Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline with Agilent 6820 GC System Using ASTM Method D3606

Application

Gasoline Analysis and Environmental Protection

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Abstract

The Agilent 6820 gas chromatographic (GC) system configured with flame ionization detector and 6-port valve is used to analyze benzene and toluene in motor and aviation gasoline. In this method, the methyl silicone packed column OV-101 and a TCEP [1,2,3-*tris*(2-cyanoethoxy) propane) are used as precolumn and analytic column respectively. The concentration of each component is calculated by reference to the internal standard (methyl ethyl ketone). Agilent Cerity NDS software is used for 6820 GC control and data analysis. This application demonstrates that calibration and precision meet or exceed the ASTM D3606 specifications.

Introduction

Benzene is classified as a toxic air pollutant. A knowledge of the concentration of benzene compounds can aid in evaluating possible health hazards to persons handling and using gasoline.

Some worldwide regulatory standards were created for monitoring and controlling fuel composition. The United States Clean Air Act (CAA) requires that the level of benzene in reformulated gasoline (RFG) must not exceed 1 volume percent. In China, Nation Standard GB17930 requires that the level of benzene in finished gasoline must not exceed 2.5 volume percent [1]. To meet the stipulated limits of benzene, quantitative determinations of benzene at all process stages is essential.

The American Society for Testing and Materials (ASTM) has published method ASTM D3606 for determining benzene and toluene in finished motor and aviation gasoline [2]. The only difference between ASTM D3606 and this application is the use of a different detector. The detector in D3606 is a thermal conductivity detector (TCD), but in this work the easier-to-maintain, flame ionization detector (FID) is used.

Experimental

Configuration

The GC system is configured with packed inlet, FID, and 6-port valve. Packed columns OV-101 and TCEP are precolumn and analytic column respectively. The configurations are listed in Table 1.

Table 1. Agilent 6820 Configuration

Standard hardware and software	
G1180A	Agilent 6820 GC
152	Packed inlet system with septum purge
215	FID
302	One manual flow controller
751	Installation and automation of one valve
700	6-port valve
335	NDS Cerity chemical software
Columns	
	Stainless Steel packed column, 2.6' × 1/8-inch OV-101 (10%) on Chromosorb WAW 80/100 mesh
	Steel packed column, 15' × 1/8-inch TCEP (20%) on Chromosorb PAW 80/100

Method Description

Methyl ethyl ketone (MEK) is added as an internal standard (ISTD) to the sample which is then introduced into a GC equipped with two columns connected in series. The sample passes through the nonpolar OV-101 precolumn first, as illustrated in Figure 1A. The six-port switching valve is in the "OFF" position. On the OV-101 column, the components are separated according to their boiling points. The lighter components including benzene, toluene, and nonaromatics up to n-octane, elute first from the OV-101 column and transfer into the polar TCEP column. After octane has eluted, the valve switches to the "ON" position, as illustrated in Figure 1B. The components heavier than octane backflush from the OV-101 to vent, while the components of interest are separated on the TCEP column. The eluted components are detected by an FID.

Instrument Conditions

Table 2 provides a list of analysis conditions.

Table 2. GC Conditions

Inlet	Packed inlet, 250 °C
Detector	FID, 250 °C
Oven temperature	90 °C
Valve temperature	80 °C
TCEP flow	N_2, 40 mL/min (~44 psi)
OV-101 flow	N_2, 40 mL/min (~44 psi)
Air flow	350 mL/min
H_2 flow	40 mL/min
Valve switch	3.02 min*
Precolumn	Stainless Steel packed column, 2.6' × 1/8-inch OV-101 (10%) on Chromosorb WAW 80/100 mesh
Analytical column	Steel packed column, 15' × 1/8-inch TCEP (20%) on Chromosorb PAW 80/100

* The time to backfush must be determined for each column system.

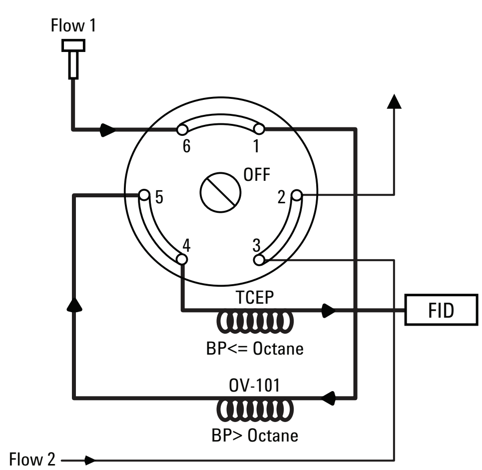

Figure 1A. Valve "OFF" Forward flow mode.

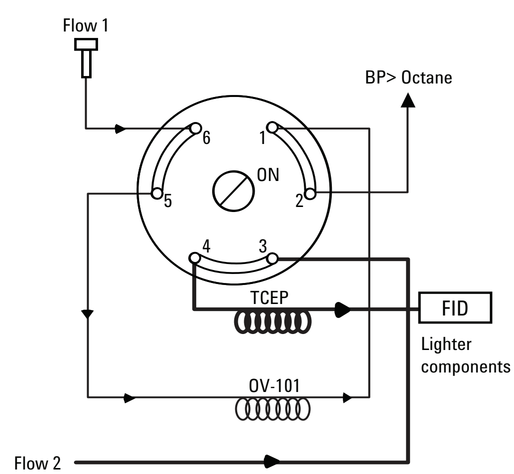

Figure 1B. Valve "ON" Backflush flow mode.

Calibration

Standard sample: seven standard samples covering the range of 0.06 to 5 volume% benzene and 0.5 to 20 volume% toluene are shown in Table 3. For each standard, the volumes of benzene and toluene listed below were added into a 100-mL volumetric flask, and diluted with isooctane.

Table 3. Range of Standard Samples

Benzene		Toluene	
Volume%	**mL**	**Volume%**	**mL**
5.00	5.00	20.00	20.00
2.50	2.50	15.00	15.00
1.25	1.25	10.00	10.00
0.67	0.67	5.00	5.00
0.33	0.33	2.50	2.50
0.12	0.12	1.00	1.00
0.06	0.06	0.50	0.50

Calibration blends: Accurately add 1.0 mL of MEK into a 25-mL volumetric flask, and fill to the mark with the first standard sample. Repeat this procedure until all blends are prepared.

Results and Discussion

Calibration

The calibration is shown to be linear. The correlation (R^2) of both benzene and toluene exceeds 0.999. Figure 2 shows a calibration curve for benzene, as an example.

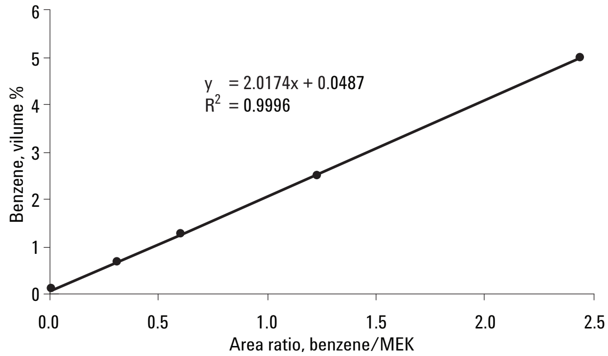

Figure 2. Calibration of curve for benzene.

Repeatability

The good separation of benzene, toluene, and MEK from other potential interferences is shown in Figure 3.

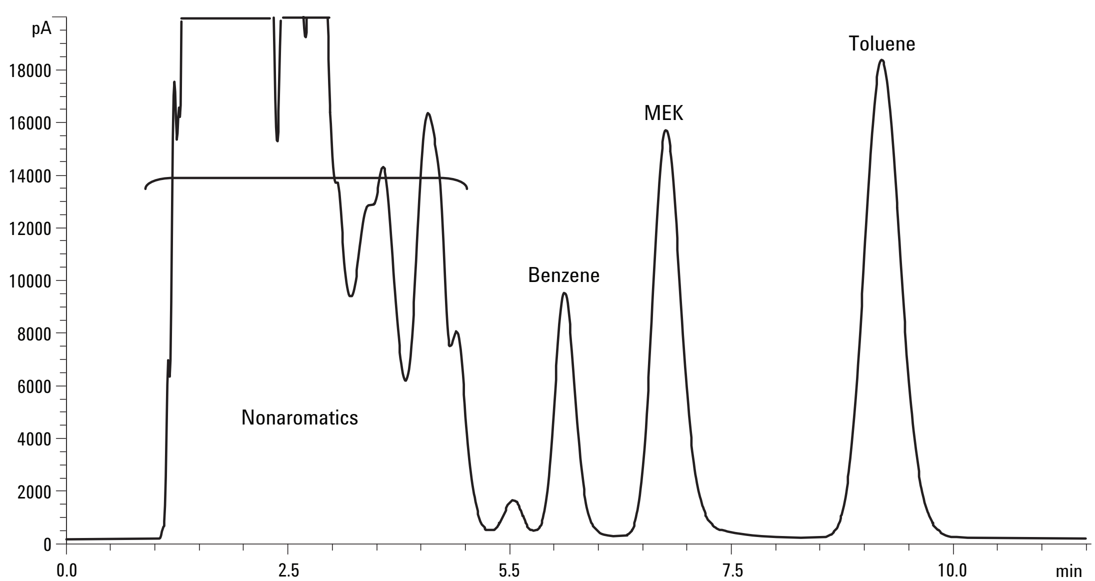

Figure 3. Chromatogram of gasoline.

Table 4 shows very good repeatability, meeting or exceeding ASTM D3606 specifications.

Table 4. Repeatability of %(V/V) for Five Runs

	Observed		ASTM D3606 specifications	
Compound	Average %(V/V)	Difference* %(V/V)	Range %(V/V)	Repeatability
Benzene	1.24	0.01	0.1–1.5	0.03 (x) + 0.01 = 0.04
	2.54	0.01	>1.5	0.03
Toluene	4.78	0.08	1.7–9	0.03 (x) + 0.02 = 0.16
	9.11	0.16	9	0.62

Note: X is the mean volume% of the component.
* Difference between maximum and minimum volume% for five runs.

Sample Injection

In this application, a manual injection technique is used. The following process is necessary so that sharp symmetrical peaks are obtained.

1. Flush the micro-syringe at least five times with sample mixture and then fill with 3 µL of sample. (Avoid any air bubbles in the syringe.)
2. Slowly inject the sample until 2.0 µL remains in the syringe.
3. Wipe the needle with tissue and draw back the plunger to admit 1 to 2 µL of air into the syringe.
4. Insert the needle of the syringe through the septum cap of the chromatograph and push until the barrel of the syringe is resting against the septum cap.
5. Push the plunger completely down and remove the syringe immediately from the chromatograph.

Cerity NDS

With Cerity NDS, it is very easy to control the instrument. It can switch the valve automatically and build the multi-calibration.

Conclusions

The Agilent 6820 GC configured FID and 6-port switch valve is used to determine benzene and toluene in finished motor and aviation gasoline. An independently heated valve system ensures heavy components in the sample not to be condensed. The result demonstrates the correlation of calibration curve for benzene and toluene exceed 0.999 and the repeatability meets or exceeds the specification of ASTM D3606.

References

1. People's Republic of China National Standards GB17930-1999.
2. ASTM D3606-99, Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography.

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