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Procedure for and results of simultaneous determination of aromatic hydrocarbons and fatty acid methyl esters in diesel fuels by high performance liquid chromatography

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Abstract

The content of aromatic hydrocarbons in diesel fuels is regulated by appropriate standards, and a further reduction in the allowed concentration of these hazardous substances in these fuels is expected. The content of aromatic hydrocarbons in diesel fuels is most often determined using standard methods EN-12916 or ASTM D-6591. The content of polycyclic aromatic hydrocarbons (PAHs) is determined from a single peak obtained using normal phase high-performance liquid chromatography (NP-HPLC), a column of the NH2 type, *n*-heptane as the eluent, refractive index detector (RID) and backflushing of the eluent. However, the methods mentioned above cannot be applied when the fuel contains fatty acid methyl esters (FAME), which lately has become more common. The content of FAME in diesel oils is determined using mid-IR spectrophotometry based on the absorption of carbonyl group. However, no standard procedure for the determination of classes of aromatic hydrocarbons in diesel fuels containing FAME is yet available. The present work describes such a modification of methods EN-12916/ASTM D-6591 that provides a simultaneous determination of individual groups of aromatic hydrocarbons, total content of polycyclic aromatic hydrocarbons and the FAME content in diesel fuels. The refractive index detector (RID) and *n*-heptane as the mobile phase are still used, but backflushing of the eluent is applied after the elution of all polycyclic aromatic hydrocarbons. Additionally, ultraviolet diode array detection is used for the exact determination of low contents of polycyclic aromatic hydrocarbons and to confirm the presence of FAME in the analyzed fuel.

Keywords: Diesel fuels; Simultaneous determination of aromatic hydrocarbons and FAME; Normal phase-high-performance liquid chromatography (NP-HPLC); Refractive index and spectrophotometric detection and determination (RID/UV-DAD)

1. Introduction

Fresh vegetable oils and waste fats of vegetable and animal origin begin to play an important role as a starting material for renewable fuel components in the form of their fatty acid methyl esters (FAME). FAME is mixed with crude oil origin fuel oils in varying ratios. Sometimes it is used instead of the diesel fuel produced from crude oil. In addition, attempts are made to use vegetable oils directly as a diesel fuel. In many countries, diesel fuels already contain up to 30% of FAME. Soon, FAME is to be an essential component of diesel fuel in Poland [1]. At the same time, the allowable content of polycyclic aromatic hydrocarbons in diesel fuels is being limited to 11% and a further reduction in the allowed content of these hazardous compounds is anticipated.

A standard procedure for the determination of FAME in diesel fuels involves mid-IR Fourier transform spectroscopy (FTIR) and makes use of the measurement of intensity of the absorption band of carbonyl bonds [2]. Solid-phase extraction (SPE) can also be used for the determination of total content of FAME in diesel fuels. Such a procedure is described in European standard method PN-EN-ISO 5508 [3], dealing with the quality control of FAME. In this case, SPE is applied for sample preparation in order to determine each type of fatty acid esters by means of gas chromatography (GC). The total content of FAME could

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be determined gravimetrically, following evaporation of solvent, which elutes FAME from the SPE column. However, the procedure would be tedious and potentially erroneous due to the risk of partial evaporation of fatty acids esters.

The literature search reveals two different approaches which could possibly be used for the determination of FAME content in diesel fuels. The first approach involves the determination of individual fatty acid methyl esters in oils. The analysis is then carried out by high resolution capillary gas chromatography with flame ionization detection (GC–FID) [4–10]. The GC–MS technique is used for the identification and determination of each fatty acid ester in FAME, or else only the values of retention times, particularly in the form of Kovats' retention indices and response factors for each fatty acid standard are used. The analysis is time-consuming and tedious, especially when applied to determine the FAME content in diesel fuel. In this case an isolation of the FAME group by SPE (similar to method PN-EN-ISO 5508 [3]) would have to precede the final determination. The second approach makes use of two-dimensional gas chromatography (2D-GC), which is particularly well suited for the separation and determination of very complex mixtures of substances, including the determination of hydrocarbon composition of medium boiling fractions of crude oil, coal distillation products, and FAME [11–15]. This approach could also be used for the identification and determination of each fatty acid methyl ester in diesel fuel and consequently for the determination of total FAME content; however, it would require specialized instrumentation for two-dimensional gas chromatography. The two approaches are advantageous for the determination of individual fatty acids as well as their isomers in oils or fats. By contrast, the total FAME content in diesel fuel can be determined in a faster and simpler way by means of HPLC, using the procedure described in this paper.

At present, the determination of aromatic hydrocarbons in diesel fuels is generally carried out by means of normal phase high-performance liquid chromatography (NP-HPLC) with refractive index detection (RID), NH_2 column, *n*-heptane as the eluent and column backflush. The procedure is adopted from method IP-391 [16] and then transferred to the following standard methods: EN-12916 [17] and ASTM D 6591 [18]. However, the applicability of these standard methods does not include the diesel fuels containing FAME. The procedure described in the present work enables the simultaneous determination of groups of aromatic hydrocarbons and FAME in diesel fuels of crude oil origin, which contain up to 30% of FAME. The procedure makes use of the standard equipment for the determination of groups of aromatic hydrocarbons in diesel fuel according to methods EN-12916 or ASTM D 6591 and IP 391-95. However, two HPLC detectors connected in series are used: the refractive index detector (RID) and the photometric detector, preferably UV-DAD.

The additional UV detector plays a dual role: it determines the point of switching the flow direction of the mobile phase in the column and detects the presence of FAME in the tested sample of diesel fuel. It also enables the determination of FAME content over a range from 0.1%. The UV detector is particularly suitable for the determination of very low contents of polycyclic aromatic hydrocarbons. This detector can also be used to determine the olefin content, when the technology of production of components for the tested diesel fuel is known.

2. Experimental

2.1. Materials

Solvents and eluents: *n*-Heptane for HPLC (Merck, Germany or POCH, Poland).

Calibration standards: Cyclohexane (Merck, Germany), phenanthrene (Fluka, Switzerland), *o*-xylene, 1-methylnaphthalene (Merck, Germany), all of 99.8% or better purity; samples of technical FAME, extracted from rapeseed oil, meeting the requirements of method PN-EN 14213 [6].

Solutions used for calibration and investigations:

- Calibration solutions A–D in *n*-heptane, prepared according to EN 12916 standard method (ASTM D 6591 and IP 391-95) in 50 mL volumetric flasks, and containing cyclohexane, *o*-xylene, 1-methylnaphthalene and phenanthrene with concentrations of individual components ranging from 0.05 to 26.00 mg/mL and FAME with the concentration close to that of *o*-xylene. Concentrations of calibration standards were selected according to recommendations of the above standard methods, allowing the determination of the content of the following groups: mono-aromatics (MA) – up to 50% (m/m), diaromatics (DA) – up to 20% (m/m), polycyclic aromatics (PA) – up to 7.0% (m/m) and FAME up to 30% (m/m).
- Solutions of samples of diesel fuel of crude oil origin (production-LOTOS S.A., Poland), were prepared in 10 mL volumetric flasks using the mobile phase (*n*-heptane) as the solvent. Concentrations: 50.0 mg/mL of diesel oil free of FAME or containing between 1 and 15 mg/mL of FAME. Diesel fuels were produced by hydrorefining and/or hydrocracking "Russian Blend" crude oil and up to 20% "Rozewie" crude oil from the Baltic Sea.
- Samples of other diesel fuels both containing and free of FAME were also used in this work, including about 40 samples of diesel fuels obtained over the 1994–2005 period through participation in the interlaboratory proficiency studies, mostly from the USA.

2.2. Apparatus

A LaChrom Merck-Hitachi (Darmstadt, Germany) gradient liquid chromatograph equipped with a L-7100 four-channel pump, a 7450 A UV–vis diode array detector, an L-7490 refractive index detector, an L-7350 thermostat with a 7350i cooling system, a Rheodyne RH-7725i injection valve with a 20 μL sample loop, a HSM chromatography management software (Merck-Hitachi, Darmstadt, Germany) and a V 7226 six-port two-channel backflush valve (Knauer, Berlin, Germany) to switch the flow direction of the mobile phase, were used in the present work. A LiChrospher NH_2 5 μm (250 mm × 4 mm i.d.; Merck, Darmstadt, Germany) HPLC column was used.

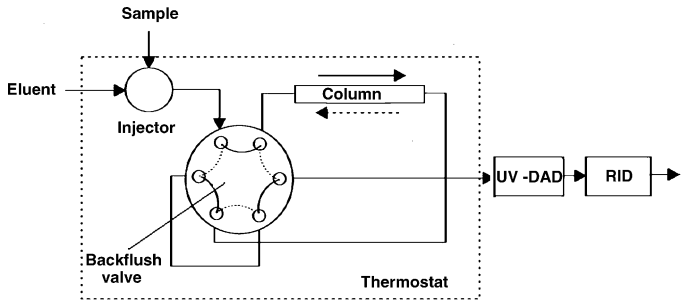

Fig. 1. Schematic diagram of the HPLC apparatus with backflush used for the determination of class composition of diesel fuel: paraffins/olefines/mono-/di-/tri- and above aromatics hydrocarbons/fatty acids methyl esters.

2.3. Procedure

A schematic diagram of the HPLC apparatus is shown in Fig. 1. Two HPLC detectors connected in series were used: ultraviolet-diode array detector followed by RID. The HPLC separation was carried out at 20 °C, using the mobile phase (*n*-heptane) flow rate of 0.8 mL/min. A transport lag time between the detectors was determined experimentally (0.26 min for the flow of 0.8 mL/min). The lag time between the column outlet and the input to the flow cell of the UV-DAD detector was also determined experimentally (8 s).

The retention time of polycyclic aromatic hydrocarbons was determined using the ultraviolet-diode array detector from the UV spectrum over the 200–400 nm range. The elution time of the last group of polycyclic aromatic hydrocarbons present in diesel fuel, reduced by 8 s, was treated as the moment of reversing the flow direction of the mobile phase in the column (backflush point). This procedure ensured elution of all aromatic hydrocarbons from the column and, at the same time, elution of all the FAME components as a single peak. The recovery of FAME using column backflush was determined experimentally and found to be equal to $100.2 \pm 0.4\%$.

Quantitative determination of each group of aromatic hydrocarbons as well as FAME was accomplished using the calibration curve method based on peak areas. Aromatic hydrocarbons were determined using the procedure described in methods EN-12916 or ASTM D-6591. The peak area corresponding to FAME was measured after switching the flow direction (backflush). Standard solutions "A" through "D", used for calibration, contained cyclohexane, *o*-xylene, 1-methylnaphthalene and phenanthrene. In addition, each of the standards contained FAME at concentrations ranging from 0.05 to 30 mg/mL, similar to concentration of *o*-xylene in a given standard solution.

The concentration of hydrocarbons in standard solutions was half of that used in method EN-12916 to compensate for doubling the volume of sample loop (20 μL) compared to the volume provided by the standard method (10 μL). The peak areas were found to be the same for the sample loop volume of 10 μL and standard solutions of concentrations given in the standard method and for the sample loop volume of 20 μL and the concentration of standard solutions reduced in half. The determination of FAME in a sample of diesel fuel involves switching of the flow direction following elution of all polycyclic aromatic hydrocarbons from the column and results in a single chromatographic peak corresponding to FAME. The sum of peak areas corresponding to each group of aromatic hydrocarbons as well as the FAME peak area are compared with the calibration data. The obtained results are converted to the content of individual classes of aromatic hydrocarbons (expressed in terms of the content of *o*-xylene, 1-methylnaphthalene, and phenanthrene according to method EN-12916) and FAME. Each result is the average of at least three measurements after application of the Q test at the 95% confidence level to reject outliers.

3. Results and discussion

The slopes of calibration curves along with the linear correlation coefficients for linear regression with a forced zero intercept are presented in Table 1. The calibration curves were forced through zero because the intercept values were very close to zero. This allowed reducing the number of calibration points by one and improving the accuracy of determination of low concentrations of FAME. The data were obtained using a refractive index detector (RID) for: *o*-xylene (monoaromatics, MA), 1-methylnaphthalene (diaromatics, DA), phenanthrene (tri-aromatics and above, PA) and for FAME. The calibration data for the ultraviolet-diode array detector for polycyclic aromatics (at a wavelength 260 nm) and for FAME (wavelength 210 nm) are also included in Table 1. Inspection of the data in Table 1 reveals that the peak areas in chromatograms obtained using both refractive index detection as well as UV detection at 210 nm are directly proportional to the concentrations of individual classes of aromatic hydrocarbons and FAME, respectively. Thus, the proposed procedure ensures linearity for all classes of aromatic hydrocarbons determined using refractive index detection and the linearity has already been established during

Table 1
Calibration data for the simultaneous determination of aromatic hydrocarbons and FAME in diesel oils

Group of compounds	Response factor for the refractive index detector	Correlation coefficient	Response factor for the UV-DAD detector	Correlation coefficient
Aliphatic hydrocarbons	$7.269e^{-6}$	0.9999	–	–
Monoaromatic hydrocarbons	$2.752e^{-6}$	1.0000	–	–
Diaromatic hydrocarbons	$1.503e^{-6}$	0.9999	–	–
Polyaromatic hydrocarbons	$11.39e^{-7}$	0.9986	$1.525e^{-8}$ [a]	0.9999
FAME	$3.742e^{-6}$	0.9995	$1.976e^{-7}$ [b]	0.9981

[a] Response factor determined at 260 nm.
[b] Response factor determined at 210 nm.

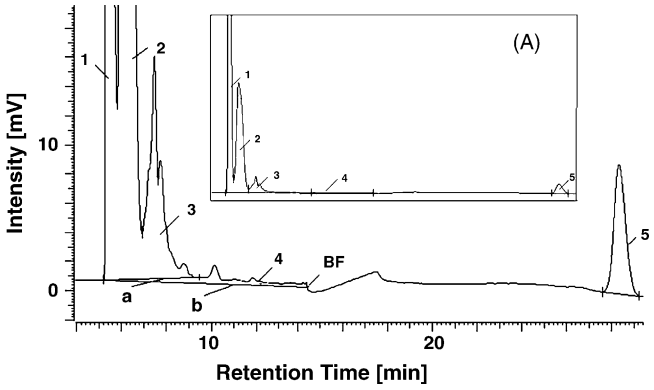

Fig. 2. Typical chromatograms obtained with RID to determine the class composition of diesel fuel (Eurodiesel), containing about 7% (m/m) FAME. Chromatogram shown in insert A has sensitivity lowered by a factor of eight. Column: LiChrospher NH2 5 μm, 250 × 4 mm i.d.; mobile phase flow rate 0.8 mL/min; temperature 20 °C; volume injected 20 μL; sample concentration 0.05 g/mL; backflush point 14 min. Peaks: (1) paraffins + naphthenes + olefins (PNO); (2) monoaromatic hydrocarbons; (3) diaromatic hydrocarbons; (4) polyaromatic hydrocarbons; (5) fatty acid methyl esters (FAME); BF, backflush; lines (a and b) are the baselines for peak integration, leading to different contents of groups of aromatic hydrocarbons: line a, drawn according to the procedure described in method EN 12916 (underestimated content of MA, and particularly of DA); line b, drawn in order to determine the content of PA (at the same time, it allows correct determination of MA and DA; see text for further details).

the development of method IP 391 [4]. Linearity of calibration curves was also confirmed for FAME with the use of both the refractive index and UV detector (at 210 nm) as well as for polycyclic aromatic hydrocarbons determined at 260 nm.

A typical HPLC-RID chromatogram of group-type separation for low-sulfur diesel fuel produced by LOTOS S.A. (sulfur content below 50 ppm) with an addition of about 6% (m/m) FAME is shown in Fig. 2. The purpose of column backflush is to elute strongly retained components as a single peak (the same way it is accomplished in method EN 12916 for polyaromatic hydrocarbons, but this time FAME are eluted as the "last" group). In general, backflush is used to elute those sample components which are soluble in the mobile phase, but undergo strong sorption in the stationary phase. After introducing onto the column a sample of diesel fuel containing FAME, all hydrocarbon components of the sample are eluted directly, whereas fatty acid methyl esters are strongly sorbed on the column packing and require backflush to be eluted from the column as a single peak. The retention time of the FAME peak is twice that of backflush point.

Two alternative ways of drawing baseline for peak integration (lines a and b) are depicted in Fig. 2. Line (a) corresponds to integration performed according to the recommendations of method EN 12916 (IP 391-95), whereas line (b) corresponds to integration used in the present work (drop integration from the end of line (a) to the end of line (b)—group of peaks labeled 4). It follows from Fig. 2 that the integration method recommended by method EN 12916 (IP 391-95 or ASTM D-6591) results in underestimated contents of monocyclic aromatic hydrocarbons and, to an even greater extent, in low content of dicyclic hydrocarbons (baseline (a) in Fig. 2). The procedure proposed in this work requires a different mode of integration (baseline (b) in Fig. 2), thus allowing correct determination of the contents of groups DA and MA. The difference in content of mono- and dicyclic aromatic hydrocarbons, resulting from the two different modes of peak integration for typical diesel oil is 0.08 and 0.25%, respectively, which amounts to 0.5 and 5% of relative content of the respective groups in a sample of diesel fuel. In addition, Fig. 2A shows a chromatogram obtained for the same sample of diesel fuel, but at a lower sensitivity of the RID detector. Such chromatograms are often included in reports with the results of determination of group composition of diesel fuels.

The difference between true content (determined from the signal of UV-DAD) and approximate content of polycyclic aromatic hydrocarbons (determined using the RID) can amount to about 0.1% by mass which is ca. 20% of the relative content of this group of hydrocarbons in diesel fuel. The values obtained using the UV detector at 260 nm do not deviate by more than ±5 relative percent from the concentration determined using method EN 12916 (switch of flow direction following the elution of dicyclic aromatic hydrocarbons).

A UV-DAD chromatogram of a sample of the same diesel fuel with an addition of FAME is presented in Fig. 3. Inspection

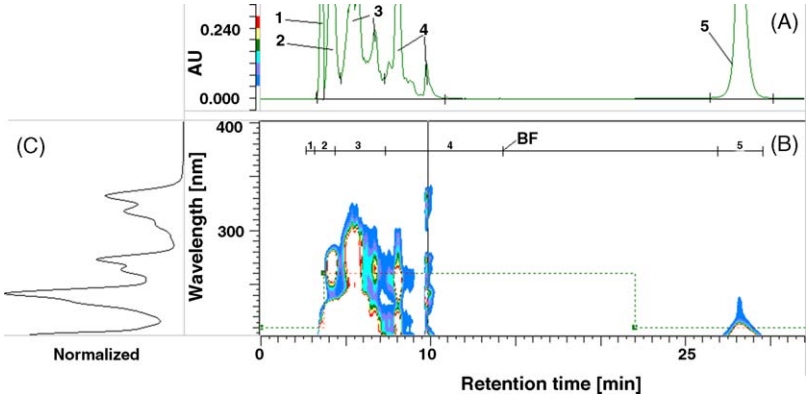

Fig. 3. Separation of diesel fuel EuroDiesel containing about 7% FAME. For chromatographic conditions, see Fig. 2. (A) UV-DAD chromatogram with programmed wavelength (210, 260 and 210 nm), marked with dotted line in (B); (B) three-dimensional UV-DAD chromatogram; (C) spectrum of the group of pyrene derivatives with the retention time of about 12 min, characteristic of diesel fuels obtained by catalytic hydrocracking. For peak labels, see Fig. 2.

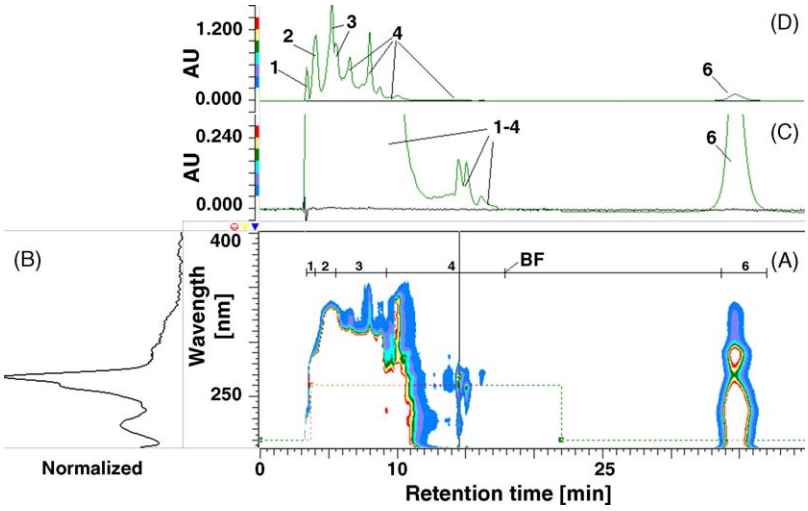

Fig. 4. UV-DAD chromatogram for diesel fuel produced by catalytic hydrorefining, free of FAME, but containing chrysene and its derivatives and also a substantial concentration of resins. (A) Three-dimensional UV-DAD chromatogram; (B) UV spectrum of chrysene and its alkyl derivatives; (C) so-called best chromatogram, obtained using the wavelength program as in Fig. 3, but at a 10 times higher sensitivity; (D) chromatogram as in (C), but at about 50 times lower sensitivity. Chromatographic conditions and peak labels as in Figs. 2 and 3, except for peak 4—chrysene and its alkyl derivatives.

of the chromatogram reveals that using so-called peak grouping obtained at 260 nm, the content of tri- and polycyclic aromatic hydrocarbons can be determined much more accurately and with better precision than with application of the RID detector. Fig. 3 also demonstrates the advisability of horizontal drawing of the integration baseline. Fig. 3B and C reveal that the tested diesel oil also contains pyrene derivatives. Careful inspection of the spectra shows a low content of unsubstituted pyrene as well. This is characteristic of diesel fuels obtained through hydrocracking. These substances do not occur in diesel fuels obtained as a result of hydrorefining.

Diesel fuels of crude oil origin always contain aromatic hydrocarbons-derivatives of phenanthrene and anthracene. Some types of diesel fuels also contain derivatives of pyrene (Fig. 3) and, sometimes, of chrysene (Fig. 4). The use of ultraviolet-diode array detection and monitoring the UV spectra to detect trace concentrations of these groups of aromatic hydrocarbons allows correct determination of the backflush point. The elution of all polycyclic aromatic hydrocarbons must take place before reversing the flow direction of eluent in the column in order to avoid interference of polyaromatics with FAME. Diesel fuels stored for a long period of time or containing straight fractions from distillation of crude oil (without hydrorefining and/or hydrocracking) may contain resins, whose peak can overlap with that of FAME. When using the procedure outlined in method EN 12916, the resin peak can overlap with that of polyaromatics. This can result in high results for the content of FAME in diesel fuel (and of the content of PA if the flow direction is switched after elution of diaromatic hydrocarbons).

The investigations described in this paper revealed that the content of resins in hydrorefined diesel fuel stored for about 3 years can correspond to about 0.5% by mass of the FAME content. Chromatograms of diesel fuel, which does not contain FAME, but was stored for 3 years, are shown in Fig. 4. Chromatograms A and C in Fig. 4 (three-dimensional (A) and with programmed wavelength at 260 and 210 nm (C)) were obtained using the UV-DAD at a very high sensitivity. A chromatogram with the wavelength programmed at 260 and 210 nm at a very low sensitivity setting is shown in Fig. 4D, while the spectrum of chrysene or its alkyl derivatives is depicted in Fig. 4B. In practice, the error due to overestimating the content of FAME in diesel fuels as a result of high content of resins (and possible overestimation of the content of polyaromatics in case of method EN 12916 (or ASTM D-65910)) can be ignored, because the FAME content in diesel fuel typically exceeds 10% by mass and then the contribution of resins to the FAME peak is small (less than 5% of the FAME content). At the same time, diesel fuels, which have been stored for a long time and thus contain a measurable content of resins, are seldom analyzed.

Comparison of three-dimensional chromatographic peaks obtained with backflushing of the eluent and shown in Figs. 3–5b reveals that it is easy to distinguish the asymmetric peak observed at up to about 220 nm and attributed to FAME from those attributed to resins. The latter peaks appear either in the region up to 250 nm (Fig. 3) or up to 350 nm (Fig. 4), depending on the UV-DAD sensitivity. It is apparent from the chromatograms that the samples of diesel fuel, whose chromatograms are shown in Figs. 3 and 5a, contain FAME, whereas the samples in Figs. 4 and 5b do not. The UV spectra over the 200–380 nm range corresponding to the maxima of peaks 5 and 6 from Fig. 5a and b, respectively, are shown in Fig. 6 (spectra 1a and 1b in Fig. 6 are those of FAME and 2a and 2b are those of resins). It is apparent that the FAME content of (6% by mass—peak 5 in Fig. 5a) is affected only slightly by the peak of resins in diesel fuel after hydrorefining (peak 6 in Fig. 5b).

A comparison of the spectra in Fig. 6 also shows that the identification of FAME and resins in diesel oil can be accomplished not only by using the ultraviolet-diode array detector—on the

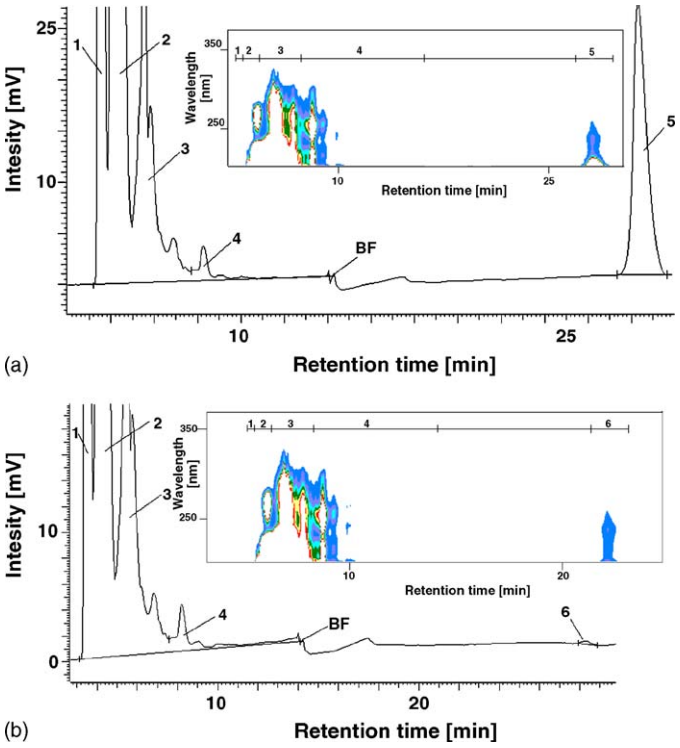

Fig. 5. RID and three-dimensional UV-DAD (insert) chromatograms of reference diesel fuel, stored for 2 years at room temperature. (a) Diesel fuel containing ca. 7% FAME; (b) diesel fuel free of FAME, but containing a substantial content of polar compounds. Separation conditions, integration baselines and labels of chromatographic peaks as in Fig. 2, except for peak 5—polar substances, so-called resins (R).

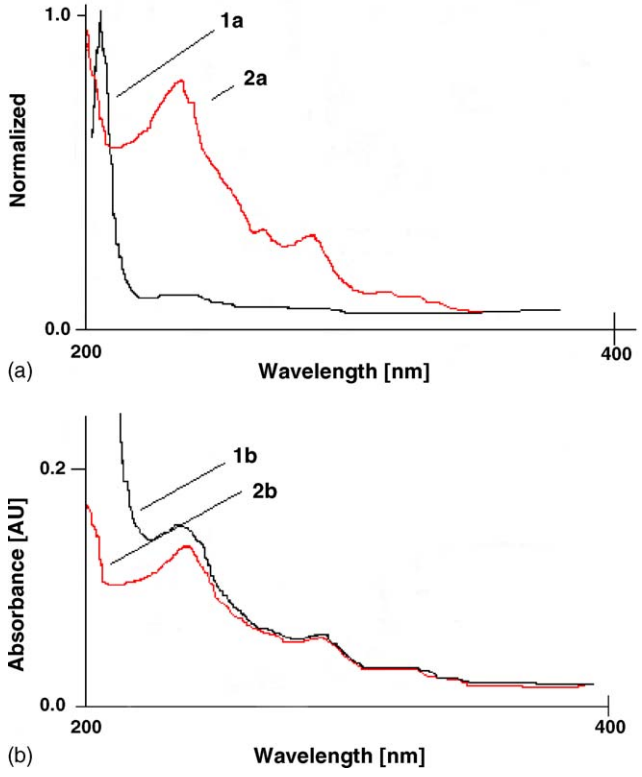

Fig. 6. UV spectra corresponding to the peak maximum of compounds eluted using backflush. (1a and 1b) FAME spectra; (2a and 2b) resin spectra; (6a) normalized spectra (see text for explanation) and (6b) raw spectra.

basis of 3D chromatogram obtained with the flow direction switching in the HPLC column (high absorbance and asymmetry of the peak over the 200–220 nm range). A variable-wavelength UV detector allowing acquisition of a UV spectrum for the band of substances eluted under backflush conditions can be used instead. The peak attributed to FAME can be readily distinguished from the resin peak or the presence of both groups established based upon the UV spectrum over the 200–380 nm range (Fig. 6a and b). The normalized spectrum (the largest absorbance is assigned a value of 1) shown in Fig. 6a is particularly useful, as it reveals that FAME strongly absorb UV radiation at wavelengths below 215 nm, while resins have a negligible absorbance in this region. However, for samples of diesel oil with high content of resins and low content of FAME, quantitative determination of the two groups using the above approach would be inaccurate. In this case, it would be preferable to solve a system of equations for the absorbance at 210 and 240 nm using approximate values of experimentally determined molar absorptivities of FAME and resins. However, such calculations are usually not required in analytical practice. Fig. 3C (spectrum corresponding to peak 4 with the retention time of 12 min) and Fig. 4 (peaks with retention times ranging from 13.5 to 16.5 min as well as the chrysene spectrum in Fig. 4B) reveal that the investigated diesel fuels can contain the alkyl derivatives of pyrene and possibly unsubstituted pyrene or even alkyl derivatives of chrysene and chrysene. In the analysis of such diesel fuels, the backflush point should be increased to about 14 min or even to about 17 min to ensure complete elution from the column of polycyclic aromatic hydrocarbons prior to switching the flow direction.

This study demonstrated that the calibration curve for tri- and polycyclic aromatic hydrocarbons should be prepared using phenanthrene and the UV detection at 260 nm. The variability of response factors for polycyclic aromatic hydrocarbons (UV detection at 260 nm) determined in a large number of different diesel fuels (about 50), both produced by LOTOS and obtained over the period 1994–2005 through participation in the interlaboratory proficiency studies organized by ASTM, did not exceed ±2.5%. Thus, the use of UV detection can significantly improve the accuracy and precision of determination of low concentrations of polycyclic aromatic hydrocarbons compared with the refractive index detection. The elution of this group of hydrocarbons as a single peak, according to method EN-12916 and using the RID detector allows the determination of low PA content; however, FAME cannot be determined at the same time, so the investigated diesel fuel cannot contain FAME. Inspection of Figs. 3 and 4 reveals that the peak heights of polycyclic aromatic hydrocarbons obtained by using the UV detection at 260 nm are significantly higher than those obtained with the RI detector (cf. Fig. 2). Without elution of this group of hydrocarbons as a single peak and using backflush, the detection limits for polycyclic aromatic hydrocarbons are 0.01 and 0.5% by mass for the UV and RI detection, respectively.

It should be pointed out that for samples of diesel fuel containing high concentrations of tri- and polycyclic aromatic hydrocarbons (above 2.5% PA), it could prove necessary to dilute the sample introduced into the HPLC column below 0.5 g/mL hep-

tane to ensure that none of the peaks exceeds the upper detection limit and the linear dynamic range of the UV detector.

The possibility of using a similar calibration procedure making use of the UV detector at 260 nm and other wavelengths to determine low contents of mono- and diaromatic hydrocarbons in diesel fuel was also investigated. However, the values of response factors for these groups of aromatic hydrocarbons in the UV region depend to a large extent on the technology of production of diesel fuel and on the origin of crude oil, from which this diesel oil was obtained. For this reason, the detection conditions providing the same values of response factors for these two groups of hydrocarbons and for all types of diesel oils could not be found. The obtained results indicate that peak integration over the 210–250 nm wavelength range could be helpful, as it appeared to be effective in the determination of olefin content in gasoline [21]. However, further work is required. This approach would be useful only for the determination of very low contents of these groups of hydrocarbons in diesel oils.

4. Conclusions

This work presents the procedure for simultaneous determination of content of aromatic hydrocarbons groups and of FAME in diesel fuels of petroleum origin, which contain FAME using normal phase high-performance liquid chromatography (NH_2 HPLC column) with two detectors connected in series: UV-DAD followed by RID. Elution of all the FAME components as a single peak obtained using column backflush The backflush valve should be switched after the time corresponding to elution of the entire group of tri- and polycyclic aromatic hydrocarbons reduced by lag time between the column outlet and the input to the flow cell of ultraviolet-diode array. If diesel oils of increased concentration of sulfur compounds contain pyrene and its derivatives as well as chrysene and its derivatives, the backflush valve should be switched after elution of the peaks of these substances.

In diesel fuels with a high content of polycyclic aromatic hydrocarbons (i.e. over 0.5% by mass), the content of this group can be determined using the refractive index detector (RID) without backflush. However, the present work demonstrated that the response factors for polycyclic aromatic hydrocarbons, obtained with the use of the UV detector at 260 nm, are independent of either the technology of production of diesel fuel components or the origin of crude oil, from which the fuel was produced. At the same time, the sensitivity of UV detector is much higher for this group of substances than the sensitivity of the refractive index detector. The UV detection at 260 nm is preferred in case of simultaneous determination of polycyclic aromatic hydrocarbons and FAME. In this case, the backflush valve should be switched after elution of polycyclic aromatic hydrocarbons. The UV detection provides a considerably higher accuracy and precision than the refractive index detection. The detection limits for polycyclic aromatic hydrocarbons when using the ultraviolet-diode array detector and the RID detector are about 0.01 and 0.3%, respectively. The determination of content of mono- and diaromatic hydrocarbons using UV detection at 260 nm or at other wavelengths is not recommended because the response factors for these groups of hydrocarbons are strongly dependent on the technology of production of diesel fuel and on the source of origin of crude oil, from which the diesel fuel was obtained.

The use of ultraviolet-diode array detector in series with the refractive index detector for the determination of content of aromatic hydrocarbons and FAME in diesel fuels is advantageous, because it provides correct and precise determination of the backflush point in the HPLC column, confirmation of the presence of fatty acid methyl esters, and detection of the presence of resins, occurring as a result of long-term storage and determination of their content as well as their distinction from FAME.

The method of peak integration for mono- and dicyclic aromatic hydrocarbons recommended in method EN-12916 (line (a) in Fig. 2) results in a slight underestimation of the content of monoaromatic hydrocarbons and in a somewhat higher underestimation of the content of diaromatic hydrocarbons. The integration procedure suggested in the present work ensures correct determination of individual groups of aromatic hydrocarbons in diesel fuel (line (b) in Fig. 2).

The advantage of the procedure proposed in this work is the possibility of using standard laboratory instrumentation for the simultaneous determination of groups of aromatic hydrocarbons and FAME. This instrumentation (except for UV-DAD) is already available in refinery laboratories for the determination of group composition of diesel oils free of FAME according to method EN 12916 (ASTM D-6591) [17,18], and for the determination of aromatic hydrocarbons in jet fuel (JET A1) according to method ASTM D-6379.

References

[1] Liquid Eco-Fuels and Eco—Components for their Production Bill, 24 July 2002—the Sejm Publication no. 760.
[2] PN-EN 14078 Standard, Liquid petroleum products, Determination of fatty acid methyl esters (FAME) in medium distillates—the IR spectroscopy method.
[3] PN-EN-ISO 5508 Standard, Fatty acid methyl esters, analysis in oils, vegetable and animal fats—GC method.
[4] D. Nightingale, J.B. Blumberg, G.J. Handelman, J. Chromatogr. A 732 (1999) 495.
[5] R.O. Adolf, J. Chromatogr. A 1033 (2004) 369.
[6] M. Schreiner, H.W. Hulan, J. Chromatogr. A 1045 (2004) 197.
[7] R.O. Adolf, J. Chromatogr. A 764 (1997) 337.
[8] J.A.G. Roach, M.M. Mossoba, M.P. Yurawecz, J.K.G. Kramer, Anal. Chim. Acta 465 (2002) 207.
[9] F.J. Senorans, E. Ibunez, Anal. Chim. Acta 465 (2002) 132.
[10] S.H. Chen, Y.J. Chuang, Anal. Chim. Acta 465 (2002) 145.
[11] J. Beens, U.A.Th. Brinkman, Trends Anal. Chem. 19 (4) (2000) 260.
[12] L. Mondello, A. Casilli, P.Q. Tranchida, P. Dugo, G. Dugo, J. Chromatogr. A 1019 (2003) 187.
[13] H.G. Janssen, W. Boers, H. Steenbergen, R. Horsten, E. Floter, J. Chromatogr. A 1000 (2003) 385.
[14] H.J. Geus, I. Aidos, J. Boer, J.B. Luten, U.A.Th. Brinkman, J. Chromatogr. A 910 (2001) 95.
[15] S.A. Mjos, J. Chromatogr. A 1061 (2004) 201.
[16] IP 391-95 Standard, Petroleum products – determination of aromatic hydrocarbon types middle distillates – high-performance liquid

chromatography method with refractive index detection, Institute of Petroleum, United States, 1995.
[17] PN-EN Standard-12916, Petroleum products – determination of aromatic hydrocarbon types in middle distillates – high-performance liquid chromatography method with refractive index detection, Polish Standards Committee, Wydawnictwo Ars Boni Sp.zo.o, Warszawa, 2003.
[18] ASTM D-6591 Standard, Standard test method for determination of aromatic hydrocarbon types in middle distillates – high-performance liquid chromatography method with refractive index detection, ASTM International, United States, 2001.
[21] M. Kamiński, R. Kartanowicz, A. Przyjazny, J. Chromatogr. A 1029 (2004) 77.