

Low Level Oxygenates in Liquefied Petroleum Gas (L.P.G.):

Introduction:

Oxygenates such as alcohols and ethers can adversely affect the efficiency of many of the sophisticated catalysts in use today. Even part-per-million levels of these oxygenated compounds can cause significant loss of catalytic efficiency which, in turn, means lost profitability. For this reason, it is critical to measure very low levels of these oxygenated compounds in a variety of process streams used in today's refineries and petrochemical plants. In addition, it is sometimes necessary to run samples which contain heavier hydrocarbons for low level oxygenates. However the heavier hydrocarbons, if introduced directly onto the oxygenate column, can adversely impact the health of the LowOx column. For these reasons, a custom built, dual column, instrument was configured for oxygenates analysis.

Experimental:

The customer had a Hewlett Packard 5890 Series II gas chromatograph (G.C.) configured for single injection L.P.G. analysis. This instrument was re-configured with a L.P.G. sampling valve, a column switching valve, a methyl siloxane pre-column and a Varian LowOx secondary column. The extremely high retention of the LowOx column for oxygenates is critical to the success of this application. Dual flame ionization detectors (already installed) were initially used to identify the valve switching time and to ensure that the siloxane column is completely clear of hydrocarbons. The second FID was eventually shut off since only the oxygenates are of interest in this analysis. The oven in this method is temperature programmed to fully elute the oxygenates off the LowOx column and to clean the siloxane column of hydrocarbons. Due to the high temperatures used in the column oven (too high for the valve), a secondary valve oven was installed on top of the GC to hold the switching valve at an isothermal temperature appropriate for the valve and application.

Results:

Below is a overlaid chromatogram from the customer's instrument showing a single injection of the 30 p.p.m. standard in propane and a 3 times stacked injection of the same standard. Note the excellent retention characteristics of the oxygenate peaks and their undistorted peak shapes which reflects the highly retentive nature of the LowOx column. Note also the significantly higher signal from the stacked injection which yields a better signal to noise ratio. The second to last peak has the poorest peak shape but this peak is actually a co-elution of three different oxygenated compounds. Note also the poor baseline of the red chromatogram is a result of it being the first run of the day.

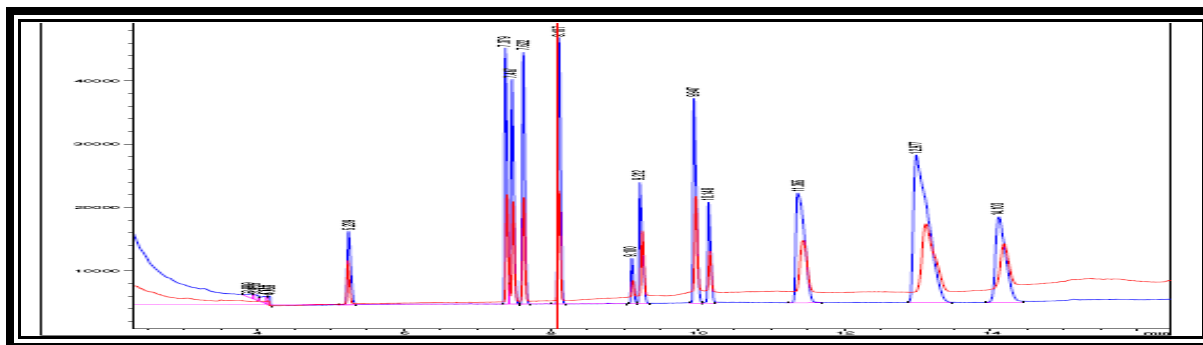


Figure 1: Overly of a single and stacked (3-times) injection of an oxygenate standard in propane.

Conclusion:

By utilizing the unique characteristics of the Varian LowOx column, in conjunction with a dual column custom configured gas chromatograph, it is possible to obtain low part-per-million detection limits of oxygenates which are detrimental to catalyst efficiency.