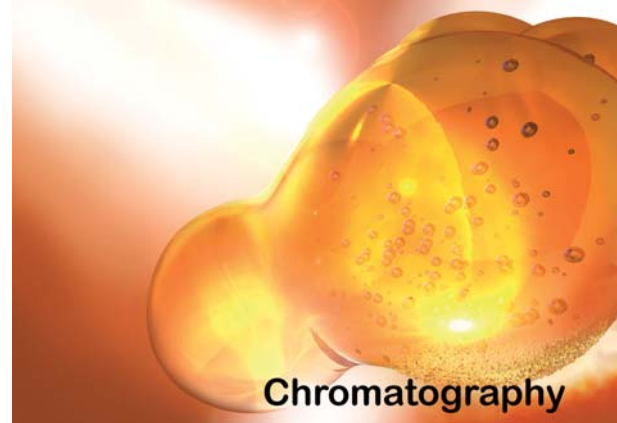


Application Note



Biodiesel Quality Control
According to DIN EN 14105
Determination of free and total glycerol and mono-, di,
Triglyceride continents (reference method)
Part 3: Optimization of the gas chromatographic method

Introduction:

After leak check and conditioning of the instrument a first sample can be injected. The DIN EN 14105 recommends a non-polar column with length of 10m, ID (inner diameter) 0.32mm, film thickness 0.1 μ m. This is a good column to start with but most operators prefer a longer column (12 to 25 m). With smaller ID a better resolution can be achieved even with a shorter column (e.g. 12m HT-5, ID 0.22mm, 0.1 μ m). Generally smaller ID allows a faster chromatography but optimizing of the gas chromatographic method might need more time.

Gas chromatographic Method:

GC: GC-2010AF with OCI

Sampler: AOC-20i

Column: HT5, 25m, ID 0.32mm, df 0.1 μ m
with retention gap ID 0.53mm

Carrier gas: Helium
Control Mode: Velocity
Injection Mode: Direct
Linear velocity: 50cm/s
Septum Purge: 3ml/min

OCI temperature program:

Rate [°C/min]	Temperature [°C]	Hold Time [min]
	60.0	1.00
20.00	380.0	3.00

OCI Advanced Settings Fan: 100°C

FID settings:

Temperature: 400°C
H2 flow: 47ml/min
Air Flow: 400 ml/min
Makeup Flow: 30ml/min (He)
Sampling Rate: 40ms
Filter Time Const.: 200ms

Oven temperature program:

Rate [°C/min]	Temperature [°C]	Hold Time [min]
	65.0	1.00
15.00	170.0	0.00
8.00	270.0	0.00
15.00	390.0	9

Equilibrium Time: 0.5min

Auto sampler:

Solvent for biodiesel samples is heptane. The life time of micro syringes with biodiesel can be extended if regularly the syringe is rinsed with a polar solvent (e.g. methanol) besides heptane. With AOC-20i+s this can be automated by using the three vial wash option. If no AOC-20s is used optional three wash stations can be inserted into the AOC-20i long rack. The wash cycle could be 1xheptane, 1xmethanol and 1x heptane again.

AOC-20i settings:

Injection volume: 1 μ l
Rinses Solvent Post-run: 2
(using three vial wash option)
Rinses Post-Run: 3
Rinses with Sample: 2
Plunger Speed (Suction): Low
Plunger Speed (Injection): High
Syringe Insertion Speed: High
Injection Mode: Normal
Pumping Times: 5

Next step would be optimization of the method according to the used column. First step is injection of standard solution 4 (highest concentration).

The standard contains one representative component for each group of glycerides.

Used naming	Alternative naming
Glycerin	
Butanetriol (ISTD1)	
Monoolein	1-Mono [cis-9-octadecenoyl]-rac-glycerol (monoolein)
Tricaprin (ISTD2)	1,2,3-Tridecanolyglycerol
Diglyceride	1,3-Di[cis-9-octadecenoyl]glycerol (diolein)
Triglyceride	1,2,3-Tri[cis-9-octadecenoyl]glycerol (triolein)

Tab1: Naming of biodiesel components

Butanetriol and Tricaprin are added as internal standard. Even in the refrigerator the stock solutions for the standards alter slowly. That is the reason for the additional peaks in the chromatogram.

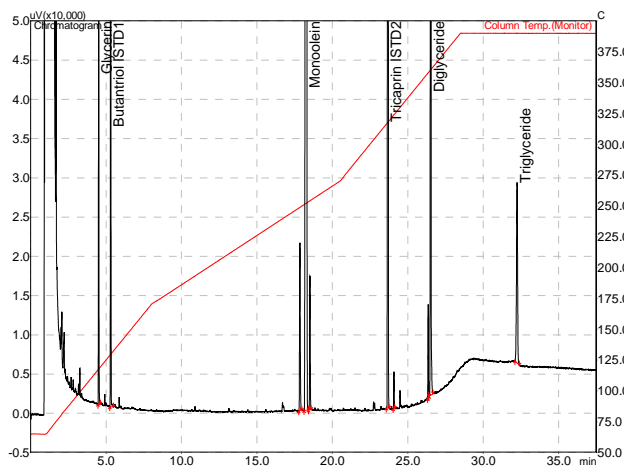


Fig. 1: Chromatogram standard solution 4

Since the glycerin concentration counts significantly in the final evaluation a good separation from the solvent peak is crucial (see fig. 1, more than 1 minute between solvent peak and glycerin).

Typically the baseline drift becomes steeper if the oven temperature rises above 340°C (see fig. 1 chromatogram time 23-26min). Fortunately the drift is not too big here therefore it is acceptable that the diglycerides elutes within this drift. A bigger drift could affect the integration accuracy of the whole group of diglycerides which elute from 23 to 24 minutes. In such cases an increase of the linear velocity (up to 70cm/s) or changing of the oven temperature might help.

The oven temperature program can be slowed down by changing the end tempera-

ture (see blue marked temperature in line two and three tab. 2).

Rate [°C/min]	Temperature [°C]	Hold Time [min]
	65.0	1.00
15.00	170.0	0.00
8.00	300.0	0.00
10.00	390.0	X

Tab2: Ganges of oven temperature program

Alternatively the temperature rate in line 4 can be decreased (see red marked rate in tab. 2). Possible is also a combination of both. In any case the hold time X in line 4 must be adjusted so that the chromatogram time does not become too long but that the triglyceride signals are still recorded.

Extending the temperature program has the disadvantage that the triglycerides remain too long on the column. It might happen that the peak disappears completely or becomes very small.

After optimizations of the temperature program the standard solution 1 (lowest concentration) must be injected to check the detection limits.

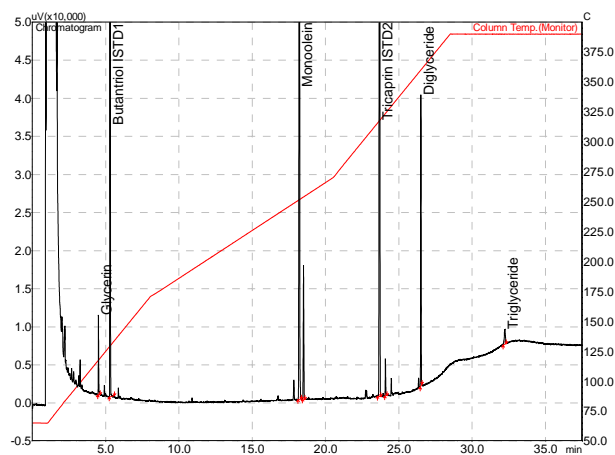


Fig. 2: Chromatogram standard solution 1

In the high temperature range the FID noise is 40µV. Peak height of the triglyceride peak is 2002µV. Thus the signal to noise ratio is 50. This is acceptable for a 0.32mm column but could be improved by accelerating the chromatography for example using a higher linear velocity.