Application of high-performance liquid chromatography with ultraviolet diode array detection and refractive index detection to the determination of class composition and to the analysis of gasoline

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Abstract

A method of effective application of normal-phase high-performance liquid chromatography (NP-HPLC) with ultraviolet diode array detection (DAD) and refractive index detection (RID) for the determination of class composition of gasoline and its components, i.e. for the determination of content of alkenes, aromatic and saturated hydrocarbons in gasoline meeting modern quality standards, has been developed. An aminopropyl-bonded silica stationary phase was used along with *n*-hexane or *n*-heptane as the mobile phase. A DAD signal integrated over the 207–240 nm range was used to determine alkenes. This eliminates the necessity of separating alkenes from saturates, because the latter do not absorb UV radiation above 200 nm. The content of aromatic hydrocarbons is determined by means of a refractive index detector. Calibration was based on hydrocarbon type composition determined by the fluorescent indicator adsorption method, ASTM D1319. The results obtained by the developed method were found to be consistent with those obtained by fluorescent indicator adsorption or by a multidimensional GC method (PIONA) (ASTM D5443). The method can be applied to gasoline meeting recent quality standards, irrespective of refining technology used in the production of gasoline components, including gasoline with various contents of oxygenates. The developed method cannot be used to determine the hydrocarbon type composition of gasoline that contains as a component the so-called pyrocondensate, i.e. the fraction with a boiling point up to 220 °C, obtained through thermal pyrolysis of distillation residues of crude oil or coal and, consequently, does not meet the quality standards. The paper includes the procedure for identification of this type of gasoline.
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1. Introduction

Finished gasoline is a mixture of light hydrocarbons with a boiling point up to 220 °C. Fractions with the boiling point of gasoline obtained through atmospheric distillation of crude oil do not meet modern quality standards. Therefore, the production of gasoline is based on mixing several components obtained in different refining processes of crude oil and sometimes also components being waste in petrochemical processes. The former are primarily the products of such processes as hydrofinishing, alkylation, catalytic cracking, hydrocracking, catalytic reforming and isomer-

ization. As a result, the main components of gasoline are: *n*- and especially isoalkanes, cyclic hydrocarbons (naphthenes), alkenes, alkylated monoaromatic hydrocarbons with a small fraction of bicyclic aromatic hydrocarbons, oxygenates, such as ethanol, methanol, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) as well as small amounts of quality-improving additives. Modern gasoline is subject to strict specifications determining, among other things, the maximum total content of aromatic compounds and alkenes, benzene, oxygenates and other components in gasoline [1]. The group composition of gasoline is now determined using several standard analytical methods. The most common method is the fluorescent indicator adsorption method (ASTM D1319) [2], which can be described as a displacement liquid chromatography. Multidimensional

GC (ASTM D5443) [3], or Reformulyzer prEN Method 14517 [4], as well as supercritical-fluid chromatography (ASTM D6550) [5] are also used. In addition, GC is applied to the determination of selected gasoline components, e.g. benzene, toluene, and xylenes (BTX) and C_{9+} aromatic hydrocarbons (ASTM D5580) [6], which after performing calibration for the C_8 group allows the determination of total content aromatic compounds in gasoline. Correlation methods using near infrared (NIR) spectroscopy or, less often, mid-IR Fourier transform spectroscopy and NMR are also employed for the determination of individual components as well as the class composition of gasoline [7–9]. Consistency of the results obtained by several of the above methods has been reported in the literature [10,11].

Among the standard methods of class determination mentioned above, the fluorescent indicator adsorption method is still used most commonly. It is an absolute analytical method and is therefore considered a benchmark method, even though its poor precision, tediousness and time consumption are generally known. The determination takes about an hour and is relatively expensive as a result of the need for using each time two new columns packed with freshly activated silica gel.

There is a number of papers dealing with the application of HPLC and a refractive index detector, a dielectric constant detector or an infrared detector for the determination of class composition of gasoline [12–21]. In general, the principle of these methods involves separation of gasoline in an HPLC column into three groups, i.e., saturated compounds, alkenes and aromatic compounds. Activated silica gel with a high specific surface area and eluents with a very low eluent strength, such as fluoroalkanes ($\varepsilon^0 < 0$), dehydrated *n*-pentane or *n*-hexane ($\varepsilon^0 = 0$), are used primarily to achieve such a class separation. Silica gel or a strong cation exchanger modified with silver ions and a second eluent with somewhat higher eluent strength have been used to separate alkenes from other types of hydrocarbons [19,20]. Under these conditions, the degree of separation depends strongly on the water content of the eluent and on the activity of the column packing. Consequently, repeatability and accuracy of the determinations are unsatisfactory and none of the methods has been adopted as a standard method. The disadvantages of fluoroalkanes as the eluent are both their high price and high ecotoxicity. In addition, as pointed out by Miller et al. [21], there is a substantial differentiation in the refractive index value among *n*-alkanes, isoalkanes, cycloalkanes and alkenes dependent on their geometric structure and the number of carbon atoms in a hydrocarbon molecule, which can result in substantial uncertainty in the results of determination of these types of hydrocarbons when using a refractive index detector.

Several papers have also been published on the determination of class composition of gasoline using reversed-phase HPLC and UV detection [22,23]; however, these methods can only be used for specific types of gasoline and have no universal application.

The aim of this paper is to present a simple and effective procedure using normal-phase high-performance liquid chromatography (NP-HPLC) with ultraviolet diode array detection (DAD) and refractive index detection (RID) for the determination of class composition of gasoline and gasoline components, including saturated hydrocarbons, alkenes and aromatic compounds. The following assumptions were made:

(1) The determination of content of aromatic compounds in gasoline can be done the same way as in methods IP-391 or EN-12916 [24,25], i.e., using RID. A small variability of refractive index of aromatic hydrocarbons occurring in gasoline allows this assumption to be made.
(2) Separation of saturated compounds from alkenes is not necessary, because saturated compounds do not absorb UV radiation above 200 nm and the total integrated absorbance of alkenes in the UV region can most likely be correlated with their content in gasoline.
(3) The content of saturated hydrocarbons can be calculated as the complement to 100%, following the determination and taking into account so-called oxygenates.

2. Experimental

2.1. Materials

n-Hexane and *n*-heptane for HPLC (Merck, Darmstadt, Germany) with a water content of about 20 mg/l or less (determined by the Karl Fischer method) were used as the mobile phase. Standard hydrocarbons (analytical reagent grade) were purchased from two suppliers (Merck, Darmstadt, Germany; POCh, Gliwice, Poland).

2.2. Samples

About two hundred samples of different gasoline were used in the investigations. These included reference gasoline obtained through participation in the interlaboratory proficiency studies organized by ASTM, gasoline with different content of oxygenates as well as several samples of components presently or previously used for the production of gasoline, i.e., raw and hydrofinished fractions from atmospheric distillation of crude oil, the products of catalytic reforming, cracking or hydrocracking, alkylation and isomerization, obtained under various refining conditions and using various refining technologies, and sometimes also waste products from petrochemical processes and so-called pyrocondensate. In addition, "reference gasoline", prepared by mixing individual hydrocarbons, was also used.

In all the HPLC determinations, the concentration of gasoline in the sample was about 1% (v/v) when the alkenes content in a gasoline was less than 10% (v/v), while for the

components and gasoline with the alkenes content greater than 10% (v/v), the concentration of gasoline solutions was about 0.2% (v/v). The solutions were made as follows: 9.0 ml of the eluent were added to a 10 ml volumetric flask weighed on an analytical balance. Next, 100 μl or 20 μl of a gasoline were injected beneath the eluent surface using a 100 μl or a 20 μl gas-tight syringe, respectively, the flask reweighed, and the volume was made up to 10.0 ml with the eluent, followed by another weighing. The true volume concentration of gasoline was then calculated from the weighing data, mass of gasoline and eluent, and their densities. Care was taken to ensure that both the gasoline and the eluent (solvent) had the same known temperature.

2.3. Apparatus

A Merck–Hitachi (Darmstadt, Germany) gradient liquid chromatograph equipped with a L-7100 four-channel pump, a 7450A UV-Vis diode array detector, a RID 7490 refractive index detector, a 7350 thermostat with a 7350i cooling system, a Rheodyne model RH-7725i injector with a 20 μl sample loop, a V7226 six-port two-channel backflush valve (Knauer, Berlin, Germany) to switch the flow direction of the mobile phase, were used in the present work. Two HPLC columns were used: LiChrospher NH$_2$ 5 μm (250 mm × 4 mm i.d.; Merck) and Spherisorb S3 NH$_2$ 3 μm (250 mm × 4.6 mm i.d.; Waters, Milford, MA, USA). Stainless steel capillaries with an inside diameter of 0.12 mm and a length less than 0.5 m were used to connect the backflush valve to the HPLC column and the injection valve. A schematic diagram of the HPLC apparatus is shown in Fig. 1.

A multidimensional gas chromatograph (AC Analytical Controls, Rotterdam, The Netherlands), configured as a PIONA analyzer, was also used in the investigations.

2.4. Procedures

2.4.1. Fluorescent indicator adsorption

For each gasoline or gasoline component sample, the total content of saturated hydrocarbons, alkenes and aromatic compounds was determined by the fluorescent indicator adsorption method according to the procedure described in ASTM standard method D1319.

2.4.2. Multidimensional gas chromatography (PIONA)

For many samples of gasoline and gasoline components, the total content of saturated hydrocarbons, alkenes and aromatic compounds was determined by multidimensional GC configured for PIONA, according to the ASTM standard D5443.

2.4.3. HPLC

The HPLC separation was carried out at 20 °C, using the mobile phase flow rate of 1.0 ml/min (n-hexane or n-heptane). A HPLC–DAD chromatogram of gasoline recorded without backflush was used to determine the moment of reversing the flow direction of the mobile phase in the column (backflush point). During the determination of class composition of gasoline, the backflush valve was switched immediately after the elution of paraffins and alkenes, but prior to the elution of monocyclic aromatic hydrocarbons. In this way, the elution of all aromatic compounds and polar gasoline components, such as ethanol or other oxygenates, in the form of one zone was ensured. The HPLC column used for this purpose must ensure complete separation of alkenes from monocyclic aromatic hydrocarbons. In practice, an aminopropyl-bonded silica column with such a selectivity that the resolution R_s for the peaks of cyclohexane and o-xylene, calculated from a HPLC–RID chromatogram is greater than 5.0, is sufficient.

A DAD system in the absorbance integration mode from 207 to 240 nm was used for the determination of alkenes. Correlation between the UV detector signal at specific wavelengths: 210, 216 and 225 nm, and the alkenes content was also investigated. A refractive index detector was used to determine the aromatic hydrocarbons.

The elution order of the alkenes was determined using standards [26]. Due to a limited number of standards available, the literature data on retention and range of absorbance of UV radiation by various low-molecular-mass alkenes were also used [27–29].
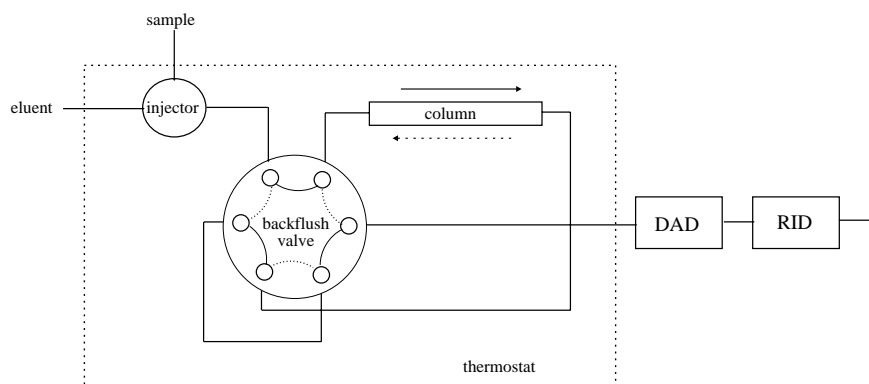

Fig. 1. Schematic diagram of the HPLC apparatus with backflush used for the determination of class composition of gasoline.

Calibration of the method of determination of class content was based on at least 15 various gasoline and gasoline components samples, for which the content of saturated hydrocarbons, alkenes and aromatic hydrocarbons was determined at least twice by the fluorescent indicator adsorption method. Calibration coefficients for alkenes and aromatics were determined from the dependence of peak areas on the volume content (% (v/v)) of the investigated group of hydrocarbons.

3. Results and discussion

Integration over the 207–240 nm wavelength range ensures acquisition of the signal from all alkenes present in gasoline, i.e., monoalkenes and isolated dienes, having somewhat different regions of UV absorption. While the UV absorbance of monoalkenes approaches zero at ca. 220 nm, non-conjugated and conjugated dienes absorb UV radiation up to ca. 240 and 260 nm, respectively [27,28]. The DAD signal obtained in the signal integration mode over the 207–240 nm range was found to be proportional to the total alkenes content in gasoline and in such gasoline components as: the products of fluid catalytic cracking (FCC), catalytic hydrocracking (CHC), continuous catalytic reforming (CCR) or hydrofinishing as well in the gasoline fractions of crude oil. This most likely results from the fact that the molar absorptivity values of low-molecular-weight alkenes in typical gasoline depend only weakly on the structure and the number of carbon atoms in alkenes molecules. The wavelength range for signal integration for the alkenes was selected in such a way as to ensure the consistency of results obtained by the described method with those obtained by the fluorescent indicator adsorption method. Similar relationships determined for gasolines and their components on the basis of chromatograms obtained at a single wavelength of 210 nm, 216 nm or 225 nm were much less favorable. It was established during calibration of the method that for alkenes the coefficient of determination (R^2) for the calibration curves prepared for single wavelengths were lower than those for the calibration curves obtained using signal integration over the wavelength range of 207–240 nm.

Fig. 2 shows examples of chromatograms for blended gasoline (A and B) and for frequently used gasoline components: reformate (C and D), fluid catalytic cracking product (E and F) and for pyrocondensate (G and H) normally not used for gasoline blending. The latter product is a condensate of volatile hydrocarbons originating in the process of pyrolysis of vacuum residue of crude oil or coal tar, which cannot be presently used as a gasoline component due to the high benzene content (15–25%) as well as the presence of styrene and alkenes with conjugated double bonds. Inspection of integrated HPLC–DAD chromatograms for alkenes reveals that the ratio of content of monoalkenes to isolated dienes varies depending on the kind of gasoline and the content of different components. In spite of this, the determina-
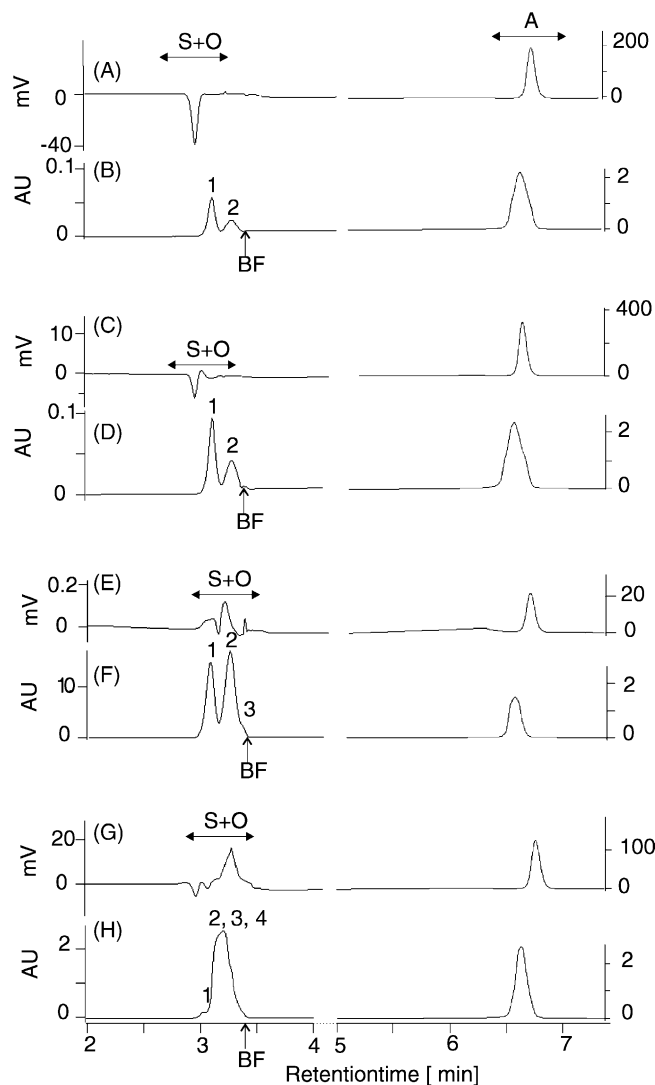

Fig. 2. Chromatograms of gasoline (A and B), gasoline components: product of continuous catalytic reforming—CCR (C and D); product of fluid catalytic cracking—FCC (E and F) and pyrocondensate (G and H). Chromatographic conditions: as described in Section 2; backflush (BF) 3 min 25 s; eluent: *n*-heptane. Chromatograms A, C, E and G were obtained using a refractive index detector, while chromatograms B, D, F and H were obtained using DAD in the integration mode over the range 207–240 nm. Peaks: S + O—saturates + alkenes, elution range 2.9–3.4 min; A—aromatic hydrocarbons, elution range 6.3–6.8 min; 1, monoalkenes; 2, isolated dienes; 3, conjugated dienes; 4, trienes and polyenes (including those with conjugated bonds).

tion of alkenes content was based on the total area of alkenes peaks (peaks 1 and 2 in Fig. 4) and just one response factor was used for the alkenes group. As will be shown further in the text, this approach proved to be fully justified. Refractive index values of saturated hydrocarbons and alkenes present in gasoline strongly depend on their geometric structure and the number of carbon atoms in molecules. Hence, the response of a RID detector depends on the mutual ratio of *n*-alkanes, isoalkanes, cyclic alkanes and alkenes in the analyzed gasoline [21]. An increased content of isoalkanes in gasoline results in negative peaks in RID chromatograms.

On the other hand, an increased content of *n*-alkanes and cyclic alkanes as well as alkenes, result in a positive RID signal. As a result, the determination of total content of saturated compounds and alkenes is not possible when using the refractive index detector.

Refractive indices for alkyl derivatives of benzene, i.e., for monocyclic aromatic hydrocarbons occurring in gasoline, do not significantly depend on the nature or number of alkyl substituents in molecules. In addition, the variability of the values of refractive index for bicyclic aromatic hydrocarbons does not exceed a few percent. At the same time, the ratio of mono- to bicyclic aromatic hydrocarbons in gasoline is approximately constant. Considering the fact that the content of bicyclic aromatic hydrocarbons in gasoline does not exceed several percent, it seems justified to use the refractive index detector for the determination of total content of aromatics in gasoline and also not to use separate calibration for mono- and diaromatic hydrocarbons. Separate calibration for mono- and diaromatic hydrocarbons cannot also be used when the calibration of the method of class determination of gasoline is based on the results obtained by the fluorescent indicator adsorption method, since the latter method enables only the determination of total content of aromatic compounds in the investigated samples of gasoline and the separate determination of content of mono- and diaromatic compounds is impossible.

When determining the class composition of gasoline containing oxygenates, a characteristic decline of the baseline in the form of a broad negative peak is observed in HPLC–RID chromatograms during the elution of aromatic hydrocarbons. This is associated with the elution from the column of MTBE, ethanol (EtOH) and other oxygenates present in gasoline. These substances have lower refractive indices than the mobile phase; hence the negative peak. This baseline decrease is more pronounced when using *n*-heptane as the eluent than when using *n*-hexane. This is due to the fact that the difference in refractive index values between the eluent and oxygenates is greater for *n*-heptane than for *n*-hexane. The existence of baseline decline during the elution of aromatic hydrocarbons allows to confirm the presence of oxygenates in the investigated gasoline and to estimate their content as well as type. A considerable width of the negative peak reveals the presence of alcohols in gasoline, while a relatively narrow negative peak indicates the presence of ethers only. Unfortunately, the baseline dip due to the oxygenates reduces the peak area of aromatics. It was established experimentally that in the case of gasoline samples containing up to 10% of MTBE or up to 5% of EtOH, the underestimation of aromatics depending on their content does not exceed 1% (v/v). When the oxygenates content exceeds 2.5%, a correction of about 0.5% (v/v) or 0.75% (v/v) should be added to the determined content of the aromatics when their content in gasoline is in the 15–30% (v/v) range or higher than 30% (v/v), respectively. Fig. 3 shows an example of HPLC–RID chromatograms for two samples of gasoline containing oxygenates, i.e., MTBE (Fig. 3A) and EtOH (Fig. 3B) as well as
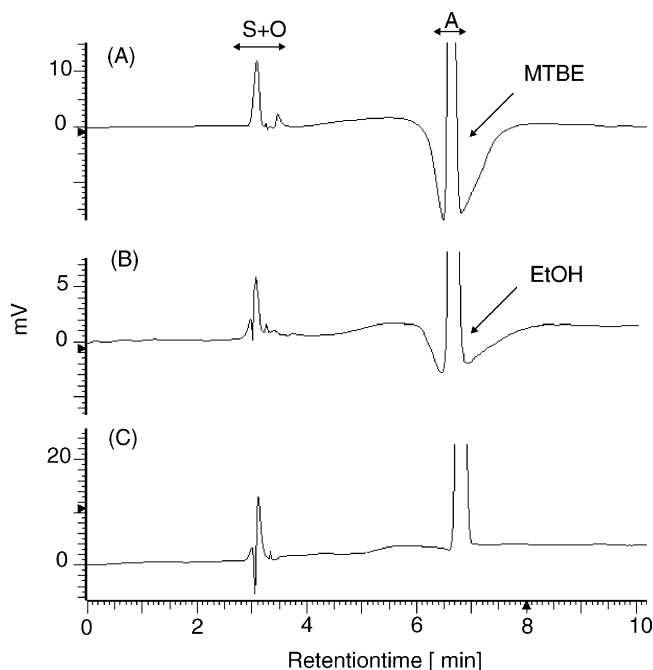

Fig. 3. Chromatograms obtained with RID for gasolines with various content of oxygenates: (A) gasoline with 10% (v/v) MTBE; (B) gasoline with 0.6% (v/v) EtOH and (C) gasoline without oxygenates. Chromatographic conditions: as described in Section 2; backflush (BF) 3 min 25 s; eluent: *n*-hexane. Peak assignment as in Fig. 2.

for gasoline containing no oxygenates (Fig. 3C). The exact determination of kind and concentration of oxygenates in gasoline must be carried out, for instance, by ASTM methods [30–32].

The determination of content of saturates (*S*) in gasoline is based on subtracting from 100% the sum of content of alkenes (*O*), aromatic hydrocarbons (*A*) and oxygenates (Ox), according to the following Eq. (1):

$$S = 100 - (O + A + \text{Ox}) \quad (\% \ (\text{v/v})) \tag{1}$$

3.1. Qualification of gasoline for the determination of class composition based on the identification of some groups of substances in gasoline

The method of determination of class composition of gasoline presented in this paper cannot be applied to gasoline not meeting modern quality standards. This takes place when gasoline contains, among other components, pyrocondensate and has, therefore, high benzene content and contains styrene and other aromatic alkenes or when gasoline has an additive containing ca. 1–3% of conjugated dienes. The method presented herein can also yield inaccurate results for gasoline containing large amounts of naphthalene, biphenyl and their derivatives compared to monoaromatic hydrocarbons. As a rule, the content of diaromatic hydrocarbons in gasoline does not exceed 5% of the content of monoaromatic hydrocarbons and calibration was performed for such gasoline samples only. A

high content of other components usually not used to blend gasoline, such as a straight run fraction of a high aromatic crude oil, can result in inaccurate results of determination of class composition of gasoline using the presented method.

In case of a gasoline with a completely unknown origin, the applicability of the presented method to the determination of class composition can always be tested by using the ASTM method D1319 (FIA) and comparing the results obtained. However, an alternative procedure using HPLC was also developed that allows avoiding erroneous determination of class composition of gasoline samples of unknown origin and composition. To this end, a preliminary identification and qualification of the gasoline under study as being suitable for the determination of class composition by the developed method should be carried out without switching the backflush valve. The qualification criteria were established for alkenes and, additionally, for aromatic hydrocarbons, using three-dimensional HPLC–DAD chromatograms, the examples of which are shown in Fig. 4. An inspection of the chromatogram for pyrocondensate in Fig. 4D reveals the presence of several peaks with retention times ranging from 2.9 to 3.2 min corresponding to substances absorbing strongly UV radiation at ca. 250 nm with the UV absorption extending all the way up to 280 nm. These peaks correspond to aliphatic and cyclic alkenes with conjugated double bonds, as found by additional analyses using GC–MS. The range of UV absorbance up to 280 nm indicates the presence of trienes or polyenes [27]. These substances are practically absent in the other investigated components shown in Fig. 4, i.e. CCR and FCC, as well as in other gasoline components used according to modern specifications and in crude oil.

The content of even less than 0.05% of dienes, trienes and polyenes with conjugated double bonds in gasoline results in a high absorbance integrated over the 207–240 nm range, and the alkenes content calculated on this basis is significantly high. In addition, the analysis of pyrocondensate by GC–flame ionization detection using the modified ASTM method D5580 yielded high benzene content (15–25%) and a substantial concentration of styrene (ca. 3.5%).

As a result, as seen in Fig. 5, the presence in a HPLC–DAD chromatogram integrated over the 207–240 nm range of an unresolved peak with a retention time from about 2.9 to about 3.2 min and the UV absorption spectrum at about 3.2 min characteristic of conjugated dienes reveals that the class composition of a gasoline sample cannot be determined by the method described herein. It follows from Figs. 4D and 5C that the peak with retention time of about 3.7 min, corresponding to elution of styrene and substances of similar structure, is characteristic of pyrocondensate only. Thus, the presence of styrene and styrene-like substances in gasoline is an additional criterion disqualifying the presented method for the determination of class composition.

It should also be emphasized that the presence in a HPLC–DAD chromatogram integrated over the 207–240 nm range
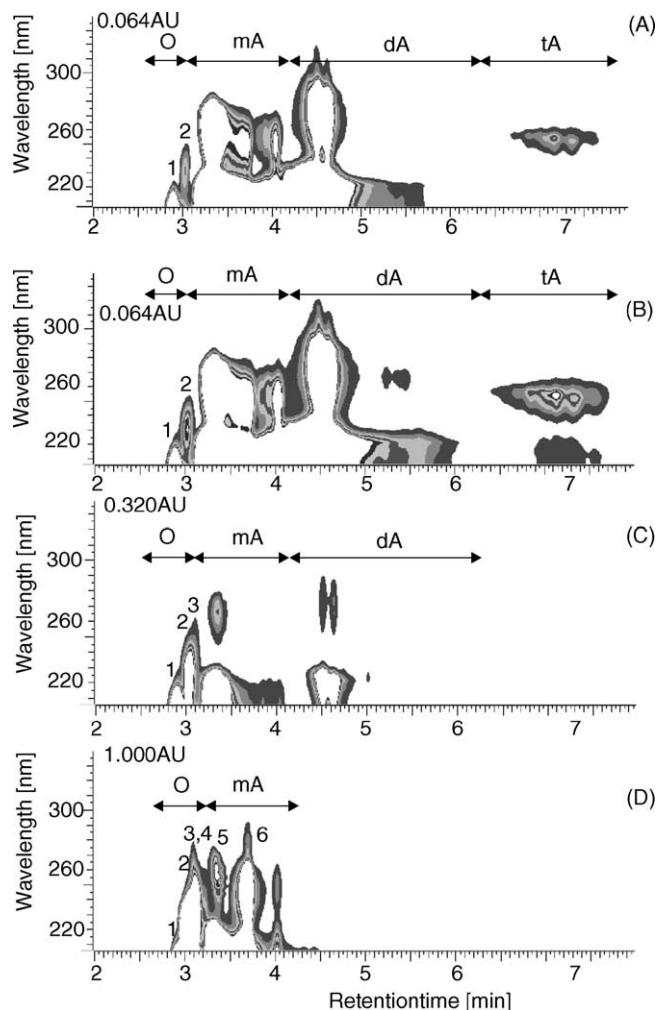

Fig. 4. Three-dimensional HPLC–DAD chromatograms of gasoline (A), product of catalytic reforming (B), product of fluid catalytic cracking (C) and pyrocondensate (D). Chromatographic conditions: as described in Section 2; eluent: *n*-hexane. Elution ranges: O, alkenes; mA, monoaromatic hydrocarbons; dA, diaromatic hydrocarbons; tA, triaromatic hydrocarbons; 1, monoalkenes; 2, isolated dienes; 3, conjugated dienes; 4, trienes and polyenes (including those with conjugated bonds); 5, benzene and 6, styrene and substances with similar structure.

of peaks corresponding to diaromatic hydrocarbons (peak 7 in Fig. 5) with heights exceeding that of the peak corresponding to monoaromatic hydrocarbons (peak 4 in Fig. 5.) is a warning that the gasoline contains an excessive fraction of diaromatic hydrocarbons–naphthalene derivatives and the determination of aromatics content can result in a considerable error.

The outlined procedure for gasoline qualification for the determination of class composition, however, using a column more selective than an aminopropyl-bonded silica, i.e. KH_2PO_4-modified aminopropyl-bonded silica or silica gel [26], can be successfully used to detect gasoline adulteration and to control hydroconversion processes of gasoline fractions [33].
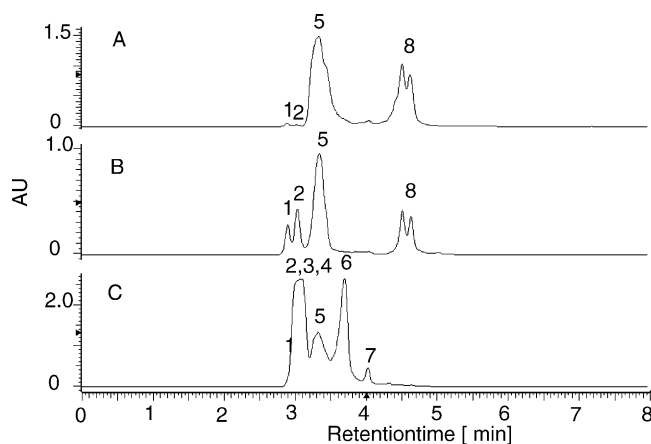
Fig. 5. HPLC–DAD chromatograms in the signal integration mode over the range 207–240 nm for product of catalytic reforming (A); product of fluid catalytic cracking (B) and pyrocondensate (C). Chromatographic conditions: as in Fig. 4. Peaks: 1, monoalkenes; 2, isolated dienes; 3, conjugated dienes; 4, trienes and polyenes (including those with conjugated bonds); 5, monoaromatic hydrocarbons; 6, styrene and substances with similar structure; 7, unidentified substance(s), most likely aromatic alkene(s); 8, diaromatic hydrocarbons, naphthalene derivatives.

3.2. Comparison of the results of determination of class composition of gasoline by the HPLC, fluorescent indicator adsorption and PIONA methods

The statistical data of correlation between the results of determination of alkenes and aromatic hydrocarbons in gasoline and gasoline components obtained by the HPLC, fluorescent indicator adsorption and PIONA methods are given in Table 1.

It follows from the data in Table 1 that for alkenes present in gasoline meeting modern quality standards, the DAD signal integrated over the 207–240 nm range is strongly correlated with the content of alkenes determined by the fluorescent indicator adsorption method. This is true for different gasolines, produced using different refining technologies and obtained from different refineries.

There is also a correlation between the volume contents of aromatic hydrocarbons determined by the fluorescent indicator adsorption and the presented NP-HPLC method. A

good agreement between the aromatics content determined by the fluorescent indicator adsorption method and HPLC with RID in fuels such as gasoline, kerosene or diesel oil has already been reported in the literature and the present results are only an additional confirmation of earlier reports [12,13,19].

The agreement of the results obtained by the fluorescent indicator adsorption and PIONA methods has already been demonstrated in the literature. Since the calibration of the HPLC method was based on the results obtained by the fluorescent indicator adsorption method, the consistency of the results of PIONA and HPLC methods is to be expected. Therefore, the content of alkenes and aromatics was determined using PIONA method for some samples only.

However, an analytical bias was observed in our laboratory for the results of determination of aromatics by the PIONA method compared to the results obtained by the fluorescent indicator adsorption method and, consequently, by the HPLC method. When the alkenes content in the investigated gasoline does not exceed several percent, the contents determined using PIONA method are slightly lower compared to those determined by the HPLC method. These discrepancies may result from the instability of activity of the column and group traps of the PIONA analyzer and, consequently, inaccuracy in peak assignment to respective classes as well as neglecting some alkenes occurring at low concentrations in the investigated gasoline samples containing alkenes up to 8% (v/v). Above this range, the results of determination of alkenes by HPLC are in a good agreement with PIONA. The explanation for underestimation of aromatics by the presented HPLC method as compared to the PIONA method can also be found in reference [11].

3.3. Analytical characteristics of the procedure for determination of class composition of gasoline using NP-HPLC

The detection limits for the HPLC method when using *n*-hexane as the eluent determined for the signal-to-noise ratio of S/N = 10 for gasoline samples at a concentration of 1% (v/v) are 0.05 and 0.01% (v/v) for aromatic and

Table 1
The statistical data of correlation between the results of determination of alkenes and aromatic hydrocarbons in gasoline and gasoline components obtained by the HPLC, fluorescent indicator adsorption and PIONA methods

		HPLC–fluorescent indicator adsorption		HPLC–PIONA	
		Alkenes	Aromatic compounds	Alkenes	Aromatic compounds
Range of correlation (% (v/v))		0.1–38	20–70	0.3–8.0	5.0–70
Number of data points	n	204	204	11	11
Slope	b	1.0157	1.0067	0.7786	1.0464
Intercept	a	0.0431	−0.0881	0.1081	1.5186
Coefficient of determination	R^2	0.9989	0.9879	0.9921	0.9824
Standard deviation of slope	S_b	0.0030	0.0101	0.0259	0.0466
Standard deviation of intercept	S_a	0.0292	0.4207	0.0881	2.1497
Residual standard deviation	S_{xy}	0.2615	0.9819	0.1976	2.6217

Table 2
Calibration equations when using *n*-hexane or *n*-heptane as the eluent

Class	Range of calibration (% (v/v))	Calibration equation when using *n*-hexane	R^2	Calibration equation when using *n*-heptane	R^2
Alkenes	0.3–15.0	(% (v/v)) = $A \times 3.292 \times 10^{-6}$	0.9926	(% (v/v)) = $A \times 2.888 \times 10^{-6}$	0.9937
Aromatic hydrocarbons	5.0–70.0	(% (v/v)) = $A \times 3.246 \times 10^{-5}$	0.9898	(% (v/v)) = $A \times 3.182 \times 10^{-5}$	0.9902

A: peak area.

unsaturated hydrocarbons, respectively. The sensitivity of RID for aromatic hydrocarbons is somewhat lower when *n*-heptane is used as the eluent, the detection limit being equal to 0.1% (v/v). In practice, there are no significant differences in using *n*-hexane or *n*-heptane as the eluent although, as can be seen in Table 2, the calibration coefficients are slightly different. When using concentrations of gasoline in the eluent other than 1% (v/v), the dilution factor needs to be taken into account. The use of *n*-heptane as the eluent is more advantageous, because it allows utilizing the same HPLC apparatus for the determination of class composition of jet fuel and diesel fuel according to the standard IP-391 method and *n*-heptane is less toxic.

The precision of determination of content of alkenes and aromatic hydrocarbons is compiled in Table 3. It follows from the data in Table 3 that the relative standard deviations for aromatic hydrocarbons and alkenes are less than 1% and less than 3%, respectively, thus being much improved compared to the precision of the fluorescent indicator adsorption method [2] and the PIONA method [3].

In case of determinations of class composition of gasoline containing oxygenates, the time of backflush must be extended by about 5–10 min in order to ensure a complete removal of polar gasoline components from the column. In this case, a correction of about 0.5% (v/v) or 0.75% (v/v) has to be added to the determined value of content of aromatic compounds content in gasoline when this content is in the 15–30% (v/v) range or it exceeds 30% (v/v), respectively.

The column used for the developed HPLC method must meet the specifications of standard method IP-391, i.e., the resolution between the peaks of cyclohexene and *o*-xylene should be no less than 5.0.

Following about 500 determinations of class composition of gasoline without oxygenates and about 100 determinations of gasoline containing oxygenates, i.e., when the

separation of alkenes from aromatic hydrocarbons visibly deteriorates, the HPLC column has to be periodically reactivated by passing acetone (ca. 10 column volumes) and then equilibrating it again with *n*-hexane or *n*-heptane to achieve the initial activity (ca. 100 column volumes).

Our experience indicates that the absorbance of *n*-hexane or *n*-heptane in the range 200–210 nm increases with time and also depends on the batch of eluent. Consequently, it is recommended to apply quality control measures, including periodic (once a week or when a new batch of eluent is used) check of calibration for alkenes using reference gasoline samples or other quality control samples.

4. Conclusions

(1) This paper demonstrates the applicability of NP-HPLC with DAD and RID for the determination of total content of alkenes and aromatic hydrocarbons in gasoline and gasoline components meeting modern quality standards and describes the analytical procedure required.

(2) The use of DAD eliminates the need for separation of alkenes from saturated hydrocarbons, since the latter compounds do not absorb UV radiation above 200 nm. The signal of UV detector integrated over the range 207–240 nm was found to be proportional to the alkenes content in samples of gasoline and gasoline components meeting modern quality standards.

(3) The developed method can also be used for the determination of class composition of gasoline containing oxygenates, such as EtOH, MTBE, etc. However, in this case the time of backflush must be extended to ensure a complete elution of polar compounds from the HPLC column. Calculation of the content of saturated hydrocarbons in the presence of oxygenates requires a separate determination of the content of oxygenates in gasoline. A correction accounting for the content of aromatic hydrocarbons also has to be introduced.

(4) The results of determination of alkenes and aromatic content by the presented HPLC method are in agreement with those obtained by the fluorescent indicator adsorption method as well as the PIONA method; however, our investigations indicate that the PIONA method yields slightly higher contents of aromatic hydrocarbons and slightly lower contents of alkenes than the other two methods.

(5) An advantage of the described method is the use of the same class separation conditions as in IP-391 method.

Table 3
Precision of determination of general class composition of gasoline and gasoline components using the HPLC method

Sample	Aromatic hydrocarbons (% (v/v))	R.S.D. (%)	Alkenes (% (v/v))	R.S.D. (%)
1	22.4 ± 0.2	0.83	33.1 ± 0.4	1.51
2	35.1 ± 0.2	0.79	3.9 ± 0.03	0.87
3	43.6 ± 0.3	0.96	1.0 ± 0.05	2.90
4	66.7 ± 0.4	0.79	1.2 ± 0.02	1.62

The number of independent determinations was no less than 6; the confidence intervals were calculated at the 95% confidence level.

This allows using the same liquid chromatograph for the determination of general class composition of gasoline as well as for the determination of content of aromatic hydrocarbons in fuels boiling from 150 to 400 °C, including jet fuels and gasoil.

(6) The procedure for determination of alkenes described in this paper can be extended to higher boiling material, such as jet fuel or gasoil. The experiments did not establish the existence of a single universal calibration. Instead, at least three different values of calibration coefficients depending on the boiling point range of a fuel and the refining technology of its components were found.

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