Determining Benzene in Finished Gasoline and Refinery Streams to Comply with CAA Requirements: ASTM Method D 3606

Application

Gas Chromatography

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Abstract

An Agilent 6890 Series gas chromatographic system (GC, Agilent ChemStation and automatic liquid sampler) was used as the foundation of the AC Benzene/Toluene in Gasoline Analyzer. The analyzer separates and detects benzene, methyl ethyl ketone (MEK, an internal standard), and toluene in finished gasoline. Sample analysis through full report takes approximately 10 minutes. A complete description of the instrument configuration, analysis conditions, and results are given.

Introduction

The United States Clean Air Act of 1990 (CAA) establishes guidelines for fuel composition. To meet the requirements of the CAA, the U.S. Environmental Protection Agency (USEPA) introduced programs aimed at reducing atmospheric levels of carbon monoxide, nitrogen oxide, ozone, and hydrocarbons. Petroleum refiners around the world are adapting their operations to accommodate the U.S. environmental regulations.

To reduce emissions of toxic compounds by motor vehicles, one program mandates the quantification of toxic compounds found in gasoline. The reformulated gasoline (RFG) program requires lowering the total aromatics, benzene, and olefin content in the gasoline pool. The CAA classifies benzene as a toxic air pollutant; the level of benzene in RFG must not exceed 1 volume percent. To meet the stipulated limits of benzene, a quantitative determination of benzene at all process stages is essential.

The EPA prescribed ASTM Method D 3606-92[1] as the single regulatory test method for determining benzene concentrations in gasoline. The AC Analytical Controls Benzene/Toluene in Gasoline Analyzer separates benzene from both light and heavy hydrocarbons, the internal standard, and toluene in one analysis, and meets all the specifications of ASTM D 3606-92. The analyzer may also be used to measure benzene and toluene concentrations in other gasoline-related refinery streams. Knowledge of benzene and toluene concentrations in refinery streams allows refiners to optimize their production processes.

The AC Benzene/Toluene Analyzer consists of the Agilent 6890 Series GC configured with two GC columns and a single thermal conductivity detector (TCD).

Experimental

The complete configuration for the AC Benzene/Toluene Analyzer is given in table 1. The ChemStation performs system control and data analysis.

Electronic pneumatics control (EPC) is used to control carrier gas to both columns and gases to the TCD. The 6890 Series automatic liquid sampler is used to maximize precision in sample introduction into the packed column injection port. The Agilent ChemStation provides instrument control, data acquisition and report generation.

Table 1. AC Benzene/Toluene in Gasoline Analyzer Configuration

Hardware and Software	
G1540A	6890 Series GC
Opt 102	Packed column inlet with EPC control
Opt 220	TCD 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 packed column (0.8 m x 3.2 mm od)
Micropacked TCEP column (4.6 m x 3.2 mm od)

Valves
Six-port rotary switching valve

AC Application
Calibration standards
Reference gasoline
Optimized methods
Software including methods
Calibration and certification data
Operating manual
Performance guarantee

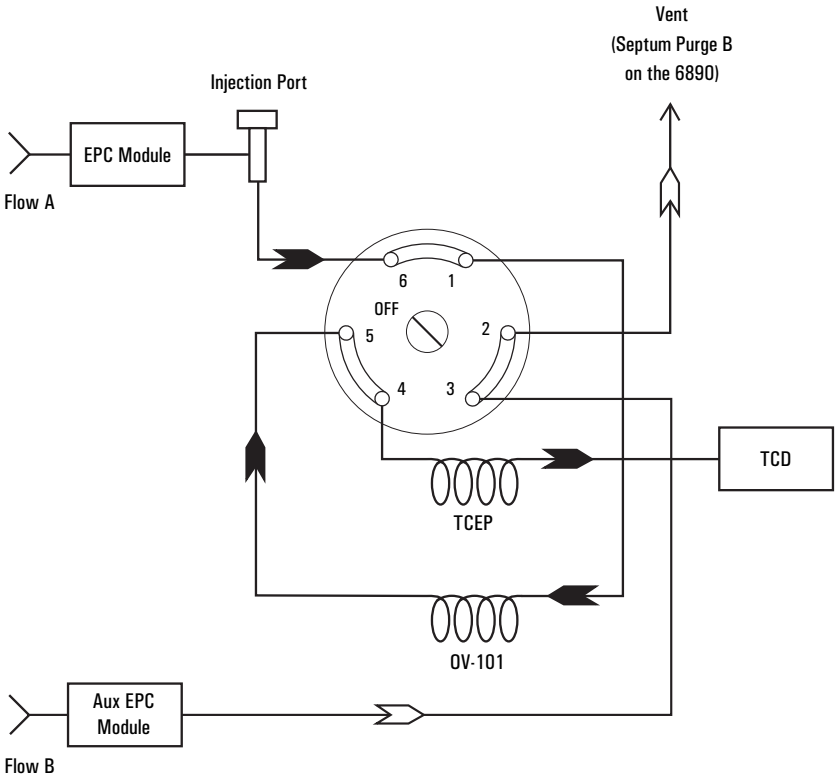

Figure 1. Flow path during and immediately after sample introduction; the six-port switching valve is in the OFF position. Sample is separated by boiling point in the first column. Lower-boiling components, including benzene, toluene, the internal standard MEK, and hydrocarbons up through the boiling point of e-octane, transfer to the the TCEP column.

Method Description

During analysis, the sample flows from the inlet to the nonpolar column, as illustrated in figure 1, with the six-port switching valve in the "OFF" position. This nonpolar column separates components according to their boiling points; the lighter components, including benzene, toluene, and non-aromatics up to n-octane, elute first from this column and transfer into the polar TCEP column. After elution of n-octane from the first column, the valve switches to the "ON" position, as illustrated in figure 2. With the valve ON, heavier components backflush from the OV-101 column to vent while separation of the components of interest continues in the TCEP column. Flow to the TCEP column is controlled by the B channel of auxiliary EPC.

Table 2 provides a list of analysis conditions.

Table 2. Gas Chromatographic Operating Parameters

Injection port temperature:	200°C
TCD temperature:	200°C
Packed column temperature:	145°C
Carrier gas:	Helium
Linear gas rate:	6 cm/s
Sample size:	2 µL
Volume flow rate:	Approx 30 mL/min
Column head pressure:	Approx 200 kPa (30 psi)
Total cycle time:	10 min
Valve switch:	Approx 0.75 min

Calibration

The ASTM D 3606-92 test method requires calibration before routine sample preparation and analysis. Seven levels of benzene within the range of 0.1 and 5.0 volume percent, and seven levels of toluene within the range of 0.5 and 20.0 volume percent, are required to calibrate response including detection limits and linearity. Methyl ethyl ketone (MEK) is used as the the internal standard for calibration standards and samples. Results are reported in volume percent relative to the internal standard.

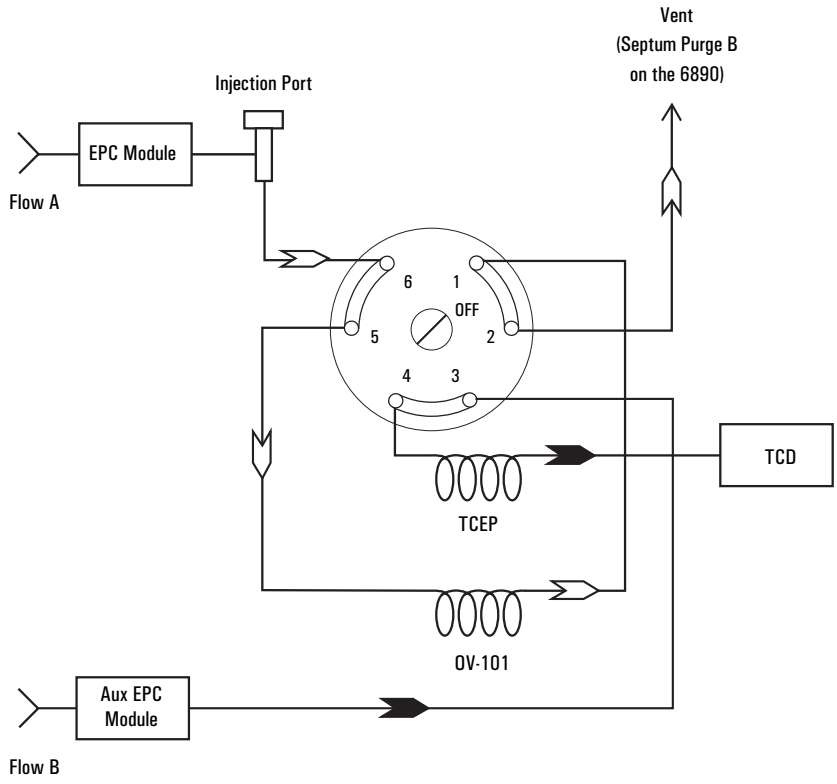

Figure 2. **Flow path after the six-port switching valve has been turned ON. Flow through the first column is reversed to backflush higher-boiling sample components. Auxiliary EPC provides flow to the second column that separates the components of interest.**

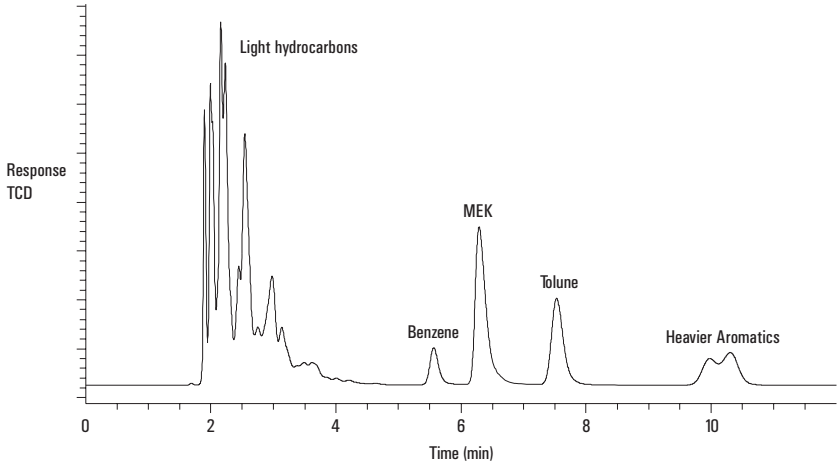

Figure 3. **A typical chromatogram that shows the separation of benzene, toluene, and MEK from other potential interferences.**

Results

Figure 3 illustrates a typical chromatogram for the analysis of benzene in gasoline, derived by the AC Benzene/Toluene in Gasoline Analyzer. The analyzer meets or exceeds the repeatability and reproducibility requirements of ASTM D 3606-92 as shown in table 3.

Table 3. Repeatability and Reproducibility of the AC Benzene/Toluene Analyzer

Component	Repeatability	Reproducibility
Benzene	0.03 liquid	0.23 x measured value
Toluene	0.62 liquid volume%	1.15 liquid volume volume %

Conclusion

The AC Benzene/Toluene in Gasoline Analyzer complies with the sole test approved by the USEPA for benzene analysis in gasoline. Its robust components (e.g., packed columns) and low maintenance configuration ensure trouble-free routine operation. The repeatability and reproducibility of the analyzer meet or exceed USEPA standards.

The AC Benzene/Toluene in Gasoline Analyzer is applicable for all finished motor gasolines and most gasoline-related refinery streams. The analyzer provides a simple approach for the determination of benzene content in gasoline and makes use of the features available on the Agilent 6890 Series GC.

References

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

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