Determining Aromatics in Finished Gasoline: ASTM Method D 5580

Application

Gas Chromatography

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Abstract

An Agilent 6890 Series gas chromatography system, including the Agilent ChemStation and automatic liquid sampler, was optimized to perform aromatics analysis according to ASTM Method D 5580-94. This standard method is for the analysis of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene (BTEX), C_9+ aromatics, and total aromatics in finished gasolines and some gasoline-related streams. A description of a guaranteed analyzer for D 5580 is given, with which analysis through full report takes approximately 45 minutes. The configuration, conditions, and sample chromatograms are presented.

Introduction

In 1990 the United States initiated the trend to improve air quality with the Clean Air Act (CAA). Legislation similar to the CAA is pending in other states in the U.S. and in other countries. The CAA is expected to serve as a guideline for setting pollutant limits and the corresponding test methods.

The CAA established guidelines for reformulated gasoline (RFG) in order to control ground-level ozone and toxins formation. The U.S. Environmental Protection Agency (USEPA) also established standards for the maximum allowable concentration of ground-level ozone. When areas exceed that allowable concentration, they are in nonattainment of the ozone standard and suffer specific consequences.

Beginning on January 1, 1995, the CAA requires certification of all RFG sold in ozone nonattainment areas and specifies a maximum concentration level of benzene (benzene is a health hazard and carcinogen) and a maximum allowable concentration of aromatics (aromatics lead to poor combustion and increased exhaust emissions).

The USEPA identified test methods for seven properties of RFG and requires testing of each batch of RFG for these. Of the identified test methods, however, no single method is suitable for addressing all requirements for reformulated gasoline. The sole USEPA regulatory method for measuring benzene concentrations in finished motor and aviation gasoline is ASTM D 3606-92[1]. However, if the gasoline contains oxygenates, they interfere with the determination of benzene and toluene. Similarly, ASTM Method D 4815-94[2], for the determination of oxygenated components, does not allow quantification of benzene.

ASTM D 5580-94[3, 4] eliminates the interference caused by the presence of ethanol and methanol when analyzing aromatics. In addition, ASTM is currently working on a revision of D 5580-94 to further improve the method. The California Air Resource Board (CARB) requires D 5580 as the analytical method for benzene quantitation in gasolines sold in California. The method requires two separate analyses; the first analysis quantifies benzene and toluene, and the second analysis determines ethyl-benzene, o-xylene, p/m-xylene, and the C_9 and heavier aromatics content. Summing the results of bothanalyses determines the total aromatics content.

The **AC Aromatics Analyzer** is a guaranteed analyzer for ASTM D 5580, is based on the Agilent 6890 Series gas chromatograph (GC), and is available through and supported by Analytical Controls[5], an Agilent Channel Partner. The AC Aromatics Analyzer consists of a 6890 Series GC configured with a split/splitless inlet, a ten-port valve, two chromatographic columns, and a single flame ionization detector (FID).

Experimental

The complete configuration for the AC Aromatics Analyzer appears in table 1. The Agilent ChemStation performs system control, data analysis, and reporting.

A micropacked TCEP column preseparates aromatics from non-aromatics in the same boiling point range. The capillary column then separates the aromatics. It is possible to use an extra detector, a thermal conductivity detector (TCD), to facilitate the determination of the valve backflush and to reset times and monitor the separation of the polar TCEP precolumn. See figure 1 for the flow diagram of the system.

ASTM D 5580 requires all standards and samples to be prepared by mass using 2-hexanone as an internal standard.

The Agilent ChemStation in a Microsoft® Windows™ environment controls the AC Aromatics Analyzer and automates all aspects of the calibration, sample analysis, and data reporting.

Table 1. AC Aromatics Analyzer Configuration

Hardware and Software	
G1540A	6890 Series GC
Opt 112	Capillary split/splitless inlet with EPC control
Opt 210	FID with EPC control
Opt 301	Three channels of auxiliary EPC
Opt 403	GPIB communication cable
G1916A	6890 Series automatic liquid sampler
G1875AA	Single-instrument GC ChemStation
Columns	
Methyl silicone fused silica capillary column	30 m x 0.53 mm, 5-µm HP-1
Micropacked TCEP precolumn	560 mm x 0.38 mm id, 20% on chromosorb PAW 80/100
Valves	
Ten-port rotary valve	
AC Application	
Calibration standards	
Reference gasoline	
Method development	
Software including methods	
Calibration and certification data	
Operating manual	
Performance guarantee	

Method Description

For the first of two analyses, a reproducible volume of sample containing the internal standard, 2-hexanone, is injected onto a pre-column containing a polar liquid phase (TCEP). C_9 and lighter non-aromatics elute from the pre-column and are vented, including 1-methylcyclopentene and ethers such as MTBE, ETBE, and TAME. It is possible to use a TCD before the vent to monitor the progress of this preliminary separation. Figure 1 shows the valve configuration and flow path during injection.

The TCEP precolumn backflushes just before the elution of benzene and directs the remaining portion of the sample onto a nonpolar capillary column for separation and FID quantitation. Benzene, toluene, and the internal standard elute in the order of their boiling points and are detected by an FID. Figure 2 shows the flow path during backflush.

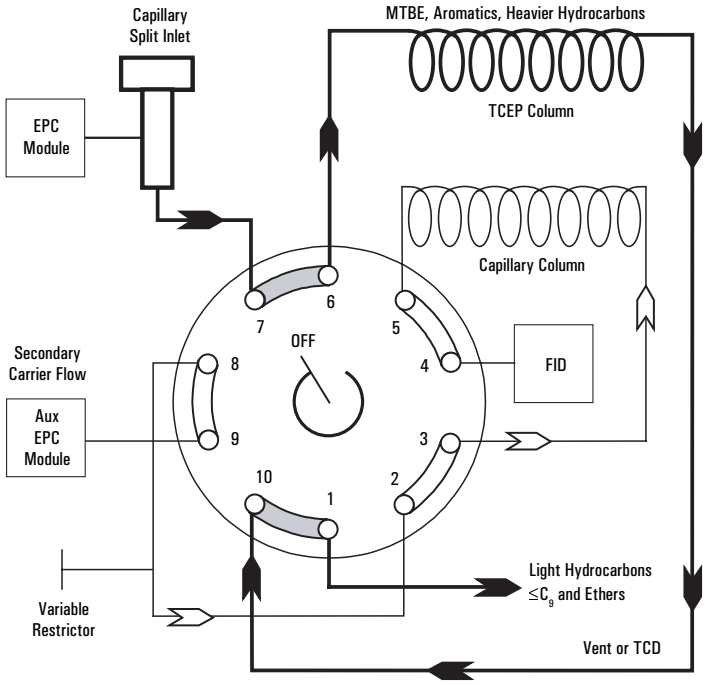

Figure 1. Sample flow path during sample injection.

Immediately after the elution of the internal standard from the capillary column, the flow through it is reversed to backflush the remainder of the sample (a mixture of hydrocarbons with boiling points above that of C_9) from the column to the FID. Although detected, this peak is not quantitated because it contains both aromatic and non-aromatic hydrocarbons. Figure 3 illustrates the valve position during backflush from the capillary column.

The analysis repeats a second time allowing the C_{12} and lighter non-aromatics, benzene and toluene, to elute from the polar TCEP precolumn to vent. A TCD is recommended to monitor this separation. The TCEP precolumn backflushes just before the elution of ethyl-benzene and directs the remaining aromatic portion into the capillary column. The internal standard and C_8 aromatics components elute in the order of their boiling points and are detected by an FID. Immediately after o-xylene elutes, the flow through the nonpolar WCOT column reverses to backflush the C_9 and heavier aromatic components to the FID. During backflush, pressure is increased to minimize the time required to remove all components from the column. Table 2 gives the chromatographic operating parameters.

Results

Figure 4 is a chromatogram of the first portion of a gasoline analysis-elution of benzene, toluene, 2-hexanone, and backflushed hydrocarbons. Figure 5 is a chromatogram of the second separation-elution of 2-hexanone, ethylbenzene, p/m-xylene, and C_9 + higher-boiling aromatic components. The oxygenates contained in the gasoline did not interfere with the aromatics analysis.

Electronic pneumatics control (EPC) helps minimize analysis time by speeding up the elution of higher-boiling components during capillary column backflush. Total analysis time (two separations plus the report) is approximately 45 minutes.

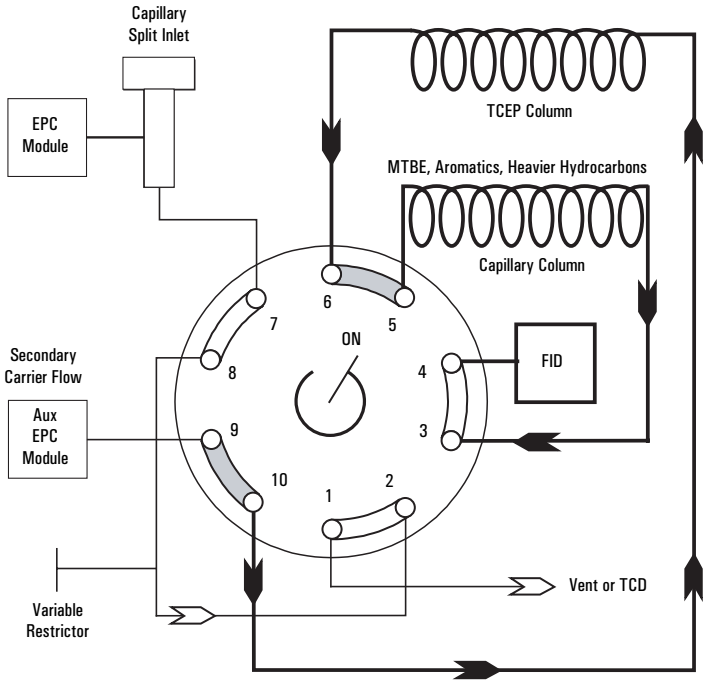

Figure 2. Backflush of micropacked TCEP column onto nonpolar capillary column for analysis of aromatics.

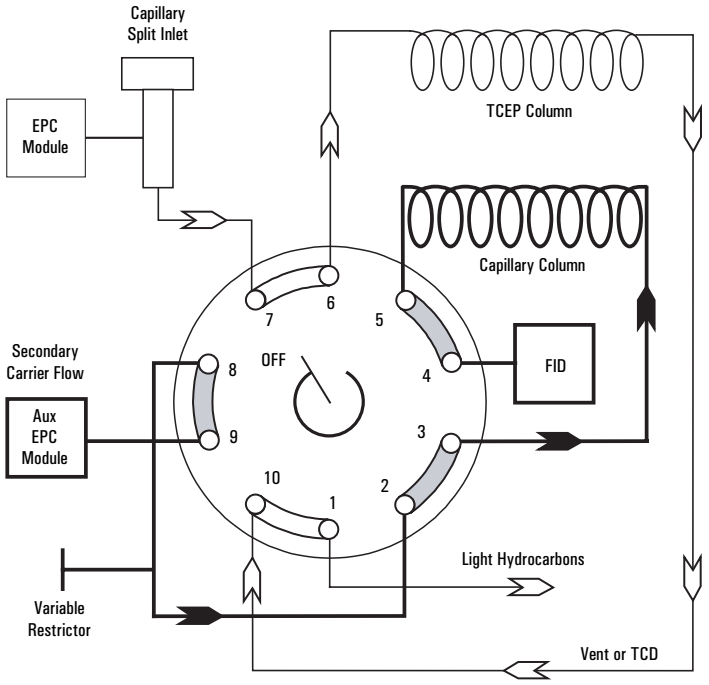

Figure 3. Backflush of the capillary column to elute >C_8 aromatics and >C_{10} hydrocarbons (first analysis) or >C_9 + aromatics (second analysis) to the FID.

Conclusion

The AC Aromatics ASTM D 5580 Analyzer is applicable for analysis of all finished motor gasolines and some gasoline-related refinery streams. The analyzer provides a simple approach to determining the benzene content in gasoline with-out interference from oxygenates. Capillary column technology provides excellent separation capability. The optimal configuration of the 6890 Series GC system reduces operator involvement and improves the accuracy of the results.

Table 2. Gas Chromatographic Operating Parameters

Injection port temperature:		200°C
FID temperature:		250°C
TCD temperature:		200°C
Oven temperature (both packed TCEP and WCOT column temperature	*Initial*	60°C (6 min)
	Program rate	2°C/min
	Final	120°C
Valve temperature:		80°C
Carrier gas:		Helium
Split ratio:		11:1
Sample size:		1 µL
Flow to TCEP precolumn:		10 mL/min
Flow to WCOT capillary column:		10 mL/min
Split vent flow:		100 mL/min

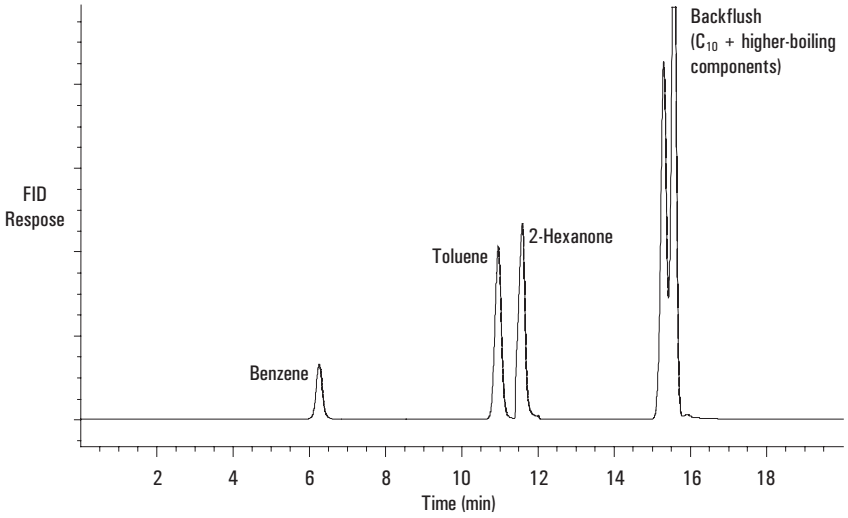

Figure 4. First analysis: separation of early-eluting aromatics.

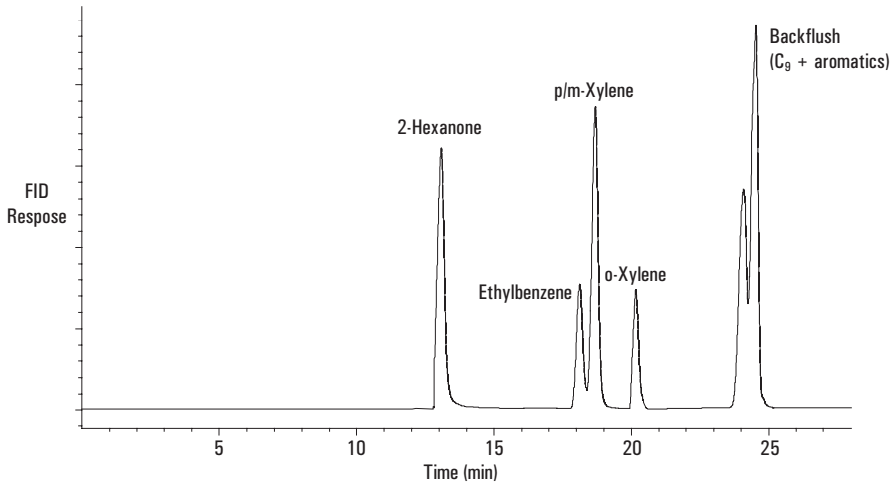

Figure 5. Second analysis: separation of later-eluting aromatics.

References

1. ASTM D 3606-92; *Test Method for the Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography*, American Society for Testing and Materials, Philadelphia, Pennsylvania.

2. ASTM D 4815-94; *Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography*, American Society for Testing and Materials, Philadelphia, Pennsylvania.

3. ASTM D 5580-94; *Test Method for Determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C_9 and Heavier Aromatics and Total Aromatics in Finished Gasoline by Gas Chromatography*, American Society for Testing and Materials, Philadelphia, Pennsylvania.

4. Vince Giarrocco, "Analysis of Benzene, Toluene, C_8 Aromatics, and Total Aromatics in Finished Gasoline by GC Using ASTM D 5580-94," Agilent Technologies, Inc., Application Note 228-293, Publication No. (43) 5963-5048E, November 1994.

5. AC Analytical Controls, Innsbruckweg 35, 3047 AG Rotterdam, The Netherlands, and 3494 Progress Drive, Bensalem, Pennsylvania 19020 USA.

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