When the German Shimadzu office in Berlin received a request for the analysis of Biodiesel in 1999 from the town of Wittensborn/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 51620) and for the determination of methanol in fatty acid methyl esters (DIN 51609) and for the determination of glycerine, methanol, mono-, di- and triacylglycerides in biodiesel. Today the following standards have been submitted as Euronorm-drafts:

- DIN EN 14112 ‘Determination of methanol content in fatty acid methyl ester (FAME)’
- DIN EN 14125 ‘Determination of free and total glycerine and mono-, di- and triacylglyceride content in FAME’
- DIN EN 14153 ‘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.

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 prize and production costs. In middle European countries, rape-seed is the main raw material. First the oil is pressed from the seeds. The rapeseed oil molecule consists of the tri-substituted alcohol glycerine in which each of the 3 OH-groups is substituted by a fatty acid group. Viscosity is high at 60°C. 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.

The biodiesel end-product may contain a maximum of:

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

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:

- 0.25 % total glycerin.

Malvolta
APPLICATION

Tank up in the rapeseed fields

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

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 51620) and for the determination of methanol in fatty acid methyl esters (DIN 51620). 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 14125 ‘Determination of free and total glycerine and mono-, di- and triglyceride content in FAME’
• DIN EN 14135 ‘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 oxygen 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 CO2 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 98 % C-18, a high cetane number (54 - 58) and is an ideal self-igniting fuel. All in all, a real alternative to 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 (J50), 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.

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 51628)
- 0.8 % mono-
- 0.4 % di-
- 0.4 % triacylglyceride,
- 0.02 % free glycerine and
- 0.25 % total glycerine.

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

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

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The DIN EN 14105 standard can be employed for FAME from rapeseed oil, sunflower oil and soya oil. The analytes glycerides as well as the mono-, di- and triglycerides are silylated 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 (5 % diphenylpolysiloxane) 10 m x 0.32 mm ID x 0.1 mm film (5 % diphenylpolysiloxane) 10 m x 0.32 mm ID x 0.1 mm film high-temperature column.

The determination 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 (5 % diphenylpolysiloxane) 10 m x 0.32 mm ID x 0.1 mm film (5 % diphenylpolysiloxane) 10 m x 0.32 mm ID x 0.1 mm film high-temperature column.

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.

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

During the analysis of the monoleins, 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 monoleins 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.
The DIN EN 14105 standard can be employed for FAME from rapeseed oil, sunflower oil and soya oil. The analytes glyceride as well as the mono-, di- and triglycerides are split by 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 (up to 400 °C) and PID with hydrogen as carrier gas. Quantification is carried out via calibration using two internal standards, 1,2,4-butantriol and 1,2,4-butantriol 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 triglycerides 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.

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