「Application Note」

Analysis of MTBE, ETBE, TAME, DIPE, tert-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by ChroZen GC According to ASTM D4815

- GC Application

Abstract

Octane number is a measure of the knock resistance of gasoline. The higher the octane number, the lower knock resistance. Therefore, the gasoline with high octane number is marketed as a premium gasoline. Generally, 8-15% of fuel additives in the form of alcohol or ether are added to gasoline to increase the octane number.

Not like other additives such as olefins that can generate toxic pollutant like formaldehyde and acetaldehyde, oxygenates help fuel to burn more efficiently and reduce emission of air pollutants.

Generally, alcohols and ethers such as methyl tert-butylether (MTBE), ethyl tert-butylether (ETBE) and ethanol are used for oxygenates. Among those oxygenates, most commonly used methyl tert-butylether (MTBE) produces nitrogen oxides and aldehydes causing air pollution, it is required to be regulated by ASTM D4815 to determine % concentrations.

In this study, ethers, alcohols and other oxygenates in gasoline were analyzed by ChroZen GC with 10-port switching valve referring to ASTM D4815.

Instruments and Software

· ChroZen GC System

Item	Description	Part No.
Oven	ChroZen GC Mainframe Assembly with UPC Detector Board Unit	6701012502
UPC	UPC Packed Manifold Block Assembly for ChroZen GC	6701012660
Inlet	Capillary Inlet Assembly for ChroZen GC	6701012550
Detector	FID Assembly for ChroZen GC	6701012590
	TCD Assembly for ChroZen GC (Option)	6701012570
Liquid Autosampler	ChroZen PAL LSI system for liquid injection	6501011590
	Mounting Kit for ChroZen GC	PAL3-Kit-YI6700
Valve	Automatic gas valve, 2-Pos / 10-Port, 250 µL sample loop, E type	6501011140
CDS	YL-Clarity software for single instrument of YCM GC	5301011020
	Autosampler control of YL-Clarity	5301011040
Column	20% TCEP on 80/100 Chromosorb PAW	19040
	Rxi-1 (30 m, 0.53 mm, 5µm)	10179

Fig 1. ChroZen GC

Columns

Column 1 : 20% TCEP on 80/100 Chromosorb PAW (0.56 m, 750 mm, 1/16")

Column 2 : Rxi-1 (30 m, 0.53 mm, 5 µm)

Standards

ASTM® D4815 Quantitative Calibration kit

① D4815 Valve Timing Mix (Part No. 47212)

- MTBE (Methyl *tert*-butyl ether)
- DIPE (Diisopropyl ether)
- MCP (Methyl cyclopentane)
- ETBE(Ethyl *tert*-butyl ether)
- n-Hexane

② D4815 Quantitative Calibration Mix 1-5

(Part No. 47205, 47206, 47207, 47208, 47209)

- *tert*-Butanol
- MTBE (Methyl *tert*-butyl ether)
- DME (1,2-Dimethoxy ethane) — ISTD
- *tert*-Amlyalcohol (2-Methyl-2-butanol)
- Ethanol
- Isooctane : Xylene (65 : 35)

③ D4815 Qualitative ID Mix (Part No. 47213)

- Methanol
- Ethanol
- IPA (iso-Propanol)
- *tert*-Butanol
- n-Propanol
- MTBE (Methyl *tert*-butyl ether)
- *sec*-Butanol
- DIPE (Diisopropyl ether)
- iso-Butanol
- ETBE(Ethyl *tert*-butyl ether)
- *tert*-Amlyalcohol (2-Methyl-2-butanol)
- DME (1,2-Dimethoxy ethane)
- n-Butanol
- Benzene
- TAME (tert-Amylmethyl ether)

Sample Preparation

Take 0.5mL of DME (internal standard) in a 10mL of volumetric flask and dilute with gasoline to the volume.

Instrument Conditions

GC conditions	
Column	Column 1 : 20% TCEP on 80/100 Chromosorb PAW (0.56 m, 750 mm, 1/16”) /N_2 : 3.5 mL/min, 26.533 psi Column 2 : Rxi-1 (30 m, 0.53 mm, 5 μm) / Split 1:5 / N_2 : 3 mL/min, 2.156 psi
Inlet	200 ℃
Oven	Oven temperature program : 60°C (7 min) → 5°C/min → 120°C (0 min) → 20°C/min → 150°C (6.5 min)
Detector	FID : 300 ℃
	Air : 300mL/min
	H_2 : 30mL/min
	Make up (N_2) : 20mL/min
Valve (GSV/10port /250μL)	60°C / Switching time (On) : 0.44 min / Reset time (Off) : 17.5 min

Table 1. GC Conditions

Liquid Autosampler Conditions	
Pre Wash	Wash Solvent – 4μL
	Wash Cycle – 3
Load Sample	Air Gap Volume – 0μL
	Sample Rinse Cycles – 3
	Filling Strokes Count / Volume – 5 / 3μL
Inject Sample	Injection Mode – Normal
	Injection Flow Rate – 100μL/s
	Injector Penetration Speed – 100mm/s
Post Wash	Wash Solvent – 4μL
	Wash Cycle – 3

Table 2. Liquid Autosampler Conditions

Summary of Test Method

Alcohols and ethers in gasoline were analyzed by ChroZen GC/FID with column switching valve and two types of column were used; micro-packed TCEP as a pre-column and PDMS (Dimethylpolysiloxane) non-polar column according to ASTM D4815. In TCEP (tris(2-carboxyethyl)phosphine) column, lighter hydrocarbons are vented out but heavier hydrocarbons are retained. The remained heavy hydrocarbons are backflushed from TCEP to Rxi-1 column by switching the valve for separation so that the FID (Flame Ionization Detector) can detect the oxygenates. The valve switching process in three steps is described by valve position as follows.

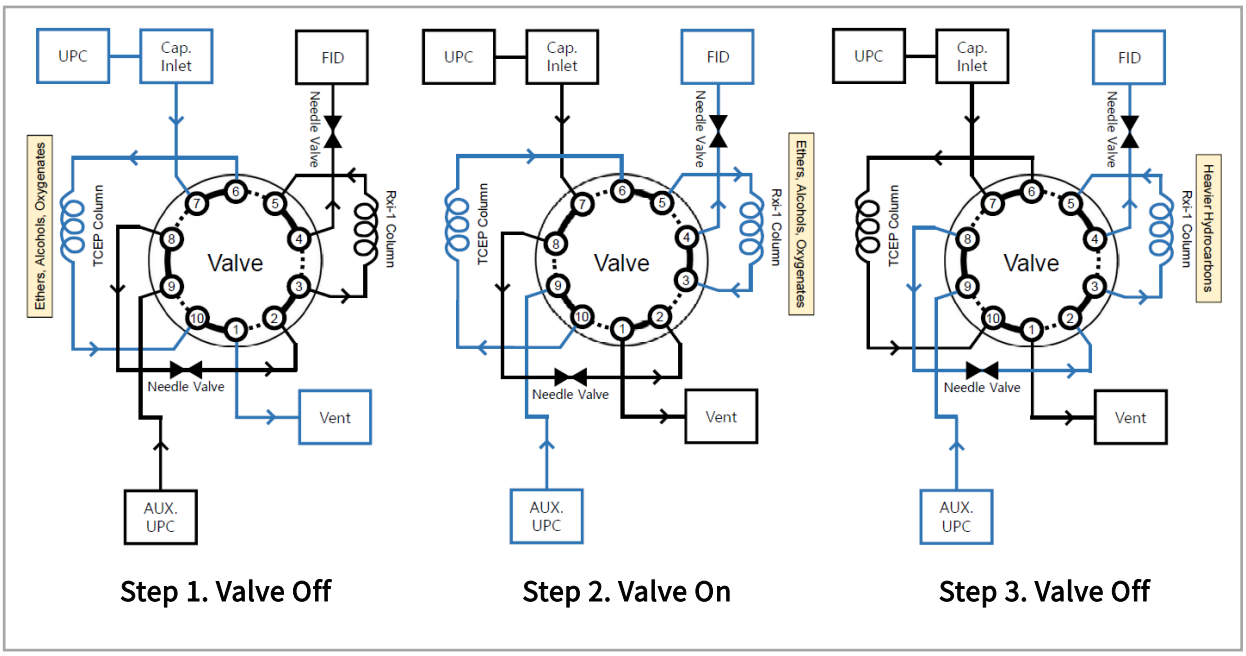

Fig 2. switching time setting of 10-port valve

Step 1. Valve Off

A D4815 Valve Timing Mix standard (47212) including DME (internal standard) is injected to the GC and moves to the TCEP column. Light hydrocarbons vent out but heavy hydrocarbons and oxygenates are still retained in the TCEP column.

Step 2. Valve On (0.44 min)

When methylcyclopentane (MCP) elutes but MTBE and DIPE still remain in TCEP column, the valve position is changed Off to On. Ethers and alcohols including MTBE, DIPE are backflushed

into Rxi-1 column and separated according to the boiling point. And then they are detected by FID. (The chromatogram is shown in Figure 4)

Step 3. Valve Off (17.5 min)

Once the valve switching time setting is finished, it is ready to analyze the D4815 Qualitative ID Mix standard (47213). The valve position is changed to Off again after the TAME vents out from the Rxi-1 column. And then heavier hydrocarbons in Rxi-1 column are backflushed to elute as the composite peak.

Determining of Backflush Time

Determining proper backflush time depends on the completely eluted time of MCP without changing the peak area of MTBE, DIPE, ETBE. The result with the valve switching time range of 0.38 - 0.52 min is shown in the figure 3. When the valve switching time is 0.38 min, all of the compounds in D4815 valve timing mix standard (MTBE, DIPE, ETBE and MCP) is detected, meaning that MCP has not been removed all. The later the valve switching time, the more eluted MCP and the peak area of MCP gets reduced. MCP is completely eluted at valve switching time of 0.44 min. If the valve switching time is later than 0.44 min, it is difficult to get the accurate result due to the incorrect ether detection. Therefore, the valve switching time for backflush is set to 0.44 min in this study.

Fig 3. detection by valve switching time using D4815 valve timing mix standard (47212)

Oxygenate Mixture Analysis

This is the result of oxygenates determination. All oxygenates such as MTBE, TAME, DIPE, ETBE and the C1-C4 alcohols in D4815 qualitative ID mix standard (47213) are separated well. The ChroZen GC is the optimized system to analyze oxygenates in gasoline according to ASTM D4815.

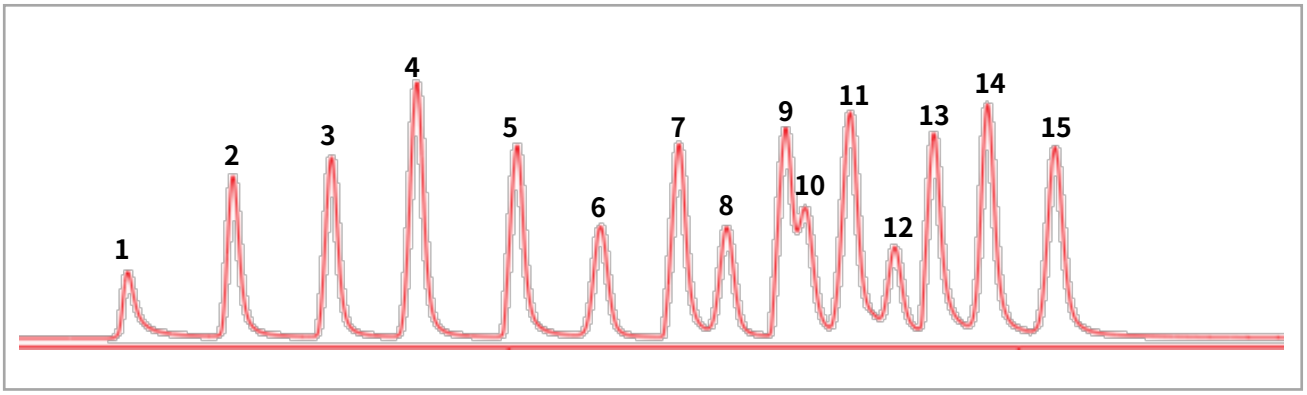

Fig 4. chromatogram of oxygenates using D4815 qualitative ID mix standard (47213)

1. Methnaol, 2. Ethanol, 3. iso-Propanol, 4. tert-Butanol, 5. n-Propanol, 6. MTBE, 7. sec-Butanol, 8. DIPE, 9. iso-Butanol, 10. ETBE, 11. tert-Amylalcohol, 12. DME, 13. n-Butanol, 14. Benzene, 15. TAME

Compound	Average (mass %)	Repeatability	Repeatability from ASTM D4815 specification
Ethanol	6.293	0.062	$0.06(X^{0.61}) = 0.184$
tert-Butanol	6.468	0.090	$0.04(X^{0.56}) = 0.114$
MTBE	3.401	0.063	$0.05(X^{0.56}) = 0.099$
tert-Amylalcohol	6.867	0.110	$0.04(X^{0.61}) = 0.130$

* **Repeatability** : The difference between maximum and minimum mass %

X = mass % of the component

Table 3. repeatability for ten runs

Calibration Curve

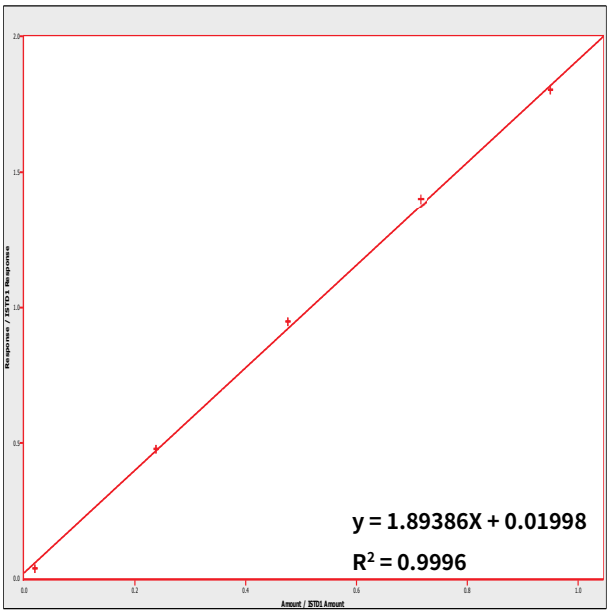

Fig 5. calibration curve of *tert*-amylalcohol

The calibration curve for each oxygenate plotted by five-point is established, as an example for tert-amylalcohol (1.19, 4.75, 2.38, 3.56, 0.095 wt %). It shows great linearity as the correlation coefficient over 0.999.

According to ASTM D4815, the absolute value of the y-intercept must be at a minimum and the mass % of oxygenates must be less than or equal to 0.1 mass % for an optimum calibration.

< The calculation of mass % oxygenate >

$W_i = (b_i / m_i) * (W_s / W_g) * 100$

W_i : mass of oxygenate i (%)

W_s : mass of internal standard (g)

W_g : mass of gasoline sample (g)

b_i : the absolute value of y-intercept

The following calculation is an example of *tert*-amylalcohol from figure 5 (b_i = 0.01998, m_i = 1.89386).

mass of internal standard (W_s) = 0.4 g (0.5 mL)

mass of gasoline sample (W_g) = 7 g (9.5 mL)

$$W_i = (0.01998 / 1.89386) * (0.4 / 7) * 100 = \mathbf{0.06\ mass\ \%}$$

$$W_i < 0.1 \text{ mass } \%$$

As the result, mass % of tert-amylalcohol (W_i) is 0.06, which is less than 0.1 mass %. And mass % of all other oxygenates are all under 0.1 mass %. (MTBE : 0.091 mass %, tert-butanol : 0.056 mass %, EtOH : 0.085 mass %)

Result

According to ASTM D4815, the absolute value of the y-intercept must be at a minimum and the mass % of oxygenates must be less than or equal to 0.1 mass % for an optimum calibration. We verified an optimized calibration curve of all components in calibration standard (ethanol, *tert*-butanol, MTBE and *tert*-amylalcohol) by satisfying the criteria from ASTM D4815.

For determining the concentration of MTBE, we confirmed the linearity of calibration curve from the result of R^2 = 0.999 and mass % = 0.07% and the concentration was calculated using the calibration equation. % Concentration of MTBE in gasoline sample was determined 7.87 wt %.

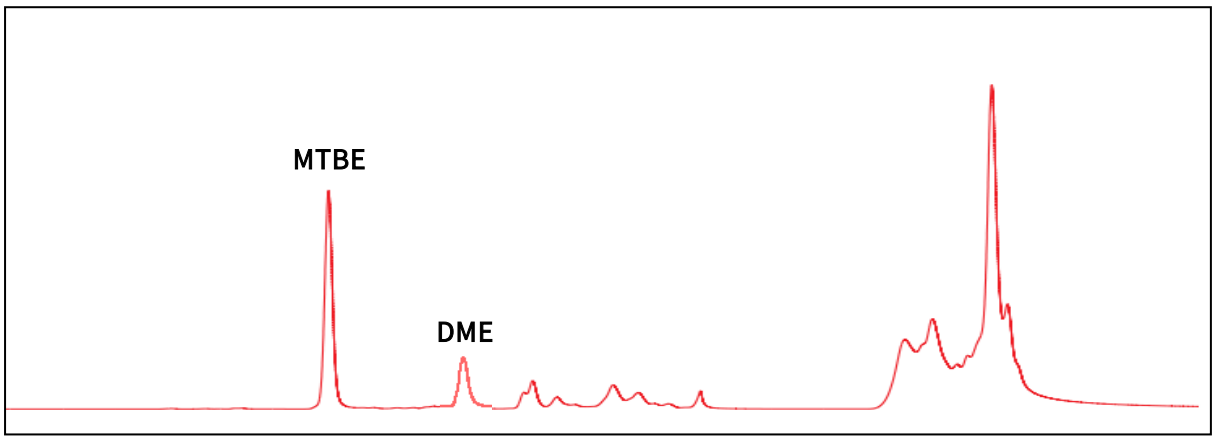

Fig 6. chromatogram of gasoline sample

Conclusion

The analysis of oxygenates in gasoline by ChroZen GC with 10-port switching valve guarantees great repeatability and linearity by satisfying the specification of ASTM D4815. The correlation coefficients of calibration curve for all compounds in the calibration standards wer determined to greater than 0.999 and the mass % of all components were under 0.1 mass %. Therefore, the ChroZen GC is the optimized system to analyze oxygenates in gasoline with the superior data reliability.

Reference

- ASTM D4815 Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amylalcohol and C1 to C4 Alcohols in gasoline by Gas Chromatography

- Ministry of Environment, Korea
http://me.go.kr/mamo

- Young In Chromass' application note
[ASTM Method D4815 Oxygenates Analysis in Gasoline]

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