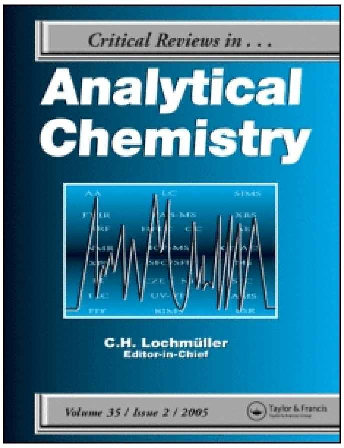

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High-Performance Liquid Chromatography in Group-Type Separation and Technical or Process Analytics of Petroleum Products

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High-Performance Liquid Chromatography in Group-Type Separation and Technical or Process Analytics of Petroleum Products

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Our work includes a critical analysis of current knowledge about the use of high-performance liquid chromatography (HPLC) in the analysis of group-type composition of petroleum products of different volatility and the possibilities of HPLC employment for technical and process analysis in the petrochemical-refining industry and related industries. Aside from volatility of petroleum products, the information about group-type composition is of some importance in the processing and refining of petroleum; quality control of fuels, oils, and other petroleum products; and for determination of sources of environmental pollution. It is important to obtain precise and exact information about the greatest number of possible hydrocarbons groups in the investigated petroleum material. We have reviewed and scrutinized both the standardized methods of determination of the group-type composition of petroleum products of different volatility and those described in the scientific literature. The methods employing a normal-phase high-performance liquid chromatography technique (NP-HPLC), which is particularly useful for group-type separation, make up the vast majority. Based not only on the literature data but also on our own research, we should state that together with increase of range of both a boiling point of petroleum material and degree of refining a possibility of group-type separation becomes more difficult, and all the more our knowledge about a field of control of the group-type separation of petroleum products by means of HPLC is unsatisfying. We also have referred to results of our own research, the aim of which was to elaborate the new selective conditions of group-type separation of petroleum products of different volatility by means of the HPLC multicolumn distribution systems, when evaluating that they introduce an essential progress to the knowledge about a field of control of the analytic problems being a subject of the present review work.

Keywords determination of group-type composition, petroleum products of different volatility, normal-phase high-performance liquid chromatography (NP-HPLC)

Petroleum and its fractions belong to the most complicated of analytical samples in view of the very large number of substances that they contain. It is not possible to separate, identify, and determine all the components of low-volatile fractions of petroleum. Gases and light petroleum fractions of boiling point to about 220°C can be considered exceptions, because in those cases we can successfully use gas chromatography (GC). A system of several columns and valves as well as a so-called olefin trap and a microreactor for hydrogenation of olefins, which together make up a so-called PIONA analyzer (1) or so-called "reformulyzer" (2), is employed. A very efficient 100-m tubular column can also be used. In this case a procedural rule consists of distribution of all components of the investigated sample, identification of components with the use of GC-MS or Kovat's indexes, and calculation of group-type composition by

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means of totalization of concentrations of the all components belonging to particular hydrocarbon groups.

In the case of fractions only a little higher than boiling point, their complete separation into particular components, the employment of a two-dimensional chromatography, and a very long period of analysis could be required. In the case of high-boiling petroleum fractions, the complete separation of all the components has been impossible until now. However, the GC cannot be used directly for the group-type separation of petroleum products because, in the case of GC, retention depends more on the boiling point of the substance than on a group participation of the substance. For most tasks concerning petroleum-derived products, the separation of petroleum products into single components is not necessary. It is sufficient to determine the group-type composition, that is, to determine content of the following groups of substances: saturated hydrocarbons separated into n-aliphatic (nP), isoaliphatic (iP), cyclic (so-called naphthenes, N) hydrocarbons, aliphatic and cyclic olefins (O), mono- (A_1) di- (A_2), tri- and more (A3+) cyclic aromatic hydrocarbons, polar compounds (so-called resins, R) and asphaltenes (A_{ph}). Exemplary structures of the above-mentioned hydrocarbon groups are presented in Figure 1. This figure also illustrates a conception of the group-type composition and a principle distinguishing it from the conception of group structural composition. The most polar function group occurring in a molecular structure or molecule itself determines its group participation. The conception of the group-structural composition refers to determination of the content of carbon atoms linked in the particular chemical structures. A content of so-called paraffin, naphthene, aromatic and so forth carbon should be quantified to determine the group-structural composition, while to determine the group-type composition we should quantify adequately a content of substances belonging to the groups of paraffin (P), naphthene (N), aromatic (A) and so forth hydrocarbons. Estimation of group participation becomes complicated when different functional groups of similar polarity are contained in the molecule.

The information about the group participation of petroleum material (raw material or product) is of different application in the case of technical and process analysis as well as in the case of quality control in the refining/petrochemical industry. Among other things, this involves

- determination of the optimum refining technology or other way of processing;
- selection of the optimum conditions of the processing and refining processes' control;
- in the case of quality control for evaluation of compatibility to requirements of fuels, oils, and other products and also petroleum raw materials;
- the important data for evaluation of the used raw material and product properties, herein petroleum, fuels, oils, lubricants, paraffin, asphalt and so forth.

The group participation also determines fundamental and often sufficient information about both the type and source of environmental pollution with the petroleum products, especially pollution of soil and water. The group participation is also of a similar meaning in the case of looking for a place of installation failure in the refining/petrochemical industry or in a storage place. The data about the group participation also makes it possible or at least easy to identify the fuel or oil falsification and to determine the method of committing an offense of this type (3–5).

Thus far, the following techniques and analytical methods have been employed for determination of the group participation: GC, adsorption liquid chromatography, supercritical fluid state chromatography, thin-layer chromatography with quartz bars coated with sorbent layer (6–12). However, the adsorptive techniques are of particular meaning and especially in the normal-phase liquid chromatography (NP-HPLC). In this case, systems of the reversed phases do not matter as much, because the order of elution depends on a degree of hydrophobicity of molecules and not on their group-type composition.

In view of a possibility of both automatization of analytics and obtaining precise and repeatable data, the NP-HPLC should serve for determination of the group-type composition. There have been many studies of this type in the literature. Their results will be discussed in detail later in this work. In this introduction, we should emphasize that only the IP-391 method (13) and the identical EN 12916 (14), ASTM D-6379 (15), and ASTM D-6591 (16) methods have been applied in recent years for determination of content of the chosen aromatic hydrocarbon groups in diesel oils and jet engine fuels. However, the majority of analytical procedures for determination of the petroleum products' group-type composition by means of the HPLC technique described in the scientific literature have not found application until now. In particular, they have failed in the case of group analysis of the low-volatile petroleum products of a high degree of refining. An increase in difficulty of obtaining the satisfactory group-type separation has been caused by the existence of more and more weak adsorptive interactions as well as more and more strong steric hindrances, especially in the case when the increase of both the molecular mass and boiling point of the petroleum material takes place. These separative difficulties still increase with an increase in the degree of refining, because an increase in the number of both branched chains and naphthalene rings takes place. In consequence, the sorptive interactions are weaker and weaker.

A LITERATURE REVIEW OF THE METHODS OF DETERMINATION OF VOLATILE AND MEDIUM-VOLATILE PETROLEUM MATERIALS (A FINAL BOILING POINT ADEQUATE TO 220°C AND 350°C)

Standard Methods

The most important standard methods of determination of both the group-type composition and a content of specified groups of hydrocarbons in the volatile and medium-volatile

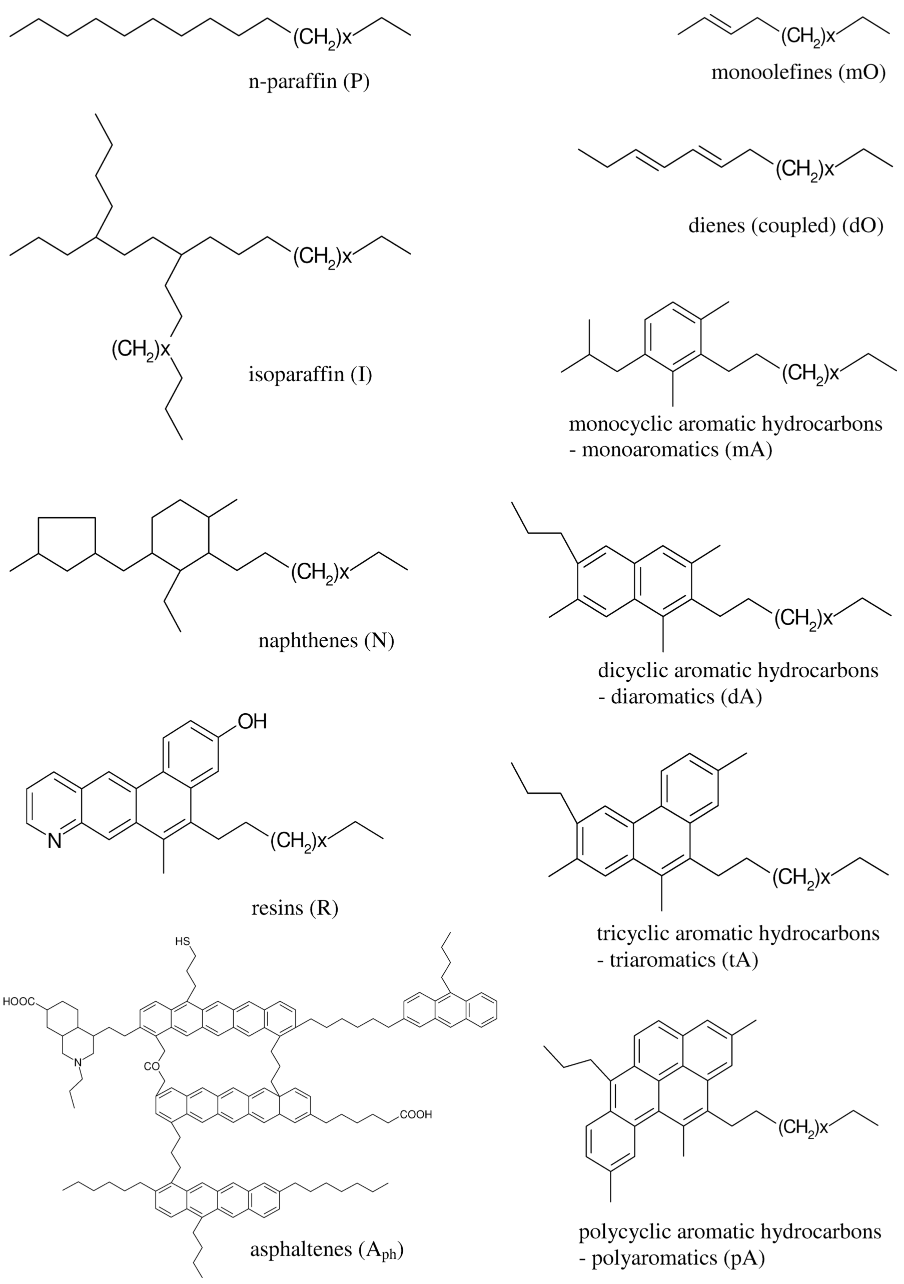

FIG. 1. Exemplary structures of groups of substances in petroleum and in products of its refining.

petroleum materials are compiled in Table 1. Attention was paid not only to a range of employment of these methods but also to their restrictions, defects, and advantages.

Methods Described in the Scientific Literature

The determination of group-type composition of petroleum products for the purpose of characterization of their compatibility to requirements described in specifications is, as a rule, made in compliance with the commonly respected procedures described in standards. Some suggestions of new solutions and procedures for determination of the group-type composition described in the scientific literature make an alternative to standardized methods. The most important methods of determination of the group-type composition of the volatile and medium-volatile petroleum materials are presented in Table 2.

Columns packed with silica gel and anhydrous mobile phases of very low elution strength (i.e. fluoroalkanes, n-pentane, or n-hexane) are used in methods concerning determination of the group-type composition of gasoline, aviation fuels, and diesel oils. It is possible to carry out the group-type separation between alkanes, olefins, and aromatic compounds under these

TABLE 1
The most important standard methods for determination of the group-type composition or of the content of specified groups in the volatile and medium-volatile petroleum products

Product	Standard no.	Separation/detection technique	Determined groups	Remarks
Gasoline	ASTM D5443 (17) ASTM D2427 (18) PrEN-15517 (19) "Reformulyzer"	GC/FID	P/I/A/N/O(C_4-$C_{12)}$ P/O/N/A, P/N/A P/N/O/A/zwizki tlenowe	• The use of gas chromatography is not possible in the case of higher-boiling petroleum products (petroleum, diesel oils)
Aviation fuels, petroleum	ASTM D1319 (20)	FIA	P/N/O/A	• Incorrect precision • Considerable labor intensity and time consuming of carried out determinations • Expensive analysis because of the use of columns packed with a freshly activated sorbent each time
Diesel oils	ASTM D 5186-91 (21)	SFC	PN/O/A	• Incorrect precision • Considerable labor intensity and time consuming of carried out determinations • Expensive analysis because of the use of columns packed with a freshly activated sorbent each time
	IP 391 (22) EN-12916 (23) ASTM D 6591 (16)	HPLC/RI	PNO/mA/dA/pA	• Exact and precise method • Determination of only a few groups of hydrocarbons, (i.e., mono-, di-, and polyaromatic) is possible

conditions, whereas the latter compounds are eluted in the reverse elution mode (24–30). Distributive systems with application of the silica gel and eluent of very low elution strength lead to the poorly repeatable results. The "drying" of eluent and control of its water content is necessary, and separation between the both groups of saturated hydrocarbons and olefins decrease with increase of the range of boiling points of the investigated material (18).

Moreover, especially a refractometric detector is used for determination of the content of the each hydrocarbon group. Indexes of refraction within saturated and olefin hydrocarbon groups are characterized with relatively high variability, depending on the number of carbon atoms and geometrical structure of molecule. Thus, it is necessary to determine the response factor for these groups based on the nature of the analyzed petroleum fraction. In view of the lower value of the refraction index of fluoroalkanes in relation to hydrocarbons, only fluoroalkanes used as eluent make it possible to determine the low content of olefins by means of a refractometer. Nevertheless, in the case of the use of a refractometer, results of determination of the saturated hydrocarbon groups content $(P + N)$ usually complement to 100%, in view of different response factor values of these hydrocarbon groups. Stationary phases with silica gel modified with silver (I) and copper (II) ions were applied for the group-type separation of light petroleum distillates. At that time, paraffin and naphthenes were not separated and olefins were eluted in the reverse elution mode (29, 32, 33, 35). Attempts were made to determine the content of aromatic hydrocarbons and some oxygen additives by means of the HPLC technique in reverse system, a spectrophotometric detector in the UV range, and a refractometric detector (40–45). However, it appears that this method can be considered useful only for determination of some components of gasoline or groups of specified oils and it does not find any applications for the group-type composition determination.

A combination of supercritical fluid state chromatography (diesel oil separation into the PN/mA/dA/pA groups) with gas chromatography for the final analysis of each fraction was successfully used for determination of the group-type composition (46). The other approach, leading to the diesel oil separation into the PN/mA/dA/pA groups, is the solid-phase extraction on silica gel. The program of gradient elution of dichloromethane in n-pentane was employed and the obtained fractions were analyzed by means of the GC-FID or GC-MS techniques (47). However, these two approaches are exceptionally labor intensive and rather useless in view of the process analysis and determination of the group-type composition.

A result of the present knowledge about a field of determination of the group-type composition of volatile and

TABLE 2
Compilation of the high-performance liquid chromatography (HPLC) methods for group-type composition of the petroleum products with boiling point to 350°C existing in literature

Reference no.	Separation/ detection technique	Stationary phase	Mobile phase	Degree of group separation	Range of application, remarks
(25)	HPLC/RI	SiO_2	FC 72 (the C_6F_{14} isomers)	PN/O/A	Petrol, petroleum, diesel oils. Separation of mono- and diolefins, which are eluted in the reverse elution mode; calibration of method basing on the FIA method. Response factors of hydrocarbons groups were calculating in this way.
(26)	HPLC/RI, IR	SiO_2	FC 72 (the C_6F_{14} isomers)	PN/O/A	A procedure similar to the one described in the work (40). Application for determination of the group-type composition of gasoline. Restrictions on the use of refractometric detector for determination of the content of saturated and olefin hydrocarbons were described in detail.
(27)	HPLC/RI	SiO_2	n-hexane	PN/mO/dO/A	Fuel oil, a product of hydrocracking of a final boiling point to 360°C. Calibration based on fractions collected in preparative scale. PN and O fractions were collected by means of the FIA method. A fraction of aromatic hydrocarbons was collected by means HPLC in preparative scale.
(28)	HPLC/RI	SiO_2	FC-87 (the C_6F_{14} isomers)	PN/O/A	Gasoline, aviation fuels. Limited separation of olefins and aromatic hydrocarbons; for example, cyclodienes are eluted with aromatic hydrocarbons.
(29)	HPLC/IR	SiO_2 SiO_2-Ag	CCl_4	PN/O/A	Gasoline, petroleum. Response factors were determined based on reference for gasoline. Good compatibility of results to the FIA method.
(30)	HPLC/RI GC-FID	SiO_2	n-hexane	PN/O/A/R	Gasoline, diesel oils. Precolumn with stationary phase of the CN type is applied for the purpose of trapping of resins, which afterward are eluted in the reverse elution mode. In the case of diesel oils, separation of the PN group from olefin group is very poor.
(31)	HPLC/RI	$-NH_2$	n-heptane	PN/mA/dA/pA	Gasoline, petroleum, diesel oils. Calibration of method based on fractions collected in the preparative scale.
(32)	HPLC/RI/UV	SiO_2 SiO_2-Ag	FC-72 n-pentane	PN/O/A	Gasoline. Reverse elution of aromatic hydrocarbons. Response factors were determined for hydrocarbon group. Applicability of silica gels of different specific surfaces was investigated in the case of group-type separation.
(33)	HPLC/DCD	SCX-Ag	Freon 123 (2,2-dichloro-1,1,1,-trifluoroethane)	PN/A/O	Gasoline, petroleum, diesel oils; calibration based on the prepared mixture of saturated, olefin, and aromatic hydrocarbons. A problem arises when, for example, the diesel oil contains aromatic hydrocarbons of a number of rings higher than three (e.g., pyrene).

(Continued on next page)

TABLE 2
Compilation of the high-performance liquid chromatography (HPLC) methods for group-type composition of the petroleum products with boiling point to 350°C existing in literature *(Continued)*

Reference no.	Separation/ detection technique	Stationary phase	Mobile phase	Degree of group separation	Range of application, remarks
(34)	HPLC/RI/UV-DAD	SDB	n-pentane n-hexane	P/O/N/mA/dA	Separation of gasoline and aviation fuels. An “experimental” stationary phase based on polymer of the styrene-divinylbenzene type was used. However packing of this type is not commercially available. Standard hydrocarbons show the group order; there is a lack of information on petroleum products. Coelution of olefin group and both paraffin and naphthene hydrocarbons.
(35)	HPLC/RI	SiO_2 SiO_2-Ag SiO_2-Cu	Fluorinert FC-72 (the C_6F_{14} isomers) n-pentane	PN/O/A	Gasoline, diesel oils. Only the PNO groups are separated from aromatic hydrocarbon group in the case of fuels. FC-72 is too weak as eluent for olefins trapped on silica gel modified with copper ions. The use of silica gel of the very high specific surface of about 800 m^2/g is required for the system.
(36)	HPLC/DCD	SDB* SiO_2-Ag	Envron 123 (2,2-dichloro-1,1,1-trifluoroethane)	P+I//N/O/A	Gasoline, petroleum. Multicolumn system five columns of the SDB type were used for separation of saturated paraffin from naphthene hydrocarbons (P + I/N).
(37)	HPLC/RI	CN SiO_2-Ag	n-hexane	PN/mA/dA/O	Gasoline, petroleum. A sample cannot contain triaromatic hydrocarbons because they will coelute with olefins, which are eluted in the reverse elution mode. Only the separation method is described, the lack of results of quantitative determination.
(38)	HPLC/RI/UV-DAD	$-NH_2$ SiO_2	n-hexane	PN/mA/dA/pA PN/A	Diesel oils of 250° to 350°C. Calibration based on synthetic mixtures formed with mixing of two petroleum materials of known compositions. Semipreparative conditions. Materials did not contain olefins.
(39)	HPLC/UV/RI	—CN SDB* SiO_2	n-hexane	P/A/R	Gasoline diesel oils. A task of a column of the CN type is to trap resins, which are then eluted in the reverse elution mode; a task of a column of the SiO_2 type is to separate into PN/O/A groups; polymeric sorbent of the SDB type makes possible the P/N separation. A coelution of dienes with aromatic hydrocarbons is a defect of this solution. Olefins and saturated hydrocarbons are incompletely separated. The UV detector was used for detection of olefins. There is the weak group-type separation in the case of heavier fractions of petroleum (e.g., diesel oils and vacuum distillates).

*Packing of this type is not commercially available.

medium-volatile petroleum materials is that, in the case of the determination of the total content of n-paraffins, isoparaffins, and naphthenes, and also the total content of n-olefins and cycloolefins as well as the total content of aromatic hydrocarbon groups, the chromatography with eluent in supercritical state is applied based on procedure described in the ASTM D-5443 standard (1). Moreover, the technical analytics have at their disposal a methodology described in the IP-391 (13), EN-12916 (14), and ASTM D-6591 (16) standards concerning the routine determination of mono-, di-, and polycyclic hydrocarbons in aviation fuels and diesel oils. However these two methods have a series of defects (Table 2) and they also are insufficient in view of the demand of the petrochemical-refining industry. So we can state that, until now, we have not had at our disposal a standardized method of determination of the content of saturated hydrocarbons with their partition into subgroups, olefin hydrocarbons, and aromatic hydrocarbon groups at the same time and by means of the HPLC technique, and also the procedures described in the scientific literature have not found acceptance to such degree that they can obtain the status of a standard.

A LITERATURE REVIEW ON DETERMINATION OF GROUP-TYPE COMPOSITION OF PETROLEUM PRODUCTS OF THE TRUE BOILING POINT (TBP) IN THE RANGE FROM 350°C TO 650°C

Low-volatile petroleum products contain a great number of chemical compounds of a complicated chemical structure. Hydrocarbons have numerous aliphatic chains, in which the number, length, and branching increase when the refining degree increases and the fraction is of lower volatility. The group-type separation of these petroleum products is, as it was mentioned in the introduction, an especially difficult analytical task. So-called steric hindrances occur and consequently the interactions between the molecule and the sorbent surface are very weakened.

Standard Methods

The standard methods for determination of the low-volatile petroleum materials group-type composition are: the classic liquid column chromatography, HPLC in preparative scale, supercritical fluid state chromatography, and mass spectrometry (48–54). The most important standardized methods for determination of the low fractions group-type composition are compiled, discussed, and scrutinized in Table 3.

The adsorptive liquid chromatography with the use of preparative glass columns of a diameter of 12–13 mm packed with silica gel, aluminium oxide, and/or bleaching earth as well as multistage elution is, first of all, used for routine determination of group-type composition of low-volatile materials. The mobile phases of increasing elution strength are applied. Collected fractions are gravimetrically determined after evaporation of eluent (56–59). Separation is carried out with application of the column, which each time is packed again with freshly activated adsorbent. Preparation of the column and carrying out the one determination, according to a procedure described in the PN-72/C-04025 (56), ASTM D-2007 (57), or ASTM D-2549 (58) standards, lasts at least 8 h. Great quantities of toxic and expensive solvents are used, and the obtained results are not precise.

An incorrect precision is caused by the unique method of injection of sample to the column, uniqueness of the degree of activity of sorbent, and especially by uniqueness of packing degree of the column and distribution of the column packing porosity. The profile of liquid flow in column (not entirely piston, often of paraboloidal type or otherwise distorted and variable) (62), bears unfavorably on both the separation degree and results of determinations. It has been proved in the literature that these methods do not provide the full separation of particular hydrocarbon groups in high-refined petroleum products such as base oils (63).

The IP-386 is the only method of determination of the group-type composition of petroleum heavy fractions by means of both HPLC in semipreparative scale and the refractometric detector (55). Only summary content of paraffin, naphthenes, and olefins (if they occur) as a one group, and the content of aromatic compounds including resins as a second group, can be determined gravimetrically after eluent evaporation by means of the described procedure (55).

The mass spectrometry is used for determination of the group-type composition of vacuum distillates, especially vacuum diesel oils, in the range of boiling points of 350°C to 550°C (60, 61). The ASTM D-3239 (60) and ASTM D-2786 (61) methods describe the analytical procedure and its employment. It is necessary to separate the investigated material by means of the ASTM D-2549 method (i.e., by means of the column chromatography in preparative scale) before the group-type composition analysis according to these standards (58).

The methods of determination of the heavy petroleum products, group-type composition by means of liquid chromatography are compiled in Table 3. These methods are routinely used in refining laboratories in spite of such defects as a low precision of determinations and considerable labor intensity. An absolute (i.e., gravimetric determination) of content of each hydrocarbon group is the advantage of these methods and because of this they are considered as the reference methods. The obtained results of group-type composition have been used by many authors of publications on determination of low-volatile petroleum materials group-type composition for determination of the response factors of each hydrocarbon group when, for example, the final determination is carried out by means of the HPLC in analytical scale or the TLC-FID techniques.

METHODS OF GROUP-TYPE SEPARATION OF HIGH-BOILING PETROLEUM PRODUCTS DESCRIBED IN THE SCIENTIFIC LITERATURE

Many techniques and results from the research on determination of the group-type composition of low-volatile petroleum materials have been reported in the scientific literature. Possibilities of employing the following techniques have been

TABLE 3

The compilation of standardized methods of determination of the petroleum products' group-type composition with boiling point in the range of 350°C to 650°C

Standard	Separation technique/method of final determination	Determined groups	Range of application	Remarks
IP-368 (55)	HPLC/RI/by weight	PNO/AR	• Determination of the heavy fractions of petroleum boiling at the range of 350°C to 650°C	• Incomplete separation into groups of compounds (summary determination of paraffin, naphthenes, and olefins as a one group as well as aromatic compounds inclusive of resins as a second group) • Low accuracy • Gravimetric determination (after evaporation of eluent)
PN-72/C-04025 (56)	LC/by weight	PNO/mA/dA/pA/R		• They require column packed with a freshly activated adsorbent each time • Incorrect precision caused by uniqueness of sorbent activity degree and particularly by the method of packing and distribution of packing porosity in column • Incompletely paraboloidal and variable profile of liquid flow in column unfavorably affects the degree of separation and results of determinations • Gravimetric final determination (after evaporation of solvent) • The use of great quantities of toxic and expensive solvents • Chromatographic analysis lasts at least 8 h
ASTM D 2007 (57)		PNO/AR		
ASTM D 2549 (58)		PNO/AR	• Determination of group-type composition of petroleum products of boiling point above 260°C	
ASTM D 4124 (59)		$PN/A//A_f$	• Determination of asphalt group-type composition • Determination of group-type composition of vacuum distillates and base oils after elimination of asphaltenes by means of precipitation in n-heptane (in the case of heavy vacuum distillates).	
ASTM D 3239 (60)	MS	$A_1/A_2/A_3/A_4/A_5/A_6^{*}$	• Vacuum distillates, especially vacuum diesel oils in the range of true boiling point of 350°C to 550°C	• Separation of the investigated material is necessary (according to the ASTM D 2549 standard) before analysis of group-type composition according to these standards
ASTM D 2786 (61)		$P/N_1/N_2/N_3/N_4/N_5/N_6^{**}$		

*$A_{1\text{-}6}$, number of aromatic rings in molecule.

**$N_{1\text{-}6}$, number of cyclic rings in molecule.

investigated: the classic liquid column chromatography (LC), normal-phase high-performance liquid chromatography (NP-HPLC), thin-layer chromatography (planar-TLC), and the TLC-FID techniques with quartz bars coated with stationary-phase and flame ionization detector. There also have been works concerning the use of supercritical fluid state chromatography (48–54).

The most important methods for determination of the petroleum products group-type composition in the range of boiling points from 350°C to 650°C described in scientific literature are presented in Table 4. The important information with regard to conditions of separation and critical opinion concerning the quoted methods is also presented in this table.

By reason of the mentioned difficulties with the group-type separation resulting from reduction of interactions with the sorbent surface, systems of several HPLC columns connected in series and packed with adsorbents of a strong group affinity as well as the mobile phases of as low as possible elution strength have been used for determination of the group-type composition of low-volatile petroleum fractions by means of the HPLC technique (64).

Silica gel (65, 66) or aluminium oxide, which differ with respect to both the degree of hydration and acidity (63, 67), were first applied as the stationary phase. The hydrocarbons' retention and selectivity of these sorbents, especially in relation to separated substances, intensely depend on the water content on the sorbent surface as well as in the mobile phase. The defects of these adsorbents are their ease in deactivation and change in their activity by reason of the durable sorption of polar compounds, so-called resins, and asphaltenes. The elution of resins groups is usually carried out in elution mode with the use of polar solvent. A prolonged conditioning of the column with the use of initial eluent is then necessary (68, 69). Employment of stationary phases with function groups linked chemically to silica gel has been proposed in many later works. There also have been investigations on the possibility of group-type separation of low-volatile petroleum products by means of the normal phase adsorption chromatography (NP-HPLC) with the use of stationary phases of the type of $-NH_2$ (68, 70–77), $-CN$ (81–88), $-NO_2$ (81–84) and others, for example, with the use of ligand-exchange chromatography (35, 68, 85, 86).

The employment of columns, packed with adsorbents with nitroamine or cyano groups, permits partial separation of aromatic compounds with regards to the number of aromatic rings in the molecule. However, the separation achieved by authors of cited works has been only partial and obtained almost exclusively for petroleum products of the low-refining degree. The increase of retention with increase of the number of aromatic rings has been observed. Not only isocratic elution, but also elution with a change in mobile phase composition, has been employed. A modification of silica gel surface with silver (35, 65) and copper (35) has been suggested in some works for the purpose of both group-type separation improvement and better separation of olefin groups from monoaromatic hydrocarbons. Cation-exchange columns with bounded silver ions also have been employed (33, 85, 86). Stationary phases containing the silver ion are extremely selective in relation to olefins, especially when the silver ion is linked to the cation exchanger.

A coupling between HPLC and mass spectrometry was used for determination of group-type composition of petroleum heavy fractions. The so-called moving belt interface (MBI) was applied for the purpose of evaporation of the mobile phase (82). A technique of ionization in a magnetic field (field ionization) was used for determination of the paraffin-naphthene fraction of base oil by Liang and coworkers (83). Hsu and coworkers applied the thermospray interface (TSP) and chemical ionization of aromatic compounds from vacuum distillates (84). These techniques resulted in information on content of different hydrocarbon groups in heavy petroleum products. However, expensive apparatus is required. The use of so-called MBI for the purpose of evaporation of the mobile phase and introduction of a sample into the mass spectrometer is limited to substances of boiling point to about 550°C. The coupling of HPLC and mass spectrometer through so-called ISP does not show such restrictions.

From information compiled in Table 4, a method using the HPLC technique providing satisfactory separation of heavy naphtha fractions into such groups as paraffin, naphthene, olefin mono- and dipolyaromatic hydrocarbons and resins (P/N/O/mA/dA/pA/R) has not been elaborated until now. In the case of base oils, even a satisfactory method of group-type separation of paraffin-naphthene-olefin, mono- and dipolyaromatic hydrocarbons and resins (PNO/mA/dA/pA/R), has not been elaborated.

None of the HPLC techniques of group-type composition determination described in literature met until now an acceptance in a form of the standard adequate for vacuum distillates and base oils. Results of determination of base oil group-type composition specifying the hydrocarbon groups PN/mA/dA/tA/pA/R, with the use of the AC Heavy Distillates Analyser offered by the Analytical Control Company (96) (the HPLC technique in column switching system with UV-DAD and LLDS detectors) showed that, in view of low values of recovery degree, the suggested method cannot be directly used for determination of group-type composition of high-refined products (97). After all, the Analytical Control Company withdrew an offer for an application and apparatus of this type. There probably were two reasons for this: (1) a sorbent with dinitroanilinopropyl group (DNAP), on which substances forming very strong charge transfer complexes underwent sorption irreversibly; and (2) a lack of unambiguous correlation between the content of determined hydrocarbon groups and signal of the laser light scattering detector (LLSD).

It also was proved that decrease of separation temperature even to -20°C does not influence improvement in selectivity of investigated stationary phases, though values of retention factor (k) increase significantly. However, a considerable peak broadening takes place which results in reduction of resolution (98).

Cebolla and coworkers elaborated a method of determination of paraffin and aromatic hydrocarbon content in vacuum

TABLE 4

Methods of determination of the low-volatile petroleum fractions' group-type composition by means of liquid chromatography described in the scientific literature

Referene no.	Separation/ detection technique/ method of determination	Applied stationary phases	Applied eluents	Range of applications	Separated groups of chemical compounds	Remarks
(63)	LC/detector UV/by weight	Al_2O_3	Pentane, ethyl ether:pentane 1:1 pentane:benzene 3:1 benzene:methanol 1:1	Fractions of vacuum distillation, atmospheric residue	PNO/mA/dA/pA/R	One of the first published works. The dA and pA hydrocarbons groups contain a small quantity of sulfur compounds. Sorbent must be reactivated before the next analysis. The UV detector is used only to determine boundaries of elution between hydrocarbon groups. The technique does not find application for the group-type separation of atmospheric residue.
(67)	HPLC/UV detector	Al_2O_3	n-Hexane, methyl chloride	Base oils	mA/dA+pA+R	Only the content of mA was determined quantitatively, reactivation of sorbent is necessary. Separation of aromatic hydrocarbons groups in base oils and *brightstock* is practically insignificant. Calibration basing on samples of petroleum materials of a known content of monoaromatic compounds.
(65)	HPLC/UV and RI detector/by weight	SiO_2 SiO_2/Ag^+	Cyclohexane benzene:cyclohexane 1:4 benzene:methanol 2:3	Vacuum distillates, vacuum residues	PN/O/A	Separation in preparative scale with the use of two columns of dimensions 610 × 7.8 [mm]. Resins eliminated *off-line* in column packed with cation exchanger, anion exchanger, and Attapulgus clay. Recovery values amount to only 77% in the case of some kinds of materials.

(68)	HPLC/RI detector/by weight	$-NH_2$	n-hexane	Vacuum distillates of TBP > 450°C	$PON/A/R/A_f$	Asphaltenes are determined after their elimination by means of precipitation in n-hexane. Distribution into hydrocarbon, groups is very poor, especially between saturated and aromatic hydrocarbons. It is questionable whether all the resins are eluted with n-hexane in the reverse elution mode.
(87)	HPLC/UV and IR detector	SiO_2	n-hexane ethanol	Petroleum, vacuum distillates	PNO/A/R	The use of automated analyzer of group-type composition in preparative scale by means of fraction collector; possibility of automated analysis up to 20 samples. Resins are trapped in precolumn; column packed with SiO_2 makes it possible to separate saturated and aromatic hydrocarbons in the reverse elution mode. Then resins are eluted with ethanol, which is supplied by means of individual pump. Elimination of asphaltenes from analyzed petroleum materials samples is necessary.
(69)	HPLC/UV and IR detector	$-CN$ SDB SiO_2	n-hexane	Vacuum residues of the light petroleum	PN/A/R	Reverse elution of R, sorbent of the CN type—trapping of resins, SiO_2—separation of PN/O/A, SBD—separation of P/N, dienes interfere with A, olefins not completely separated from PN, UV detection, not correct separation in the case of more heavy petroleum fractions.

(Continued on next page)

Table 4
Methods of determination of the low-volatile petroleum fractions' group-type composition by means of liquid chromatography described in the scientific literature (*Continued*)

Referene no.	Separation detection technique/ method of determination	Applied stationary phases	Applied eluents	Range of applications	Separated groups of chemical compounds	Remarks
(70)	HPLC/UV and IR detector	$-NH_2$ $-CN$	n-hexane cyclohexane: chloroform	Vacuum distillates	PN/AR lub PA/R	Separation of PN/AR—n-hexane as eluent, PA/R—cyclohexane: chloroform (85:15, v/v). Asphaltenes eliminated by means of precipitation in n-hexane. Logging of two chromatographs, with the use of two different eluents, is necessary in order to determine the group-type composition of PN/AR. The proposed procedure is not practical. Calibration factors were determined basing on vacuum distillates of the known group-type composition.
(88)	HPLC/UV and RI detector	$-NH_2$:$-CN$ 2:1	n-pentane, MTBE	Petroleum	PN/A/R	Reverse elution (by means of MTBE) was applied to rinse resins fraction from the column. Incomplete separation between groups.
(71)	HPLC/UV and RI detector/by weight	$-NH_2$	n-hexane	Petroleum	PN/A/R	The preparative scale. The complete group-type separation of standard substances for the investigated stationary phase was not obtained with what results from the k value.
(9)						

HPLC/RI detector	—CN SiO_2	n-hexane	Petroleum	PN/A/R	The gel permeation chromatography (GPC) was applied for the preliminary separation.	
(90)	HPLC/LC-FID detector	—CN —CN/—NH_2	n-hexane, MTBE	Vacuum distillates of TBP > 350°C	PN/AR	Calibration: LC-FID detector based on preparative collected fractions. The reverse elution of R with the use of MTBE as eluent from the CN column, reverse elution of aromatic hydrocarbons from the —CN/—NH_2 column (n-hexane as eluent). A lack of compatibility between obtained results and reference method. A necessity for elimination of asphaltenes by means of precipitation in n-heptane.
(91)	HPLC/RI and LC-FID detector	—NH_2 —SCX-Ag	n-hexane	Base oils, vacuum distillates of TBP > 375°C	PN/AR	A lack of compatibility between determinations and reference methods, too little information on the group-type composition. Polar components, so-called resins, probably undergo irreversible sorption on the SCX-Ag column.
(35)	HPLC/UV and RI detector	SiO_2/Ag^+ lub SiO_2/Cu^{2+}	Fluorinet FC-72 (C_6F_{14} isomers), n-pentane	Vacuum distillates, after cracking distillates, vacuum residues	PN/O/A	Fluoroalkanes were applied as eluent. SiO_2/Ag^+ is characterized with greater group selectivity than SiO_2/Cu^{2+}. Incomplete group-type separation occurs in the case of heavy fractions even with the use of SiO_2/Ag^+. The reverse elution of arenes. A very low solubility of petroleum heavy distillates in FC 72 is a problem.

(Continued on next page)

Table 4
Methods of determination of the low-volatile petroleum fractions' group-type composition by means of liquid chromatography described in the scientific literature (*Continued*)

Referene no.	Separation detection technique/ method of determination	Applied stationary phases	Applied eluents	Range of applications	Separated groups of chemical compounds	Remarks
(72)	HPLC/UV and RI detector	$-NH_2$	n-hexane	Vacuum distillates	PNO/mA/dA/pA/R	A content of olefins was determined based on the UV detector indications with analytical wavelength of 200 nm. However, these results are not compared to reference methods.
(33)	HPLC/DCD detector	−SCX-Ag	Freon 123 (2,2-dichloro-1,1,1-trifluoroethane)	Distillates of TBP<400°C	PN/O/A	Reverse elution of olefins, a heavy cost of eluent.
(81)	HPLC/UV detector	$-NO_2$	n-hexane:methyl chloride	Shale oil	mA/dA/pA	Gradient elution. The $-NO_2$ sorbent makes it possible to separate arenes with regard to the number of aromatic rings in the molecule even in the case of aromatic hydrocarbons from base oils. In view of a strong retention of arenes—the good separation of PNO/A.
(82)	HPLC/FI-MS	−DNAP	n-hexane	Paraffin-naphthene fraction of base oils	P/I $N_1/N_2/N_3/N_4/N_5/N_6$	*A moving belt interface* was used for *on-line* connection of HPLC with a high-resolution mass spectrometer (HR-MS). Field ionization (FI) was employed as a source of particle excitation. Only a fraction of paraffin-naphthene hydrocarbons was separated, from both aromatic hydrocarbons and resins, by means of the HPLC technique.

(92)	HPLC/RI	—TENF	FC-77 (C_7F_{16} isomers), TFTCE (2,2,2-trichloro-1,1,1-trifluoroethane)	—	$N_1/N_2/N_3/N_4$	Naphthene separation with regard to the number of rings. TFTCE is added to eluent in order to increase hydrocarbon solubility in the mobile phase (which the FC-77 is).
(83)	HPLC/TSP-MS	—DNAP	n-hexane, dichloromethane, isopropanol	Vacuum residues	mA/dA/tA/pA	The PN content was not determined. Aromatic compounds were separated into groups by means of the HPLC technique. It is impossible to determine the content of paraffin-naphthene hydrocarbons.
(84)	HPLC/TSP-MS	—DNAP	n-hexane, dichloromethane, isopropanol	Vacuum distillates of 340°C–510°C	mA/dA/tA/pA	Mass spectrometer made it possible to identify the aromatic compounds of sulfur. Only qualitative determinations.
(86)	HPLC/LC-FID	—SCX-Ag —CN	n-hexane, cyclohexane, dichloromethane	Vacuum distillates, base oils	PN/mA/dA/pA/R	Gradient elution. The results obtained for petroleum products by means of HPLC/LC-FID are comparable to results obtained with the use of the MS detector. A lack of reference to the standard methods. Suggested procedure appears to be optimal and, first of all, simple.
(93)	HPLC/DCD	—DNAP SiO_2	Freon 123 (2,2-dichloro-1,1,1-trifluoroethane)	Heavy distillates	PN/mA/dA/pA	Very poor group-type separation of the low-volatile materials.
(69, 70)	HPLC/UV-DAD	—NH_2	n-hexane:isopropyl ether	Vacuum diesel oil of 300°C to 480°C	mA/dA/tA	Incomplete group-type separation. The lack of data on quantitative determination.
(88)	HPLC/UV-RI	—NH_2	n-hexane	Petroleum	PN/mA/dA/pA+R	The quantitative determination based on fractions collected during separation in preparative scale. The incomplete separation between both saturated and aromatic hydrocarbons. It is uncertain whether the all resins are eluted under conditions of reverse elution.

(Continued on next page)

Table 4

Methods of determination of the low-volatile petroleum fractions' group-type composition by means of liquid chromatography described in the scientific literature (*Continued*)

Referene no.	Separation detection technique/ method of determination	Applied stationary phases	Applied eluents	Range of applications	Separated groups of chemical compounds	Remarks
(71)	HPLC/UV-RI	$-NH_2$	n-hexane	Vacuum diesel oil	PN/mA/dA/pA	The analytical procedure for determination of the content of aromatic hydrocarbons is similar to the IP-391/EN-12916 standard.
(89)	HPLC/UV-DAD	$-NH_2$	n-hexane	Vacuum diesel oil	mA/dA/pA	Incomplete group-type separation.
(94)	HPLC/UV/by weight	$-NH_2/H_3PO_4$	n-hexane, acetic acid, isopropanol	Heavy diesel oils	PNO/A/R1/R2	The separation of resin fractions into the Ż1 group (inactive and acidic resins) and the Ż2 group (resins of basic nature).
(46, 50)	TLC/FLD	SiO_2	n-hexane, toluene, dichloromethane	Deasphaltizate of vacuum residue, base oil	PN/A/R	TLC plates are impregnated with a fluorescent dye berberine sulfate, which is responsible for amplification of emission of radiation in the presence of saturated compounds (a wavelength of 450–550 nm). The amplification of emission of radiation is in proportion to the content of saturated compounds in the investigated material. The incomplete group-type separation in the case of heavy fractions. The "semiquantitative" technique.
(95)	TLC/FID	SiO_2	n-hexane, toluene, dichloromethane: methanol 95:5 v/v	Vacuum residues > 530°C	$PN/A/R/A_f$	Results obtained by means of the TLC-FIC technique are not consistent with results obtained according to the ASTM D 4124 method.

distillates and base oils with the use of the high-performance thin-layer chromatography on plates (HPTLC) with silica gel impregnated with berberine sulfate. This dye increases the fluorescence intensity in the presence of alkanes. A densitometer (so-called "scanner") was used for detection (99, 100). This is a promising method, but there is more estimation than determination of group content of substances in investigated material with regard to results.

The TLC-FID technique (i.e., the use of thin-layer chromatography on quartz bars coated with sorbent layer and flame ionization detector) has found application in determination of vacuum distillates group-type composition of boiling point above 300°C, especially in the case of base oils, vacuum residues, and asphalt (101, 102). The group-type separation up to baseline has been obtained in practice. More volatile components can evaporate during chromatogram development and bar drying, and also in a detector chamber. Comparatively low precision, especially during determination of low group contents, is a defect of the TLC-FID technique. Repeatability reaches relative 35% when the content determined group is about 2.5% by weight (103).

THE DETECTION AND CALIBRATION PROBLEM IN DETERMINATION OF GROUP-TYPE COMPOSITION OF PETROLEUM PRODUCTS

There is another problem connected with possibility of effective application of HPLC for group-type separation of petroleum products besides the difficulty with obtaining the sufficient selectivity of separation. It is the problem of detection and calibration. Obtaining an analytical signal from all groups of substances and the signals' proportionality to the content of the group are necessary, as well as the method of calibration which makes it possible to obtain exact and precise results.

Detectors applied to determine the content of individual hydrocarbons are presented in Table 5. Special attention was paid to restrictions in application of specified detectors.

Table 5 shows that a lack of a universal detector for determination of group-type composition of the petroleum products is an essential problem. Employment of such a detector could enable us the use of simple standardization, as is possible (with a satisfactory accuracy) in the case of gas chromatography applied for hydrocarbons with the use of flame ionization detector (GC-FID); for example, for so-called simulated distillation (SIMDID) (106). On that account, the gravimetric method is most often used as method of determination of group content of low-volatile petroleum products. The method consists of weighing of hydrocarbon groups obtained in preparative scale after evaporation of eluent. It is a labor-consuming and, more importantly, expensive methodology, because of the use of large volumes of eluent components. The method cannot be applied in relation to volatile petroleum products, and in the case of products of medium volatility it is inaccurate because a part of the sample evaporates.

From among instrumental methods of detection and calibration, the method of standardization has been applied when taking into consideration response factors of refractometric detector (RI) for determined groups. The flame ionization detector for liquid chromatography (LC-FID) (64) should also find application, but it has not been offered at by known producers of HPLC apparatuses.

The other way to solve the problem of group-type composition calibration is to use substances which are representatives of particular hydrocarbon groups, as was suggested by the authors of the IP-391, EN-12916, ASTM D-63591, and ASTM D-6591 standards for determination of the content of particular aromatic compounds (13–16). Content of monocyclic hydrocarbons has been determined in terms of o-xylene, dicyclic hydrocarbons—in terms of 1-methyl-naphthalene and tricyclic hydrocarbons as well as those of higher number of rings (A3+)—in terms of phenanthrene. The authors have investigated applicability of some other techniques and calibration methods for determination of the group-type composition of petroleum products with employment of HPLC (26, 107). It was proved that, for determination of group-type composition of the resin-free petroleum materials, the use of refractometric detector and standardization, considering response factors of detector, is possible. The response factor can be calculated based on an absolute value of refractive index of the particular groups of hydrocarbons when separating the same sample, using two eluents of very similar elution strength and selectivity but varying with refraction factor (e.g., with application of heptane and hexane as eluents). We can calculate these factors based on the same principle, which was suggested by Synovec for determination of individual substances by means of RI and two eluents which vary with refraction factor (108).

It was also proved that application of the flame ionization detector for liquid chromatography (LC-FID) and standardization method should be an advantageous solution to the problem of detection and calibration in the case of determination of low-volatile petroleum products group-type composition (109).

Our research also showed that a laser light scattering detector (LLSD) (104, 105) should not be applied for determination of the group-type composition of low-volatile petroleum products, not because of its nonlinear characteristics which can be compensated, but for the fact that the obtained results are of poor repeatability (110). Unfavorable repeatability of this detector is probably caused by oscillation of properties of surface-active eluant fractions consisting of many substances that consequently results in formation of microdrops which are differ with regard to size despite the same concentration of a determined group, particularly so-called resins and polycyclic aromatic hydrocarbons.

SOME RESULTS OF THE LAST INVESTIGATIONS AND DIRECTIONS FOR FURTHER RESEARCH

The presented review shows that the HPLC is potentially the best separative and analytical technique for determination of group-type composition of petroleum products of different volatility, especially including high-boiling petroleum products.

Table 5
Detectors applied for determination of the content of individual hydrocarbon groups

Type of detector	Remarks
UV-VIS	• It is not sensitive in relation to hydrocarbons, which do not contain chromophoric groups, so not to paraffin and naphthenes • Application for determination of group-type composition of petroleum products is limited • It is impossible to obtain the signal, which is unambiguously correlated with the content of the determined group (33)
IR	• Application of the narrow group of eluents is required (e.g., perchloromethane) • This technique of detection is used only in the case of a few methods cited in the scientific literature concerning determination of gasoline group-type composition (19, 26)
RI	• Relatively universal detector, but application of isocratic elution is necessary • Used for determination of petroleum product group-type composition in the whole range of volatility • It is characterized by a low sensitivity and, consequently, determination of content of hydrogen group at a level below about 1% is inaccurate (48, 64)
DCD	• Application of isocratic separation conditions is necessary • Application of eluents, which are characterized by a value of dielectric constant at least twice lower than that of determined groups (e.g., trifluoroethane) (103)
LLSD	• limited application for group-type separation in view of response nonlinearity and influence of properties of surface-active components of eluant on sensitivity; application is possible only in the case of nonvolatile substances (104, 105)
MS	• Different techniques of ionization and high-ionization energies (higher than in the case of the classic mass spectrometers) are required for the purpose of defragmentation of saturated and aromatic hydrocarbons (82, 83, 84)
LC-FID	• Wide range of response linearity • Sensitive to all groups of determined hydrocarbons • It can be employed under conditions of the gradient and jump elution (23, 64, 89)

It also shows that the knowledge in the field of application of HPLC for determination of petroleum products group-type composition is unsatisfactory. It has induced the authors of this review work as well as other research teams to take further research pursuing elaboration of optimal conditions of resolution and determination of group-type composition in the case of petroleum products of different volatility by means of HPLC and with distinction of main groups and subgroups of hydrocarbons (24, 107, 109, 111, 112). The continuing research is being carried out in two different directions.

The first direction applies to selection of new sorbents as well as employment of systems of several HPLC columns of special selectivity and a system of column switching during elution and group-type separation. The group selectivity of sorbents of the NH_2 type (i.e., $-(CH_2)_3$; NO_2: $-(CH_2)_3$-Ph; NO_2 (Ph-phenyl); NH_2-KH_2PO_4; SiO_2; CN: $-(CH_2)_3$-CN; DNAP: $-(CH_2)_3$-An-$(NO_2)_2$ (An-aniline); SiO_2-Cu^{2+}, SiO_2-Ag^{2+}, SCX-Ag) has been investigated. The possibility of employing ligands exchange chromatography for petroleum products group-type separation also has been studied (112–114). These works are being applied especially to investigations not only of possibilities but also elaboration of adequate conditions of separation into subgroups of these hydrocarbon groups, which until now were determined together by means of HPLC or SFC; for example, in the case of separation of olefins group into n-olefins, iso-olefins, cycloolefins, coupled dienes (113) and/or in the case of separation of paraffin groups into n-paraffin (n-P), iso-paraffin (I-P), and cycloparaffin hydrocarbons (N) as well as separation of sulfur, oxygen, and nitrogen compounds as individual groups.

Despite the essential progress in our knowledge in the field of applications of HPLC for group-type separation of petroleum products, we cannot admit that full success has been achieved. Research of this type should be continued. Also the group selectivity of commercially available and new elaborated stationary phases should be better known. This type of investigation will allows us, among other things, to state that in the case of some substances the order of elution is improper. For example, in the case of a sorbent of the Purospher NH_2 type, triphenylmethane (tricyclic aromatic hydrocarbon) is eluted within a range of elution of dicyclic aromatic hydrocarbons . However, in the case of silica gel, we have observed the improper order of elution of diaromatic hydrocarbons (e.g., diphenylmethane is eluted after phenenthrene, anthracene, and their derivatives). It undermines the sense of application of silica gel for group-type separation of aromatic hydrocarbons into subgroups (111). Based on these results, we can state that there is a need for application of column-switching systems during group-type separation of petroleum products (115) when taking into consideration the particularly

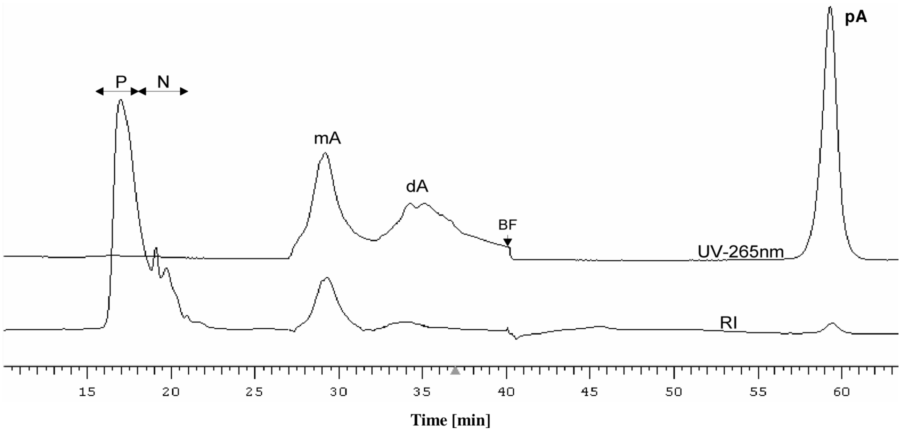

FIG. 2. Chromatograms of group-type separation of SAE 10 base oil, obtained using the (IR) detector-lower and UV-265 nm detector-upper and presented excluding resins. The HPLC multicolumn system with column switching was used (152, 79). Separation of the following groups of hydrocarbons: P/N/mA/dA/pA. System of columns: a Lichrospher CN column (250 × 4 mm, 5 μm, Merck), two Lichrospher SiO_2-$Cu(NH_3)_2$ columns connected in series (250 × 4 mm, 5 μm, self-obtained) and two Lichrogel PS1 columns connected in series (250 × 7 mm, 5 um, Merck); Eluent: n-hexane, flow: 1 mL/min; Temperature: 20°C; Volume of sample: 20 μL; Concentration of sample: 50 mg/mL; Sequence of column switching: a CN column disconnected after 6 min from inlet to a $SiO_2(NH_3)_2$ column, outlet from SiO_2-$Cu(NH_3)_2$ columns disconnected from PS1 column and elution of PNO fraction from the PS1 column to 23rd min, elution of the mA and dA groups from SiO_2-$Cu(NH_3)_2$ column from 23rd min to 40th min (elution only through the SiO_2-$Cu(NH_3)_2$ columns—elution of hydrocarbons of the mA and dA groups from about 27th min), the reverse elution of polyaromatic hydrocarbons (pA) through the SiO_2-$Cu(NH_3)_2$ columns from 40th min.

beneficial selectivity of silica gel in relation to separation of the groups of paraffin, naphthenes, and olefins (109).

The group-type separation of base oils (devoid of the resins group) was realized by means of the multicolumn HPLC device with column-switching system, which was described in Ref. (116). A chromatogram obtained for the SAE 10 base oil is presented in Figure 2. It shows that we can separate and determine the (NP + iP)/N/mA/dA/pA) groups during a time of about 60 min. In the case of standard procedures (55–71), we can distinguish only a smaller number of groups (P + N/mA/pA). The analysis lasts about 8 h and the obtained results are not accurate and not precise.

The elaborated methodology, which will be described in detail in the paper which is being prepared for publication (107), is characterized by the possibility of application of different sorbents and columns during both the group-type separation and change of columns sequence, which are used for separation of particular hydrocarbon groups. Consequently, this makes possible use of the method not only for determination of group-type composition but also for determination of group-type composition of liquid products of processing of coal, natural asphalt, bituminous shales, and secondary vegetable metabolites of different polarity (e.g., for isolation of fractions of lipids, phospholipids, and other groups of substances from natural sources).

The second direction of the last and most likely future research is based on the successes of proteomics (115, 117). The trend of the research involves separation of all components of an investigated sample by means of two-dimensional chromatography of the type GC-GC, HPLC-GC, HPLC-HPLC-GC-GC with the use of extremely selective and high-performance chromatographic columns and (MS) technique for identification and determination of the content of substances (118).

NOMENCLATURE

A_f	Asphaltenes
API	American Petroleum Insitute
ASTM	American Society for Testing and Materials
CN	Bonded phase: dihydroxypropyl
dA	Dicyclic aromatic hydrocarbons (diaromatics)
DAD	Photodiode array detector
DCD	Dielectric constant detector
DNAP	Bonded phase: dinitroanilinopropyl phase
dO	Olefins containing two double bonds in molecule (dienes)
EN	European Standard
FIA	Fluorescent indicator adsorption
FID	Flame ionization detector
FTIR	Fourier-transform-infrared spectrometry
GC	Gas chromatography
GC-FID	Gas chromatography with flame ionization detector
GC-FTIR	Gas chromatography with Fourier-transform-infrared spectrometry
GC-MS	Gas chromatography/mass spectrometry

GCxGC	Two-dimensional gas chromatography
HPLC	High-performance liquid chromatography
HPLC-DAD	High-performance liquid chromatography with photodiode array detector
HPLC-DAD-RI	High-performance liquid chromatography with photodiode array detector and refractometric detector
HPLC-GC/FID	High-performance liquid chromatography combined with gas chromatography and flameionization detector
HPLC-LC/FID	High-performance liquid chromatography with flame ionization detector
HPLC-LLSD	High-performance liquid chromatography with laser light scattering detector
IP	Institute of Petroleum
IR	Infrared detector
LC	Liquid chromatography
LC-FID	Flame ionization detector for liquid chromatography
LLSD	Laser light scattering detector
mA	Monocyclic aromatic hydrocarbons (monoaromatics)
mA/dA/pA	Groups of hydrocarbons: monocyclic aromatic, dicyclic aromatic, and polycyclic aromatic hydrocarbons
mO	Olefins containing a one double bond in molecule (monoolefins)
MS	Mass spectrometry, mass spectrometer
MTBE	Methyl tert-buthyl ether
N	Naphthene hydrocarbons (naphthen es)
NH_2	Bonded phase: aminopropyl phase
NO_2	Bonded phase: nitrophenyl propyl phase
NP-HPLC	Normal-phase high-performance liquid chromatography
NP-HPLC-UV-DAD-RI	Normal-phase high-performance liquid chromatography combined with UV spectrophotometric and photodiode array detector as well as refractometric detector
O	Olefins
P	Paraffin hydrocarbons (paraffin)
pA	Polycyclic aromatic hydrocarbons (polyaromatics)
PIONA, P/I/O/N/A	Groups of hydrocarbons: n-paraffin, isoparaffin, olefin, naphthene, aromatic hydrocarbons
PN	Polish Standard
PN/A/R/A_f	Groups of hydrocarbons: paraffin + naphthene and aromatic hydrocarbons, resins, asphaltenes
PN/mO/dO/A	Groups of hydrocarbons: n- + isoparaffin + nahthene hydrocarbons, monoolefins, dienes, aromatic hydrocarbons
PN/O/A	Groups of hydrocarbons: n- + isoparaffin + naphthene, olefin, aromatic hydrocarbons
PN/O/A/R	Groups of hydrocarbons: n- + isoparaffin + naphthene, olefin, aromatic hydrocarbons, resins
PNA, P/N/A	Groups of hydrocarbons: n- + isoparaffin, naphthene, aromatic hydrocarbons
PNO/mA/dA	Groups of hydrocarbons: n-+ isoparaffin + naphthene + olefin, monocyclic aromatic, dicyclic aromatic hydrocarbons
PNO/mA/dA/pA	Groups of hydrocarbons; n-+ isoparaffin + naphthene + olefin, monocyclic aromatic, dicyclic aromatic, polycyclic aromatic hydrocarbons
PNO/mA/dA/pA/R	Groups of hydrocarbons: n- + isoparaffin + naphthene + olefin, monocyclic aromatic, dicyclic aromatic, polycyclic aromatic hydrocarbons, resins
PNO/mA/dA/tA/pA/R	Groups of hydrocarbons: n- + isoparaffin + naphthen + olefin, monocyclic aromatic, dicyclic aromatic, tricyclic aromatic, polycyclic aromatic hydrocarbons, resins
PON	Vacuum diesel oil
PONA,P/O/N/A	Groups of hydrocarbons: n- + isoparaffin, olefin, naphthene hydrocarbons
PS1	Polymer of the type of polystyrene-divinylbenzene
R	Resins
RI, RID	Refractometric detector
RP-HPLC	Reverse-phase high-performance liquid chromatography
SAE10	Base oil, class of kinematic viscosity of 4.9–5.2 mm^2/s at 100°C
SBD	Polymer of the type of polystyrene-divinylbenzene
SCX-Ag	The strong ion exchanger (cationite) with silver compounds
SFC	Supercritical fluid chromatography
SiO_2	Silica gel
SiO_2-Ag^+	Silica gel modified with silver (I) ions
SiO_2-Cu^{2+}	Silica gel modified with copper (II) ions
TLC-FID	Thin-layer chromatography with quartz bars coated with stationary phase and with flame ionization detector
TNAP	Bonded phase: trinitro aniline propyl phase
UV	Ultraviolet radiation, UV spectrophotometric detector
UV-DAD	UV spectrophotometer combined with photodiode array detector

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