Determining Oxygenates in Gasoline: ASTM Method D 4815

Application

Gas Chromatography

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Abstract

An Agilent 6890 Series gas chromatographic system (GC, ChemStation, and automatic liquid sampler) was used as the foundation of the AC Oxygenate Analyzer. The analyzer determines individual ethers and alcohols in finished gasolines according to ASTM Method D 4815-94[1] and takes advantage of the unique features of the 6890 Series GC. An analysis through full report takes 15 minutes. A complete description of the instrument configuration, analysis conditions, and chromatograms is given.

Introduction

The 1990 Clean Air Act Amendments (CAA) establish guidelines for fuel composition with the intent of reducing atmospheric levels of carbon monoxide, nitrogen oxides, and hydrocarbons. The Amendments include a reformulated gasoline (RFG) program that is in effect from January 1995 to March 1997. RFG is specifically targeted to reduce levels of ozone. The simple model on which the regulations are based requires a minimum content of 2 wt% oxygen in RFG. The California Air Resources Board (CARB) has designated ASTM D 4815-94 as the test method for oxygenate quantification in all gasoline sold in California.

The AC Oxygenate Analyzer from AC Analytical Controls is an analyzer based on the 6890 Series GC system and designed to perform ASTM D 4815. It tests all finished motor gasolines for oxygenates listed in table 1 to determine regulatory compliance and to ensure uniform product quality. Individual ethers are quantified from 0.1 to 20.0 mass % and individual alcohols from 0.1 to 12.0 mass % in one analysis.

Table 1. Scope of the AC Oxygenate Analyzer

Ethers	Alcohols
Methyl tert-butylether (MTBE)	Methanol
Diisopropylether (DIPE)	Ethanol
Ethyl tert-butylether (ETBE)	Isopropanol
tert-Amylmethylether (TAME)	n-Propanol
	Isobutanol
	tert-Butanol
	sec-Butanol
	n-Butanol
	tert-Pentanol (tert-amyl alcohol)

Experimental

The AC Oxygenate Analyzer consists of the 6890 Series GC configured with two GC columns, a split/splitless inlet, a ten-port sampling valve, and a flame ionization detector (FID). The complete configuration is given in table 2.

Table 2. AC Oxygenate Analyzer System 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 column (30 m x 530 µm id, 2.65 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-Specific Components	
Calibration standards	
Reference gasoline	
Optimized Methods	
Software including methods	
Calibration and certification data	
Operating manual	
Performance guarantee	
Instrument Control and Data Acquisition	
ChemStation	

The micropacked TCEP column pre-separates the low-boiling non-polar components from the polar and higher-boiling nonpolar components. The nonpolar capillary column then separates the polar components, including the oxygenates, according to their boiling points. Electronic pneumatics control (EPC) is used for faster backflush of the TCEP column. This reduces the analysis time by approximately 40%.

The Agilent ChemStation runs in a Microsoft® Windows™ environment, controls the AC Oxygenate Analyzer, and automates all aspects of data handling and data reporting.

Calibration

Detector response is calibrated using several levels of the oxygenates to be analyzed and a single level of an internal standard such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether). After analyzing this standard, the analyzer generates a standard curve automatically that includes detection limits and linearity. The internal standard is also added to the samples to be analyzed, and their results are reported in mass percent.

Method Description

Figure 1 shows the valve configuration and sample flow path during injection. The sample first passes into the TCEP column where the low-boiling and nonpolar components, those eluting before methyl-cyclopentane, pass directly to vent. The column retains polar compounds, beginning with DIPE and MTBE, and higher-boiling components.

The valve then switches, and components trapped in the TCEP column backflush to the nonpolar capillary column for separation and analysis, as shown in figure 2. This column performs a boiling point separation on components through benzene and TAME. After TAME elutes from the nonpolar column, the valve switches to backflush the components remaining on the capillary column to the detector as one unresolved peak at increased head pressure (higher flow). Although detected, this backflush fraction is not quantified. By using EPC to increase pressure during the last backflush, total analysis time is reduced by approximately 40%. Figure 3 illustrates the valve position during the backflush from the capillary column when using pressure programming. Table 3 gives the chromatographic operating parameters.

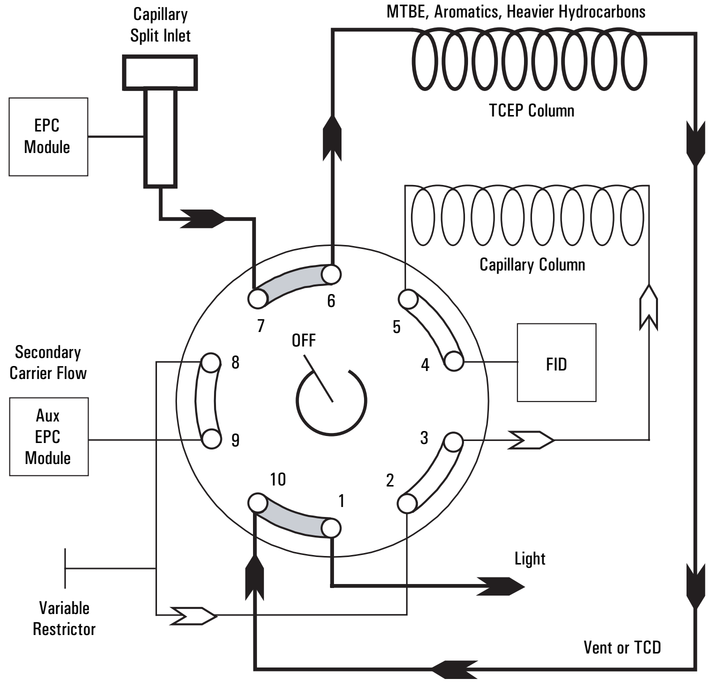

Figure 1. Sample flow path during and directly after sample injection. Low- polarity volatiles pass through the polar TCEP column and are vented. Polar components and higher-boiling apolar components are trapped in the TCEP column.

Results

A report listing results in mass percent is generated automatically at the end of each run. Targeted ethers are reported from 0.1 to 20.0 mass % and targeted alcohols from 0.1 to 12.0 mass %. Figure 4 shows a typical chromatogram for an ether blend. Figure 5 is a typical chromatogram of an alcohol blend, showing good resolution and lack of interferences.

The AC Oxygenate Analyzer meets and exceeds the repeatability and reproducibility standards set by ASTM D 4815-94. A summary of analysis precision is shown in table 4.

Conclusion

The AC Oxygenate ASTM D 4815 Analyzer provides a rapid, accurate analysis of oxygenates in finished gasolines including RFGs, taking advantage of 6890 Series GC system automation to reduce operator involvement, increase sample throughput, and improve accuracy of the results. The electronic pneumatics control of the 6890 Series GC helps achieve a 40% reduction in analysis time through the use of pressure programming. Capillary column technology yields excellent separation of targeted oxygentates.

References

1. *ASTM D 4814-94, Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol, and C1 to C4 Alcohols in Gasoline by Gas Chromatography*, American Society of Testing and Materials, Philadelphia, Pennsylvania.

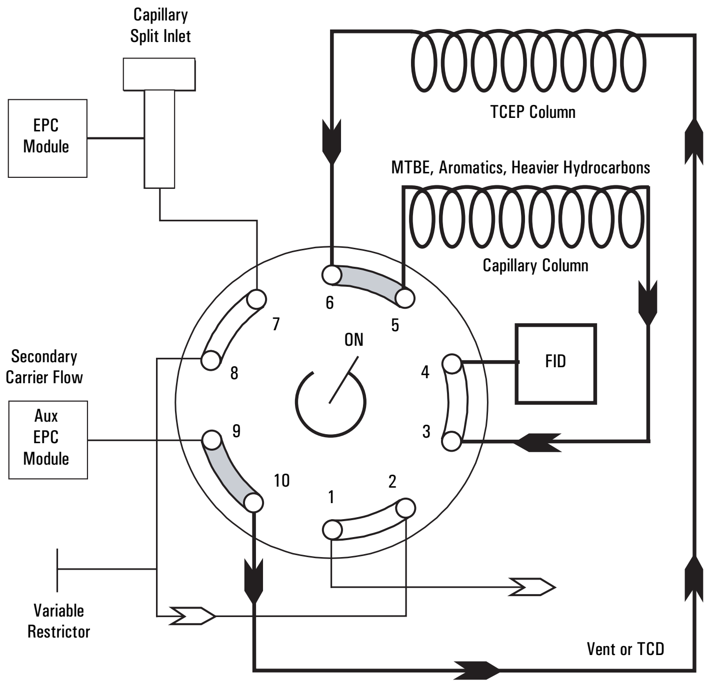

Figure 2. Flow path of polar and medium-volatility compounds backflushed from the TCEP column to the capillary column for separation and analysis.

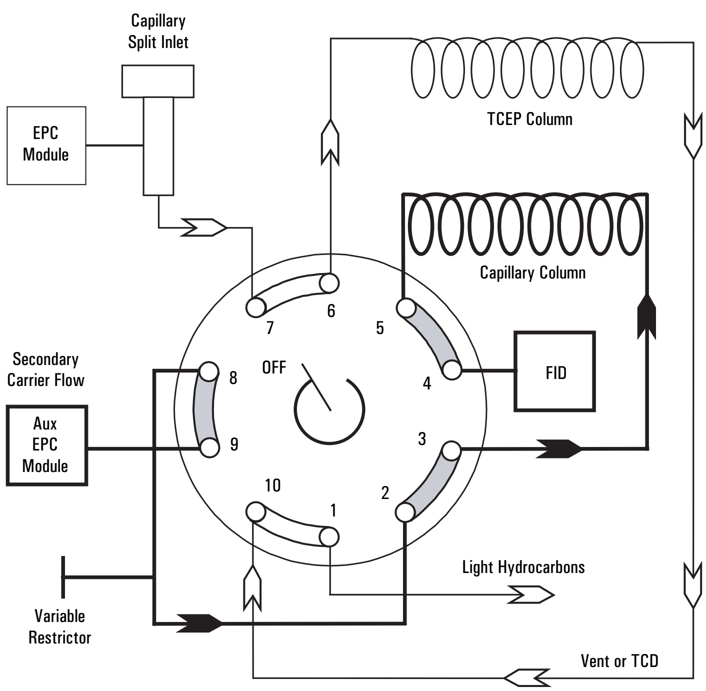

Figure 3. Final backflush of heavy hydrocarbons from the capillary column. Column head pressure is increased through programming via EPC to reduce run time.

Table 3. Gas Chromatographic Operating Parameters

Injection port temperature:		200ºC
FID temperature:		250ºC
TCD temperature:		200ºC
Nonpolar WCOT capillary column temperature:	Initial:	60ºC (6 min)
	Program rate:	2ºC/min
	Final:	115ºC
Polar TCEP precolumn temperature (isothermal):		60ºC
Valve temperature:		80ºC
Carrier gas:		Helium
Split ratio:		15:1
Sample size:		1.0-3.0 µL
Flow to TCEP precolumn:		5 mL/min
Flow to WCOT capillary column:		5 mL/min
Split vent flow:		100 mL/min
Makeup flow:		18 mL/min

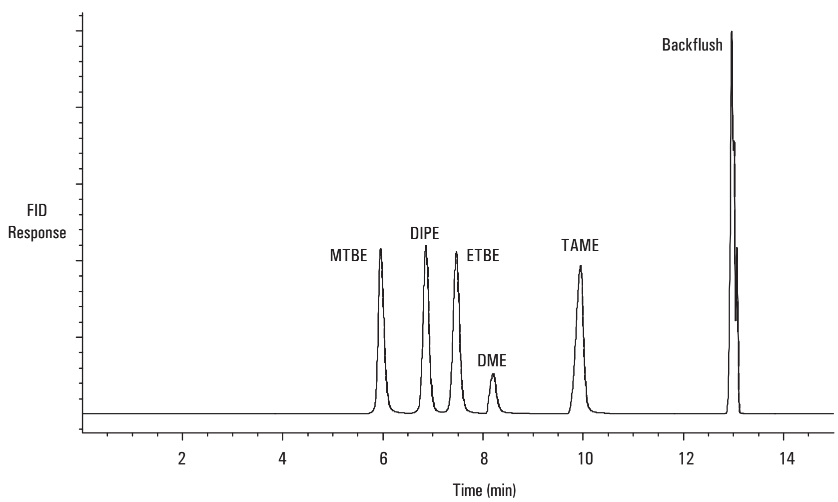

Figure 4. Typical chromatogram of an ether gasoline blend.

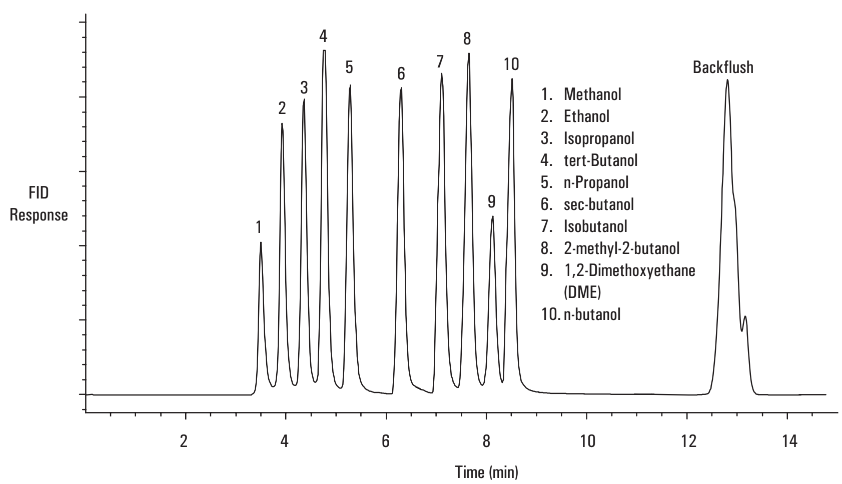

Figure 5. Typical chromatogram for alcohol gasoline blend.

Table 4. ASTM D 4815-94 Precision with the AC Oxygenate Analyzer (X = Oxygenate Concentration in Mass %)

Component	Repeatability	Reproducibility
Methanol (MeOH)	0.09 ($X^{0.59}$)	0.37 ($X^{0.61}$)
Ethanol (EtOH)	0.06 ($X^{0.61}$)	0.23 ($X^{0.57}$)
Isopropanol (iPA)	0.04 ($X^{0.56}$)	0.42 ($X^{0.67}$)
tert-Butanol (tBA)	0.04 ($X^{0.56}$)	0.19 ($X^{0.67}$)
n-Propanol (nPA)	0.003 ($X^{0.57}$)	0.11 ($X^{0.57}$)
MTBE	0.05 ($X^{0.56}$)	0.12 ($X^{0.67}$)
sec-Butanol (sBA)	0.003 ($X^{0.61}$)	0.44 ($X^{0.67}$)
DIPE	0.08 ($X^{0.56}$)	0.42 ($X^{0.67}$)
Isobutanol (iBA)	0.08 ($X^{0.56}$)	0.42 ($X^{0.67}$)
ETBE	0.05 ($X^{0.82}$)	0.36 ($X^{0.76}$)
tert-Pentanol (tAA)	0.04 ($X^{0.61}$)	0.15 ($X^{0.57}$)
n-Butanol (nBA)	0.06 ($X^{0.61}$)	0.22 ($X^{0.57}$)
TAME	0.05 ($X^{0.70}$)	0.31 ($X^{0.51}$)
Total Oxygen	0.02 ($X^{1.26}$)	0.09 ($X^{1.27}$)

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