

Analysis of Low Level Oxygenates (LOWOX) in Liquefied Petroleum Gas (LPG)

Application Note

AN0009

INTRODUCTION

The determination of sub to high ppm levels of ethers, alcohols, aldehydes and ketones in different hydrocarbon matrices is a recurring challenge in the petroleum refining and petrochemical industry. The SCION low level oxygenates analyser is designed and optimised to quantify ppm and sub levels of ethers, alcohols, ketones and hydrocarbons in gas, liquid and LPG samples.

Oxygenates can be present in hydrocarbon streams for a variety of reasons. For example, methanol is added to crude oil to reduce the formation of hydrates during transportation and storage. Clean up processes like hydro-treating are used in an attempt to remove oxygenated compounds. Even at sub ppm trace levels, oxygenates quickly degrade or destroy expensive catalysts in downstream polymerisation processes.

The SCION LOWOX analyser measures oxygen containing hydrocarbons with a boiling range up to 100°C. Higher boiling components may be present in the sample but will not be measured; the sample final boiling point is 250°C.

ASTM D7423 is a standard test method for determination of oxygenates C₂-C₅ in hydrocarbon matrices. Although the LOWOX method used in this application is not the ASTM test method, due to different inlet configuration, reference will be made for repeatability testing.

EXPERIMENTAL

Configured with both a gas sampling valve and liquid valve, the SCION 456 GC is capable of simultaneously injecting gas, liquid and LPG samples without the need for reconfiguration.

Two high performance capillary columns are digitally controlled with a fluidic switch coupled to an FID. The sample is injected via the appropriate sampling valve onto the first of the two columns. The lighter fraction, containing oxygenates with a boiling point lower than 100°C, is separated from the rest of the stream components whilst the heavier components are backflushed to vent.

The lighter component fraction is then transferred onto the LOWOX column using the fluidic switch. The LOWOX column is used to separate individual oxygenated components from the bulk hydrocarbons.

The LOWOX analyser is capable of operating in two modes; the wide range mode and the MTBE mode. In MTBE mode, only the components up to MTBE including the lighter components will be measured whereas in the wide range mode all components lighter than Propylether will be measured.

Varying concentrations of a multi components standard mixture is used for the calibration curve. The linear working range for the oxygenates is 0.50mg/kg to 100mg/kg. Table 1 shows the analytical conditions of the SCION 456 analyser.

Table 1. Analytical Conditions

Variable	Setting
Injector	Direct, Liquid Sampling Valve (0.2µL)
Backflush	After 3.7 minutes
Carrier Gas	Helium
Oven	50°C (5 mins), 10°C/min to 240°C 60°C/min to 50°C
Columns	1: 25m x 0.53mm x 0.5µm Sil 5 CB 2: 10m x 0.53mm x 10µm LOWOX
Detector	275°C

RESULTS

A LOWOX calibration standard (wide range mode and MTBE mode) was analysed using the SCION Oxygenates analyser. The wide range chromatogram is shown in Figure 1 whereas Figure 2 shows the MTBE range chromatogram. Table 2 details peak identification. Post analysis each of the oxygenates are automatically quantified and reported by the Compass Chromatography Data Handling Software.

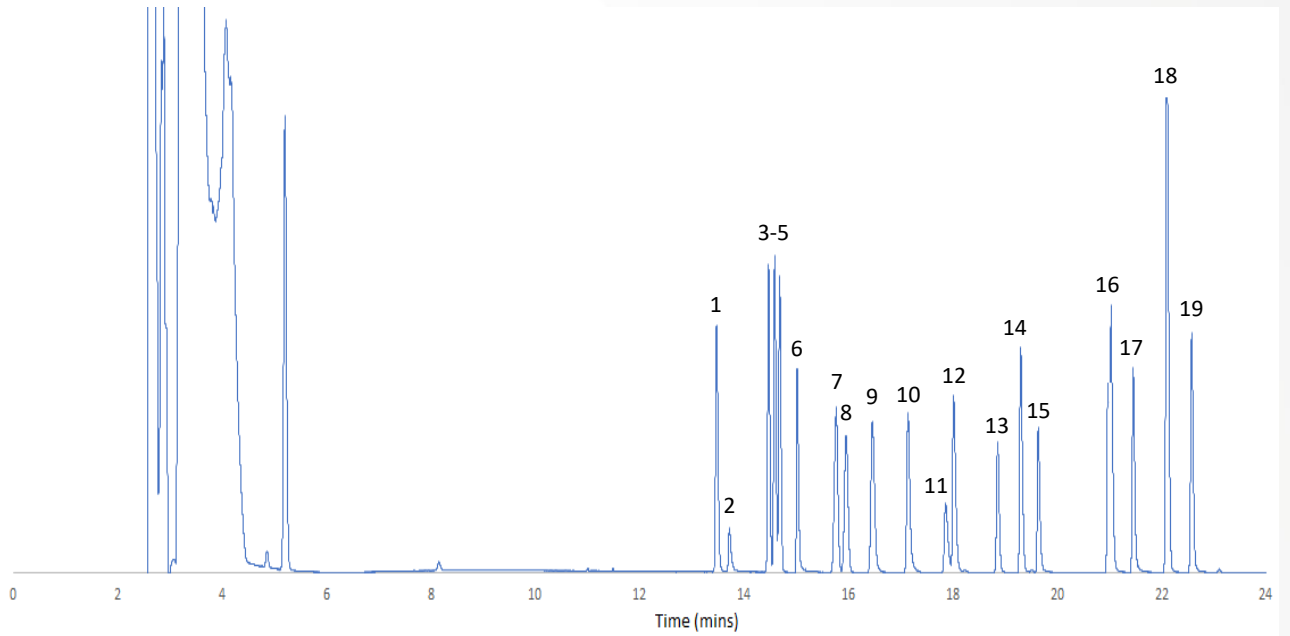


Fig 2. Wide Range Chromatogram

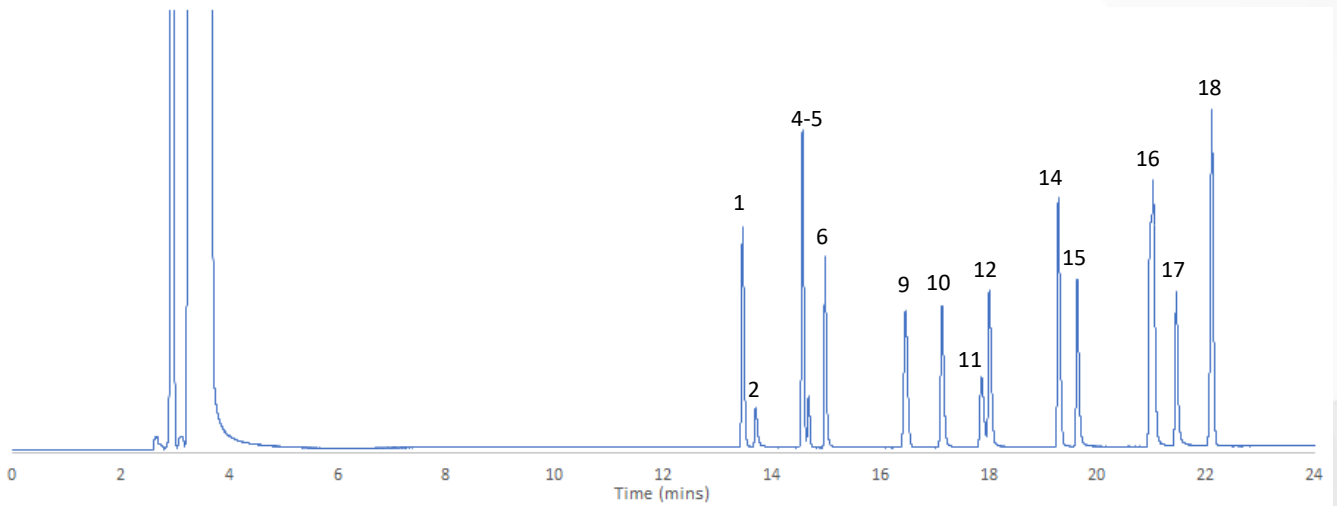


Fig 3. MTBE Chromatogram

Table 2. Peak Identification of wide range and MTBE calibration sample.

Peak ID	Compound
1	Diethyl Ether
2	Acetaldehyde
3	ETBE
4	MTBE
5	DIPE
6	Propanal
7	TAME
8	Propylether
9	Isobutyraldehyde
10	Butyraldehyde
11	Methanol
12	Acetone
13	Valeraldehyde
14	Methyl Ethyl Ketone
15	Ethanol
16	Propanol + Iso-Propanol
17	Allyl Alcohol
18	Tert Butanol Alcohol + Iso-Butanol
19	1-Butanol

The 19 components found in the sample are clearly separated and defined. The GC conditions were optimised to ensure complete separation of the three critical peaks; ETBE, MTBE and DIPE, all of which have a resolution of 1 or greater, in wide range mode. Maximum resolution is vital to ensure accurate quantification of each oxygenated compound.

ASTM D7423, the standard test method for determining oxygenates in hydrocarbon matrices, specifies that repeatability of the oxygenate system must be validated using ten consecutive runs for a standard blend containing 25ppm of each component. The RSD% of the area for each component must be less than 2.5%. Although this application was not ran to ASTM D7423 specification, the repeatability was tested under those conditions. Repeatability data for the three critical components can be found in Table 3.

Table 3. Peak Area repeatability data of three critical peaks

	ETBE	MTBE	DIPE
1	12646.5	11615.9	12388.7
2	12642.9	11624.2	12378.1
3	12714.1	11657.1	12432.4
4	12625.8	11615.3	12351.5
5	12752.8	11687.6	12374.7
6	12721.4	11619.4	12425.3
7	12682.4	11654.5	12394.3
8	12611.8	11613.1	12363
9	12653.1	11627.2	12373.1
10	12728.4	1667.9	12410.9
Mean	12678	11638.2	12389.2
Std Dev	46.2	25	25.2
RSD%	0.36	0.22	0.20

The SCION Oxygenates analyser shows excellent repeatability with ten consecutive injections having an RSD% of <0.40 for the three critical peaks.

CONCLUSION

The SCION Oxygenates analyser is a dedicated solution for accurate determination of trace oxygenates in hydrocarbon matrices. The ability to be operated in both wide range mode and MTBE mode allows the Oxygenates analyser to be highly selective. Due to its selectivity, large amounts of sample can be introduced onto the LOWOX column and combined with the sensitive FID, low level detection of oxygenated compounds is made easy. The repeatability performance exceeds that of the requirements of ASTM D7423.