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Fast and simple method for determination of fatty acid methyl esters (FAME) in biodiesel blends using X-ray spectrometry

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ABSTRACT

The determination of fatty acid methyl esters (FAME) in diesel fuel blends is an important aspect of production and blending process as well as quality control of distribution operations. In this study, energy-dispersive X-ray fluorescence spectrometer (EDXRF) is used for the first time for determination of FAME in biodiesel blends. The principle of the method is based on intensity difference of X-ray radiation scattered from hydrocarbons and from FAME. The experiment shows that coherent and incoherent radiation, commonly applied for evaluation of the average atomic number of the sample with light matrix, cannot be applied for FAME determination. However, the application of scattered continuous radiation gives excellent correlation between FAME concentration and intensity of scattered radiation. The best results are obtained if continuum is collected in the range of energy between 10.5 and 15.0 keV for rhodium X-ray tube, operated at 35 kV. Linear relationship between the FAME concentration and the inverse of scattered continuous radiation is obtained with the correlation coefficients of 0.999. Standard deviation of measurement is ca. 0.46% (v/v) of FAME and detection limit is 1.2% (v/v) for 600 s counting time and 50% dead-time loss using Si-PIN detector. The investigation shows that crucial issue in determination of FAME in biodiesel blends using EDXRF spectrometer is the precision of measurements resulting from the counting statistics. Therefore, much better results (0.20% (v/v) standard deviation and 0.52% (v/v) detection limit) can be expected if higher intensity of primary radiation is applied and X-ray spectrum is collected by silicon drift detector of high input count rate. For concentration of FAME from 10 to 100% (v/v), the differences between reference method (Fourier transform infrared spectrometry) and the proposed method usually do not exceed 1% (v/v) of FAME. The proposed method is fast, simple and enables FAME determination in wide range of concentration up to 100% of FAME without any sample treatment.

1. Introduction

Depletion of fuel fossil reserves, increasing demand for energy and increasing requirements related to limitation of contaminants emission and environment protection create new challenges in terms of automotive fuel production. Therefore, biological origin fuels are developed and wider and wider applied [1,2]. For example, European Union countries are obliged to use increasing amount of biofuels – 6.20% of biofuels in 2011 and 10% biofuels in 2020 [3]. To fulfill these requirements in the case of diesel engine vehicles [4,5], fatty acid methyl esters (FAME, called biodiesel) are used. FAME are usually produced in a transesterification process from vegetable oil (rapeseed, soy, palm, sunflower or jatropha oils), animal origin fat (tallow) or fatty wastes (frying oil). The final product is a mixture of esters of various chain lengths (12–24) and various numbers of unsaturated bonds (0–3), which depends on the raw material taken for production and the used technology. FAME, fulfilling requirements of specification [6,7], can be used in pure form (B100) or blended with diesel oil of petroleum origin. Some amount of biofuel is added to diesel oil without special labeling, which means that it does not influence the work of engine significantly and does not cause necessity of any engine modification. The amount, established in specifications for diesel oil, is at the level of a few percent, e.g. 7% (v/v) [4] or 5% (v/v) [5]. Higher amount of biodiesel added to fuel needs labeling. Various mixtures of FAME and petroleum origin oil are developed as fuel for diesel engine vehicles, e.g. B20 (20% of FAME [8]) and B30.

The determination of FAME concentrations in diesel fuel blends is an important aspect of production and blending process as well as quality control of distribution operations. Several methods for assessing biodiesel quality and quantification of methyl esters, as well as mono-, di- and triglycerides have been reviewed in [9,10]. In the midst of modern techniques applied in FAME determination, the following ones can be listed: gas chromatography–mass

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spectrometry [11], gas chromatography with flame ionization detector [12], high-performance liquid chromatography [13–15], electrospray mass spectrometry [16]. The analysis using aforementioned techniques is usually hampered beacause of complexity of the biodiesel sample. Therefore, the non-specificity of the technique is an advantage in determination of total amount of FAME. Recently, the UV fluorescence spectrometry has been proposed for biodiesel quantification without prior sample preparation [17]. Reddy et al. demonstrated a method based on the natural radiocarbon (^{14}C) abundance of biodiesel blends in the range B0 to B100 [18]. Borges et al. proposed determination of FAME content in diesel fuel blends from its dynamic viscosity value [19]. Chuck et al. [20] evaluated effectiveness of three spectroscopic techniques (FT-IR, refractive index and UV–vis) to determine the blend level of biodiesel samples and to ascertain further structural information relating to the fatty acid profile and alcohol moiety of the biodiesel present.

Infrared spectroscopy (IR) is most frequently applied for determination of total amount of FAME in diesel fuel blends in industrial laboratories. Two standard methods for FAME determination are based on IR measurements: EN 14078 (FT-IR spectrometer with a standard transmission liquid cell) [21] and ASTM D73713 (FT-IR spectrometer with a liquid attenuated total reflectance (ATR) sample cell) [22]. Since nonlinear relationship between FAME concentration and absorption is observed for a wide range of blends, the samples have to be diluted (EN 14078) or three separate partial-least-squares models have to be applied (ASTM D73713). EN 14078 method of FAME determination with FT-IR transmittance spectroscopy is the method officially approved for FAME determination in diesel fuel blends [4,5,8], therefore the method was chosen as a reference method in this work. The advantage of the method is also its non-specificity (strong absorption at ca. 1745 cm^{-1} due to the ester carbonyl bond regardless of type of FAME), simple sample preparation (only dilution is required) and low cost.

The aim of this study is the development of a new analytical method of FAME determination in biofuel blends based on the difference in the intensity of X-ray radiation scattered from hydrocarbons and from FAME. Non-specificity of X-ray spectrometry (XRS) with the use of scattered radiation should be an advantage in total amount of FAME determination.

2. Experimental

The X-ray measurements were performed with the laboratory-constructed energy-dispersive X-ray fluorescence (EDXRF) spectrometer described in details in [23]. The samples were excited by an X-ray beam from the air-cooled side-window Rh target of the X-ray tube of 125 μm thickness Be window (XTF 5011/75, Oxford Instruments, USA). The X-ray tube was supplied with XLG high-voltage generator (Spellman, USA). The X-ray spectra emitted by the sample were collected by a thermoelectrically cooled Si-PIN detector (XR-100CR Amptek, Bedford, MA, USA) of 6 mm^2 active area, 500 μm crystal thickness and 12.5 μm Be window thickness. The resolution of the Si-PIN detector cooled to the temperature of ca. −55 °C was 149 eV at 5.9 keV. The detector was coupled to a multichannel analyzer (PX4 Amptek, Bedford, MA, USA).

The Fourier transform infrared measurements were performed using FT-IR spectrometer Mattson 3020 (USA) working in a transmission mode and cells made of NaCl with path length of 0.1 cm. Spectra were recorded in the range from 4000 cm^{-1} up to approximately 400 cm^{-1}. The baseline was drawn as a tangent between approximately 1670 and 1820 cm^{-1}. Two-point correction was applied. The FAME contents in diesel fuel blends were determined according to EN 14078 [21]. Standard and unknown samples were measured after dilution in FAME-free middle distillates. Dilution

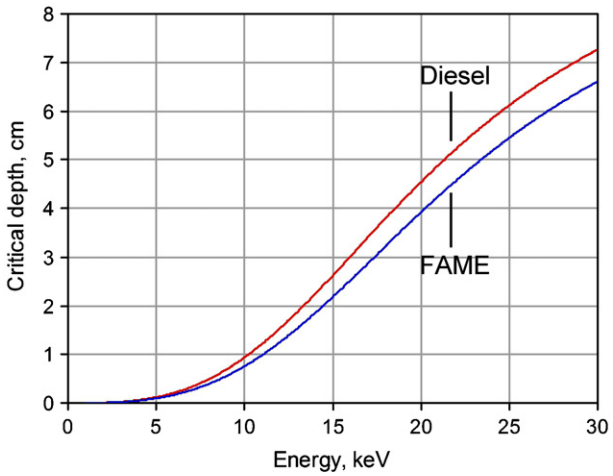

Fig. 1. Relationship between critical depth (d_{crit}) and energy of X-ray radiation. Following chemical composition for calculation of d_{crit} is assumed: diesel (14.6% H, 85.4% C, density 0.83 g cm^{-3}), FAME (13.2% H, 77.6% C, 9.2% O, density 0.88 g cm^{-3}).

coefficient was adequate to FAME content. For the routine range of concentration, from the determination limit up to 20% (v/v) of FAME, it was: 1:1 (v:v) for samples of diesel oil type and 1:5 (v:v) for samples of B10 and B20 type. For extended concentration range, the dilution coefficient was: 1:10 (v:v) for 20–40% (v:v) FAME and 1:25 (v:v) for 50–100% (v:v) FAME.

For XRS analysis, three series of standard samples of FAME concentration from ca. 0 to 100% (v/v) were prepared. Each series was prepared by mixing FAME and FAME-free solvent of different origin: series 1 by mixing standard of FAME (fulfilling requirements of EN 14214+A1:2010 [6]) with FAME-free middle distillate, series 2 and 3 by mixing FAME and pure diesel fuel from petrol stations. The prepared samples were also analyzed by FT-IR according to EN 14078.

3. Results and discussion

The proposed method of determination of FAME in biodiesel blends is based on the measurement of scattered X-ray radiation. The pure diesel fuels contain mainly carbon and hydrogen atoms (the presence of a low amount of other elements such as sulfur or heavy elements can be neglected in this study), whereas FAME, beside carbon and hydrogen, contain oxygen (ester carbonyl bond). Taking into account the differences in scattering properties of oxygen and the other elements, i.e. carbon and hydrogen, the X-ray scattered radiation can be used for determination of FAME in biodiesel blends.

3.1. Volume of the sample

The sample preparation is limited to pouring biodiesel into a sample cup covered by Mylar foil with thickness of e.g. 6 μm. Although sample preparation is very simple, one parameter such as penetration depth can have critical influence on analysis, especially if the X-ray spectra are collected in wide range of energy (up to 30 keV). Sample thickness should be greater than critical depth (thickness d_{crit} of the sample which emits 99% of radiation intensity) for any radiation energy of interest. Then, distribution of scattered spectra does not depend on sample thickness. Unfortunately, in the X-ray analysis of such light matrix samples (H, C and O) the critical depth can reach very high values especially for high energy. Fig. 1 shows that calculated critical depth equals to ca. 4–4.6 cm for 20.21 keV (Rh K_α radiation) or even 6.6–7.3 cm for 30 keV. Such great sample thickness cannot be assured using

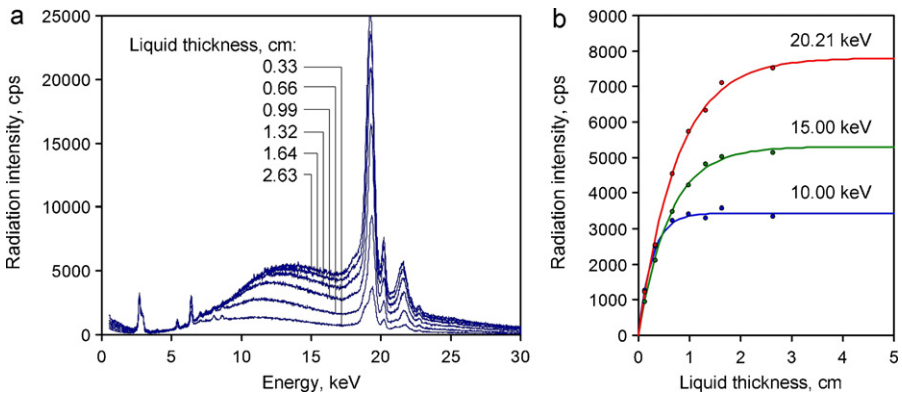

Fig. 2. Experimental data for diesel sample of various thicknesses (sample volume of 5, 10, 15, 20, 25 and 40 mL in cuvette of 4.4 cm diameter). (a) Spectral distribution of scattered radiation (Rh target X-ray tube operated at 45 keV). (b) Relationship between scattered radiation intensity and sample thickness.

commercial sample cups whose heights are usually in the range from 2 to 4 cm. The experimental results presented in Fig. 2a show that with greater sample thickness not only the intensity of scattered radiation increases but also spectral distribution considerably changes. Fig. 2b confirmed theoretical calculation that sample thickness should not be smaller than ca. 4.5 cm for 20.21 keV and 2.7 cm for 15 keV. Because in our study the spectral region of interest is located between 9 and 15 keV (see Section 3.3), the thickness of the samples should not be smaller than 2.7 cm. In practice, we applied the samples of ca. 3 cm thickness i.e. 45 mL of fuel in cups of diameter 4.4 cm. Under this condition, the spectral distribution up to 15 keV does not depend on sample thickness.

3.2. Measurement conditions and dead-time correction

The average atomic numbers of the biodiesel samples are very low (from 5.27 to 5.52). Thus, high intensities of scatter spectra are observed. Because the radiation scattered from the sample is collected by the semiconductor detector (Si-PIN) in the whole energy range, the high count rate and the dead-time loss can be expected. Unfortunately, the small input rates for which the output rate linearly increases cannot be applied because of the low precision of the measurement. In our case, the voltage and current of the X-ray tube were fixed to obtain dead-time loss of ca. 50%. Particular attention should be drawn to correction of the dead-time loss. Only then, accurate results can be obtained. Si-PIN detector in our EDXRF spectrometer with 1 mm collimator reached ca. 50% dead-time loss for the biodiesel samples if X-ray tube was operated at 45 kV and 700 μA. Because in our study the spectral region of interest is located between 9 and 15 keV (see Section 3.3), the excitation conditions can be optimized to obtain high intensity of the scattered radiation and better precision of the measurement in this energy region. Thus, the measurements were also performed using X-ray tube operated at 35 kV and 1300 μA. The dead-time loss was kept the same (ca. 50%). For these conditions, as Fig. 3 illustrates, a lower intensity of characteristic radiation of X-ray tube and higher intensity of continuum in the range from 9 to 15 keV were observed. Two regions of continuum scattered radiation marked in Fig. 3 are discussed in Section 3.3.

3.3. Selection of the region of X-ray spectrum

Fig. 4 presents X-ray spectra of pure diesel and FAME and also the difference between these spectra. As it can be observed, there are considerable differences in two regions of the spectra:

- In the range of energy from 18 to 23.2 keV – this region covers coherently and incoherently scattered characteristic radiation of the X-ray tube, i.e. Rh Kα and Rh Kβ lines.
- In the range of energy from 9 to15 keV – this region covers scattered continuous radiation.

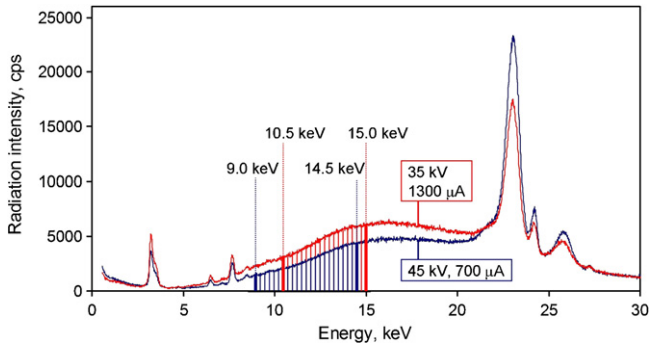

Fig. 3. X-ray spectra of diesel sample provided by rhodium target X-ray tube operated at 45 kV, 700 μA and 35 kV, 1300 μA.

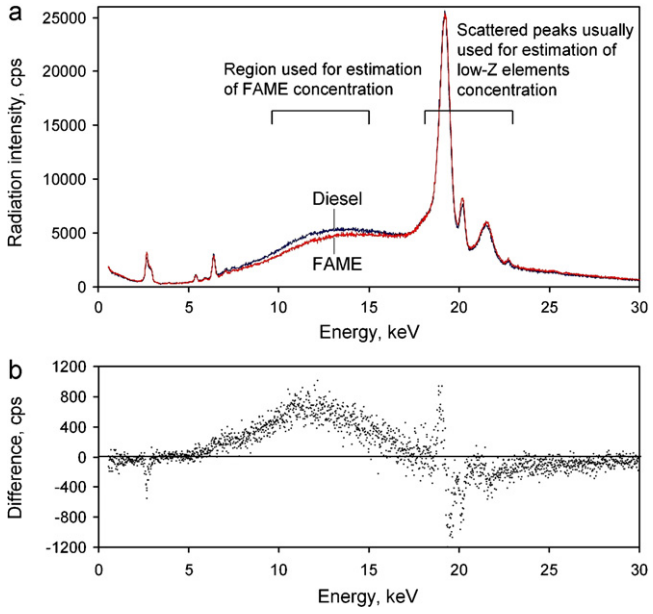

Fig. 4. X-ray spectra of pure diesel and FAME (a) and difference between these spectra (b).

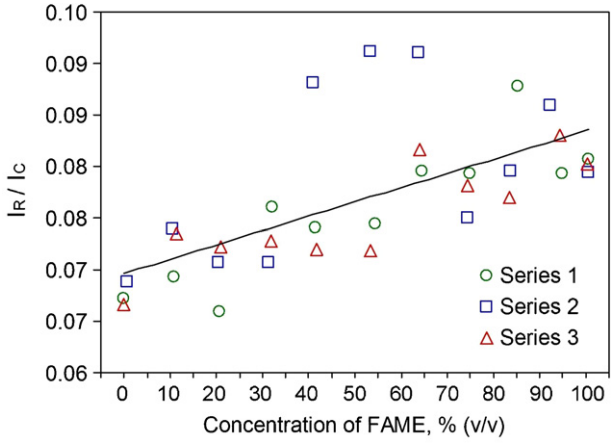

Fig. 5. Relationship between I_R/I_C ratio and FAME concentration in prepared reference samples.

The first region is commonly applied to evaluate the so-called 'dark matrix' i.e. matrix of undetectable (by EDXRF) low-Z elements, e.g. H, C and O. In these methods, the ratio of coherent I_R (Rayleigh scattering) to incoherent radiation I_C (Compton scattering) is used for the determination of the average atomic number of the sample: $Z_{av} = a \times (I_R/I_C)^n$, where a and n are experimental factors determined during calibration. Z_{av} is usually applied to evaluate 'dark matrix' in fundamental parameters method. In some cases, the ratio I_R/I_C can be used for determination of concentration of undetectable elements, e.g. carbon and hydrogen in hydrocarbons and petroleum [24]. To follow this idea, the application of the ratio I_R/I_C should give satisfactory results in determination of FAME in biodiesel blends. Unfortunately, the results for three series of prepared reference samples presented in Fig. 5 indicate the uselessness of I_R/I_C method for determination of FAME. The very high dispersion of the points can be explained by too low sensitivity of I_R/I_C in the case of FAME–diesel system, taking into account the precision of the measurements (Z_{av} varies from 5.27 to 5.52 for the samples from pure diesel to pure FAME). Moreover, the samples of thickness ca. 3 cm are not thick enough for radiation of energy from 18 to 23.2 keV. Although I_R/I_C ratio depends slightly on sample thickness (coherent and incoherent radiation have similar energy), even slight deviation of I_R/I_C can have crucial influence on FAME determination.

The second region, for which significant difference between X-ray spectra of pure diesel and FAME is observed, covers the energy of radiation from ca. 9 to 15 keV. The source of the continuum is the coherent and incoherent scattering of the X-ray tube radiation by the sample. The shape and intensity of the spectrum depend both on the initial shape of the X-ray tube spectrum (target, kV, mA) and on the sample composition. Fig. 4 shows that intensity of continuum in this range of X-ray spectrum is lower for FAME than for pure diesel. It results from the higher absorption of X-ray radiation in oxygen than in carbon or hydrogen. Thus, for the higher concentration of oxygen in the samples, the lower intensity of continuum in this range of X-ray spectrum should be observed. Taking into account this relation, the continuum can be used for determination of FAME in biodiesel blends. Fig. 6 presents experimental data for prepared calibration samples. In contrary to the I_R/I_C method, the utilization of continuum gives excellent correlation between FAME concentration and intensity of scattered radiation. The relationship is as follows:

$$\frac{1}{R_{cont}} = K \times C_{FAME} + B \quad (1)$$

where R_{cont} is a count rate of the continuum (counts per second), i.e. the total number of counts per second of the continuum in the integration window E_{min}–E_{max}, C_{FAME} is concentration of FAME in biodiesel blends expressed in % (v/v), K (second per counts per percent) and B (second per counts) are slope and intercept determined by least-squares-fit on the basis of calibration samples.

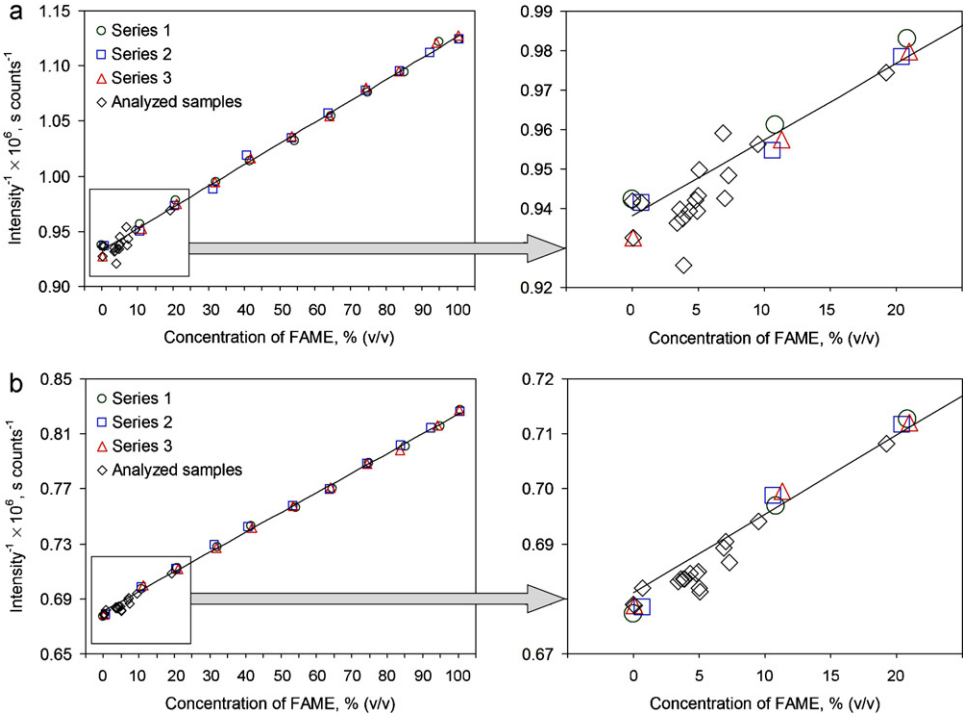

Fig. 6. Relationship between continuum scattered radiation and FAME concentration: (a) measurement conditions: 45 kV and 700 μA, integration window: 9.0–14.5 keV; (b) measurement conditions: 35 kV and 1300 μA, integration window: 10.5–15.0 keV.

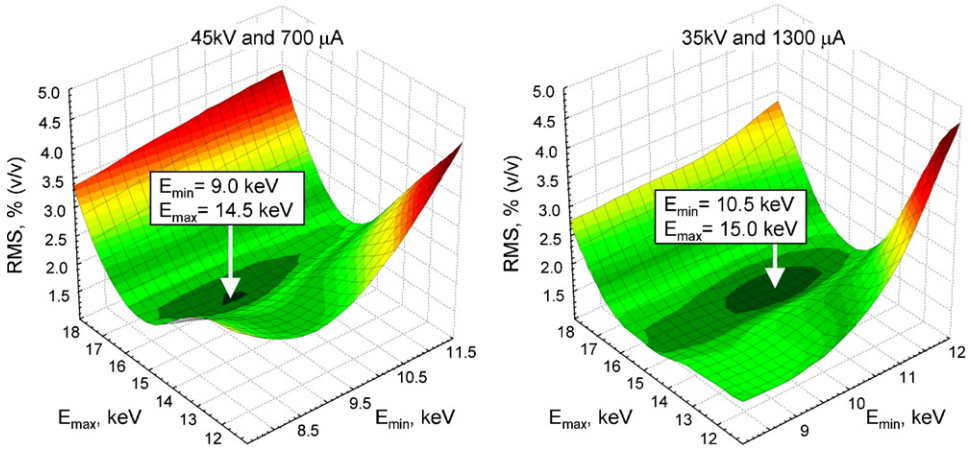

Fig. 7. Influence of integration window, i.e. E_{min} and E_{max}, on RMS.

The results presented in Fig. 6 were obtained for spectra provided by rhodium target X-ray tube operated at various measurement conditions: 45 kV, 700 μA and 35 kV, 1300 μA. For these conditions, the integration window E_{min}–E_{max} should be individually optimized to obtain the high quality results. First of all, the presence of the characteristic radiation of elements in the integration window E_{min}–E_{max} should be definitely avoided. The elements in question can be present in analyzed biodiesel as trace impurities. The strategy of selection of integration window E_{min}–E_{max} was based on calculation of RMS (root mean square of the sum of the differences between the true values of the standard concentration and the calculated values) for three series of prepared reference samples:

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{n}(C_{\mathrm{FAME\text{-}IR},i} - C_{\mathrm{FAME\text{-}calc},i})^2}{n-2}} \quad (2)$$

where $C_{\mathrm{FAME\text{-}IR},i}$ is the concentration of FAME in standard i determined by FT-IR (assumed as reference value), $C_{\mathrm{FAME\text{-}calc},i}$ is the concentration of FAME in standard i calculated from Eq. (1), n is the number of standards (in our case $n = 33$).

The RMS was calculated for various integration windows E_{min}–E_{max}. Fig. 7 shows that RMS reaches minimum value if the integration window E_{min}–E_{max} is 9.0–14.5 keV for X-ray tube operated at 45 kV and 700 μA and 10.5–15.0 keV for X-ray tube operated at 35 kV and 1300 μA. Thus, the integration window E_{min}–E_{max} can vary with measurement conditions and should be optimized for applied EDXRF spectrometer, X-ray tube, collimator etc.

3.4. Calibration, detection limit, precision and analysis of unknown samples

The calibration was based on three series of standard samples covering FAME concentration from ca. 0 to 100% (v/v). Each series was prepared by mixing FAME and FAME-free solvent of different origin. The calculated calibration parameters are presented in Table 1. As seen from the value of slopes and intercepts as well as from Fig. 6, significant differences between calibration graphs for different series of calibration samples are not observed. Thus, the origin of diesel fuel blends should not influence FAME determination. The RMS characterizing dispersion of points around the straight line are 1.8 and 1.4% (v/v) of FAME for X-ray tube operated at 45 kV, 700 μA and 35 kV, 1300 μA (integration windows 9.0–14.5 and 10.5–15.0 keV), respectively. The lower values of RMS for 35 kV and 1300 μA result from the higher intensity of the scattered radiation and better precision of the measurement. This issue was discussed in Section 3.2.

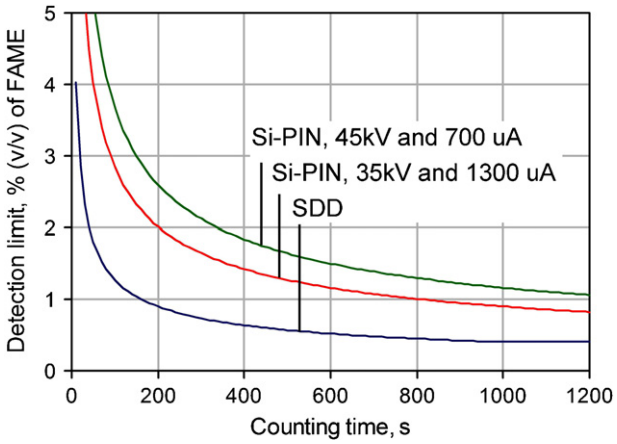

Fig. 8. Relationship between counting time and detection limit of FAME obtained using Si-PIN and SDD.

The detection limit (3 standard deviation) was calculated from Eq. (3) taking into account radiation increasing in inverse proportion to FAME concentration.

$$\mathrm{DL} = \frac{3}{K} \times \frac{1}{\sqrt{R_B^3 t}} \quad (3)$$

where R_B is the count rate of FAME-free diesel sample (counts s^{-1}) and t is the counting time.

Fig. 8 presents the relationship between detection limit of FAME and counting time. The obtained DLs with a counting time of 600 s are equal to 1.5 and 1.2% (v/v) of FAME for rhodium target X-ray tube operated at 45 kV, 700 μA and 35 kV, 1300 μA with 1 mm collimator. Some improvement of DLs can be achieved by extending the counting time up to 1200 s: 1.1 and 0.82% (v/v) of FAME for 45 kV, 700 μA and 35 kV, 1300 μA. Nevertheless, such a long time of measurement can limit the application of the proposed method in routine analysis. Much better DL can be expected if higher intensity of primary radiation is applied (e.g. coarse collimator) and X-ray spectrum is collected by silicon drift detector (SDD) of high input count rate. The predicted DL with the use of SDD is also presented in Fig. 8. The calculation of DL for SDD was performed to keep dead-time loss at the same level as in our experiment (ca. 50%, see Section 3.2) and similar energy resolution (peaking time is 25.6 μs

Table 1
Parameters of calibration curves.

Series of reference samples	Slope ($\times 10^7$ s counts^{-1} %$^{-1}$) (±std)	Intercept ($\times 10^4$ s counts^{-1}) (±std)	RMS (%, v/v)	R
X-ray tube operated at 45 kV and 700 μA, integration window from 9.0 to 14.5 keV				
Series 1	11.28 ± 0.18	5.616 ± 0.012	1.9	0.9986
Series 2	11.58 ± 0.18	5.598 ± 0.012	1.9	0.9986
Series 3	11.94 ± 0.12	5.580 ± 0.006	1.2	0.9993
Series 1–3	11.58 ± 0.12	5.598 ± 0.006	1.8	0.9986
X-ray tube operated at 35 kV and 1300 μA, integration window from 10.5 to 15.0 keV				
Series 1	8.58 ± 0.12	4.086 ± 0.006	1.7	0.9989
Series 2	8.58 ± 0.12	4.092 ± 0.006	1.6	0.9990
Series 3	8.58 ± 0.12	4.086 ± 0.006	1.2	0.9994
Series 1–3	8.58 ± 0.06	4.086 ± 0.006	1.4	0.9991

Table 2
Comparison between FT-IR and XRS analysis results.

Concentration of FAME (% (v/v) ± std)		Difference (%, v/v)	Relative difference (%)
FT-IR	XRS		
9.5 ± 0.1	9.2 ± 0.4	−0.3	3.2
11.3 ± 0.1	12.9 ± 0.4	1.6	14.2
19.3 ± 0.1	19.1 ± 0.4	−0.2	1.0
21.0 ± 0.2	21.6 ± 0.4	0.6	2.9
31.9 ± 0.1	32.3 ± 0.4	0.4	1.3
41.8 ± 0.1	42.4 ± 0.4	0.6	1.4
53.4 ± 0.2	53.2 ± 0.5	−0.2	0.4
63,9 ± 0.7	62.7 ± 0.5	−1.2	1.9
74.3 ± 0.2	74.5 ± 0.5	0.2	0.3
83.5 ± 0.6	81.7 ± 0.5	−1.8	2.2
94.3 ± 0.6	94.0 ± 0.5	0.3	0.3

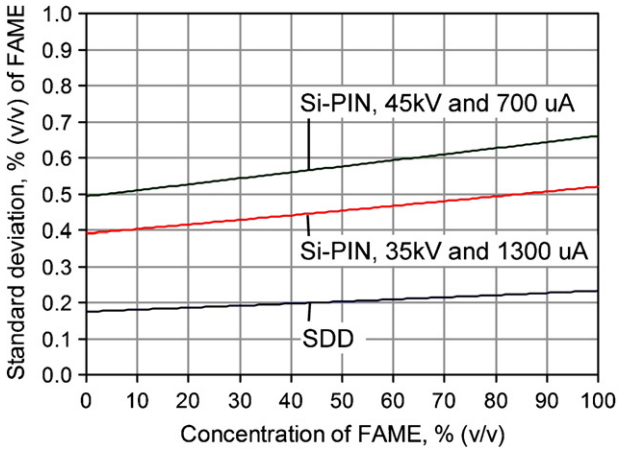

Fig. 9. Relationship between standard deviation of measurement and FAME concentration.

for Si-PIN detector, e.g. XR-100CR Amptek, and 3.2 μs for SDD, e.g. XR-100SDD Amptek). As can be observed, DL can be down to 0.52% (v/v) of FAME for 600 s counting time and SDD.

Table 2 presents exemplary analysis of biodiesel fuels performed at 35 kV and 1300 μA. The agreement between the results of FT-IR and XRS is satisfactory. The differences between these methods usually do not exceed 1% (v/v) of FAME. The mean difference between the results of FT-IR and XRS is ca. 0.67% (v/v) of FAME. It should be emphasized that bigger differences can be expected if FAME concentration is below 10% (v/v). Fig. 6 illustrates some samples of low concentration of FAME and their high dispersion around the calibration line, especially if X-ray tube operates at 45 kV and 700 μA. The mean difference between the results of FT-IR and XRS is ca. 1.76% (v/v) of FAME if rhodium target X-ray tube operates at 35 kV and 1300 μA. To improve the accuracy of analysis, separate calibration can be performed for this region. If calibration is performed in the range of 0–10% (v/v) of FAME, then the mean difference between the results of FT-IR and XRS is ca. 0.75% (v/v). Although the improvement is significant, the relative error can reach rather high value especially for very low concentration of FAME. The results obtained for X-ray tube operated at 45 kV, 700 μA and 35 kV, 1300 μA show that precision of measurements is the crucial issue in this type of analysis. Fig. 9 presents the relationship between standard deviation of measurement and concentration of FAME for counting time of 600 s. The average standard deviations of measurements are 0.56 and 0.46% (v/v) of FAME for X-ray tube operated at 45 kV, 700 μA and 35 kV, 1300 μA. As expected, lower standard deviation can be obtained if higher intensity of primary radiation and SDD are applied. Then, the average standard deviations of measurements can be down to 0.20% (v/v) of FAME for 600 s counting time. Thus, much better results in the low FAME concentration range can be obtained for higher intensity of primary radiation (e.g. using coarse collimator) and SDD. Nowadays, such detectors are applied in more modern instruments.

4. Conclusions and future perspectives

A new method is proposed for determination of FAME in biodiesel blend, the principle of which is based on difference in the intensity of X-ray radiation scattered from hydrocarbons and from FAME. In view of determination of total amount of FAME in diesel fuel blends, the advantage of the proposed method is its non-specificity. In contrary to IR method, the proposed methodology can be applied for a full range of possible blends (up to 100% of FAME) without any sample treatment (i.e. dilution). The experiments show that coherent and incoherent radiation commonly applied to evaluate the average atomic number of the sample cannot be applied for determination of FAME. In contrary to the coherent and incoherent radiation, the utilization of continuum gives excellent linear correlation between FAME concentration and inverse of radiation intensity.

The investigation shows that the crucial issue in determination of FAME in biodiesel blends by XRS is the precision of the measurements resulting from the counting statistics and appropriate selection of integration window. For concentration of FAME from 10 to 100% (v/v), the differences between FT-IR and XRS do not usually exceed 1% (v/v) of FAME. Higher differences can be expected if FAME concentration is below 10% (v/v). The accuracy of analysis in this concentration range can be improved by applying separate calibration in this region. Nevertheless, the full range of FAME concentration can be covered by improving measurement precision using higher intensity of primary radiation and SDD of high input count rate.

Because XRS is widely used for determination of sulfur in fuels, the proposed method can be base for new analytical strategy of simultaneous elemental analysis and determination of FAME using benchtop EDXRF spectrometer. The proposed method can be also applied for quality control of biodiesel using portable EDXRF spectrometer. The application range of the proposed method can be easily extended in the case of other types of biodiesel development, e.g. for analysis of fatty acid ethyl esters (FAEE) in biodiesel blends.

Patent pending

The proposed method of determination of FAME in biodiesel blend using X-ray spectrometry has been registered (P.394663) in The Patent Office of the Republic of Poland.

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