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Analysis of FAME in Diesel and Heating Oil

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1. Introduction

Fossil fuel repository is decreasing worldwide very quickly and finding new sources becomes more and more difficult. Experts are expecting that the fossil fuel will end in a few decades. This is the reason for researchers to find alternatives. Many technical improvements have already been made for car engines and also many developments have been made in the area of fuel. FAME (fatty acid methyl esters) was found as an equivalent fuel to diesel. It is also known as "Biodiesel". In Europe, it is mostly prepared from rape, palm or soy oil. In the process of biodiesel production, the glyceride bondages are broken and methyl esters of the long chained fatty acids are formed (FAME = fatty acid methyl ester). In recent years, car engines have been developed, which run with both fossil diesel and FAME.

At a time of growing globalisation and increasing financial pressure on logistics and transport companies, cross contamination is an increasing issue. It needs extensive actions to clean a tank or a truck after having loaded FAME. Very often, traces of FAME can be found in other fuels. This was the reason, why a limit for FAME in Jet A-1 fuel needed to be defined and was set at 5 ppm (mg/kg) for aircrafts (Ministry of Defence (2008). Defence Standard 91-91 and Joint Inspection Group (2011). Aviation Fuel Quality Requirements for Jointly operated System (AFQRJOS) Bulletin No. 45).

As diesel and FAME are used in one and the same engine, one would think that cross contamination is not critical. This is correct for car drivers. However, it is well known that FAME cannot be stored for more than a couple of years. The reason for this is it's hydroscopic properties and it is also a very good alimentary for fungi.

Pure fossil diesel can be stored for decades without any problems. However, when fossil diesel is stored over several years, containing small quantities of FAME, fungi growth starts quickly and the characteristics of the diesel can change drastically. First, the odour of such contaminated diesel changes, second, FAME causes sticky deposits with water on the bottom of the containers and tanks, and third, fungi which grow in the fuel cause filter clogging.

A method was developed for sample preparation and quantification of FAME in diesel.

There is a difficulty when diesel or heating oil is analysed using a gas chromatograph connected to a mass spectrometer (GC-MS). A diesel sample contains compounds, which evaporate at high temperature. The temperature limit for the analysis using GC-MS is given by the chromatographic column. As it was found that HP-Innowax[1] shows the best

[1] HP-Innowax 50m, I.D. 0.200mm, Film 0.40 µm (by Agilent J&W); as an alternative column the following can be used: TBR-WAX 50m, I.D. 0.200mm, Film 0.40 µm (by Teknokroma)

separation for FAME and the temperature limit of this column is 260°C, a solution to separate the high volatile compounds from the diesel and heating oil sample needed to be found. The highly volatile compounds, as they are found in diesel, would contaminate a GC-MS injector in standard application rapidly, and cleaning would be needed too frequently. A solid phase extraction was found to be a solution for extracting FAME from diesel or heating oil samples.

2. Preparation of standards and samples

2.1 Preparation of standards

6 fatty acid methyl esters (FAME) were used to prepare the standards. The selection of these 6 FAME was already published earlier (Institute of Petroleum (2009). Norm draft document IP PM-DY/09). These are: methyl palmiate (C16:0), methyl margarate (C17:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3). A stock solution was prepared of approximately 50 mg of each FAME dissolved in 50 g Jet A-1[2]. From this stock solution, standard dilutions were prepared at the following concentration levels: 0.1, 0.5, 1.2, 3.0, 5.0, 12, 50, and 100 mg/kg (ppm) of each fatty acid methyl ester (FAME).

2.2 Preparation of samples

FAME free diesel and heating oil samples were used for the preparation of the samples. For the method development, they were fortified by the same stock solution as used for the preparation of standards as described above. The fortified samples were prepared at the following levels: 0.2, 2.0, 10, and 100 mg/kg of each FAME.
Later, natural mixture of FAME was used for fortification. The levels of total FAME were 1.20, 7.55, and 115 mg/kg.

3. Sample treatment

Highly volatile compounds, as they are found in diesel, contaminate a GC-MS injector when used with a HP-Innowax[3] column due to temperature limits.

3.1 Solid phase extraction

The solid phase extraction cartridge (SPE) which was found to fit the best, is a Strata SI-1 Silica (55 µm, 70A)[4]. A 12-port vacuum manifold by Supelco connected to a small vacuum pump was used for the SPE sample preparation.

3.1.1 SPE column washing and conditioning

The SPE cartridges were pre-washed with approximately 10 mL diethyl ether at a speed of approximately 2 drops per second. Right after all the diethyl ether had passed the column, it was conditioned with 10 mL n-hexane at the same flow speed. Thereafter the

[2] When using Jet A-1 as a solvent, it needs to be checked to be free of FAME. Other solvents such as octane or dodecane can be used as well. It is essential, that the same solvent is used for the preparation of standards as used for the sample dilution as described in section 3.1.3.
[3] See footnote 1
[4] Strata SI-1 Silica (55 µm, 70A), 1000 mg/6 mL Part Number 8B-S012-JHC by Phenomenex.

SPE cartridge was dried by vacuum for approximately 30 to 60 seconds. Then, the vacuum was stopped and the sample was applied. Both solvents, diethyl ether and n-hexane, were discarded.

3.1.2 Application of the sample

1 mL of the diesel sample or heating oil sample was passed through the cartridge at a speed of 1 drop per second. Thereafter, the diesel residue of the sample on the SPE cartridge was washed using 10 mL n-hexane. Also here, the n-Hexane from washing was discarded as well as the diesel sample which passed the column.

3.1.3 Elution and further treatment of the sample

After the n-hexane passed the SPE cartridge, it was dried for approximately 1 minute by vacuum. Thereafter, the vacuum was stopped and the adsorbed FAME were eluted with 10 mL of diethyl ether at a speed of 1 drop per second into a test tube.
The diethyl ether was evaporated by a gentle stream of nitrogen blown via a glass pipette into the test tube. Thereafter, the sample was diluted in 1 mL of FAME free Jet A-1 fuel[5]. The walls of the test tube were washed with a pipette and all of the solution was transferred into a sample vial as quantitatively as possible, closed with a crimped lid and analysed using GC-MS.

4. Analytical method

The analytical method is very similar to the one described in Literature (Institute of Petroleum (2009). Norm draft document IP PM-DY/09 and IP 585/10). However, the measuring range was extended down to 0.1 mg/kg for each FAME as the lowest standard. The preparation of standards was thus modified in terms of solvent and calibration levels. For maximum precision, the calibration curve was split into two segments as described in section 5 of this chapter.

4.1 Instrumentation

A gas chromatograph (Trace GC Ultra) connected to a mass spectrometer (DSQ II) by Thermo Scientific was used as GC-MS System.

4.1.1 GC method

Injector:	PTV
Injection:	Split
Split Flow:	20 mL/minute
Injection volume:	1.0 µL
Injector temperature:	260°C
Carrier gas:	Helium
Analytical column:	HP-Innowax 50m, I.D. 0.200mm, Film 0.40 µm (by Agilent J&W)

[5] When using Jet A-1 as a solvent, it needs to be checked whether the solvent is really free of FAME. Other solvents such as octane or dodecane can be used as well. It is essential, that the same solvent is used for the sample dilution as used for the preparation of standards as described in section 2.1.

Oven temperature:

Start temperature:	150°C (for 5 minutes)
Heating rate:	17°C/minute up to 200°C, hold time for 17 minutes, thereafter with 3°C/minute up to 252°C
End temperature:	252°C (isotherm for 3 minute)

4.1.2 MS method

Measuring mode:	Selected Ion Monitoring (SIM)
Measuring ranges:	20.00 – 27.69 minutes: SIM of 227, 239, 270, 271 Da 27.70 – 33.49 minutes: SIM of 241, 253, 284 Da 33.50 – 35.99 minutes: SIM of 255, 267, 298 Da 36.00 – 37.29 minutes: SIM of 264, 265, 296 Da 37.30 – 39.49 minutes: SIM of 262, 263, 264, 295 Da 39.50 minutes to end of run: SIM of 236, 263, 292, 293 Da
Polarity:	positive
Detector voltage:	1518V
Software used:	Xcalibur Version 2.0.7, QuanBrowser Version 2.0.7, and QualBrowser Version 2.0.7

5. Results

The standard measurement showed that it is not possible to calculate one calibration curve over the entire concentration range. Therefore, two calibration curves were created: one for the high concentration range, approximately 5 – 100 mg/kg of each FAME and a second for the range of 0.1 to 5.0 mg/kg of each FAME. An example of the high range calibration curve is shown in Figure 1 and the low concentration range is depicted in Figure 2.

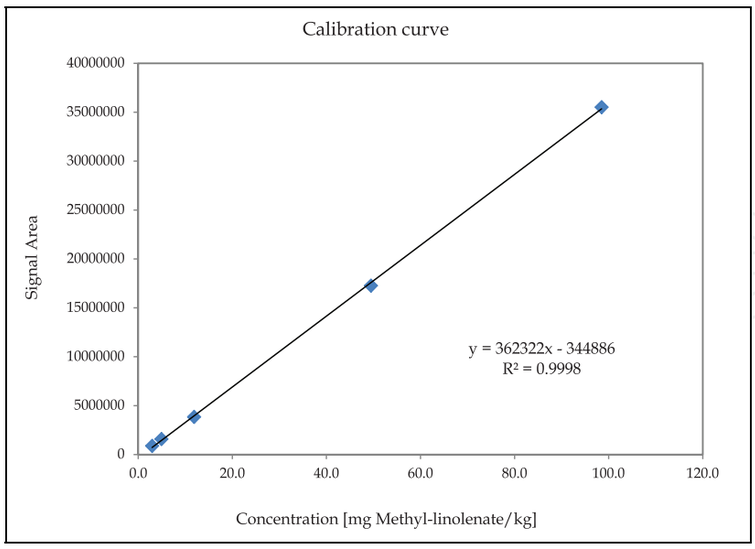


Fig. 1. Calibration curve for Methyl linolenate in high concentration range.

For each of the 6 FAME, a set of two calibration curves were calculated. Figure 3 shows the main section of the chromatograms of the standards. The depicted concentrations are 0.1,

0.5, 1.2, and 3.5 mg/kg for each FAME. The signal at approximately 26.6 minutes corresponds to methyl palmiate (C16:0), at 31.4 minutes to methyl margarate (C17:0), at 35.7 minutes to methyl stearate (C18:0), at 36.7 minutes to methyl oleate (C18:1), at 38.6 minutes to methyl linoleate (C18:2), and at 41.1 minutes to methyl linolenate (C18:3).

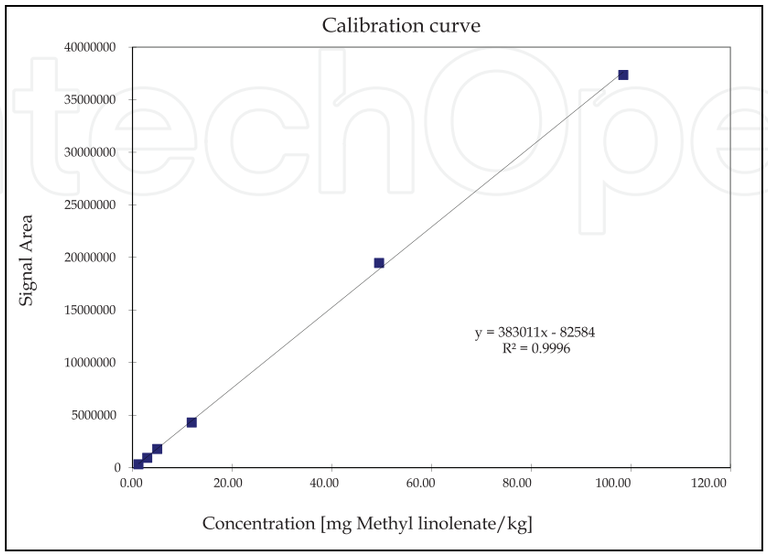


Fig. 2. Calibration curve for Methyl linolenate in low concentration range.

The expected retention time ranges are shown in Table 1 as they were also listed in the literature (Institute of Petroleum (2009). Norm draft document IP PM-DY/09 and in Purghart V. & Jaeckle H (2010). What Damage Can Biodiesel Cause to Jet Fuel? *Chimia, Volume 64, No 3*, Highlights of Analytical Chemistry in Switzerland). In the present study, slightly longer retention times were observed.

Species to be detected	**Significant SIM masses [Da]**	**Expected retention time [minutes]**
Methyl-palmitate C16:0	227, 239, 270, 271	24.9 – 26.4
Methyl-margarate C17:0	241, 253, 284	30.1 – 31.4
Methyl-stearate C18:0	255, 267, 298	34.7 – 35.5
Methyl-oleate C18:1	264, 265, 296	35.5 – 36.5
Methyl-linoleate C18:2	262, 263, 264, 294, 295	37.7 – 38.6
Methyl-linolenate C18:3	236, 263, 292, 293	40.3 – 41.1

Table 1. List of fatty acid methyl esters used as standards with the masses used for SIM detection and the approximately expected retention time ranges.

An example chromatogram of a fortified heating oil sample at a level of 2.0 mg/kg of each FAME is shown in Figure 4, the chromatogram of the one fortified at a level of 100 mg/kg of each FAME is shown in Figure 5.
A quantification of all signals is summarized in Table 2. The fortification levels were chosen to show the robustness of the method and also to cover both calibration curves with two

samples each. The fortification levels were defined as concentration of each of the 6 FAME, e.g. a fortification level of 100 mg/kg results in a total FAME concentration of 600 mg/kg as 6 FAME are considered. In later examples, fortification using natural FAME will be described. The concentration there will be given as total FAME, where the sum of 6 components is the number of interest.

As it was shown that reasonable recovery was found for each level of the fortified heating oil, samples of fortified diesel were prepared. However, if a cross contamination in a storage container or a truck occurs, then the detected signals of each fame would correspond to the FAME mixture as it comes from soy oil, rape oil, palm oil or similar. Therefore, diesel samples were prepared with natural fatty acid methyl ester mixture as commercially available. The fortification levels of total FAME were 1.20, 7.55, and 114.5 mg/kg.

An example chromatogram of a fortified diesel sample at a level of 7.55 mg/kg of total FAME is shown in Figure 6, the chromatogram of one fortified at a level of 115 mg/kg of total FAME is shown in Figure 7.

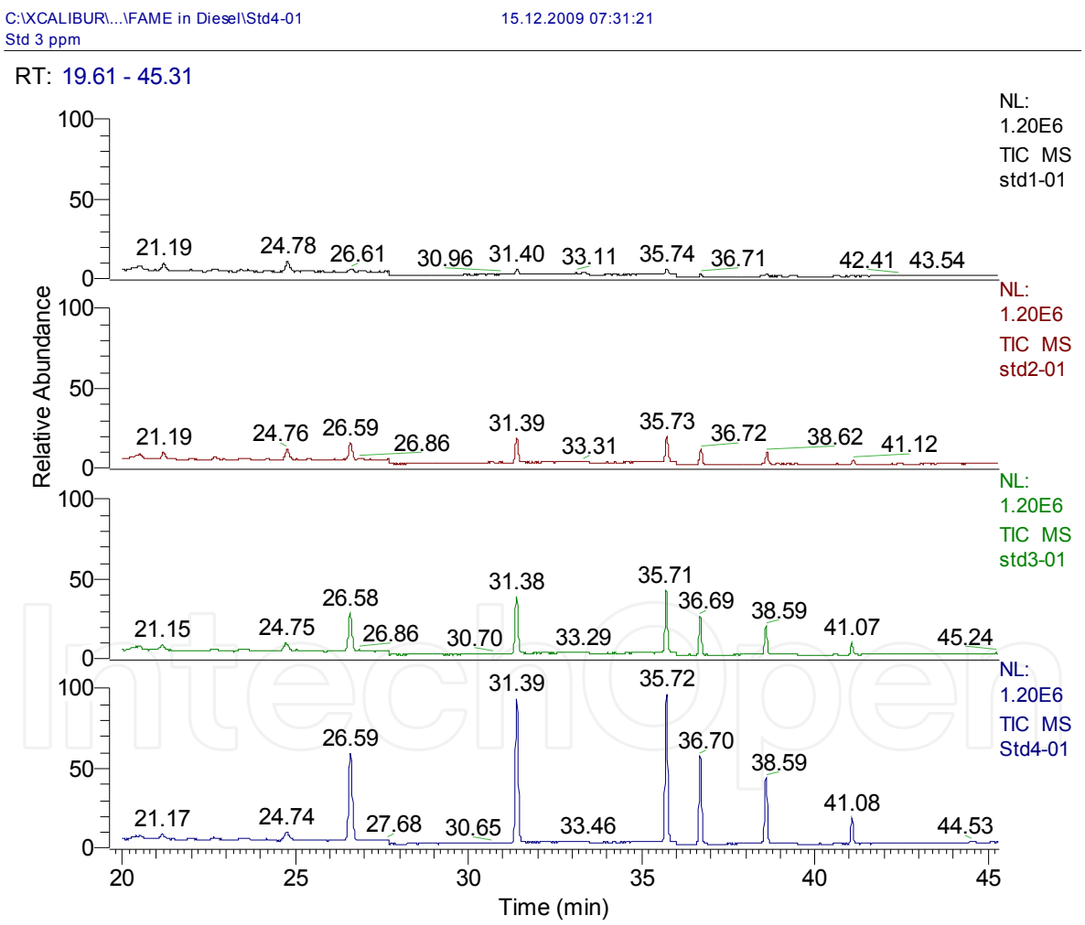


Fig. 3. Chromatograms of the standards at low concentrations i.e. 0.1, 0.5, 1.2, and 3.5 mg/kg for each FAME.

The signal at 26.56 minutes corresponds to methyl palmiate (C16:0), the signal at 35.70 minutes to methyl stearate (C18:0), the signal at 36.72 minutes to methyl oleate (C18:1), the signal at 38.59 minutes to methyl linoleate (C18:2), and the signal at 41.06 minutes

corresponds to methyl linolenate (C18:3). There is no signal at approximately 31.4 minutes, which would correspond to methyl margarate (C17:0). Generally, methyl margarate is not or only very rarely at very low concentrations present in FAME prepared from rape, palm or soy oil.

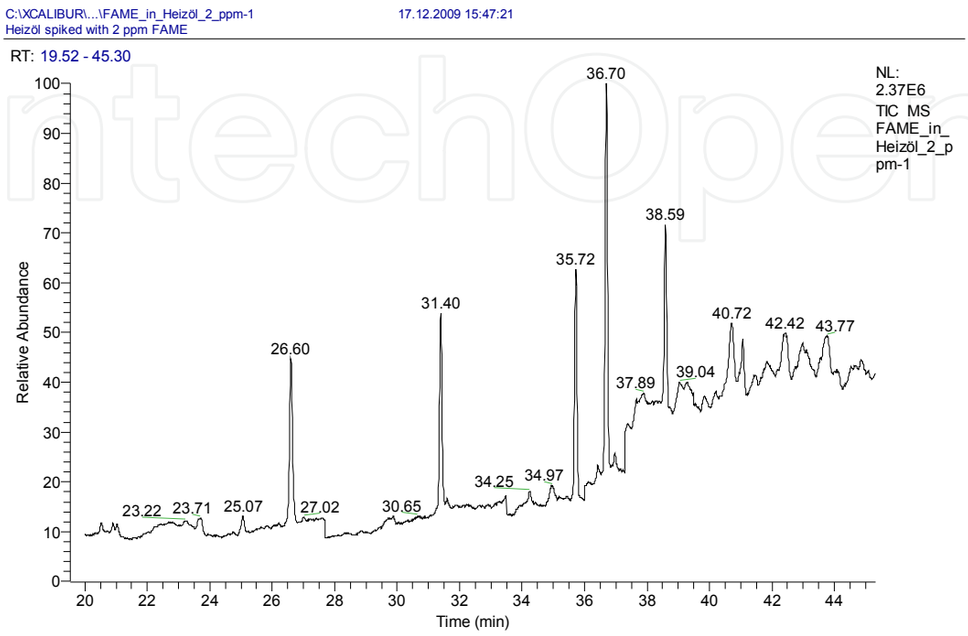


Fig. 4. Chromatogram of a fortified heating oil sample at a level of 2.0 mg/kg of each FAME.

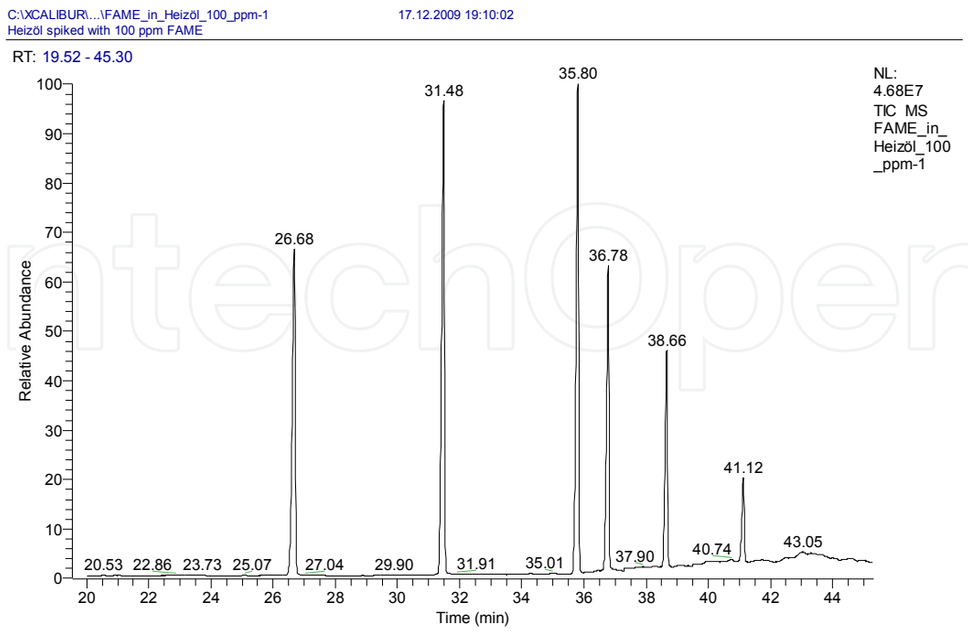


Fig. 5. Chromatogram of a fortified heating oil sample at a level of 100 mg/kg of each FAME.

Fortified level [mg/kg]	Methyl palmiate [mg/kg]	Methyl marganate [mg/kg]	Methyl stearate [mg/kg]	Methyl oleate [mg/kg]	Methyl linoleate [mg/kg]	Methyl linolenate [mg/kg]	Sum [mg/kg]
0.0	0.01	0.00	-0.02	-0.03	0.02	0.08	0.05
0.0	0.01	0.00	-0.02	0.01	0.00	0.03	0.03
0.2	0.19	0.16	0.19	0.24	0.21	0.20	1.19
0.2	0.18	0.17	0.19	0.23	0.24	0.22	1.22
2.0	1.98	2.10	1.95	1.84	2.09	2.02	11.99
2.0	1.99	2.10	1.90	2.06	2.07	1.83	11.94
10.0	9.62	11.16	9.24	9.62	9.90	10.60	60.13
10.0	9.22	10.38	9.76	9.73	9.25	10.39	58.74
100.0	104.73	103.53	94.62	99.78	102.70	105.42	610.78
100.0	104.72	102.92	94.60	99.15	100.97	101.48	603.84

Table 2. Summary of fortified heating oil samples at various levels. Each fortification level contains approximately the same amount of each FAME.

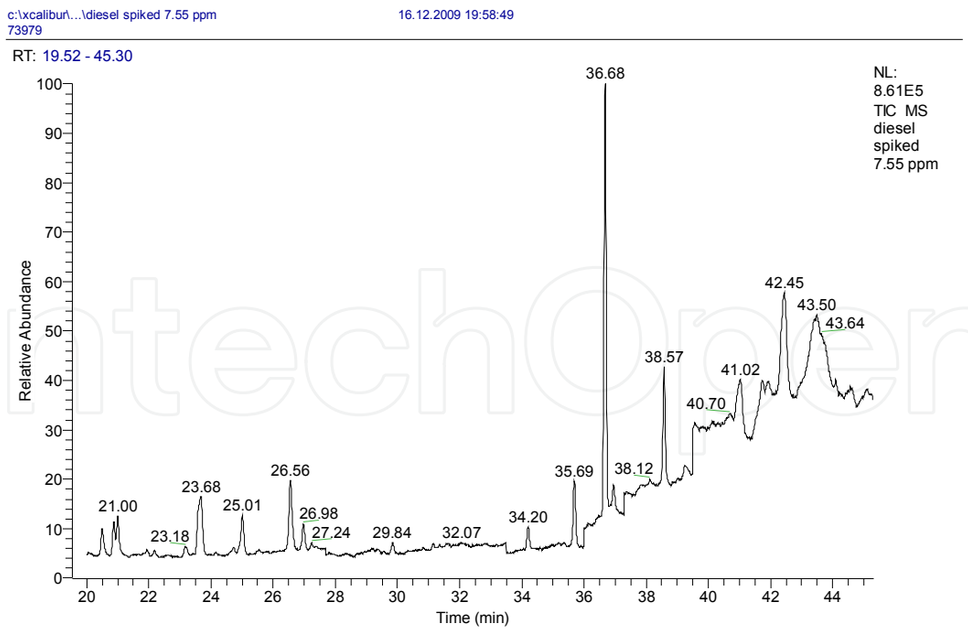


Fig. 6. Chromatogram of a fortified Diesel sample at a level of 7.55 mg/kg of total FAME.

A quantification of all signals of the fortified diesel samples is summarized in the following Table (Table 3).

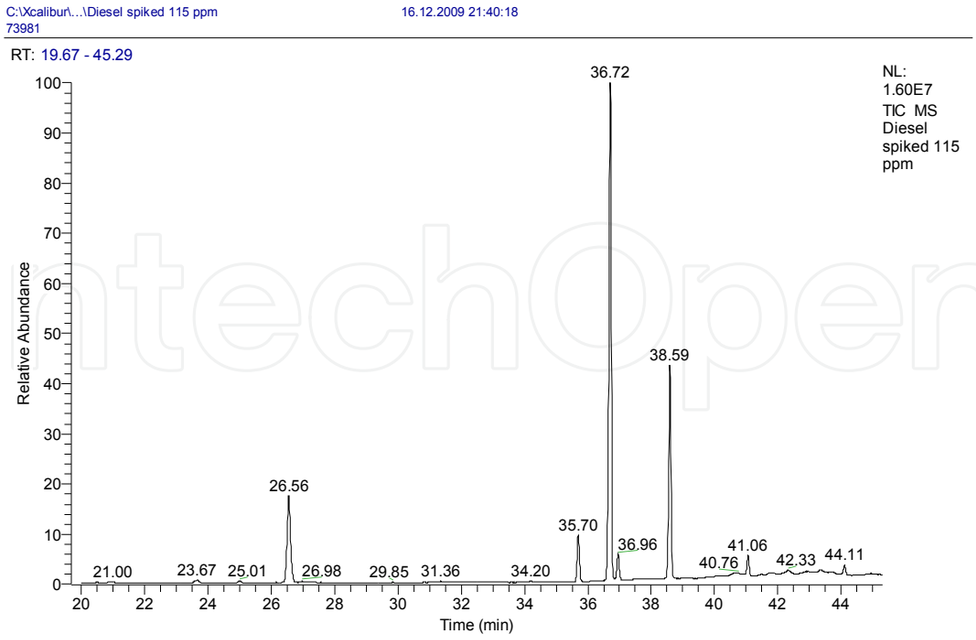


Fig. 7. Chromatogram of a fortified Diesel sample at a level of 115 mg/kg of total FAME.

Fortified level [mg/kg]	Methyl palmiate [mg/kg]	Methyl marganate [mg/kg]	Methyl stearate [mg/kg]	Methyl oleate [mg/kg]	Methyl linoleate [mg/kg]	Methyl linolenate [mg/kg]	Sum [mg/kg]
1.20	0.11	0.02	0.15	0.30	0.21	0.12	1.01
1.20	0.11	0.04	0.14	0.25	0.23	0.18	1.06
7.55	0.57	0.10	0.42	2.88	1.17	2.43	7.57
7.55	0.57	0.09	0.42	2.91	1.19	2.25	7.43
115	10.88	0.22	3.20	59.66	32.27	7.94	114.19
115	11.14	0.22	3.23	59.09	32.69	8.46	114.83

Table 3. Summary of fortified diesel samples at various levels. Each fortification level contains the sum of FAME listed in the table.

6. Conclusion

The presented analytical method for low concentration of FAME in diesel and heating oil was shown to be robust and sensitive down to low ppm level. The range of quantification was extended down to 0.1 mg/kg of each FAME. The robustness of the solid phase extraction was shown in the range of 1.2 to 600 mg/kg FAME in total. This results in a maximum total load of 600 µg FAME on the SPE cartridge.

7. References

Institute of Petroleum (2009). Norm draft document IP PM-DY/09
Institute of Petroleum (2010). Norm IP585/10

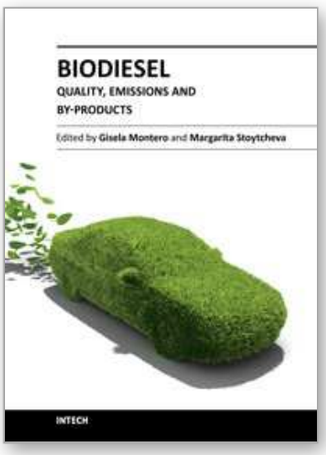
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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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