

# QUALITY CONTROL OF BIODIESEL WITH GASCHROMATOGRAPHY

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The outlook on increasing costs for mineral oil makes regenerative energy sources more interesting. Biodiesel consists of Fatty Acid Methyl Esters (FAME) produced by transesterification of natural oils e.g. rape oil. The quality control of biodiesel (DIN EN 14214) implements the measurement of residual methanol, free glycerol and glycerol esters (mono-, di- and tri-glycerides). Methods and maximum concentrations of the components are given in the standards DIN EN 14110 and DIN EN 14105.

## Instrumentation:

The methanol residue is measured by headspace analysis of biodiesel (DIN EN 14110). The norm recommends automated headspace sampling in combination with GC analysis. More sophisticated analysis is required for the determination of the glycerol and glycerol ester contents in biodiesel (DIN EN 14105). Rape oil mainly contains of four fatty acids with chain lengths  $C_{16}$  and  $C_{18}$ . Due to the boiling point range from glycerol to tri-glycerides „On Column“ is the recommended sample injection method. Additionally a high temperature column is needed. Preferred are fused silica columns with inner diameters (ID) of 0.32mm or smaller. Smaller ID allows faster analysis with better peak resolution. Standard On Column injection requires a column ID of 0.53mm. Capillary columns with smaller inner diameter therefore must be operated with a retention gap - normally a deactivated capillary of 2m length and ID 0.53mm (see fig 1). In case of the biodiesel measurements the connection retention gap to capillary column turned out to be the weak point for the gas tightness of the system. Due to the high oven temperature gradients the connection becomes often leaky.

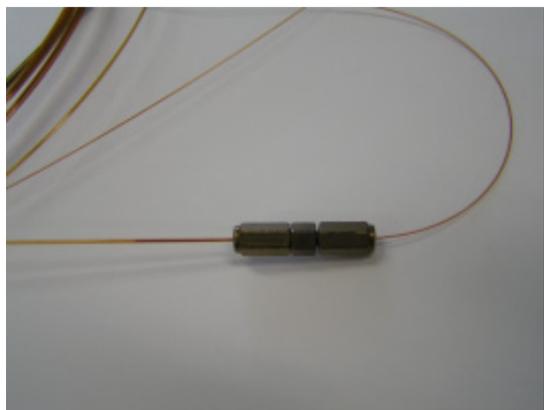


Fig 1: Capillary column with retention gap.

Much easier handling and more reliable results can be achieved using the alternative „Simple on Column Injection technique“. Injection is not

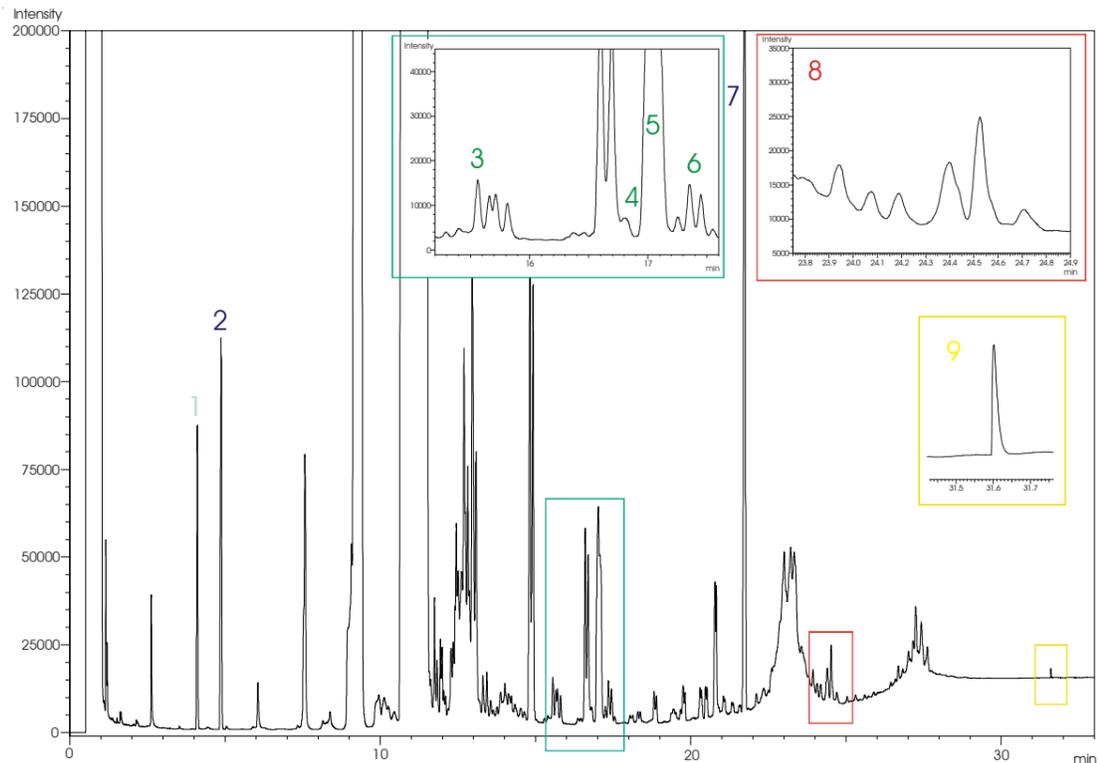


Fig 3: Biodiesel chromatogram measured with the „Simple On Column Injection technique“

1. Free glycerol, 2. Butanetriol (1st ISTD)  
Mono-glycerides: 3. Monopalmitoylglycerol (16:0), 4. Monolinoleoyl-glycerol (18:2), 5. Monooleoylglycerol (18:1), 6. Monostearoylglycerol (18:0), 7. Tricaprin (2<sup>nd</sup> ISTD), 8. Di-glycerides, 9. Tri-glycerides

performed „On Column“ but in a special designed glass liner (see fig 3). The column is fixed in the liner and additionally with a graphite ferrule on the injector body. A connection inside the GC oven is not necessary and gas tightness is no problem any more.

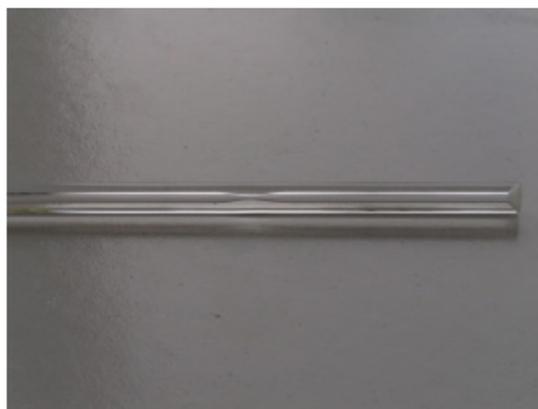


Fig 2: Liner for simple on column method

We made several biodiesel measurements using the liner and with retention gap over a longer time period. Table 1 shows the observed reproducibility ranges of areas and retention times for the components used in the calibration mixture according to DIN 14105.

## Reproducibility of areas:

Compound	Std. Deviation Liner	Std. Deviation RT-Gap
Glycerol	< 0.8 %	< 1.2 %
Butantriol ISTD1	< 0.8 %	< 0.8 %
Mono cal (Oleic)	< 0.7 %	< 1.5 %
Tricaprin ISTD2	< 0.7 %	< 1.0 %
Diglycerol	< 1.5 %	< 2.0 %
Triglycerol	< 5 %	< 7 %

## Reproducibility of Retention Times:

Compound	Std. Deviation Liner	Std. Deviation RT-Gap
Glycerol	< 0.13 %	< 0.08 %
Butantriol ISTD1	< 0.09 %	< 0.06 %
Mono cal (Oleic)	< 0.2 %	< 0.8 %
Tricaprin ISTD2	< 0.01%	< 0.02 %
Diglycerol	< 0.02 %	< 0.04 %
Triglycerol	< 0.02 %	< 0.05 %

## Conclusions:

The „Simple on Column“ injection method using a special designed glass liner proved to be a good alternative to the standard „On Column“ injection technique with retention gap.

Installation and maintenance of a system is easier with the liner and in case of the biodiesel quality control the reproducibility of the results is equal or better compared to similar measurements with retention gap.