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ANALYSIS OF FAME IN NEW FUEL SOURCES and PETROLEUM BLENDS

Traditional petroleum fluids are very complex. Recent new fuel sources only add to the complexity of fuel and petroleum characterization. Current gas phase analytical methods for petroleum fluids emphasize methods that expect non-polar analytes in the samples. These non-polar analytes mainly consist of a wide range of hydrocarbons. Exceptions include the analysis of oxygenates in finished fuels in which a defined mixture of alcohols may be added to the final petroleum fuel in the final blending stage.

New fuel source materials introduce a wide range of new analytes into the analysis and characterization of source fuel and mixed petroleum samples. These new fuel related analytes include, new functional groups, as well as more polar chemistry. While this introduces new challenges to the established petroleum analytical techniques, it also allows new opportunities for quick analysis and characterization of these new samples.

New fuel source materials are still developing and they include a wide range of plant based or refuse based materials. These initial source materials are processed to generate a stream that can be further modified and refined for fuel use. Both these source materials and the processing techniques require analytical characterization to assist in optimization. In this application, the ASAP IRD 3, a gas phase infrared detector for GC eluents, is used to provide selectivity and identification in complex samples. The IRD and accompanying software is used with an Agilent 7890 GC with split injection and capillary separations prior to IRD detection.

Ester type analytes are common from many of these source materials and processing techniques. Fortunately, these esters contain a carbonyl group with a strong and very specific infrared absorbance. GC-IRD can select these ester analytes from a complex mixture into a much simpler selective chromatogram or SWC (Selective Wavelength Chromatogram).

Here is a separation of a simple B100 (100% biodiesel) mixture in a SWC chromatogram at 1750 wavenumbers in which we see each of the 5 FAME analytes for this B100 mixture:

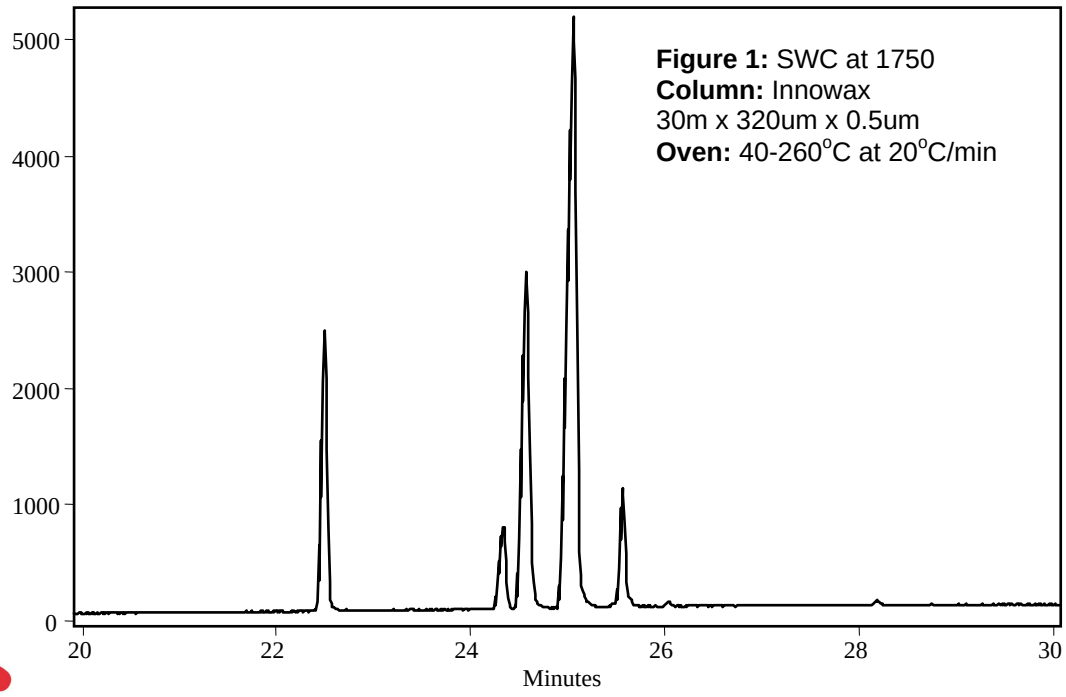

Figure 1: SWC at 1750
Column: Innowax
30m x 320um x 0.5um
Oven: 40-260°C at 20°C/min

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The GC-IRD can also look selectively for the presence of non-esterified fatty acids in B100 biodiesel or other petroleum samples. We use the GC-IRD to generate a selective SWC chromatogram at 3600 wavenumbers to selectively look for the –OH portion of a carboxylic acid. Generally, we do not want residual free fatty acids in the fuel mixture and we want complete methyl ester conversion to FAME. In this case, we do not see any detectable non-esterified fatty acids, which is the desired result.

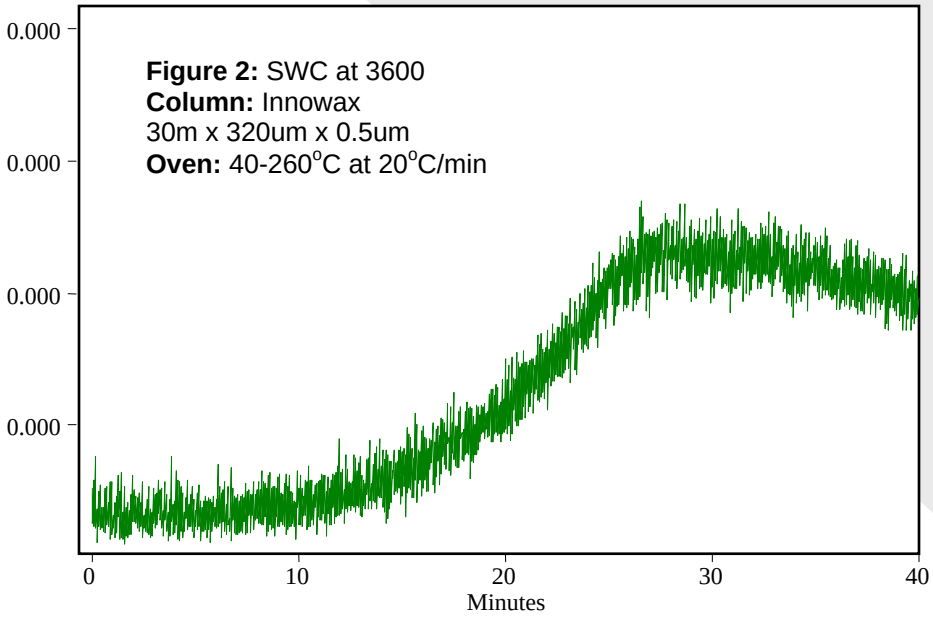

Figure 2: SWC at 3600
Column: Innowax
30m x 320um x 0.5um
Oven: 40-260°C at 20°C/min

As in this example, B100 is primarily made from FAME (Fatty Acid Methyl Esters) compounds in the C16 to C18 range. However, we can look at these same FAME analytes in hydrocarbons blends. Here is a GC-IRD separation of a FAME mixture in a selective SWC chromatogram at 1750 for carbonyl groups. The FAME is present at 0.4% in a hydrocarbon jet fuel but we do not see any response from the hydrocarbon fuel matrix.

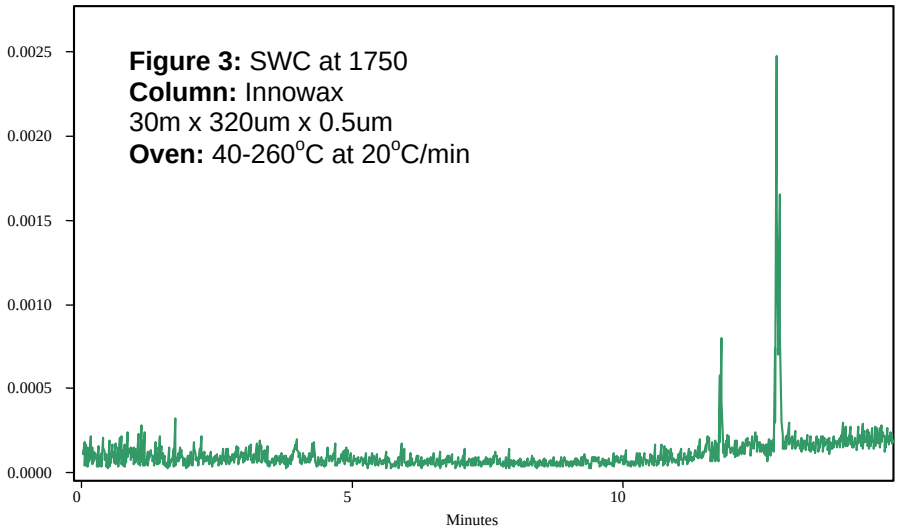

Figure 3: SWC at 1750
Column: Innowax
30m x 320um x 0.5um
Oven: 40-260°C at 20°C/min

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We can compare the selective chromatogram (SWC at 1750 for carbonyl groups) above to a Total Response Chromatogram (TRC) showing the GC-IRD separation at all IR wavelengths from 4000 to 550 wavenumbers. We can see biodiesel fatty acids near the end of the chromatogram in a hydrocarbon jet fuel matrix at 2 percent in the TRC by GC-IRD:

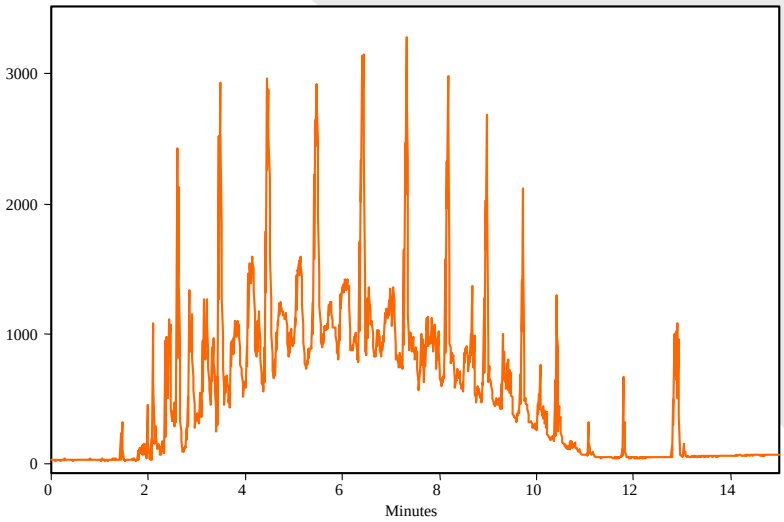
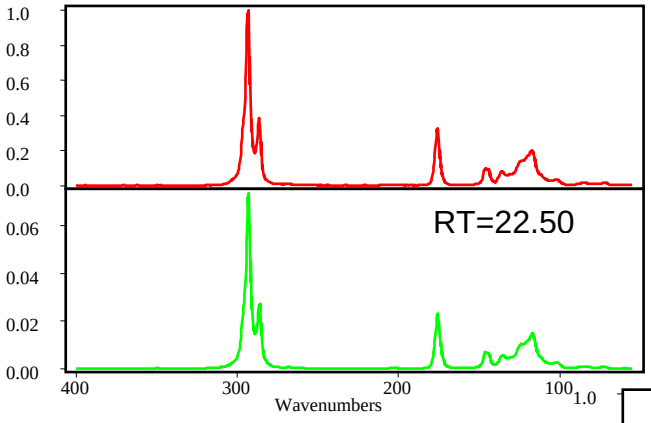


Figure 4: TRC on IRD
Column: HP-1
30m x 320um x 0.25um
Oven: 40-280°C at 20°C/min

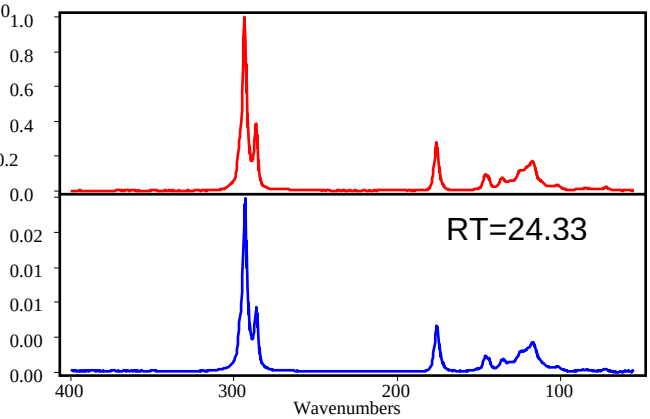
Finally, the GC-IRD can selectively look at the saturated versus unsaturated FAME analytes. We can selectively look at the double bond in an unsaturated FAME at 3070 wavenumbers.

Next, two IR spectra are shown for the saturated C16 and C18 FAME compounds:



Methylhexadecanoate or Palmatate
C16 Saturated FAME

Methyloctadecanoate or Sterate
C18 Saturated FAME



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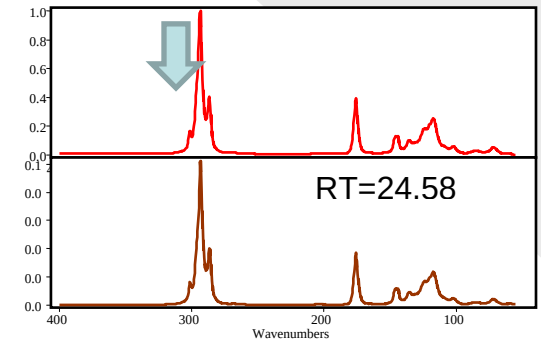
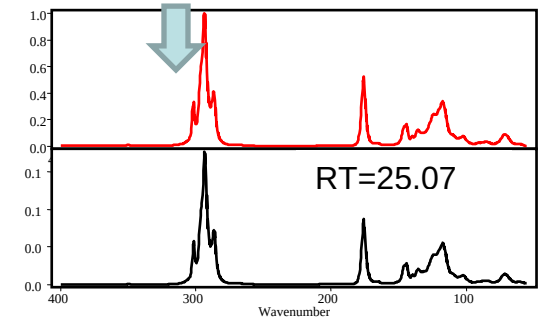
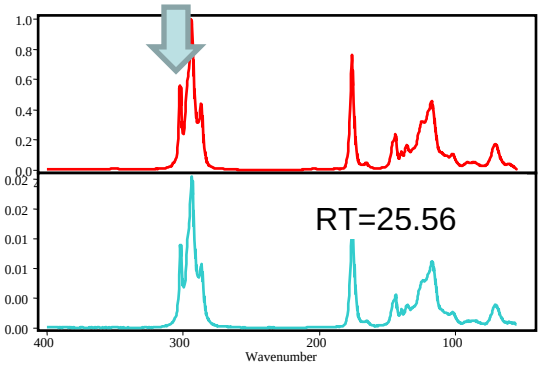
Now, IR spectra are shown for the three unsaturated C18 FAME compounds in this B100 sample:



Methyloleate
C18:1 unsaturated FAME



Methylinoleate
C18:2 unsaturated FAME



Methylinolenate
C18:3 unsaturated FAME

Conditions:

Gas Chromatograph: 40 to 260°C with split injection (5:1 and 0.5uL volume)
Column: Innowax 30m x .32 x 0.5
IRD: scan from 4000 to 550 wavenumbers at 8 wavenumber resolution, 280°C

Summary

It has been demonstrated that the GC-IRD system with the ASAP IRD 3 is very powerful tool for the analysis and characterization of new source fuel mixtures and petroleum blends.

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