Running ASTM Method D4815 for Determining Oxygenates in Gasoline on the Agilent 6820 GC

Application

Gasoline Analysis and Environmental Protection

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Abstract

The analytical method is designed for the determination of ethers and alcohols in gasolines by using the Agilent 6820 gas chromatography system. This method employs one 10-port switch valve and two columns. Specific compounds determined are: methyl tert-butylether (MTBE), ethyl tert-butylether(ETBE), tert-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, n-propanol, isobutanol, tert-butanol, sec-butanol, n-butanol and tert-pentanol. For quantitative analysis, 1,2-dimethoxyethane (DME) is used as the internal standard.

Introduction

Unleaded gasoline is produced to reduce environmental pollution. Ethers, alcohols, and other oxygenates can be added to gasoline to increase the octane number and to reduce the amount of carbon monoxide in exhaust. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. It is therefore important to develop test methods for the analysis of these oxygenates. The American Society for Testing and Materials (ASTM) has published method ASTM D4815 for the analysis of oxygenates [1]. This application follows the ASTM D4815 method. Another application note shows running methods ASTM D4815 and D5580 on a single Agilent 6890N GC [2].

Experimental

The experiments are performed on an Agilent 6820 GC system equipped with 10-port switch valve, split/splitless inlet, and flame ionization detector (FID). A micropacked column packed with polar 1,2,3 -*tris*-2-cyanothoxypropane (TECP) is used for prefraction; a nonpolar HP-1 capillary column is used for separating components of interest. In order to obtain steady gas flows, the auxiliary 2-channel gas pressure regulator (G4323A) is suggested. The configuration is listed in Table 1.

Table 1. Configuration

Hardware		
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
G4323A	Auxiliary 2-channel gas pressure regulator	1
Columns		
19095Z-123	Capillary column HP-1, 30 m, 0.53 mm, 2.65 µm	1
	Micropacked column: 56 cm x 1/16 inch, TCEP (20%)	1
Standards		
	Ethers and alcohols standards	

Method Description

1. The sample containing the internal standard (ISTD) 1,2-dimethoxyethane (DME) is injected into the GC and passes onto a polar TCEP column. The lighter hydrocarbons elute first from the column and are vented, while oxygenates and heavier hydrocarbons are retained. The switch valve is in the "OFF" position, as shown in Figure 1A.
2. After methylcyclopentane (MCP), but before DIPE and MTBE elute from the TCEP column, switch the valve to the "ON" position, as shown in Figure 1B. The components trapped in the TCEP column backflush to the nonpolar HP-1 column for separation in boiling point order.
3. After TAME elutes from the nonpolar HP-1 column, switch the valve to its original "OFF" position to backflush the heavier remainder, as shown in Figure 1C.

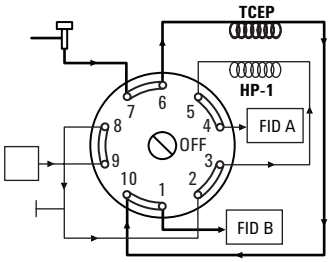


Figure 1A. Valve.

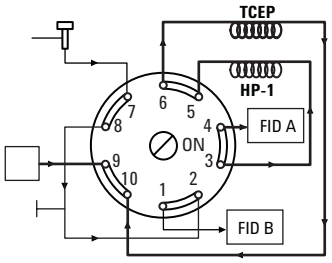


Figure 1B. Valve.

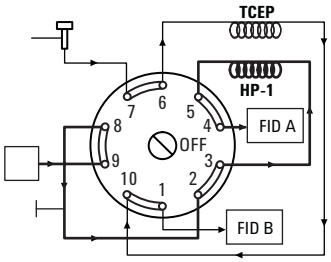


Figure 1C. Valve.

Backflush Time Setting

Setting the correct backflush time is key to this method. If valve switching is too short, C5 and lighter hydrocarbons are backflushed and interfere with the analysis of C4 alcohols. If the switching time is too long, all of the ether components are vented, resulting in an incorrect ether measurement.

Backflush time is determined experimentally by using switching times between 0.18 and 0.34 minutes. The data obtained from the backflush time setting experiment appear in Figure 2. Inspection of this data shows that the hydrocarbons, represented by MCP, are completely eluted from the TCEP column after 0.22 minutes. For this system, a backflush time of 0.22 minutes is used for analysis of DIPE, MTBE, other ethers, and alcohols. If analysis of DIPE is not required, the backflush time will be slightly longer. For this system, a backflush time of 0.28 minutes is used for the analysis of MTBE and alcohols. The valve switch, with the preferred backflush time, is controlled by the Agilent Cerity NDS software.

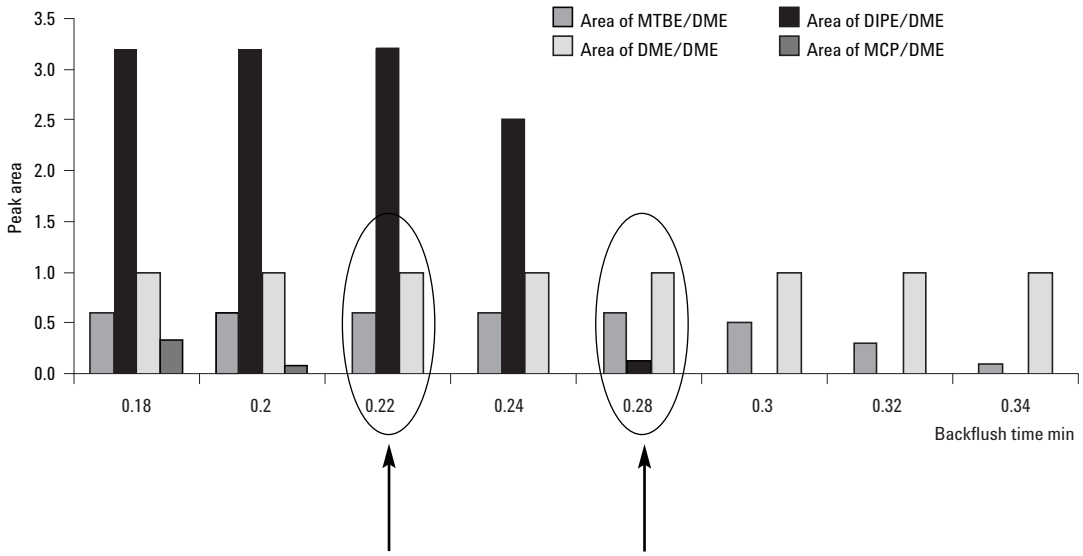
GC Conditions

The instrument conditions are listed in Table 2.

Table 2. Instrument Conditions

Inlet	Split/Splitless, 200 °C, split ratio: 15:1
Detector	FID, 250 °C, makeup: N_2,18 mL/min
Oven program	60 °C (6 min), 2 °C/min, 75 °C, 5 °C/min, 115 °C
Valve temperature	60 °C
HP-1 column flow	N_2, 3 mL/min
TCEP precolumn flow	N_2, 3.5 mL/min
Air flow	350 mL/min
H_2 flow	40 mL/min
Backflush time	0.22 min*
Precolumn	TCEP micropacked, 56 cm,1.6 mm od, 0.38-mm id
Analytic column	HP-1, 30 m, 0.53 mm, 5 µm

* Switch times should be determined for each GC system.



Backflush time of 0.22-min for analysis of DIPE. At this point, hydrocarbons represented by MCP are completely eluted from the TCEP, while the MTBE and DIPE are completely retained.

Backflush time of 0.28-min for analysis of MTBE when DIPE is not required.
At this point, very little DIPE is retained in TCEP, while the MTBE is completely retained.

Figure 2. Graphic presentation of the data from backflush time setting experiment.

Results and Discussion

Calibration and Standardization

Prepare multicomponent calibration standards of the oxygenates and concentration ranges of 0.1, 0.5, 2, 5, 10, 15, and 20 mass percent; for each oxygenate, prepare a minimum of five calibration standards. Run the calibration standard and establish the calibration curve for each oxygenate. It is easy to build the multicalibration by using Cerity NDS software. The experimental data demonstrated excellent calibration linearity; the correlation R^2 exceeds 0.99 and the y-axis intercept is at a minimum for each oxygenate. Figure 3 shows the calibration plot for tert-butanol, as an example.

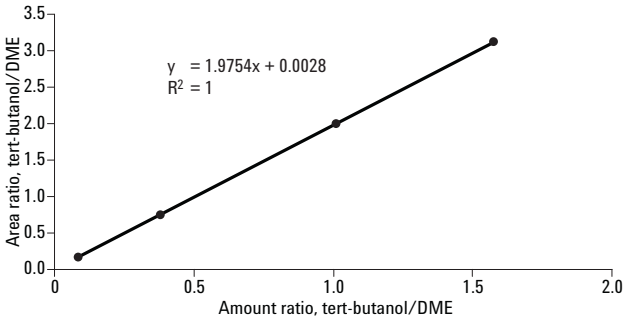


Figure 3. Calibration curve of tert-butanol.

For an optimum calibration, the absolute value of the y-intercept, b_i, must be at a minimum. In this case, when w_i is <0.1 mass%, A_i approaches zero. The equation to determine the mass percent oxygenate i or w_i, reduces to Equation 1. The y-intercept can be tested using Equation 1 below:

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

where:

w_i = mass% oxygenate i, where w_i is <0.1 mass%,

w_s = mass of ISTD added to the gasoline sample, g

w_g = mass of gasoline sample, g.

b_i = absolute value of the y-intercept for component i

m_i = mass ratio of component i in sample relative mass of standard

The following is an example of the calculation for the y-intercept (b_i) test using Figure 3 for tert-butanol, for which $b_i = 0.0028$ and $m_i = 1.9754$. A typical sample preparation may contain approximately 0.5 mL of ISTD ($w_s = 0.4$ g) and approximately 9.5 mL of gasoline sample ($w_g = 7$ g). Substituting these values into Equation 1 yields:

$$w_i = (0.0028/1.9754) \times (0.4\text{ g}/7\text{ g}) \times 100 = 0.008 \text{ mass\%}$$

Since w_i (0.008 mass%) is less than 0.1 mass%, the y-intercept b_i has an acceptable value for tert-butanol. Similarly, determine w_i for all other oxygenates. The results show that for all oxygenates, w_i is less than 0.1 mass%. (Data not shown for all compounds, only tert-butanol is shown as an example.)

Oxygenate Mixture Analysis and Repeatability

Figure 4 shows the analytical results for an oxygenate mixture. Oxygenates including MTBE, TAME, DIPE, tert-pentanol, and the C1–C4 alcohols are all well separated.

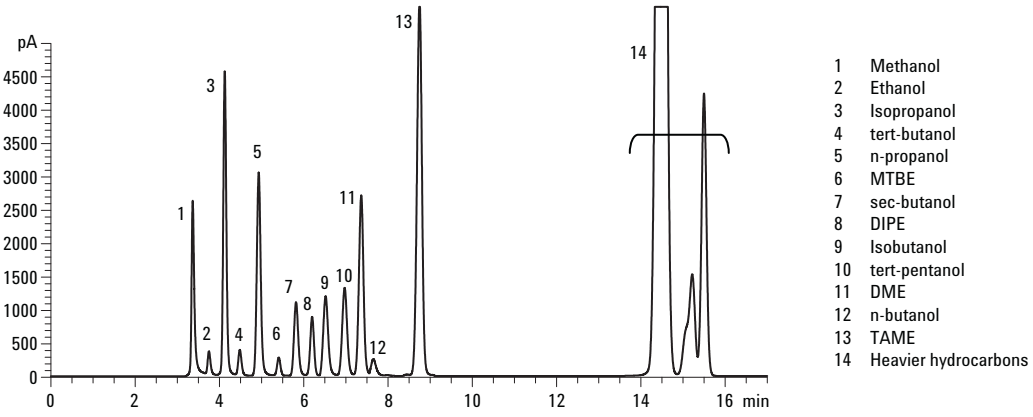


Figure 4. Chromatogram of oxygenates mix.

Table 3 shows very good repeatability, exceeding the specification of ASTM D4815.

Table 3. Repeatability for Five Runs

	Observed		ASTM D4815 specification
Compound	**Average, (mass%)**	**Repeatability***	**Repeatability**
Methanol	7.974	0.225	$0.09(X^{0.59}) = 0.306$
Ethanol	0.5391	0.026	$0.06(X^{0.61}) = 0.041$
iso-Propanol	7.958	0.012	$0.04(X^{0.56}) = 0.128$
tert-Butanol	0.4912	0.023	$0.04(X^{0.56}) = 0.027$
n-Propanol	5.0080	0.033	$0.03(X^{0.57}) = 0.075$
sec-Butanol	2.008	0.004	$0.03(X^{0.61}) = 0.046$
iso-Butanol	1.996	0.008	$0.08(X^{0.56}) = 0.119$
tert-Butanol	1.851	0.015	$0.04(X^{0.61}) = 0.058$
n-Butanol	0.488	0.004	$0.06(X^{0.61}) = 0.039$
MTBE	0.499	0.031	$0.05(X^{0.56}) = 0.034$
DIPE	1.867	0.021	$0.08(X^{0.56}) = 0.114$
TAME	16.668	0.278	$0.05(X^{0.70}) = 0.358$

* Repeatability: Difference between maximum and minimum mass%
X = mass percent of the component.

Conclusion

The Agilent 6820 GC system configured with FID, 10-port valve, and two columns is used for analysis of oxygenates including MTBE, TAME, DIPE, tert-pentanol, and C1–C4 alcohols in gasoline, following the ASTM D4815 standard method. In this GC system, an independently heated valve system ensures the heavy components in the sample are not condensed. It is very easy for the GC to control and run data analysis by using the Cerity NDS software. The experimental data demonstrates that the results exceed the ASTM D4815 calibration and repeatability specifications.

References

1. ASTM D4815, Standard Test Method for Determination of MTBE, TAME, DIPE, tertiary-Amyl Alcohol, and C1 to C4 Alcohols in Gasoline by Gas Chromatography
2. James 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

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