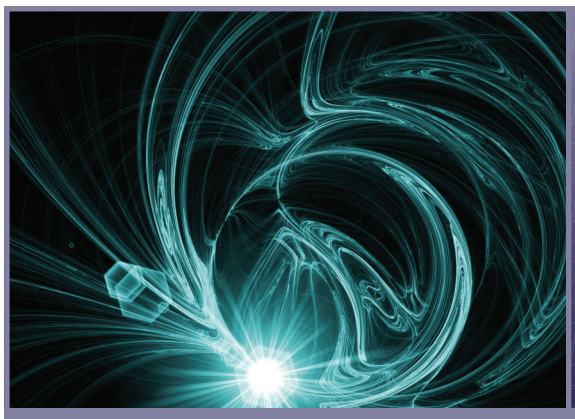

The Rapid Determination of Benzene and Toluene in Finished Gasolines Containing Ethanol Using Gas Chromatography

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The determination of benzene and toluene in gasoline is an important application in the petrochemical industry to monitor and ensure that levels of these compounds meet regulatory requirements.

Gasoline is a highly complex sample matrix and, in this instance, we want to just see the benzene and toluene content in among the hundreds of other components present. Traditionally, this analysis has been performed by gas chromatography using packed columns in a mechanical valve backflush configuration as described in ASTM method D3606-07. A non-polar precolumn allows the volatile fraction of an injected gasoline sample (which contains benzene and toluene) to elute into a second column which is polar. The heavier sample fraction, which was left in the precolumn, is removed by backflushing the precolumn out to vent. The polar analytical column retains the benzene and toluene more than the volatile hydrocarbons that also eluted into this column and so enables these aromatic compounds to be fully separated from all other components in the gasoline. A polar internal standard is added to the gasoline prior to analysis to improve the quantitative precision.

Such methods have been used for many years but the relatively recent introduction of high concentrations of ethanol in modern gasolines has caused peak-coelution issues on the polar analytical column. Alternative column sets have been developed to improve the chromatography but these have extended the analysis time.

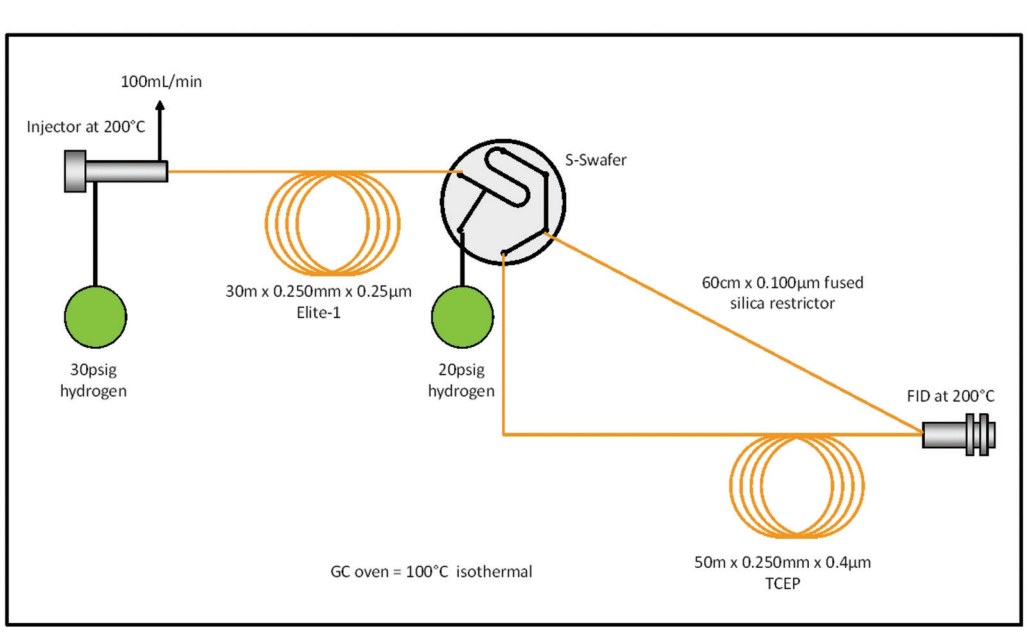

Figure 1: Analytical system used for the determination of benzene and toluene in gasoline

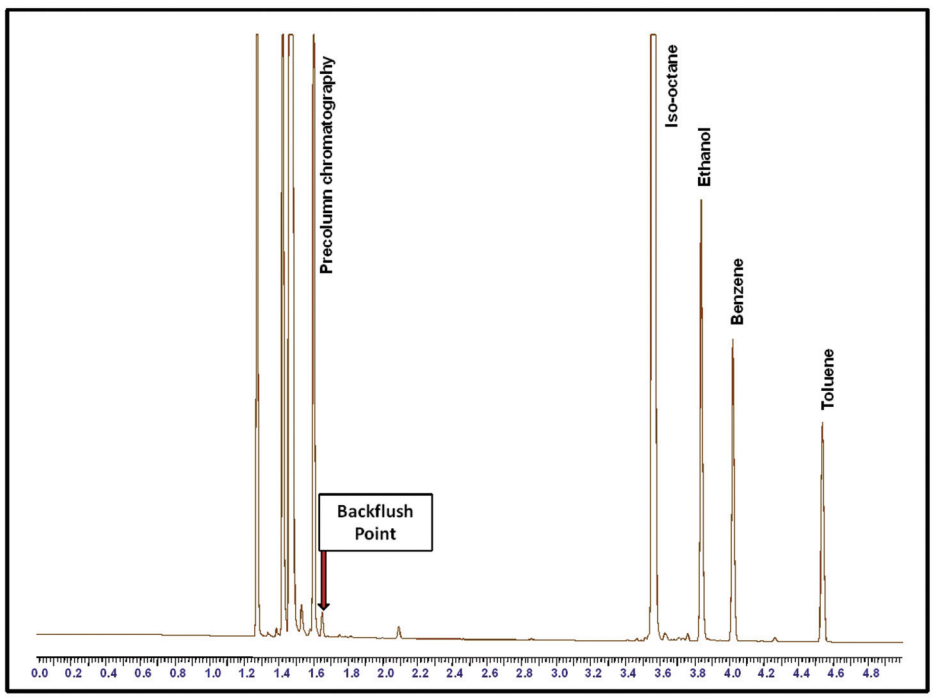

Figure 2: Chromatogram of a standard mixture without backflushing.

This article describes a similar approach to this analysis as used in the ASTM method but using high resolution capillary columns. Interference effects from ethanol have been totally eliminated and the chromatography is complete within 4 minutes while still meeting the performance requirements of ASTM method D3606-07.

Analytical Approach

Figure 1 shows a diagram of the system used for this analysis. The packed columns were replaced with narrow-bore capillary columns. A split/splitless injector was used to introduce the sample into a non-polar precolumn. A Swafer™ system was used to manage the transfer from the precolumn to a polar analytical column and to control 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. A fused silica restrictor was connected between one of the S-Swafer outlet ports and the same detector as connected to the analytical column. This provided two benefits: the gas flow rate through the first column could now be higher than through the analytical column giving flexibility in the method and, because the chromatography on the precolumn is complete before the first peak elutes from the analytical column, the detector could record both chromatograms in the same run. This makes set up much easier and provides extra confidence in the results because the precolumn chromatography is now visible in all the runs.

Figure 2 shows a chromatogram of a standard mixture without backflushing applied. The backflush point is easily identified – just after the last peak of interest has eluted from the precolumn.

Figure 3 shows the final chromatography with backflushing applied of a sample of 87-octane gasoline. 2-butanol internal standard is added to the gasoline. Even though there are hundreds of components in this sample, the method is able to eliminate all of these potential interferences from the benzene, toluene and 2-butanol internal standard peaks in just four minutes. The total analytical cycle time which includes autosampler loading and equilibration times is approximately 5.4 minutes.

The peak shapes are very symmetrical, the resolution between all the peaks is very high and the baseline is flat – these are all attributes needed for a rugged and reliable method.

Experimental Conditions

Table 1 lists the full experimental conditions developed for this analysis.

Gas Chromatograph	PerkinElmer Clarus® 680
Oven	100°C isothermal for 4 minutes. 0.5-min equilibration time
Injector	Split/Splitless or Programmable Split/Splitless. 100mL/min Split at 200°C
Detector	Flame Ionization at 200°C Air 450mL/min, Hydrogen 45mL/min Range x1, Attenuation x8
Backflush Device	S-Swafer in S6 configuration
Precolumn	30m x 0.25mm x 0.25µm Elite-1
Analytical Column	50m x 0.25mm x 0.4µm TCEP
Midpoint Restrictor	Fused silica, 60cm x 0.100mm
Carrier Gas	Hydrogen
Carrier Gas Pressure Programming	Inlet: 30psig for 1.62 minutes, then 5psig by timed event until end of run Midpoint: 20psig for 1.61 minutes then 25psig by timed event until end of run
Injection	0.3µL by Autosampler in fast mode. 4 solvent washes following injection.
Sample Preparation	1mL 2-butanol (I.S.) added to 25-mL volumetric flask and gasoline sample added to bring total volume to 25mL.

Table 1: Full experimental conditions

Analytical Performance

Good response linearity is an important requirement for this method as it will greatly simply the calibration process. Figure 4 shows the plots obtained from running D-3606 calibration standard mixtures on this system. Excellent linearity is evident.

A good method should demonstrate excellent quantitative precision. To check this on this system, a gasoline sample was run 100 times and the standard deviations were calculated for the quantitative results. These data are shown in Table 2. For each analyte, the quantitative repeatability requirements of D-3606 are easily met.

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

Table 2: Quantitative precision obtained from 100 injections of a single gasoline sample

Chromatographic peak retention time precision is a good indicator of a robust method. Table 3 shows the relative standard deviations obtained for the three components from the 100 gasoline sample runs. For such short chromatography, these results are excellent.

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

Table 3: Retention time precision obtained from 100 injections of a single gasoline sample.

Another important requirement for this method is to demonstrate that there is no interference between successive analyses. This is particularly important in cases where a concentrated sample is followed by a low level sample. Figure 5 shows chromatography of a concentrated standard mixture immediately followed by chromatography of a solvent blank.

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.

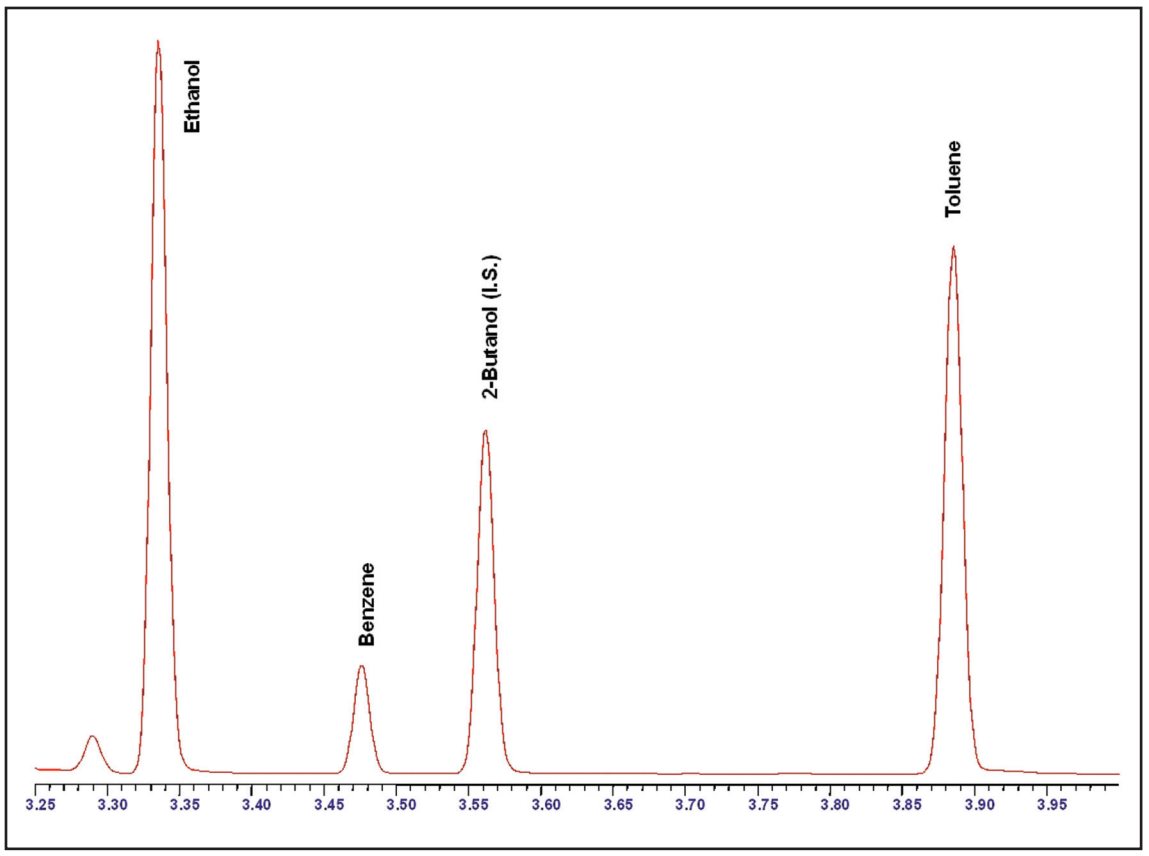

Figure 3: Analytical column chromatography of a gasoline sample with added internal standard.

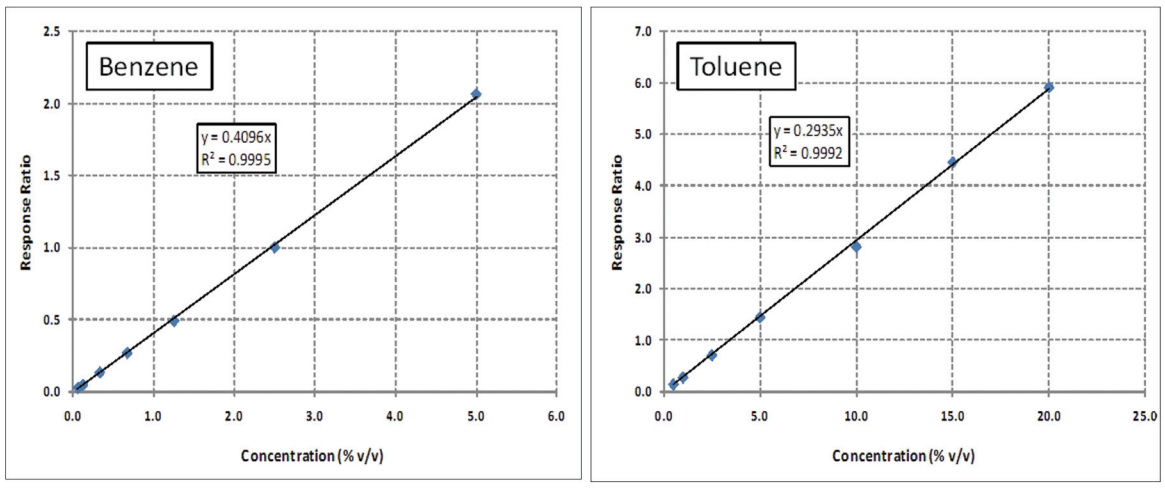

Figure 4: System calibration plots

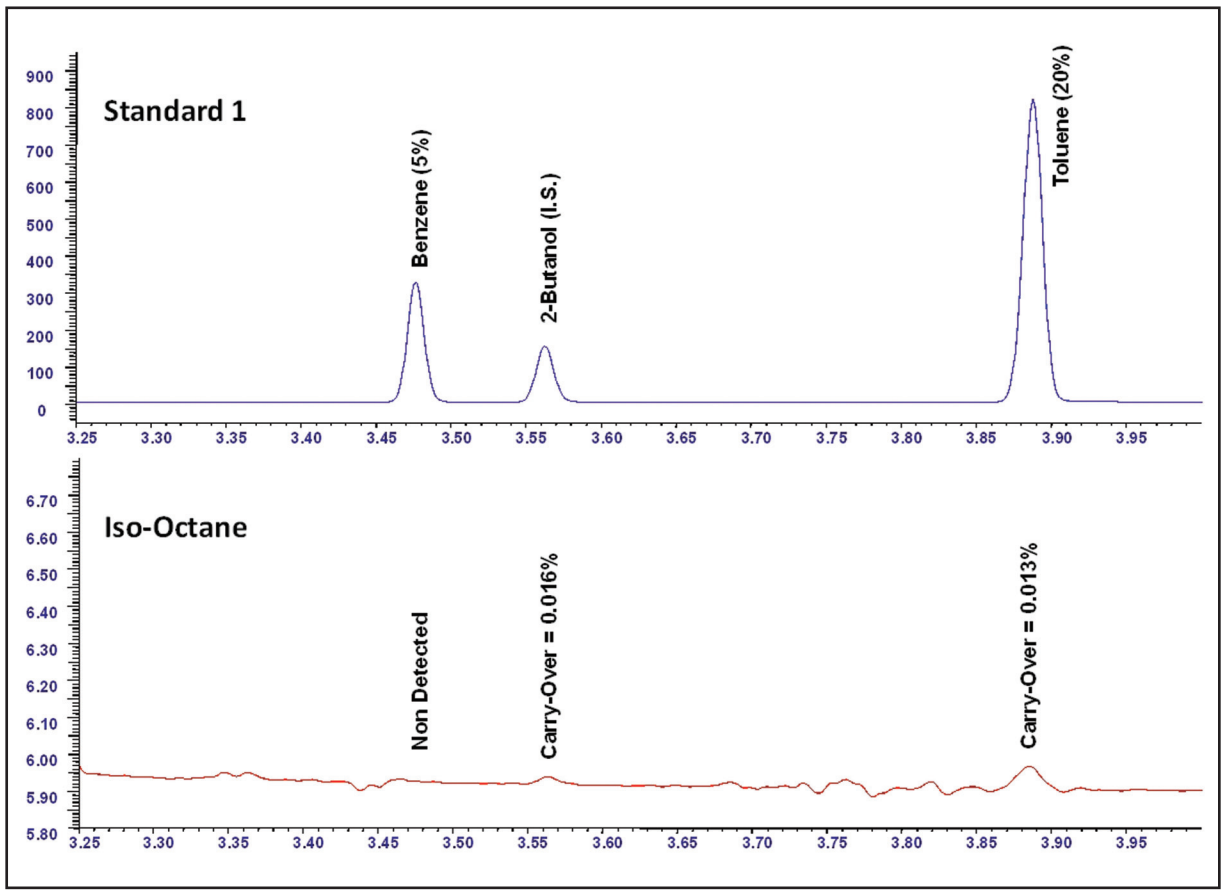

Figure 5: Chromatography of a concentrated sample followed by injection of blank solvent to test for system carry-over.

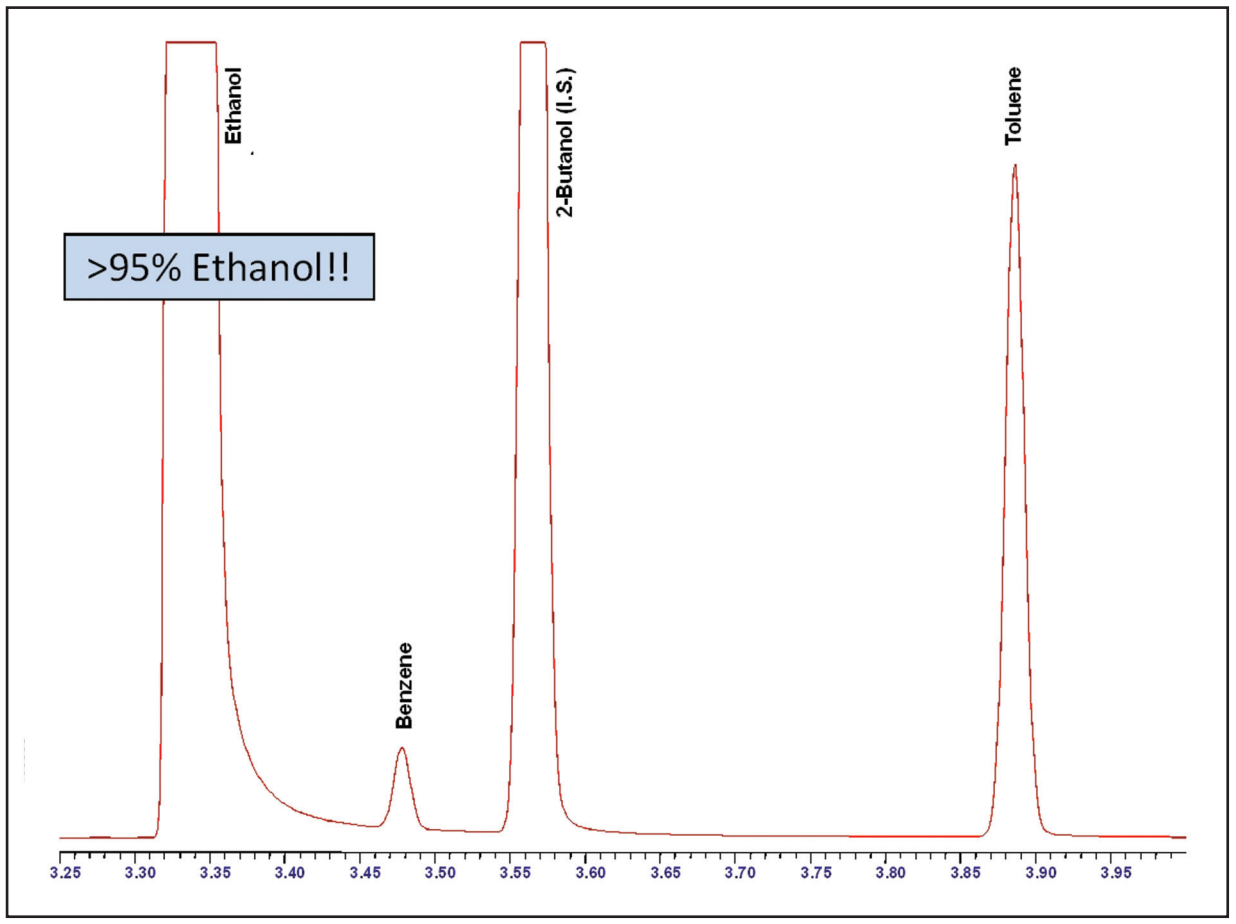

Figure 6: Chromatogram of standard mixture containing 0.05% v/v benzene and 0.5% v/v toluene in pure ethanol with added internal standard

This excellent result is due to many factors: the efficient rinsing of the autosampler syringe, the injector flowpath and the efficiency of the backflush process in removing the bulk of the sample form the system

As mentioned in the introduction, one of the big challenges with the existing D-3606 method is dealing with the presence of large concentrations of ethanol in modern gasolines. The ethanol peak elutes in front of the benzene peak. On packed columns, the ethanol peak will tail and start to interfere with the digital integration of low-level benzene peaks.

Figure 6 shows a chromatogram run on this system of a standard mixture prepared using ethanol as the solvent. In this case even though the ethanol comprises more than 95% of the sample, there is very little interference between its chromatographic peak and that of benzene at a concentration of 0.05% (the lowest calibration concentration).

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 significantly.
- 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 analysed during an 8-hour working shift.
- The method is able to analyse samples with low levels of benzene in the presence of high levels of ethanol.