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Comparison of Multi-Mode and Cool On-Column Inlets for EN 14105

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Introduction

The European Standard EN 14105:2011-07 is a method for quantifying free glycerol and residual mono-, di- and tri-glyceride content in fatty acid methyl esters (FAMEs) intended for addition to mineral oils by gas chromatography with flame ionization detection (FID). The method is applicable to a variety of FAMEs derived from rapeseed, sunflower, soybean, palm, animal oils and fats and mixtures of them. The analysis covers a wide range of boiling points from free glycerol to the triglyceride trinonadecanoate (Tri C57). The glycerol and glycerides are silylated and introduced onto the column using a cool on-column inlet (COC) in order to maximize recovery and improve peak shape. The COC is well suited for this analysis however it lacks versatility compared to inlets such as the multi-mode inlet (MMI) which can be used in a variety of introduction modes including cold-splitless which can produce results equivalent to COC. Also, the MMI is easier to maintain, similar to a standard split splitless inlet. In this study, the use of the multi-mode inlet (MMI) is investigated as an alternative to the COC by comparing results obtained for the analysis of a biodiesel B100 standard.

Experimental

Samples were prepared and analyzed in accordance with EN 14105:2011-07. For the MMI experiments, the inlet was run in cold-splitless mode starting at 88 °C for 0.1 minute and then ramping at 250 °C to 350 °C for 1 minute with a purge time of 2.5 minutes at 9.6 mL/min. For both COC and MMI analyses, the same Select Biodiesel for Glycerides UltiMetal column 15 m x 0.32 mm, 0.10 µm was used. For COC, a 2 m x 0.53 mm UltiMetal retention gap was connected to the analytical column using an inert union. The same temperature program was used for both COC and MMI starting at 50 °C for 1 min ramping to 180 °C at 15 °C/min then to 230 °C at 7 °C/min then to 370 °C at 30 °C/min for 4 minutes. The COC was set to track the oven temperature program. The FID was held constant at 380 °C. Biodiesel B100 SRM 2772 was purchased from NIST.

Results

Chromatographic Comparison

Figure 1 shows an overlay of chromatograms generated with the COC versus MMI for the analysis of the B100 SRM. The chromatograms were aligned using the first peak (glycerol) and last peak (Tri C57). Figure 2 shows the same chromatograms in expanded scale encompassing the Mono C19, Di C38 and Tri C57 gylcerides with aligned retention times. Figure 3 and 4 show a comparison of the glycerol and 1,2,4-butanetriol ISTD peaks in the calibration standard and B100 sample using the COC and MMI inlet, respectively.

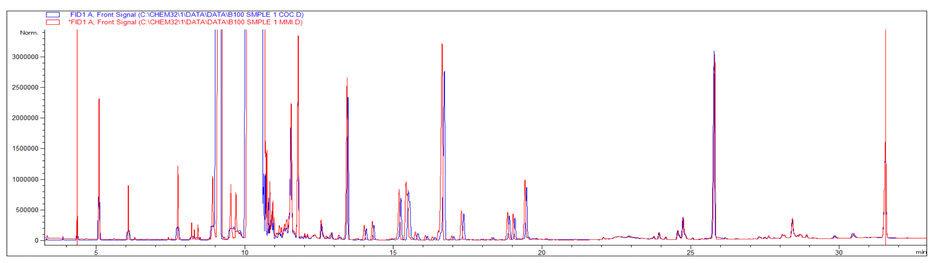

Figure 1. B100 chromatograms for COC (blue) and MMI (red) - full scale

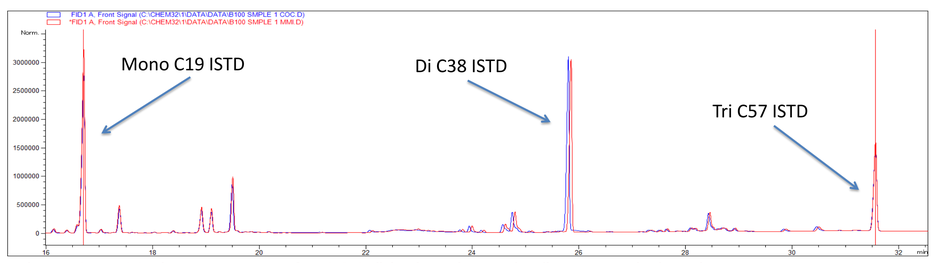

Figure 2. B100 chromatograms for COC (blue) and MMI (red) – expanded scale

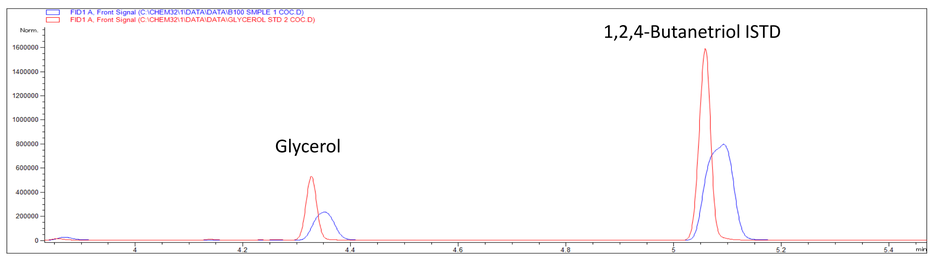

Figure 3. Glycerol and 1,2,3-butanetriol in a calibration standard (red) and B100 (blue) for COC inlet

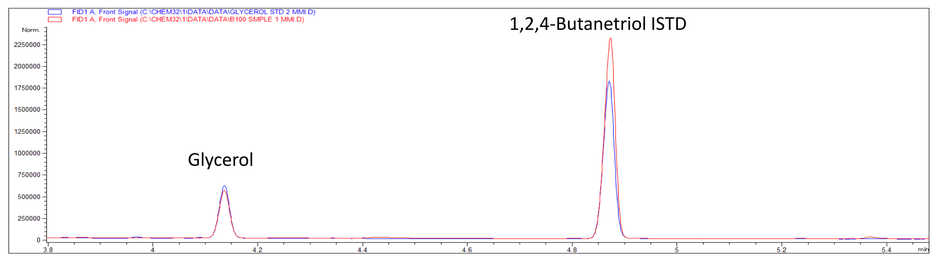

Figure 4. Gycerol and 1,2,3-butanetriol in a calibration standard (blue) and B100 SRM (red) for MMI

Quantitative Comparison

Figure 5 shows glycerol calibration curves for the MMI and COC. Table 1 lists the free glycerol, monoglyceride, diglyceride, triglyceride and total glycerol content of the B100 SRM determined using the MMI and COC for an average of two samples analyzed 8 times for a total of 16 injections. Weight percent calculations and repeatability limits were determined in accordance with EN 14105 Section 8.

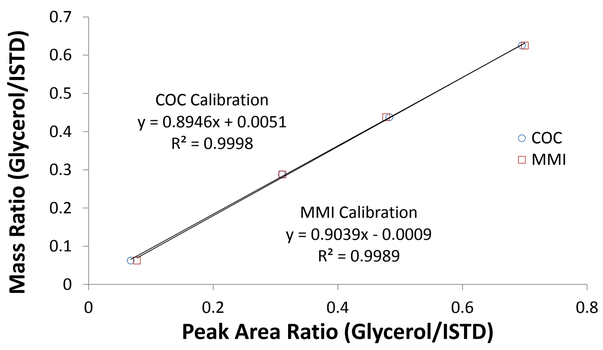

Figure 5. Comparison of COC and MMI glycerol calibration curves

Table 1. Comparison of COC and MMI glycerol and glyceride composition in the B100 SRM

Analyte Group	COC (wt%)	MMI (wt %)	Difference	EN 14105 Repeatability Limit
Glycerol	0.015	0.015	0.000	0.003
Monoglycerides	0.24	0.24	0.00	0.03
Diglycerides	0.10	0.11	0.00*	0.01
Triglycerides	0.05	0.05	0.00	0.01
Total glycerol	0.096	0.097	0.001	0.007

* Subtracted before rounding

Robustness Comparison

Figure 6 shows a comparison of the relative response factors (RRF) of Di C34 to Tri C57 for 16 replicate injections of B100 for the COC and MMI. According to the method, the RRF cannot exceed a limit of 1.8 or the system is not suitable for analysis. For the COC inlet, trimming the first 5-10 cm of the retention gap restored system performance after the 8th injection. Figure 7 shows the RRF for 50 runs using the MMI.

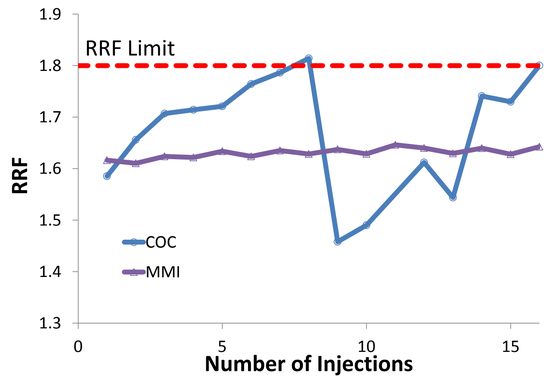

Figure 6. RRF as a function of injections for COC and MMI

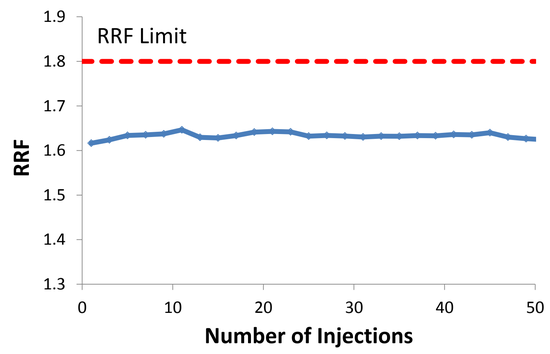

Figure 7. RRF as a function of injections for MMI

Discussion and Conclusion

Chromatographic Comparison

In comparing Figure 1, two observations are worth noting . First, no discrimination or loss of high boilers was observed for the MMI particularly for Tri C57 (Figure 2). This indicates a well optimized MMI method with virtually identical response for both inlets for high boilers. Second, an interesting phenomenon was observed for the glycerol and 1,2,4-butanetriol peaks comparing the calibration standard and B100. For the calibration standard, injection of the gylcerol and 1,2,4-butanetriol in pure heptane yields sharp peaks as a result of solvent focusing. However, peak broadening and a slight shift in retention time for these compounds was observed in the B100 sample with the COC (Figure 3). It is hypothesized that the large fraction of FAME matrix in the B100 causes a disruption in the solvent focusing characteristics. This broadening is not observed for the MMI because the glycerol, 1,2,4-butanetriol and heptane are transferred to the column at a similar vaporization points during the inlet temperature program preserving the solvent focusing effect (Figure 4).

Quantitative Comparison

As illustrated in Figures 5 and 6, quantitative results using the COC and MMI are indistinguishable based upon the repeatability reporting requirements of EN 14105.

Robustness Comparison

Figure 6 demonstrates a stark difference in robustness between COC and MMI. Only about 8 injections could be made using the COC before failing the RRF suitability criteria as specified EN 14105. It is hypothesized that the surface deactivation is removed by abrasion of the syringe needle during insertion into in the metal retention gap. Performance was restored by clipping a short portion of the retention gap the same length as the needle insertion depth. Even with careful straightening of the retention gap, this effect could not be eliminated. This was not observed with the MMI due to the different mechanism of sample introduction. Degradation of the RRF was not for observed over 50 injections (Figure 7).

Conclusion

This application demonstrates that MMI may be used as a replacement for a COC inlet for EN 14105. Quantitative results are identical and method robustness is greatly enhanced using the MMI compared to COC.