

Determination of Benzene and Toluene in Gasoline by ASTM D3606 on an Agilent 8890 GC with Capillary Columns

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Abstract

In accordance with ASTM D3606, the concentration of benzene and toluene in finished gasoline was determined on an Agilent 8890 gas chromatograph. This study used capillary columns and a midcolumn backflush with a monitor channel to ease with the setup of the backflush. This Application Note also demonstrates the use of hydrogen as an alternate carrier gas.

Introduction

The determination of benzene and toluene concentrations in gasoline is necessary for regulatory and blending purposes. In 2007, the Environmental Protection Agency (EPA) published regulations to reduce the emission of benzene from mobile sources, which included controls on passenger vehicles. The Control of Hazardous Air Pollutants from Mobile Sources final rule took effect in 2011, limiting the annual refinery average for benzene in gasoline to 0.62% by volume.¹

This Application Note follows ASTM D3606-17, Standard Test Method for Determination of Benzene and Toluene in Spark Ignition Fuels by Gas Chromatography, procedure A.² This method uses capillary columns in place of the packed columns used in procedure B. The use of capillary columns provides improved separation of benzene from oxygenates such as ethanol and butanol. A method based on capillary columns also runs the carrier gas at a reduced flow rate compared to the packed column method. D3606 procedure B recommends up to 44 mL/min carrier flow, so switching to a capillary column-based method can immediately reduce gas consumption.

An 8890 GC was equipped with a mixed-phase column set with midcolumn backflush and two flame ionization detectors (FIDs). Commonly, backflushing is performed using two segments of the same analytical column, which maintains elution order throughout the analysis. Unwanted compounds can be backflushed through the precolumn before they enter the analytical column, offering improved column lifetime and reduced cycle time. In this analysis, compounds that elute after toluene on the nonpolar precolumn will interfere

with the peaks of interest on the polar analytical column. To prevent this interference, the use of backflush in this application is essential to the separation of the peaks of interest from the complex matrix of gasoline.

Experimental

Instrumentation

Figure 1 presents a schematic of this configuration. A 30 m HP-1ms Ultra Inert precolumn is used for the initial separation of hydrocarbons while a 60 m DB-WAXetr analytical column is used to separate aromatic and aliphatic compounds. Between these two columns is a purged two-way splitter with purge gas supplied from a pneumatic switching device (PSD) to allow backflushing. The other outlet from the two-way splitter is connected to the second FID as a monitor channel.

The inclusion of the monitor channel takes some of the guesswork out of backflushing. This monitor channel, column 3, consists of a very short segment of deactivated fused silica.

The length and internal diameter of this segment were designed to match the flow rate of the analytical column, column 2. Since the flows for columns 2 and 3 are the same, the effluent from column 1 is split equally between the analytical column and the monitor channel. Compounds quickly elute from the short segment of fused silica to the second FID. This enables monitoring of compounds eluting from the precolumn with a very short time delay, simplifying the determination of the backflush time. Using a PSD also allows an easier implementation of a backflush configuration, thanks largely to its built-in purge flow.³

Chemicals and standards

A seven-level calibration standard was purchased from AccuStandard. The concentration ranges for benzene and toluene were 0.06 to 5% by volume and 0.5 to 20% by volume, respectively. The internal standard was methyl isobutyl ketone (MIBK) at 4% by volume. The lowest concentration level was used for the determination of benzene's signal-to-noise (S/N).

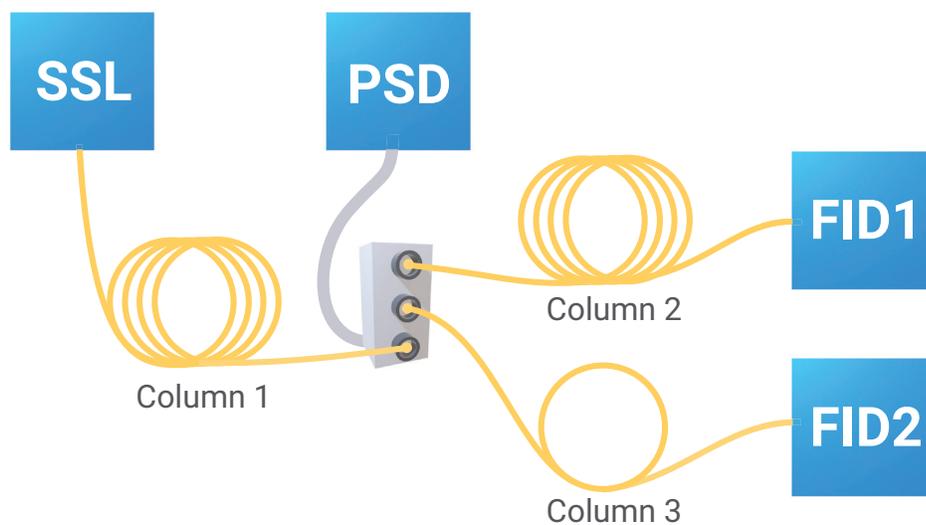


Figure 1. Schematic diagram of an Agilent 8890 GC configured for D3606. Column 1 is a 30 m HP-1ms Ultra Inert. Column 2 is a 60 m DB-WAXetr. Column 3 is a short segment of deactivated fused silica.

Neat solvents were used to prepare the backflush timing and resolution mixture (>99.99% purity, Sigma-Aldrich). This mixture was composed of 1% benzene, 20% toluene, 4% MIBK, and 20% ethanol by volume in isooctane. Regular unleaded gasoline was purchased from a local gas station. The gasoline samples were prepared by adding 1 mL of MIBK to a 25 mL volumetric flask filled to the mark with the gasoline sample.

Results and discussion

Method translation

ASTM D3606-17 only includes parameters for the use of helium as a carrier gas; however, the use of hydrogen in place of helium as the carrier gas is a quick and easy way to save on gas supply costs. This application is perfectly suited for the use of hydrogen as an alternative carrier gas, and the 8890 GC includes several safety features to reduce the risks of operating with hydrogen as a carrier gas.

Agilent GC software includes helpful tools, for example, the method translator. Method translation helps retain elution order when changing column dimensions, outlet pressure, speed of analysis, or carrier gas type. Using this tool to translate a single column method is relatively straight-forward, but with two columns in-series, the method translation requires some extra steps. Successful method translation for a multiple column configuration is best facilitated by working backwards, from the detector to the inlet. The method is first translated for the analytical column, and the resulting head pressure can then be used as the outlet pressure for the precolumn during its translation. Because the goal of this method translation was to maintain the same elution order and similar retention times,

the method translator was set to a speed gain of 1.0 instead of the translate option. This causes the translation software to retain the original method's holdup time/void time for the translated method. Figure 2 demonstrates the setup for translating the method from

helium to hydrogen carrier gas for the analytical column. Table 1 shows the final translated column flow for hydrogen carrier gas. Running with these parameters resulted in a chromatogram with very similar retention times for the peaks of interest (Figure 3).



Figure 2. Method translation for the analytical column, an Agilent DB-WAXetr, from helium carrier gas to hydrogen carrier gas.

Table 1. Method parameters for both helium and hydrogen as carrier gas.

ALS		
Syringe Volume	5 µL	
Injection Volume	0.5 µL	
Wash Solvent	Carbon disulfide	
Inlet (SSL)		
Mode	Split	
Heater	On, 250 °C	
Split Ratio	100:1	
Septum Purge	3 mL/min	
Liner	p/n 5190-6168	
Columns		
Column 1	Agilent HP-1ms Ultra Inert, 30 m × 250 µm, 0.5 µm (p/n 19091S-633UI)	
Column 2	Agilent DB-WAXetr, 60 m × 320 µm, 1.0 µm (p/n 123-7364)	
Column 3	Deactivated fused silica, 0.57 m × 100 µm	
CFT Device	2-way splitter with Pneumatic Switching Device	
Column Flow	Helium Carrier (mL/min)	Hydrogen Carrier (mL/min)
Column 1	2	1.25
Column 2	2.7	1.96
Column 3	2.7	1.96

Oven	
Gradient	75 °C hold for 8 minutes 5 °C/min to 85 °C, hold 3 minutes 40 °C/min to 140 °C, hold 0.4 minutes
Column 2 Detector (FID)	
Heater	250 °C
Air	400 mL/min
H ₂	40 mL/min (column + fuel = constant for H ₂ method)
Make-up	N ₂ at 25 mL/min
Column 3 Detector (FID)	
Heater	250 °C
Air	400 mL/min
H ₂	40 mL/min (column + fuel = constant for H ₂ method)
Make-up	N ₂ at 25 mL/min

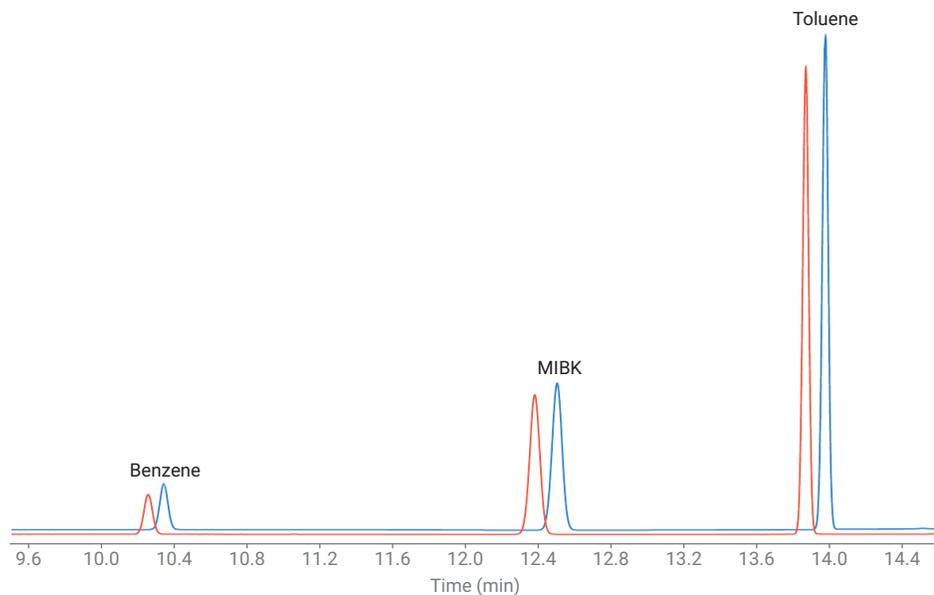


Figure 3. Overlaid chromatograms of the backflush timing standard running with helium carrier gas (blue) and hydrogen carrier gas (red).

Backflushing

The initial backflush time was determined from the monitor channel's signal. An injection of the backflush timing and resolution mixture was made, and the time that the toluene peak returned to baseline was recorded. This time was used as the starting point for optimizing the backflush time. A series of injections were made with the backflush time consecutively reduced by 0.02 minutes until the response of toluene began to decrease. The backflush timing from the injection just before the decrease in the toluene response was used as the method backflush time. Figure 4 compares injections of a gasoline sample with and without backflush. Without backflush, several peaks can be seen to interfere with the peaks of interest. The peaks eluting after toluene are of no interest, and backflushing them allows a much shorter run time.

The monitor channel simplifies the backflush time determination, but is not a requirement for this application. Alternatively, the section of deactivated fused silica can temporarily be installed in place of the analytical column for a single FID configuration.

Performance

The performance was very similar for helium and hydrogen carrier gases (Table 2). Benzene was well separated from ethanol, greatly exceeding the resolution requirement of D3606. The calibration curve correlation coefficients for benzene and toluene exceeded 0.999 for both carrier gases. The S/N for benzene also greatly exceeded the requirements of D3606. The repeatability

criteria met the 95% confidence interval for the applicable concentration ranges of benzene and toluene for six injections of calibration level 4, containing 0.67% benzene and 5.00% toluene by volume. The results for benzene and toluene from locally sourced gasoline samples were also determined to fall within the 95% confidence interval specified in D3606 across both carrier gas methods.

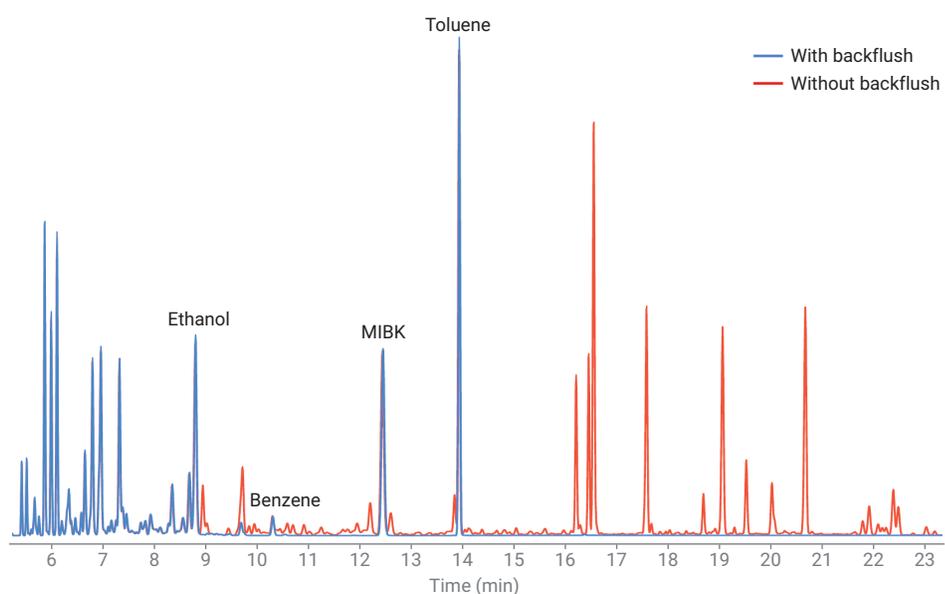


Figure 4. Overlaid chromatograms of gasoline with (blue) and without (red) backflush.

Table 2. Method performance criteria and volume percent amounts of benzene and toluene determined in locally sourced gasoline.

D3606 Performance Criteria (Limit)	Helium Method	Hydrogen Method
Ethanol/Benzene Resolution (>2)	16.8	15.7
Benzene/MIBK Resolution (>1.5)	22.5	21.7
MIBK/Toluene Resolution (>0.6)	17.2	17.2
Benzene R ² (>0.999)	0.99978	0.99954
Toluene R ² (>0.999)	0.99929	0.99925
Benzene S/N (>50:1)	200.2:1	191.0:1
Standard 4 Repeatability	Pass	Pass
Gasoline Sample Repeatability	Pass	Pass
%v/v Benzene in Gasoline Sample	0.329	0.340
%v/v Toluene in Gasoline Sample	4.170	4.154

Conclusion

Following ASTM D3606-17 Procedure A, this method is well suited for the determination of benzene and toluene in gasoline blended with up to 20% ethanol. The use of backflush is critical to the proper separation of the peaks of interest from the gasoline matrix, with the added benefit of a shorter run time and improved column lifetime. The use of both helium and hydrogen carrier gases was demonstrated to perform well and meet or exceed the requirement for ASTM D3606-17 Procedure A.

References

1. Federal Register, Vol. 72, No. 37, Monday, February 26, 2007, Rules and Regulations. Control of Hazardous Air Pollutants from Mobile Sources. *Environmental Protection Agency*, **2007**.
2. ASTM Standard D3606-17, Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography, ASTM International, West Conshohocken, PA.
3. Fitz, B. Using the PSD for Backflushing on the Agilent 8890 GC System. *Agilent Technologies Application Note*, publication number 5994-0550EN, **2018**.

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Printed in the USA, December 13, 2019
5994-1548EN
DE. 4979976852