Tank up in the rapesee

Determination of glycerine, methanol, mono-, di- and

When the German Shimadzu office in Berlin received a request for the analysis of Biodiesel in 1999 from the town of Wittenberge/ Germany, no practical information was available in this area to draw on.

Some proposed standards existed for the gas chromatographic determination of glycerine, mono- di- and triglycerides in fatty acid methyl esters (DIN 51609) and for the determination of methanol in fatty acid methyl esters (DIN 51608), the actual Biodiesel end-product. Of interest was also the gas chromatographic determination of the fatty acids as group as well as individual fatty acids and the by-product glycerine. It is clear that gas chromatography is the important analytical method for the raw material, production control and quality assurance of Biodiesel. Today the following standards have been submitted as Euronorm-drafts:

- DIN EN 14110 'Determination of methanol content in fatty acid methyl ester (FAME)'
- DIN EN 14105 'Determination of free and total glycerine and mono-, di- and triglyceride content in FAME'
- DIN EN 14103 'Determination of ester and linoleic acid-methyl ester content in FAME'.

The biodiesel industry is a growing branch of the economy which has its roots in the 1990 Gulf crisis. Biodiesel is being developed from the viewpoint that all fossil raw materials are exhaustible.

Advantages of biodiesel

Biodiesel is considered to be an environmentally safe fuel. It is manufactured from a renewable raw material, for instance rapeseed and unlike fossil diesel is virtually sulphur-free (less than 10 ppm). Biodiesel therefore guarantees a stable and long lasting effectiveness of the oxy-catalyst. Biodiesel reduces soot emissions by 50 % because it does not contain benzene or any other aromatic compounds which form soot, and it also reduces emission of PAH (polycyclic aromatic hydrocarbons). During combustion, Biodiesel emits only the amounts of CO_2 which the plants have absorbed during growth. This significantly contributes to the fact that future EURO-III exhaust standards have already been met today.

A further advantage of the biodiesel fuel is its flash point of 170 °C, which means that it is not be classified as a dangerous substance in Germany.

If Biodiesel is released by accident, it is easily biologically degradable and does not pose any danger to the soil or groundwater. From a technical point of view, Biodiesel possesses advanced lubricating properties and will protect the engine and contains, at a highly consistent composition, up to 95 % C-18, a high cetane number (54 - 58) and is an ideal self-igniting fuel. All in all, a real alternative to

d fields

triacylglycerides

exhaustible fossil fuels and other engine technologies.

Biodiesel production

Many plant oils or animal fats are suitable for biodiesel production. Important for the selection of starting material are, for instance, the melting point (CFPP), stability (JZ), availability, raw material price and production costs. In middle European countries, rapeseed is the main raw material. First the oil is pressed from the seeds. The rapeseed oil molecule consists of the trisubstituted alcohol glycerine in which each of the 3 OH-groups is substituted by a fatty acid group. Viscosity is high at 60 cSt. Transesterification with methanol, in the presence of the catalyst sodium hydroxide, breaks the oil molecules down into glycerine and fatty acid methyl esters. The fatty acid methyl esters, more accurately the rapeseed methyl ester (RME), are extracted as biodiesel. The viscosity at this point is only 4 cSt and compares well with that of fossil diesel oil.

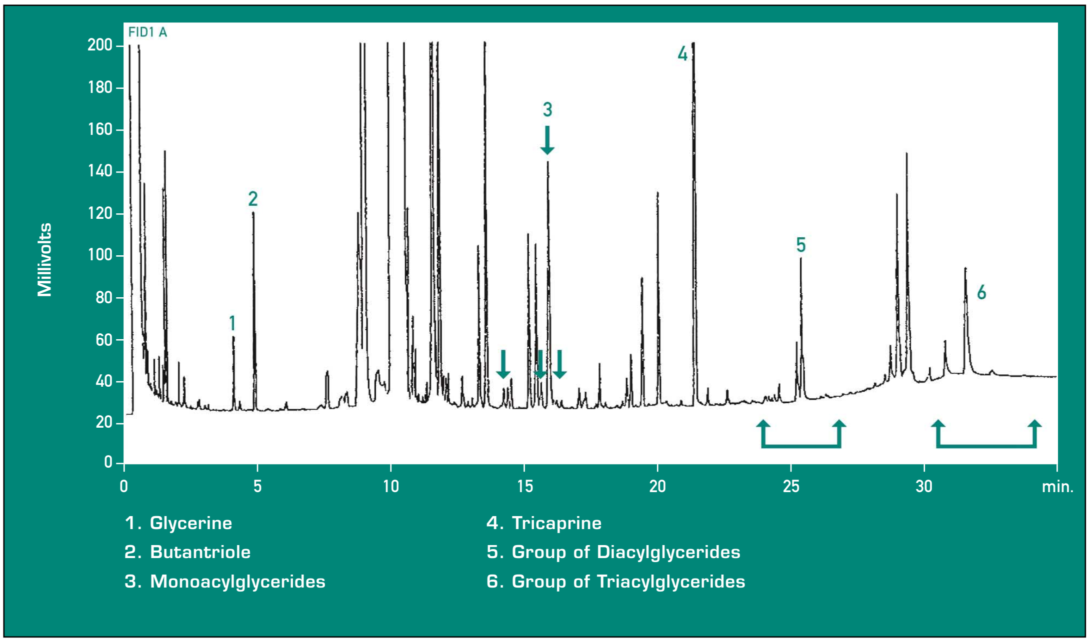

Figure 1: Example of an 'ideal' biodiesel sample. A larger representation of the three glyceride groups is shown in Figure 2

At this point it is also clear which compounds are present and what needs to be analysed. Glycerine, mono-, di- and triacylglycerides as well as methanol are determined via gas chromatography. The biodiesel end-product may contain a maximum of:

0.3 % methanol (E DIN 51608),
0.8 % mono-,
0.4 % di-,
0.4 % triacylglyceride,
0.02 % free glycerine and
0.25 % total glycerine.

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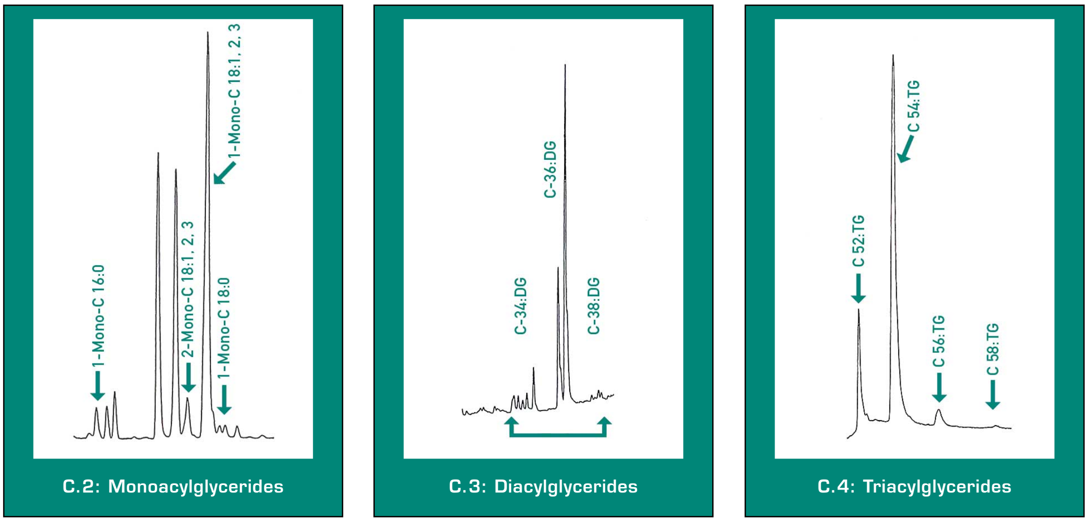

Figure 2: Enlarged representation of the glyceride groups in Figure 1

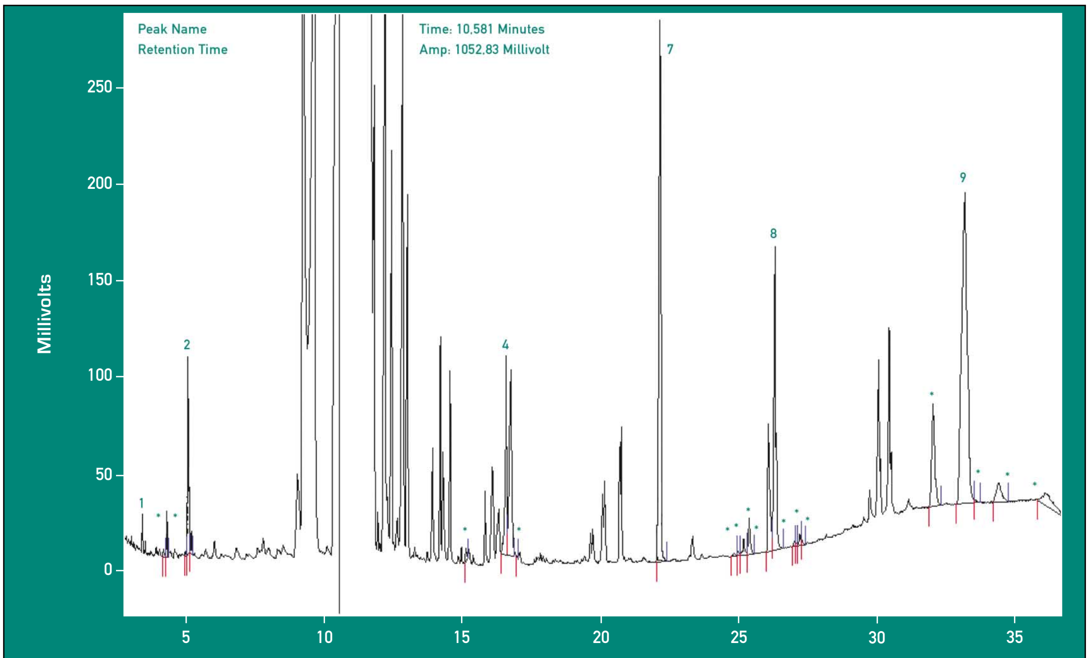

Figure 3: Example of a real biodiesel sample

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	Glycerine	4.360	0.013	mas %	54318	24142
2	Butantriole	5.126	0.958	mas %	270038	103502
3	Mono-1	15.276	0.021	mas %	27699	7464
4	Mono-Olein	16.616	0.215	mas %	487585	107963
5	Mono-2	16.789	0.456	mas %	609343	100627
6	Mono-3	17.026	0.013	mas %	17451	4660
7	Tricaprin	22.185	0.958	mas %	1379205	280208
8	Di-Olein	26.332	0.442	mas %	784718	156884
9	Tri-Olein	33.175	1.418	mas %	2149043	155477
G2	Di-Glyceride		0.705	mas %	1312150	
G3	Tri-Glyceride		1.211	mas %	2158716	
Totals			6.410	mas %	9250266	940927
Groups	1					
1	Mono-Glyceride		0.705		1142078	

Techniques and experience needed for quality control

While the determination of methanol via headspace-GC is a routine standard method, the determination of glycerine, mono-, di- and triglycerides in fatty acid methyl esters requires reliable instrumentation and considerable analytical experience.

The DIN EN 14105 standard can be employed for FAME from rapeseed oil, sunflower oil and soya oil. The analytes glycerine as well as the mono- and diglycerides are sylilated via the addition of MSTFA in the presence of pyridine and are analysed by gas chromatography via cool on-column injection, a short thin-film high-temperature column 10 m x 0.32 mm ID x 0.1 mm film (5 % diphenylpolysiloxane) (up to 400 °C) and FID with hydrogen as carrier gas. Quantification is carried out via calibration using two internal standards, 1,2,4-butantriole for the determination of glycerine and 1,2,3-tricaproglycerine (tricaprine) for the determination of glycerides (mono-, di- and tri-).

This means that a special group-type analysis must be carried out which enables the quantification of the sum of 4 components (mono) and in one time-window comprising 3 components (di and tri), using only one standard compound. The definition of a time-window for the di- and

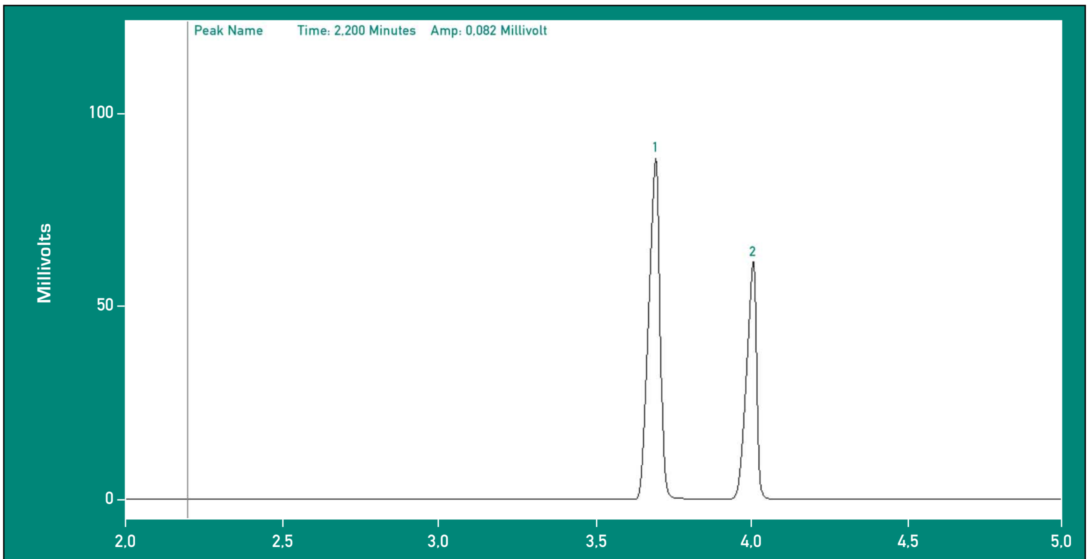

Figure 4: Example of the headspace standard: methanol with internal standard (isopropanol)

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	MeOH	3.696	0.106	mas %	222097	88352
2	iso-Propanol	4.010	1.000	mas %	141324	61611
Totals			1.106	mas %	363421	149963

trioleins is relatively uncomplicated via the setting of start- and stop functions.

During the analysis of the monooleins, it can be seen that within the defined time-window, more than the 4 signals of interest are present. This means that the signals which do not originate from the monooleins must be excluded from the group-type analysis. This is performed preferably when the undesirable signals in the group time-window are removed from the integration via the 'Integration-OFF' function.

In the following example the main signals are indicated by numbers and stars. The experienced analyst will be able to recognise and interpret the glycerine chromatogram of the respective sample.

Shimadzu's Technical Bureau in Berlin has, within its sales district, up to now equipped six biodiesel plants with gas chromatographic systems and has trained laboratory personnel in the area of biodiesel analysis. At the beginning of November 2003, users met at the Berlin office for the first exchange of ideas and discussions on biodiesel gas chromatographic analysis.

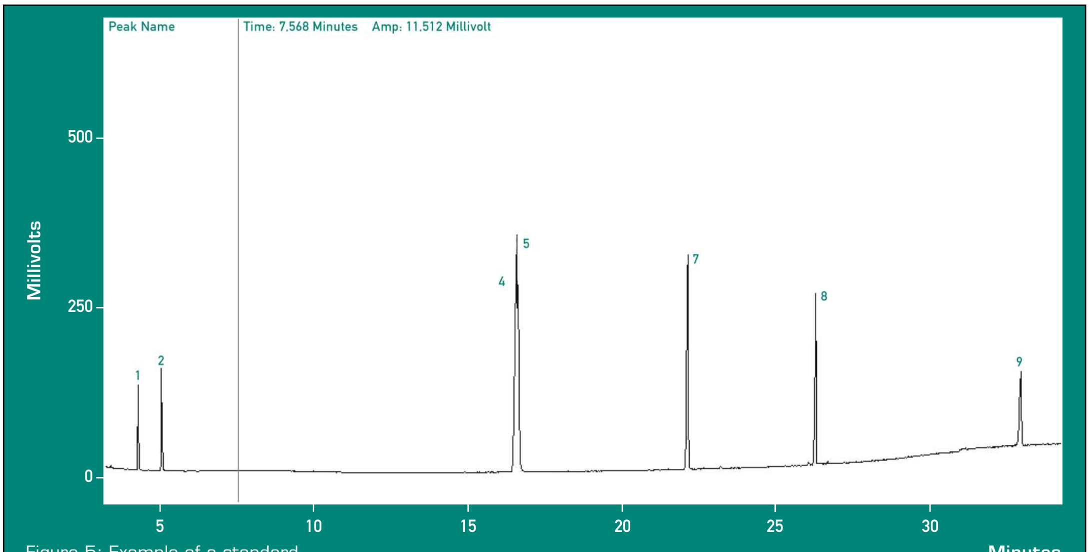

Figure 5: Example of a standard

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	Glycerine	4.323	0.001	mas %	183136	125743
2	Butantriole	5.086	0.010	mas %	235062	150214
3	Mono-1	0.000	0.000	mas %	0	0
4	Mono-Olein	16.612	0.012	mas %	1824548	349198
5	Mono-2	16.676	0.006	mas %	767237	275435
6	Mono-3	0.000	0.000	mas %	0	0
7	Tricaprin	22.179	0.010	mas %	1282202	317261
8	Di-Olein	26.315	0.005	mas %	787290	251879
9	Tri-Olein	32.978	0.004	mas %	554149	111245
G2	Di-Glyceride		0.005	mas %	815846	650779
G3	Tri-Glyceride		0.004	mas %	7100249	1580975
Totals			0.057	mas %		
Groups	1					
1	Mono-Glyceride		0.019	mas %	2591785	

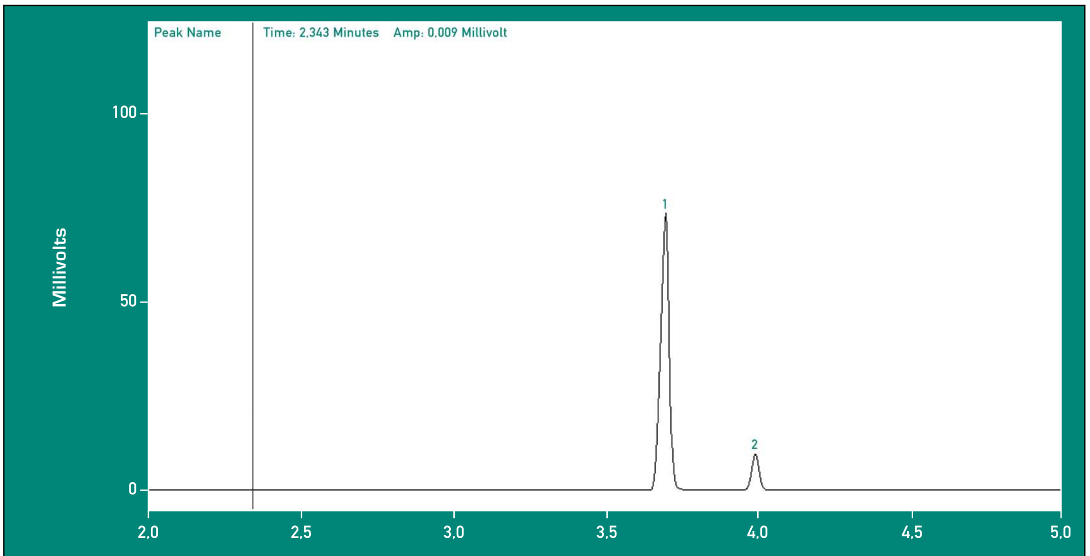

Figure 6: Example of the quantification of methanol in biodiesel

Pkno	Name	Ret. Time	Conc.	Units	Area	Height
1	MeOH	3.696	0.0159	mas %	185080	73626
2	iso-Propanol	4.010	1.000	mas %	21198	9241
Totals			1.0159	mas %	206278	82867