A New Approach to ASTM D3606 for the Analysis of Benzene and Toluene in Gasoline using Mid-Column Backflush and Hydrogen Carrier with the Agilent 7890B GC

Application Note

Hydrocarbon processing industry

Author

Roger L. Firor

Agilent Technologies, Inc.

2850 Centerville Rd

Wilmington, DE 19808

Abstract

An Agilent 7890B Series GC equipped with a mid-column backflush configuration is described for the analysis of benzene and toluene in finished gasoline. An unpurged Capillary Flow Technology (CFT) splitter is used at the mid-point between the first column a 30 m × 0.25 mm, 0.25 µm HP-1 and the polar second column a 30 m × 0.25 mm, 0.50 µm HP-INNOWax. Hydrogen carrier gas is used for the analysis at 80 °C isothermal. An Aux EPC with bleed restrictor is used to drive midpoint pressure. A dual channel configuration is described where a second FID monitors the first or precolumn chromatography. The HP-INNNOWax does an excellent job separating benzene and toluene without interference from hydrocarbons or ethanol. FID's are used for detection.

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Introduction

The determination of benzene and toluene in motor and aviation gasoline by gas chromatography as specified by ASTM D3606 is widely used for certification. [1] This method uses a packed nonpolar column for a boiling point separation which is backflushed after elution of octane. A packed or micro-packed polar 1,2,3-*tris*(2-cyanoethoxy) propane (TCEP) column then separates the aromatic from nonaromatic hydrocarbons. While this method is reliable, it can have problems with modern fuels containing ethanol due to resolution issues with benzene. Also, TCEP columns can be problematic and subject to retention time shifting in prolonged use.

Capillary columns offer a more reliable and stable analysis for a D3606 type separation and can easily separate benzene from ethanol in reformulated gasoline. In this work, an HP-INNOWax polar column is used as an alternate to a capillary TCEP. The INNOWax is a superior column for this analysis as it is not subject to the variability and sensitivity to higher boiling point hydrocarbons that is characteristic of TCEP columns. A CFT device interfaced to an AUX module on the 7890B Series GC offers precise control of hydrogen carrier flow in the INNOWax column and precise consistent control of backflush timing.

Experimental

Figure 1 shows a diagram of the single channel system used in this work. Here a purged ultimate union is used for mid-point pressure/flow control. Figure 2 shows a simple block diagram of the dual channel system where column 1 (precolumn monitor) is configured. Two unpurged splitters are used where the first serves the same function as a purged ultimate union. The AUX module is connected to the first splitter using 1/16 in stainless steel tubing and a 1/16 in siltite ferrule. The second splitter then directs equal amounts of the sample to FID's. Here, a precolumn monitor can be useful to setup and establish backflush timing. After toluene elutes, the flow in the HP-1 precolumn is reversed. Backflush timing can be established using a mixture on isooctane and *n*-nonane. Backflush time is correct when *n*-nonane just disappears from the chromatogram leaving the complete signal for isooctane.

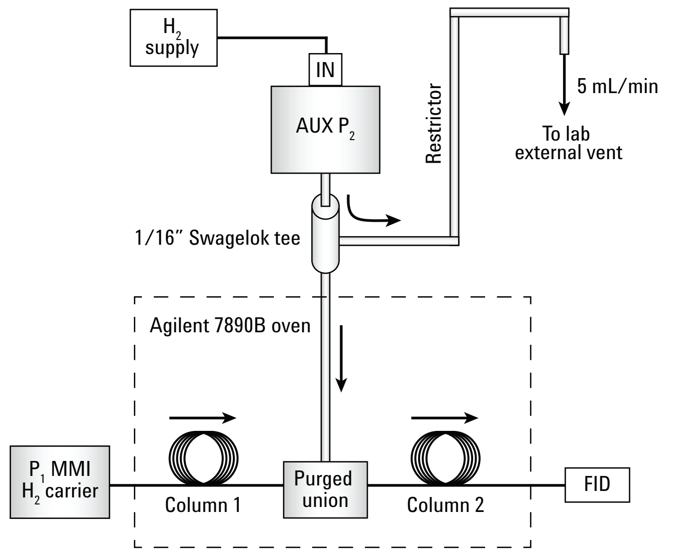


Figure 1. Single channel system diagram using a Multimode Inlet (MMI) and Purged Ultimate Union. Column 1: 30 m × 0.25 mm, 0.25 um HP-1, Column 2: 30 m × 0.25 mm, 0.50 um HP-INNOWax.

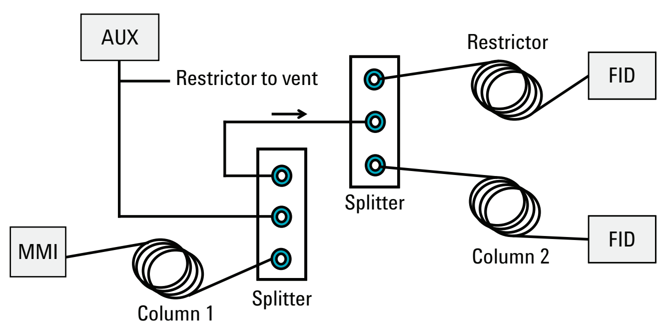


Figure 2. Block diagram of system with precolumn monitor channel showing the use of two unpurged CFT splitters. Restrictor sized for 1:1 split between the FID's.

The internal standard is 2-butanol and is well separated from benzene. A seven level calibration for benzene and toluene is established using standards from Spectrum Quality Standards. These standards contain 10.00% ethanol, 4.01% 2-butanol, benzene 0.06%–5.00%, toluene 0.50–20.0% in isooctane. 2-butanol is added to each of the unkown gasoline samples prior to injection at a concentration of 4 vol%, 40 µL 2-BuOH in gasoline to a final volume of 1 mL in a 2-mL autosampler vial.

For safety considerations, hard plumbing the AUX restrictor bleed flow and Multimode inlet (MMI) split vents to laboratory external vents ensures that hydrogen does not enter the lab.

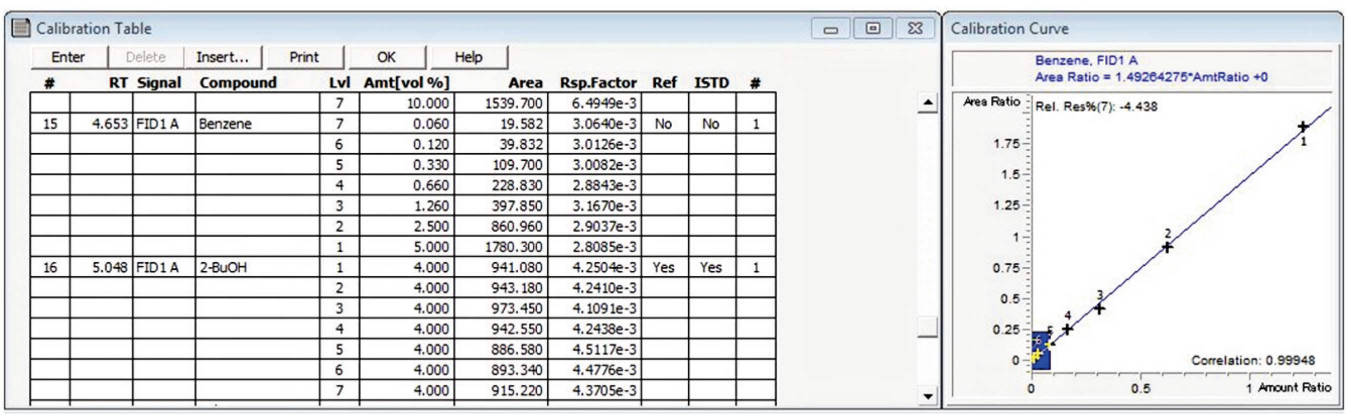
The MMI is used for sample introduction in a temperature programmed split mode. This inlet is also well suited for backflush methods. Hydrogen is demonstrated for the carrier gas and is an excellent alternative to helium. Also, some speed advantages with hydrogen can be exploited. Typical parameters used for the analysis are given in Table 1.

Table 1. System Parameters

Gas chromatograph	Agilent 7890B
Injection port	MMI
Carrier gas	Hydrogen
MMI program	250 °C (0.5 minute) to 300 °C at 200 °C/min
Split ratio	100 to 1
ALS	7693A, 0.5 µL
Oven program	80 °C isothermal
MMI	2 mL/min constant flow, 22.80 psi, for 2.57 minutes, then backflush at –2.5 mL/min
AUX	2.50 mL/min constant flow, 14.95 psi
Backflush time	2.57 minutes
FID1	350 °C
FID2	350 °C
Restrictor to FID2	0.75 m × 0.100 µm deactivated fused silica
CFT Devices	Two unpurged splitters, p/n G3180-6410
Column 1	30 m × 0.25 mm, 0.25 µm HP-1, p/n 19091Z-433
Column 2	30 m × 0.25 mm, 0.50 µm HP-INNOWax, p/n 19091N-233
Calibration standards	D3606 Set, Spectrum Quality Standards, No. 3606EB10
Gasoline samples	87, 89 and 93 octane
ChemStation	OpenLab CDS C.01.05

Results and Discussion

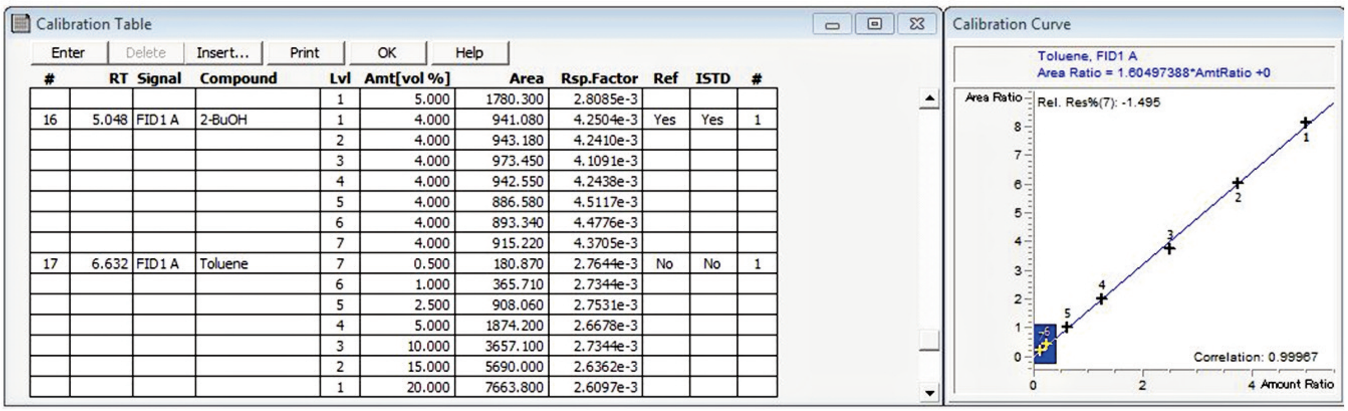
As seen in Figures 3 and 4, the calibration from both benzene and toluene is linear. Correlation coefficients for benzene and toluene are 0.9995 and 0.9997, respectively. Low and high octane samples of pump gasoline were analyzed. All samples contained ethanol.


Calibration Table

#	RT	Signal	Compound	Lvl	Amt[vol %]	Area	Rsp.Factor	Ref	ISTD	#
				7	10.000	1539.700	6.4949e-3			
15	4.653	FID1 A	Benzene	7	0.060	19.582	3.0640e-3	No	No	1
				6	0.120	39.832	3.0126e-3			
				5	0.330	109.700	3.0082e-3			
				4	0.660	228.830	2.8843e-3			
				3	1.260	397.850	3.1670e-3			
				2	2.500	860.960	2.9037e-3			
				1	5.000	1780.300	2.8085e-3			
16	5.048	FID1 A	2-BuOH	1	4.000	941.080	4.2504e-3	Yes	Yes	1
				2	4.000	943.180	4.2410e-3			
				3	4.000	973.450	4.1091e-3			
				4	4.000	942.550	4.2438e-3			
				5	4.000	886.580	4.5117e-3			
				6	4.000	893.340	4.4776e-3			
				7	4.000	915.220	4.3705e-3			

Figure 3. Pane from ChemStation showing benzene standards and seven point calibration curve.

An 87 octane gasoline was analyzed after the appropriate backflush time was established. Figure 5 shows the chromatogram. Benzene is clearly separated from potential interfering hydrocarbons and the 2-butanol internal standard.



#	RT	Signal	Compound	Lvl	Amt[vol %]	Area	Rsp.Factor	Ref	ISTD	#
				1	5.000	1780.300	2.8085e-3			
16	5.048	FID1 A	2-BuOH	1	4.000	941.080	4.2504e-3	Yes	Yes	1
				2	4.000	943.180	4.2410e-3			
				3	4.000	973.450	4.1091e-3			
				4	4.000	942.550	4.2438e-3			
				5	4.000	886.580	4.5117e-3			
				6	4.000	893.340	4.4776e-3			
				7	4.000	915.220	4.3705e-3			
17	6.632	FID1 A	Toluene	7	0.500	180.870	2.7644e-3	No	No	1
				6	1.000	365.710	2.7344e-3			
				5	2.500	908.060	2.7531e-3			
				4	5.000	1874.200	2.6678e-3			
				3	10.000	3657.100	2.7344e-3			
				2	15.000	5690.000	2.6362e-3			
				1	20.000	7663.800	2.6097e-3			

Figure 4. Pane from ChemStation showing toluene standards and seven point calibration curve.

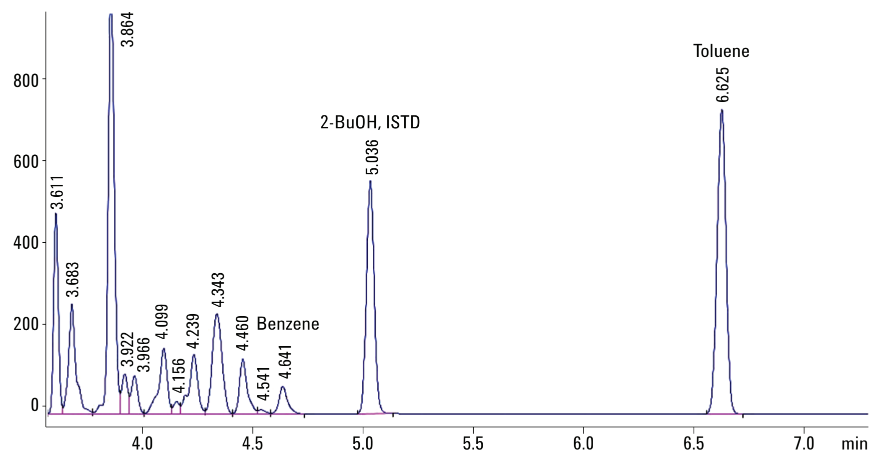


Figure 5. Zoom in on a chromatogram of an 87 octane gasoline in the benzene to toluene region.

The chromatogram shown in Figure 6 was produced using the dual channel configuration in Figure 2. The monitor channel can be useful to visualize changes in backflush times particularly when running standards used to optimize the timing such as isooctane/*n*-nonane mixes. The 0.75 m restrictor has a hold up time at 80 °C of only 0.003 minutes. While the hydrocarbons will show some retention, the timing of elution on the restrictor to FID2 will be very close to what is needed to set backflush time by monitoring the desired calibrating compounds. Alternatively, a backflush wizard software tool can be installed into OpenLab CDS that will guide the user with setup and timing of a backflush method.

In Figure 7, one of the Spectrum Quality standards used for calibration was overlaid with a 93 octane gasoline sample specifically to show the location of ethanol and confirm that it cannot interfere with the benzene determination.

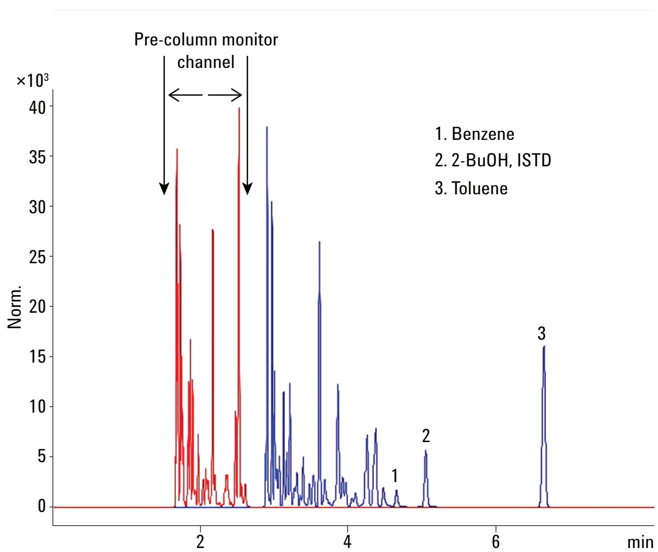


Figure 6. Dual channel chromatograms showing the precolumn monitor. The sample is 93 octane gasoline.

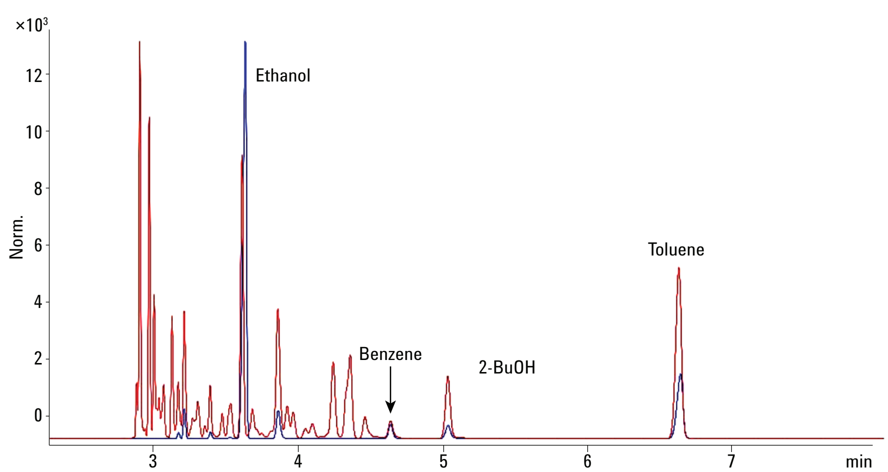


Figure 7. Overlay of a 93 octane gasoline and a calibration mix showing the retention time of ethanol.

Table 2 shows the repeatability for three independent gasoline sample preparations (sample plus internal standard) analyzed on the same system. Results for these independently prepared samples show very good agreement for both benzene and toluene determinations, differing by 2% or less. The three samples were from different gas stations.

Conclusion

An alternate to the current ASTM D3606 using capillary columns with a midpoint pressure CFT device is an easy to implement solution for the determination of benzene and toluene in gasoline. Oxygenates do not interfere with the benzene quantitation. While a capillary TCEP column could be substituted for the INNOWax second column with successful separations, it will not show the reliability and retention time stability of a wax column. A proposed revision of D3606, “Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography” that uses configurations similar to what is described in this application note is currently under development in ASTM.

Reference

1. D3606-10, “Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography”, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

Table 2. Sample Plus Internal Standard, Analyzed on the Same System

Run	Sample	Amt benzene vol %	Amt toluene vol %
1	87 Octane	0.67	3.53
2	87 Octane	0.67	3.50
1	89 Octane	0.93	6.39
2	89 Octane	0.96	6.33
1	93 Octane	0.75	8.00
2	93 Octane	0.77	7.99

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