

# Determination of Oxygenated Compounds in Gasoline in Compliance with ASTM D4815

## Application Note

AN0002

### INTRODUCTION

As mandated by the EPA and the California Air Resources Board (CARB), petroleum refiners have to incorporate some form of oxygen containing components into the gasoline they produce. The model on which the regulations are based requires 2% by weight of oxygen in reformulated gasoline. Both refiners and regulators have had to ensure that this requirement is met by the addition of certain compounds to the gasoline blend. Most of these compounds take the form of aliphatic alcohols or ethers such as ethanol and t-butyl-methyl ether (MTBE). To quantify these oxygenated additives, CARB has designated ASTM D4815 as the test method for all reformulated gasoline sold in California.

### EXPERIMENTAL

The oxygenates in gasoline analyser is a standard analyser made by SCION Instruments. The analyser complies to ASTM D4815, with all finished motor gasolines being analysed for the target compounds listed in the method. The SCION GC is equipped with two columns, a split/splitless injector, a ten port rotary valve and a single FID detector. The first column is highly polar and pre-separates the low boiling points and non-polar components from the higher boiling and polar components. The alcohols, ethers and high boiling point components are back-flushed into the second non-polar column where they are separated by boiling point order. The system utilises electronic control of the carrier gas to decrease the total analysis time by automatically increasing the pressure during the final back flush. An additional TCD detector may be added to assist in the vent line. Figure 1 shows the configuration of the instrument during injection mode, whilst Table 1 details the analytical conditions of the analysis.

Calibration standards are composed of several multi-component mixtures each containing different amounts of each of the oxygenated compounds. 1,2-Dimethoxyethane (DME) was used as internal standard.

Table 1. Analytical conditions of the GC-FID

Conditions	
S/SL	220°C, 1:15
Column 1	TCEP 0.56m 1/16 Inert Steel
Column 2	10m x 0.25mm x 0.25µm
Oven Programme	60°C (hold 12 min), 20°C/min to 120°C (1 min)
Carrier Gas	Helium, 18psi (12 mins), 4psi/min to 30psi (1min)
FID	300°C

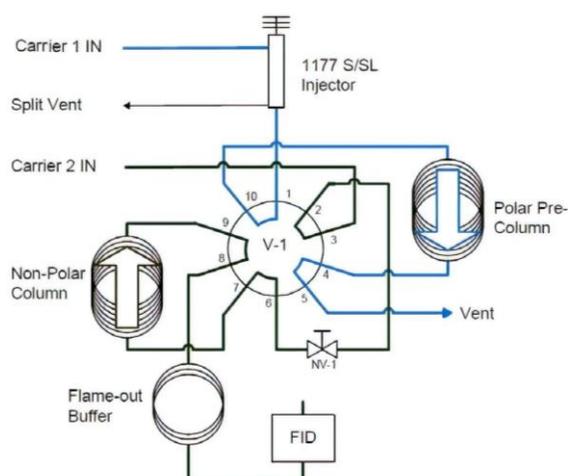


Fig 1. Schematic configuration of the analyser during injection

### RESULTS

Through the use of two columns, it was possible to separate oxygenated compounds from the gasoline matrix. The mixture contained approximately 7% by weight of each alcohol and 4% by weight of each ether. Figure 2 shows the chromatogram of the oxygenates blend. After the complete elution of benzene and TAME, the composite peak, which was back-flushed to the detector, was not quantified but used to show that the backflush was completed (as shown via a return of the signal to the baseline).

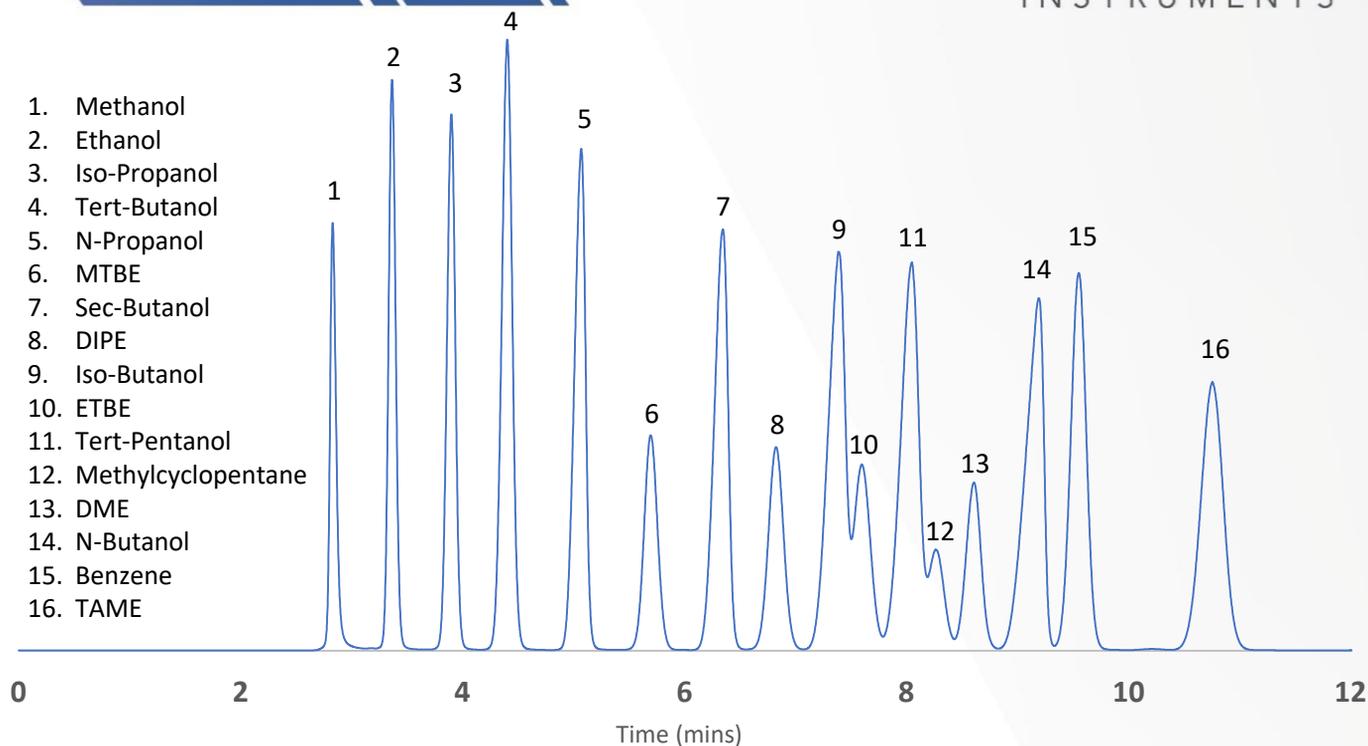


Fig 2. Separation of an oxygenates blend in accordance to ASTM D4815.

The repeatability of the system was tested via 20 consecutive injections of the oxygenate blend, in compliance to ASTM D4815. Table 2 shows repeatability summary of all components including average, standard deviation and relative standard deviations of peak area (RSD%) whilst Figures 3 and 4 show the repeatability of each injection for the oxygenate blend.

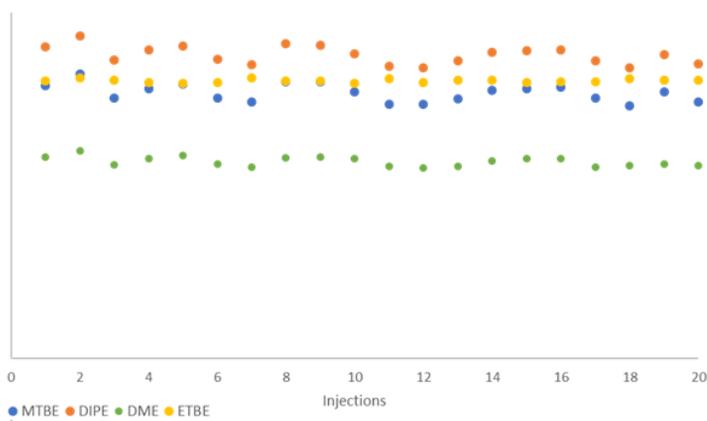


Fig 3. Repeatability of Ethers (n=20)

Table 2. Repeatability values of peak area (n=20)

	Methanol	Ethanol	Iso-Prop	Tert-But	n-Prop	MTBE	Sec-But	DIPE
Ave	10550035.6	16204624.4	17989714.5	25191395.1	21955389.7	11326538.3	22823175.3	12113303
Std Dev	131292.8	163847	166303.6	224115.4	161030.3	181041.8	163303.8	181227.5
RSD %	1.24	1.01	0.92	0.89	0.73	1.6	0.72	1.5
	Iso-But	ETBE	Tert-Pent	DME	n-But	Benzene	TAME	
Ave	27003480.3	11363420	27934080	9900323	25050641.5	22893117.1	23300700.1	
Std Dev	193776.8	141469.5	199389.3	97538	161411.5	338414.1	261082.1	
RSD %	0.72	1.24	0.71	0.99	0.64	1.48	1.12	

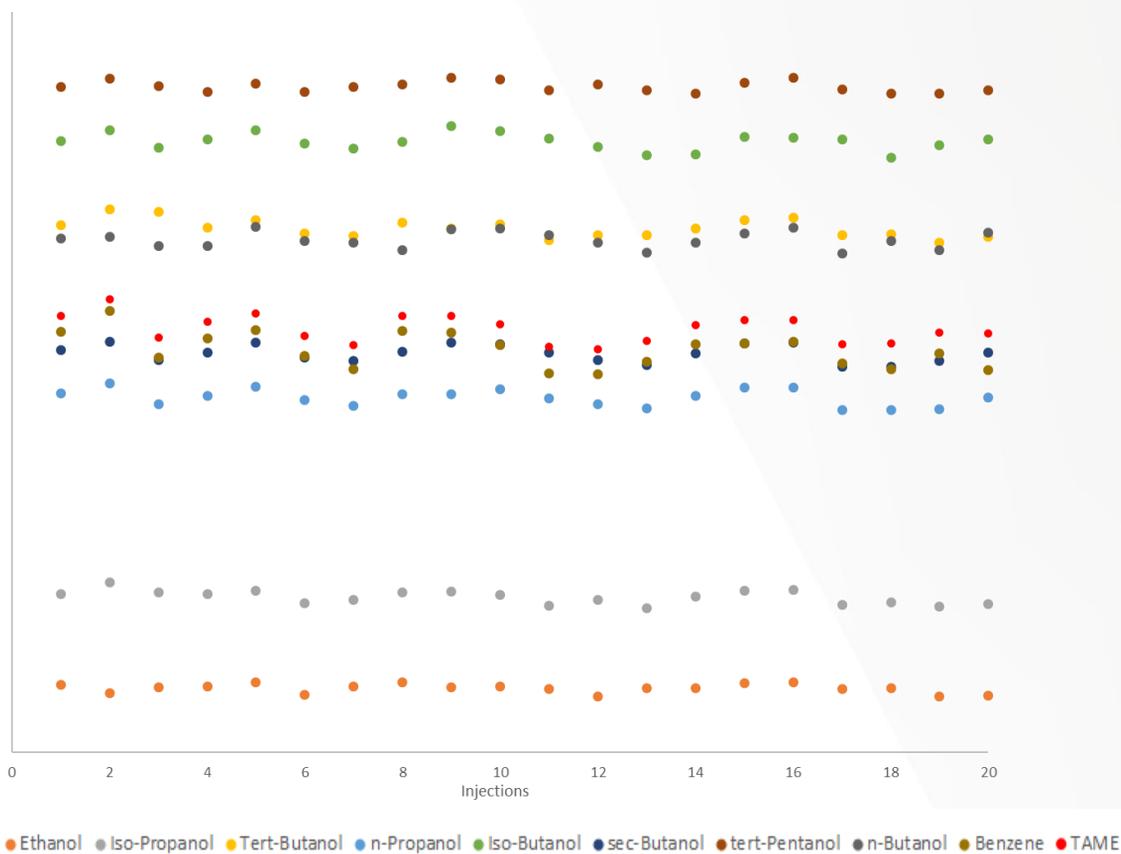


Fig 4. Repeatability of Alcohols and TAME (n=20)

The SCION analyser shows excellent repeatability over 20 consecutive injections, with the RSD% ranging from 0.71% to 1.6%, respectively.

## CONCLUSION

The SCION GC system configured with FID, a ten-port valve and two columns are used for the analysis of oxygenated including MTBE, TAME, DIPE, ETBE and C<sub>1</sub> to C<sub>4</sub> alcohols in gasoline, following the ASTM D4815 standard method. The experimental data demonstrates that separation is easily achieved using the standard analyser along with excellent repeatability values.