Determination of Methyl Esters in Diesel Oils by Gas Chromatography – Validation of the Method*

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The EU directives on the addition of bio-components to diesel oil in the form of methyl esters of fatty acids (FAME) require that the relevant laboratories should be able to estimate the content of these bio-components in oil. Assuming complexity of hydrocarbon matrix regarded, gas chromatography was selected as the corresponding analytical method allowing both quantitative and qualitative characterization of a fuel studied. For evaluation of FAME content in gasoline a standard gas chromatography with flame ionization detector and a polar capillary column was used. The proposed analytical procedure does not require special preliminary sample preparation and it is characterized by high accuracy and precision.

Transesterification of triacylglycerols is a simple process that converts vegetable oils into fuel for diesel engines. Besides the methyl esters of fatty acids, the reaction also yields bio-impurities such as acylglycerols, methanol, and the catalyst used. Such mixture represents a challenge for analysts as the impurities content is often at a level of 0.1 %. Best performance of the engine requires the purity of added esters of 98.8 % and better [1].

Ideal method for analysis of bio-components in diesel fuel should ensure effective and cheap determination of all impurities. So far, there is no method that would meet these requirements. Pioneer studies concerning analysis of such complex mixtures were based on the use of thin-layer chromatography coupled with flame ionization detection [2, 3]. Use of gas chromatography for this purpose was also proposed. Depending on the substance determined: alcohol [4], acylglycerols [4], or esters [5], packed or capillary columns and FID (Flame Ionization Detector) or MS (Mass Spectrometer) detection was employed. For analysis of esters or acylglycerols present in gasoline, HPLC (High-Performance Liquid Chromatography) was also tested using UV (Ultraviolet) and APCI-MS (Atmospheric Pressure Chemical Ionization Quadrupole Mass Spectrometer) detectors [6]. *Darnoko et al.* [7] used gel chromatography.

Proposed method was focused on determination of bio-components, *i.e.* FAME, obtained by transesterification of vegetable oils, in the diesel fuel.

EXPERIMENTAL

Standard mixtures of FAME were prepared from vegetable oil by transesterification, *i.e.* reaction of triacylglycerols from soybean oil with methanol in the presence of dissolved potassium hydroxide, according to the procedure described earlier [8]. The reaction yielded a mixture of methyl esters of the following acids: palmitic (9.99 %), stearic (3.20 %), oleic (24.89 %), linoleic (48.55 %), linolenic (4.85 %), and of other acids (8.48 %). The esters were used to prepare mixtures employed for determination of FAME in gasoline.

Internal standard solution of methyl esters of fatty acids with concentration of 10 mg cm^{-3} was prepared by dissolving a sample of esters in heptane. After each operation (internal standard addition, making up the measuring flask to the mark with heptane) the solution was weighed with the accuracy of 0.0001 g.

Weighing of standard mixtures of methyl esters was performed with the accuracy of 0.0001 g. *Standard A* contained 0.7 mass % of each of the methyl esters of the following acids: lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic in diesel oil. *Standard B* comprised 0.2 % of methyl esters of lauric, myristic, palmitic, and stearic acids and 1.2 % of the methyl esters of oleic, linoleic, linolenic acids in diesel oil. In *Standard C* content of the corresponding esters was reversed compared to the *Standard B*. 1 cm^3 of each standard solution was placed in a 10 cm^3 flask. Then,

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to each of the flasks 1 cm^3 of the internal standard solution was added and the flask was made up to the mark with heptane. After each operation the flask was weighed.

Samples of gasoline containing FAME were prepared by adding 1 cm^3 of the studied oil and 1 cm^3 of the internal standard solution to a 10 cm^3 flask and then the flask was made up to the mark with heptane.

Chromatographic analysis of samples was performed using a gas chromatograph (HP5890 Series II – Agilent Technologies) equipped with a flame ionization detector, split-splitless injector and a J&W INNOWAX capillary column (30 m × 0.32 mm × 0.5 μm). As a carrier gas helium was used with the flow rate of 2.7 cm^3 min^{-1}. Temperature program included isothermal analysis at 170 ℃, which lasted 5 min. Then a ramp of 6 ℃ min^{-1} was used to increase temperature to 230 ℃.

RESULTS AND DISCUSSION

On the basis of chromatograms of standard mixtures (Fig. 1*a*—*c*), the mean retention times of individual methyl esters were calculated relative to that of methyl heptadecanoate (Table 1). Furthermore, three chromatograms of each of the above-mentioned standard mixtures were taken to evaluate correction factor according to the equation

$$f_i = \frac{G_i A_\mathrm{w}}{G_\mathrm{w} A_i} \qquad (1)$$

where G_i and G_w represent the content of the component to be determined and that of the standard; and A_i and A_w the peak area corresponding to the component to be determined and that relative to the standard, respectively.

Components identification could be performed either on the basis of the relative retention times, or by comparing the sample chromatogram with those of the standard mixtures. Content of a given component in a sample was calculated using the equation

$$w_i/\% = \frac{m_\mathrm{w} A_i f_i}{m_i A_\mathrm{w}} \cdot 100 \qquad (2)$$

m_i and m_w being the mass of the sample and that of the standard added to the sample, respectively.

The amount of bio-components added to the diesel oil was calculated by summing up the amounts of particular esters. Qualitative analysis of samples provided information about the source of the esters added to gasoline.

Later on, the method validation parameters were determined according to [9, 10]. Accuracy of the method of internal standard was improved by using correction factors, determined for different analyte concentrations. Thus, ratio of the peak areas relative

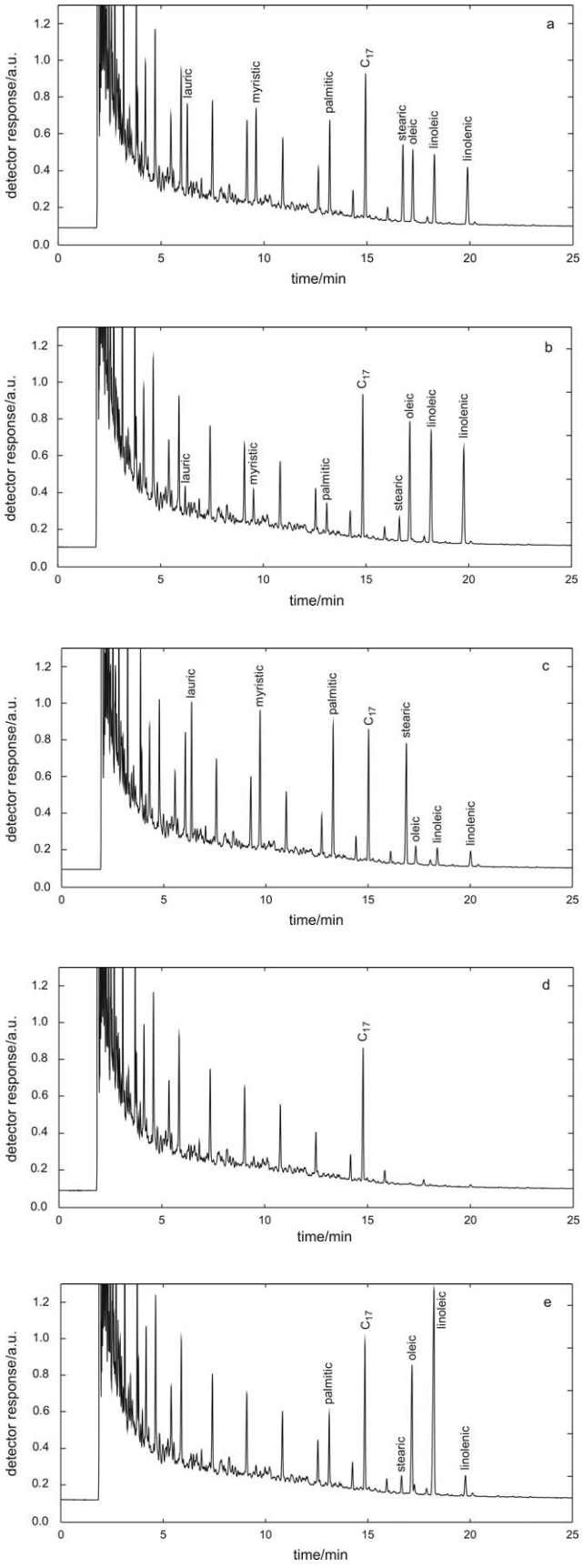

Fig. 1. Chromatograms of *Standards A* (*a*), *B* (*b*), *C* (*c*), and of diesel oil without (*d*) and with (*e*) addition of bio-components.

Table 1. Relative Retention Times of Methyl Esters of Fatty Acids

Methyl ester of fatty acid	Relative retention time
Lauric (C_{12})	0.42
Myristic (C_{14})	0.64
Palmitic (C_{16})	0.88
Heptadecanoic (C_{17})	1.00
Stearic (C_{18})	1.12
Oleic ($C_{18:1}$)	1.15
Linoleic ($C_{18:2}$)	1.22
Linolenic ($C_{18:3}$)	1.33

Table 2. Reproducibility of the Method Used for Estimation of FAME Content in Diesel Oil

FAME	Series	Mean value	Standard deviation	RSD
Palmitic	1	0.5701	0.0150	0.0263
	2	0.5645	0.0107	0.0190
	3	0.5701	0.0260	0.0455
	4	0.6187	0.0220	0.0356
Stearic	1	0.1724	0.0042	0.0242
	2	0.1730	0.0091	0.0524
	3	0.1648	0.0017	0.0102
	4	0.1685	0.0058	0.0346
Oleic	1	1.3425	0.0172	0.0128
	2	1.3266	0.0108	0.0082
	3	1.3158	0.0167	0.0127
	4	1.3402	0.0099	0.0074
Linoleic	1	2.5442	0.0216	0.0085
	2	2.5262	0.0202	0.0080
	3	2.5373	0.0149	0.0059
	4	2.5395	0.0143	0.0056
Linolenic	1	0.2627	0.0064	0.0244
	2	0.2591	0.0063	0.0244
	3	0.2619	0.0053	0.0204
	4	0.2517	0.0067	0.0268

to the given ester and internal standard could be used for verification of linearity of the detector response. Detection limit for particular esters was estimated as three times the signal to noise ratio on the basis of a chromatogram recorded for blank sample. The detection limit values were comparable for all esters and equal to 5×10^{-4} mass %.

Table 3. Statistical Indicators of the Quality of Method Used for Estimation of FAME Content in Diesel Oil

Ester determined	Mean	Standard deviation	RSD	U	k
Palmitic	0.5808	0.0288	0.0496	0.064	2.7
Stearic	0.1697	0.0064	0.0377	4.8×10^{-3}	2.2
Oleic	1.3313	0.0171	0.0129	0.023	2.1
Linoleic	2.5368	0.0181	0.0072	0.036	2.0
Linolenic	0.2588	0.0073	0.0283	4.3×10^{-3}	2.0

Reproducibility of the proposed method was assessed on the basis of the standard deviation values of the content of particular methyl esters determined in gasoline doped with bio-components from transesterification of soybean oil. Estimation of reproducibility and further statistical indicators was based on four series of experiments, during which for each experiment six independent analyses were accomplished. Measurement of each series was done on the same day. Reproducibility, calculated for each series separately as relative standard deviation (RSD), ranges between 1 % and 5 % (see Table 2).

Indirect precision was estimated as a relative standard deviation of all measured values (*i.e.* for the four series with six results in each series). As expected, the indirect precision value is higher than that of reproducibility (see Table 3) as the former one is affected by a greater number of variables (*e.g.* the time of measurements).

Extended uncertainty does not belong to the basic validation parameters. However, it is often used for the assessment of suitability of a given analytical method evaluating the results quality. Uncertainty of the proposed method was calculated according to the GUM recommendations [11] employing GUM Workbench provided by Metrodata [12]. Values of the extended uncertainty, U, and extension coefficient, k, calculated for individual FAME are given in Table 3.

Method accuracy was estimated comparing results obtained by the chromatographic analysis with the values determined by the gravimetric method as used during the reference standards preparation. Prior to the addition of bio-components to diesel samples, the

Table 4. Comparison of Experimental Data with the Reference Values Considering the Corresponding Uncertainty

FAME	Reference value, x_{ref}	Reference uncertainty, U	$\lvert x - x_{\mathrm{ref}} \rvert$	$2\sqrt{u(x)^2 + u(x_{\mathrm{ref}})^2}$
Palmitic	0.5570	0.0110	0.0238	0.0649
Stearic	0.1691	0.0026	0.0006	0.0055
Oleic	1.3420	0.0160	0.0107	0.0280
Linoleic	2.5090	0.0280	0.0278	0.0456
Linolenic	0.2607	0.0031	0.0019	0.0106

content of individual FAME in the product of soybean oil transesterification was determined chromatographically. Uncertainty of the reference standard was also assessed, and the results consistence was verified using the relation

$$|x - x_{\mathrm{ref}}| < 2\sqrt{u(x)^2 + u(x_{\mathrm{ref}})^2} \qquad (3)$$

where x is the value determined for a given ester, x_{ref} value for reference material; $u(x)$ uncertainty of result obtained from the determination of a given ester, $u(x_{\mathrm{ref}})$ uncertainty concerning the reference material.

It was found that the condition (*3*) was fulfilled for all reported FAME (Table 4). Thus, the result of measurements could be assumed consistent with the reference value.

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