

# Determining Aromatics in Finished Gasoline Using the Agilent 6820 GC System

## Application

### Gasoline Analysis and Environmental Protection

## Authors

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## Abstract

**A two-column Agilent 6820 gas chromatograph (GC), equipped with two flame ionization detectors (FID) and a 10-port valve, is used for the analysis of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9 and heavier aromatics, and total aromatics in finished gasoline. The internal standard used is 2-hexanone. This method requires two runs; the first is for benzene and toluene, and the second is for ethylbenzene, p/m-xylene, o-xylene, the C9 and heavier aromatics.**

## Introduction

Benzene and aromatics are classified as carcinogens. Regulations limiting their concentration in finished gasoline are established worldwide [1]. In order to assess product quality and to meet the clean fuel regulations, it is necessary to create the required analytical methods for benzene and other

aromatics. There are several methods available for the analysis of aromatics in gasoline. One method employs a single polar HP-INNOWax capillary column [2], and another uses a single nonpolar capillary column [3]. The latter method takes 90 minutes. The American Society for Testing and Materials (ASTM) has published analytical methods for the analysis of aromatics in gasoline. ASTM D5769 [4] employs gas chromatography/mass spectroscopy (GC/MS) for the analysis of benzene, toluene, and total aromatic content in gasoline. ASTM D3606 [5] is a GC method for the analysis of benzene and toluene in finished motor and aviation gasoline, but this method is unable to analyze for C8 or heavier aromatics. ASTM D5580 [6] is another GC method for determining benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9, heavier aromatics, and total aromatics in finished gasoline.

This application follows the ASTM D5580 method but is run using an Agilent 6820 GC. Another Agilent application note [8] cites that ASTM D4815 [7] and D5580 [6] were run on a single Agilent 6890N GC system.

## Experimental

The configuration used for this application is listed in Table 1. A column micropacked with 1,2,3-tris-2-cyanoethoxypropane (TCEP) is used for preseparating aromatics from nonaromatics in the same boiling point range. A nonpolar HP-1 column is used for separating the aromatics.



**Table 1. Configuration**

Hardware and software		
G1180A	6820 GC	1
161	Split/Splitless inlet	1
215	Flame ionization detector (FID)	2
302	One manual controller	1
751	Installation and automation of one valve	1
800	10-port switch valve	1
872	Zero dead volume (ZDV) connection of a capillary column to a valve	2
870	Adjustable restrictor	1
874	Install valve downstream from the capillary inlet capillary inlet	1
335	Cerity NDS software	1
Columns		
19095Z-623	Capillary column: HP-1, 30 m, 0.53 mm, 5- $\mu$ m	1
	micropacked column: 56 cm $\times$ 1/16-inch TCEP (20%)	1
Standard		
	Aromatics standards	

**Method Description**

This method requires two runs for a complete aromatics analysis, as described below:

**First Run**

The sample containing the internal standard (ISTD) (2-hexanone) is injected into a precolumn containing micropacked polar TCEP. With the valve in the "OFF" position, C9 and lighter nonaromatics elute from this column and are vented. FID B is used to monitor this separation. See Figure 1A.

Before the elution of benzene from the TCEP column, immediately switch the valve to the "ON" position (switch valve at  $T_1$ ). This backflushes the TCEP column and transfers the remaining compounds to the nonpolar HP-1 column. Benzene, toluene, and the ISTD elute in boiling point order and are detected by FID A. See Figure 1B.

After elution of the ISTD from the HP-1 column, switch the valve to the "OFF" position (switch

valve at  $T_3$ ). The HP-1 column-flow is now reversed to backflush the remainder of sample components (C8 and heavier aromatics, plus C10 and heavier nonaromatics) to FID A. See Figure 1C.

**Second Run**

The run is repeated a second time, allowing the C12 and lighter nonaromatics, benzene and toluene to elute from the TCEP column to the vent. FID B is used to monitor this separation. See Figure 1A.

Before the elution of ethylbenzene, immediately backflush the TCEP column, allowing the remaining sample components to enter the HP-1 column (switch valve at  $T_2$ ). The ISTD and C8 aromatics are thereby separated in boiling point order and are detected by FID A. See Figure 1B.

After the elution of o-xylene from the HP-1 column, immediately reverse the flow (switch valve at  $T_4$ ) to backflush C9 and heavier aromatics to FID A for detection. See Figure 1C.

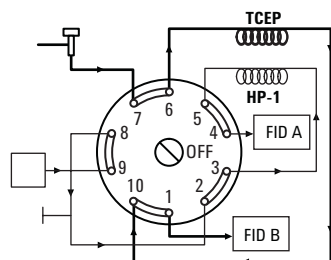
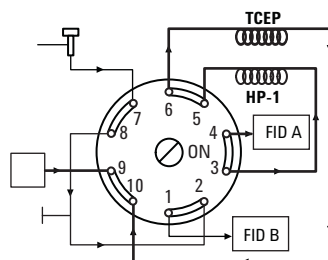
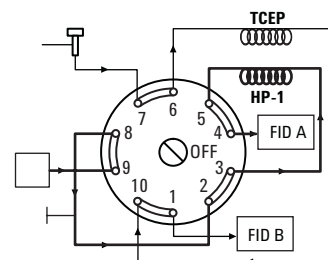
**Instrument Conditions**

The instrument conditions are listed in Table 2.

**Table 2. Instrument Conditions**

Inlet	Split/Splitless, 200 °C, split ratio: 11:1
Detector	FID, 250 °C, makeup: N <sub>2</sub> , 15 mL/min
Oven program	50 °C (10 min), 2 °C/min, 120 °C
Valve temperature	80 °C
HP-1 column flow	N <sub>2</sub> , 7 mL/min
TCEP precolumn flow	N <sub>2</sub> , 8 mL/min
Air flow	350 mL/min
H <sub>2</sub> flow	40 mL/min
Valve switch times	$T_1 = 0.5$ min, $T_2 = 1.6$ min, $T_3 = 18.5$ min, $T_4 = 29.5$ min*
Precolumn	TCEP micropacked, 560 mm, 1.6-mm od, 0.38-mm id
Analytic column	HP-1, 30 m, 0.53 mm, 5 $\mu$ m

\* Switch times should be determined for each GC system.

**Figure 1A. Valve.****Figure 1B. Valve.****Figure 1C. Valve.**

## Results and Discussion

### Valve Switch Time Setting

Appropriate valve switch time  $T_1$  and  $T_2$  must be determined experimentally. If switch time  $T_1$  and  $T_2$  are not set correctly (for example, switched too late), it is possible that part of the benzene and ethylbenzene will be vented. If switched too early, it may allow interfering compounds to enter the analytical column.

### Setting valve switch time $T_1$ and $T_2$

Set valve to the "OFF" position, and then inject 1.0  $\mu\text{L}$  of a calibration blend containing approximately 5% benzene, ethylbenzene, o-xylene, and

2-hexanone, respectively, in isooctane (the exact concentration need not be known). The correct time for  $T_1$  and  $T_2$  is just prior to the elution of benzene and ethylbenzene from the TCEP precolumn. The chromatogram is shown in Figure 2.

### Setting valve switch time $T_3$

Re-inject the calibration blend and turn the valve to backflush at time  $T_1$ . The time when the ISTD returns to baseline is called  $T_3$ , shown in Figure 3.

### Setting valve switch time $T_4$

Re-inject the calibration blend and backflush at time  $T_2$ . The time when the o-xylene peak returns to the baseline is called  $T_4$ , as shown in Figure 4.

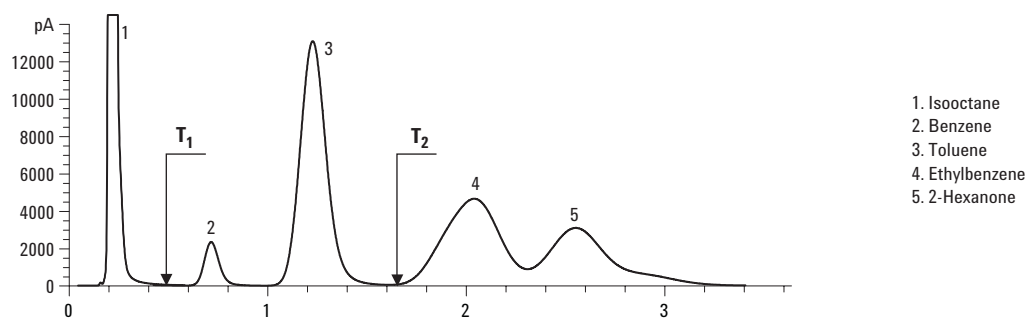


Figure 2. Setting precolumn backflush times,  $T_1$  and  $T_2$ . The compounds are detected by FID B.

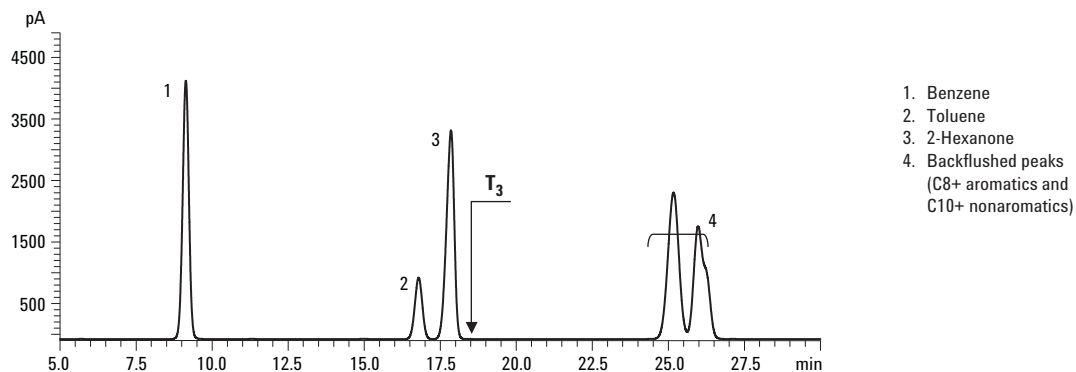


Figure 3. Setting valve switch time  $T_3$ .

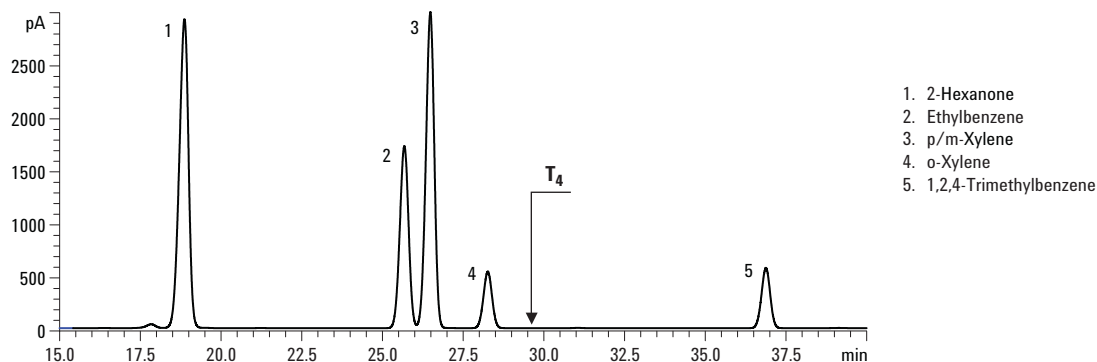


Figure 4. Setting valve switch time  $T_4$ .

## Calibration

The experimental data yields correlation coefficients ( $R^2$ ) >0.999 for each aromatic, accompanied by very low y-axis intercepts. A typical calibration curve for ethylbenzene is shown in Figure 5.

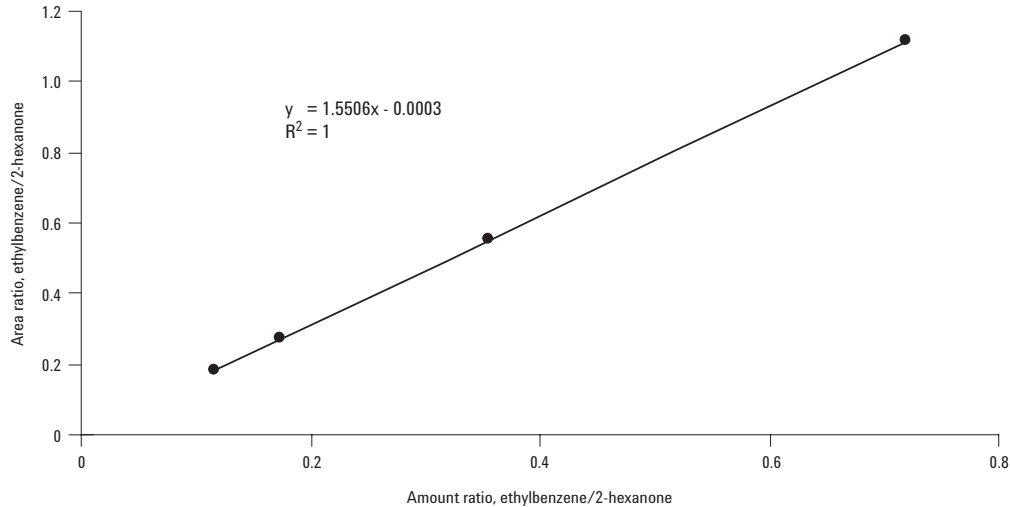


Figure 5. Calibration curve for ethylbenzene.

For an optimum calibration, the absolute value of the y-intercept ( $b_i$ ) must be at minimum. In this case,  $A_i$  approaches zero when  $w_i$  is less than 0.1 mass%. This means the mass% ( $w_i$ ) calculated for an aromatic with zero peak area must be close to zero. The y-intercept can be tested by using Equation 1 below:

$$w_i = (b_i/m_i) \times (w_s/w_g) \times 100\%$$

where:

- $w_i$  = Mass% of aromatic compound i
- $w_s$  = Mass of ISTD added, g
- $w_g$  = Mass of gasoline sample, g
- $m_i$  = Slope
- $b_i$  = Intercept
- $A_i$  = Area of the internal standard

The ASTM D5580 standard specifies that  $w_i$  must be <0.02 mass% for benzene and 0.2 mass% for the other aromatics.

The following is an example of the y-intercept test using data from Figure 5.

For aromatic i (ethylbenzene),  $b_i = 0.0003$ ,  $m_i = 1.5506$ , a typical sample preparation may contain approximately  $w_s = 0.8$  g (1 mL) of ISTD and  $w_g = 7$  g (9 mL) of a gasoline sample. Substituting these values into Equation 1 yields:

$$w_i = (0.0003/1.5506) \times (0.8 \text{ g}/7 \text{ g}) \times 100\% = 0.0022 \text{ mass\%}$$

Since  $w_i = 0.0022$  mass% is less than 0.2 mass% (the ASTM D5580 specification), the y-intercept has an acceptable value for ethylbenzene.

## Repeatability

Table 3 shows that observed repeatability meet or exceed ASTM D5580 specifications.

**Table 3. Repeatability**

Compound	Observed		ASTM D5580 specification	
	Mean, (mass%)	Repeatability *	Range, (mass%)	Repeatability
Benzene	0.852	0.009	0.14-1.79	$0.0265(X^{0.65}) = 0.024$
Toluene	6.229	0.014	2.11-10.08	$0.0301(X^{0.5}) = 0.077$
Ethylbenzene	1.614	0.009	1.57-2.65	0.029
o-Xylene	3.370	0.049	0.77-3.92	$0.0296(X^{0.5}) = 0.055$

X = mass% of mean.

\* Difference between two runs

## Conclusion

A two-column Agilent 6820 GC system equipped with 10-port switch valve, two FIDs, and Cerity NDS software is used for analysis of aromatics in gasoline. This system provides a simple approach for determining benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9, heavier aromatics, and total aromatics. The Cerity NDS software is very easy to use for instrument control and data analysis. The results demonstrate that the observed data meet or exceed the calibration and repeatability specifications of the ASTM D5580 standard method.

## References

1. The People's Republic China National Standard GB17930-1999, Unleaded Gasoline for Motor Vehicles.
2. Satoshi Ito, "Analysis of Aromatic Hydrocarbons in Gasoline and Naphtha with the Agilent 6820 Series Gas Chromatograph and a Single Polar Capillary Column", Agilent Technologies, publication 5988-9261 [www.agilent.com/chem](http://www.agilent.com/chem)
3. Cuiding Yang, et al, Test Methods of Petrochemical (RIPP test method), 1990, 233.
4. ASTM D5769-98, Standard Test Method for Determination of Benzene, Toluene, and Total Aromatics in Finished Gasoline by Gas Chromatography/Mass Spectrometry.
5. ASTM D3606-99, Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography.
6. ASTM D5580-02, Standard Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C9 and Heavier Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography.
7. ASTM D4815, Standard Test Method for Determination of MTBE, TAME, DIPE, tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography.
8. J. D. McCurry, "Running ASTM Methods D4815 and D5580 on a Single Agilent 6890N Gas Chromatograph with Nitrogen Carrier Gas", Agilent Technologies publication 5988-9153EN [www.agilent.com/chem](http://www.agilent.com/chem)

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