

Application Note # CA-270374

Determination of Oxygenates in Hydrocarbon Streams with the Bruker Low Level Oxygenates Analyzer

Introduction

The analysis of oxygenates in hydrocarbon matrices is important as these oxygenates will poison and or destroy catalysts. Oxygenates can stop or disturb (polymerization) reactions. Furthermore, oxygenates are common pollutants and tend to decrease product value. The Bruker Low Level Oxygenates Analyzer is an analytical tool to measure oxygen-containing hydrocarbons (aldehydes, ethers, alcohols and ketones) with a boiling range up to 100 °C in, especially, hydrocarbon mixtures. The system consists of a non-polar pre-column and the Lowox analytical column. The sample is injected onto the pre-column. The components having a boiling point below 100 °C are transferred onto the Lowox column.

The Lowox is a highly selective column that separates the light fraction into hydrocarbon and oxygenate fractions, and separates the oxygenate fraction into its individual components. The fraction with a boiling point above 100 °C is back-flushed from the pre-column to vent. The Lowox Analyzer is factory set with two modes: the MTBE mode and the "wide range" mode. In the MTBE mode the components up to MTBE and lighter can be measured. The wide range mode measures components lighter than propylether. The Lowox Analyzer is equipped with a liquid (LSV) and a gas injection valve (GSV), allowing the processing of gaseous, liquid and LPG type samples.

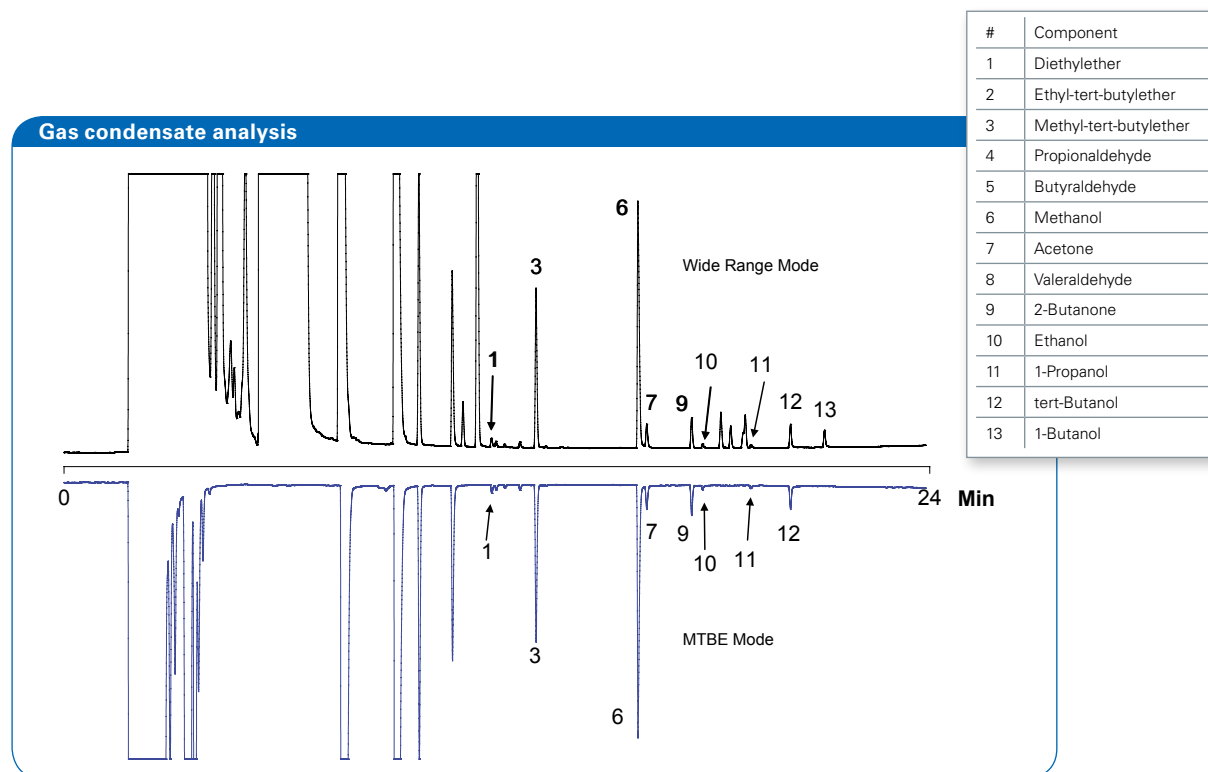


Figure 1: Wide range and MTBE mode chromatograms of ppm level oxygenates in a gas condensate.

Instrumentation

The Bruker Low Level Oxygenates Analyzer is a 450-GC based gas chromatograph and includes gas and liquid sampling valves, two high performance capillary columns including full EFC controlled (carrier) gas and Flame Ionization Detection (FID). For GC control and data handling, Galaxie™ Chromatography software was used.

Materials and Reagents

Capillary columns:

- Non-polar pre-column, 25 m x 0.53 mm
- Lowox analytical column, 10 m 0.53 mm

Samples:

- Gas condensate
- Naptha
- Toluene-xylene test mix
- Pyrolysis Gasoline (Pygas)

Conditions

Carrier gas:

- EFC flow Carrier 1: 5 mL/min
- EFC flow carrier 2: 5.3 mL/min

Column Oven:

- 50 °C (5 min) @ 10 °C/min to 240 °C, @ 60 °C/min to 50 °C

Table 1: Valve table for liquid sample injections.

Step	Time (min)	Vlv-1	Vlv-3	
1	initial	Fill	Forward	
2	0.01	Inject	Forward	
3	0.5	Fill	Forward	
4a	2.35	Fill	Back flush	MTBE mode
4b	3.2	Fill	Back flush	Wide range mode

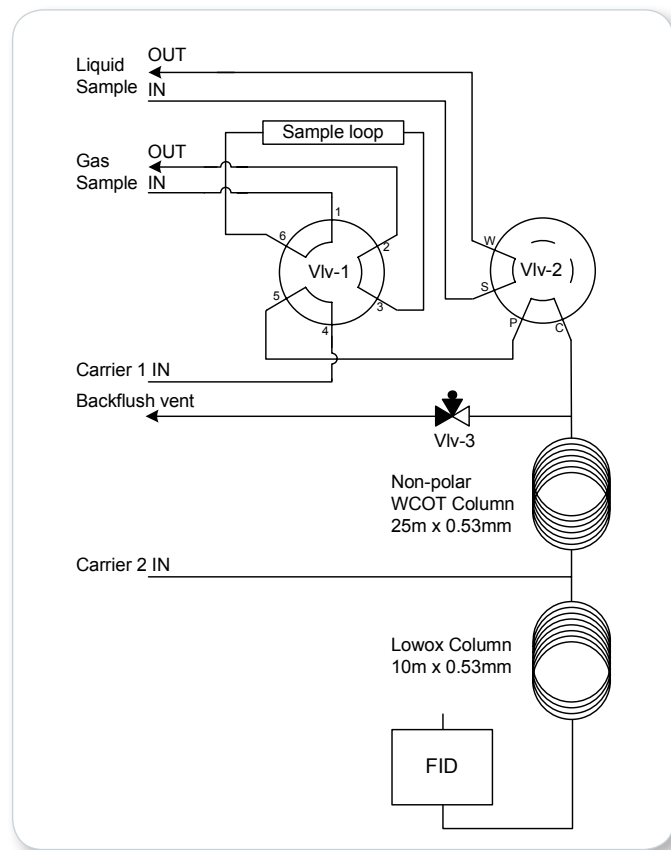


Figure 2: Plumbing scheme of the Bruker Lowox Analyzer.

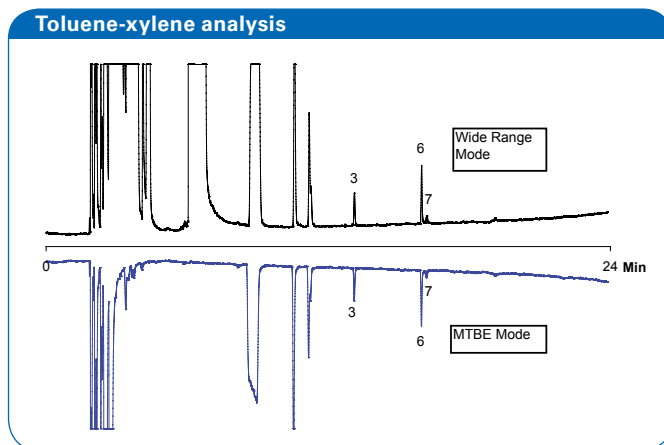


Figure 3: Low ppm oxygenates in a toluene-xylene test mix.

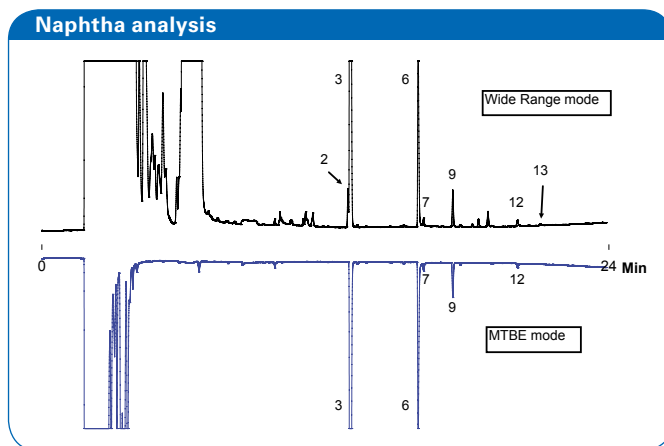


Figure 4: Ppm level oxygenates in naphtha.

Results and discussion

In MTBE mode the back-flush time is defined as the time in which the MTBE is almost back-flushed and thus elutes completely. Besides MTBE, the very low boiling components such as methyl-ethylketone and diethylether will also elute. In wide range mode, the back-flush time is defined as the time in which the propylether is almost not back-flushed. In Figure 1 the differences between the two modes are shown in the analysis of a gas condensate. The wide range mode enables elution of 1-butanol but creates potential co-elutions in the ether eluting range, and between ethanol and 1-propanol.

If MTBE and ETBE are present in different quantities the effect of choosing the right analysis mode becomes apparent (see the naphtha analysis in Figure 4). In MTBE mode the MTBE peak (#3) is nicely separated. In wide range mode, however, there is some overlap with ETBE (#2) due to the large amount of MTBE present and the resulting overloading. Figure 5 shows chromatograms in wide range and MTBE mode for the analysis of oxygenates in pyrolysis gasoline. ETBE (#2) is back-flushed in MTBE mode, enabling easy quantification of MTBE (#3) even at low concentration.

Conclusion

The Bruker Low Level Oxygenates Analyzer is a 450-GC based analyzer perfectly suited for the analysis of oxygenates in very low concentrations in different matrices. Depending on the nature of the sample and the type of oxygenates to be analyzed, the analyzer can be operated in two modes. The MTBE mode is especially suited for oxygenates with boiling points up to the boiling point of MTBE. The wide range mode allows the analysis of oxygenates up to the boiling point of propylether.

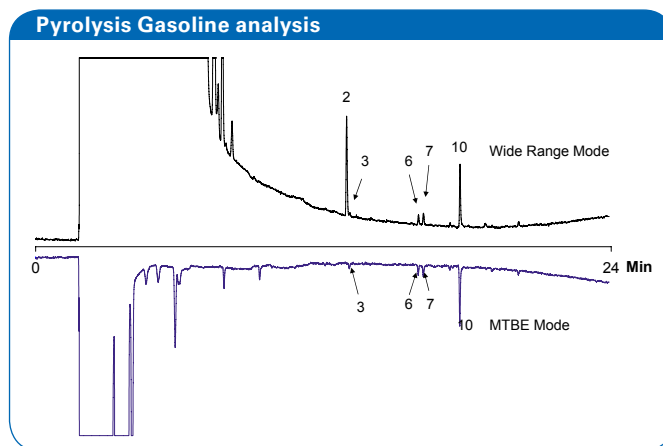


Figure 5: High ppb level oxygenates in Pygas.

References

ASTM D 5443-04, "Paraffin, Naphthene and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates Through 200°C by Multi Dimensional Gas Chromatography," ASTM International, West Conshohocken, PA, www.astm.org.

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Keywords

Oxygenates
Hydrocarbon streams
MTBE mode
Wide range mode

Instrumentation & Software

Bruker Lowox Analyzer
Galaxie™ chromatography software