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REVIEWS

Determination the Hydrocarbon Group-Type Composition of Petroleum Feedstocks and Products through Foreign Experience

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Abstract—The hydrocarbon group-type composition (saturated and aromatic hydrocarbons, resins, asphaltenes) of oil dispersed systems is predominantly determined using chromatographic methods: liquid adsorption chromatography, high-performance liquid chromatography, thin-layer chromatography with flame ionization detection. The specificity of standard procedures developed for analyzing petroleum feedstocks and products by various methods often leads to the incomparability of the results, both in terms of the nomenclature of the identified hydrocarbon groups and the determined concentrations. This review assesses chromatographic methods for analyzing the hydrocarbon group-type composition of petroleum feedstocks and products, highlighting their features, advantages, and disadvantages. The main modifications of standard procedures aimed at achieving a correlation between the results obtained by different analytical methods are described.

Keywords: hydrocarbon group-type composition, liquid adsorption chromatography, high-performance liquid chromatography, thin-layer chromatography with flame ionization detection, standard procedures, modification

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Petroleum feedstocks and products are complex multicomponent oil dispersed systems (ODSs). The initial understanding of an ODS is formed through the examination of its physical properties. To select the optimal petroleum feedstocks processing method, knowledge of its composition is essential, and the determination of the composition requires the application of a broad range of physicochemical methods [1–3].

In the analysis of ODSs, their elemental, fractional, and hydrocarbon group-type compositions are considered. Various types of ODSs exhibit a similar and a narrowly constrained range of macroelement compositions [4]. The primary components of ODSs are carbon (82.5–87.0 wt %) and hydrogen (11.5–14.5 wt %). The remaining portion consists of heteroatoms (sulfur, nitrogen, and oxygen), with their total concentration rarely exceeding 10 wt %. Trace elements (metals and nonmetals) are also present in ODSs in small quantities, and their composition varies for different petroleum feedstocks [1, 3, 5].

The fractional composition involves the distribution of hydrocarbon fractions based on the temperature ranges of their initial and final boiling points. However, the results of determining the fractional composition do not permit the assessment of the chemical nature of the ODS to identify a potential method for its processing.

Conventionally, the hydrocarbon group-type composition is understood as the subdivision of an ODS into four groups of compounds (the so-called SARA groups): saturates, aromatics, resins, and asphaltenes. Saturates consist of aliphatic nonpolar compounds, such as branched and normal alkanes (*n*-alkanes) and cycloalkanes. Aromatics are characterized by low polarity; they include compounds containing one or more aromatic or thiophene rings. Resins and asphaltenes consist of polycyclic aromatic fragments surrounded by alkyl substituents [1, 3, 4, 6–11]. Among these groups, asphaltenes have the most complex structures, and their distinguishing feature is insolubility in low-molecular-weight *n*-alkanes and, conversely, solubility in monoaromatic hydrocarbons [11, 12]. The chemical behavior of most types of ODSs depends on the concentrations of hydrocarbon groups in their composition. In this regard, the results of determining the hydrocarbon group-type composition are of particular applied significance [7–10, 13, 14]. They can give essential information about the compatibility and stability of the ODS during mixing, tendencies toward coke formation, preservation of stability, correlations with physical properties, etc. [4, 6, 11, 14–17].

The hydrocarbon group-type composition is typically determined using both absolute and relative methods of chromatographic analysis. The former methods include liquid adsorption chromatography (LAC) and solvent extraction, while the latter group comprises high-performance liquid chromatography (HPLC), thin-layer chromatography with flame ionization detection (TLC–FID), and supercritical fluid chromatography [1, 3, 4, 6–10, 13–21]. Among these, procedures of LAC, HPLC, and TLC–FID are most widely used for determining the hydrocarbon group-type composition.

Standard procedures were developed based on the aforementioned analysis methods, each with its own specificity associated with (1) the nature of the test sample (petroleum feedtocks with varying volatile hydrocarbons and asphaltene concentrations, petroleum products), (2) the peculiarities of the applied method, (3) the conditions of analysis (used eluents, adsorbents, etc.), and (4) the structural features of the chromatographic separation unit [22–38].

Depending on the selected method for analyzing the ODSs and the corresponding standard procedure, various hydrocarbon groups can be identified. These groups may differ in composition both from each other and from the SARA groups. This disparity in results can be a reason for incomparability, prompting researchers to modify standard procedures [4, 6, 8–10, 13, 14, 18, 20, 21, 39–45].

This review is dedicated to the examination of the primary chromatographic methods for determining the hydrocarbon group-type composition of ODSs, namely, LAC, HPLC, and TLC–FID, along with their respective standard procedures, with the objective to identify their characteristics, advantages, and disadvantages. Some variations of proposed modifications to standard procedures aimed at achieving a correlation between the results obtained by different methods are described.

KEY CHROMATOGRAPHIC METHODS FOR DETERMINING THE HYDROCARBON GROUP-TYPE COMPOSITION OF OIL DISPERSED SYSTEMS

Liquid adsorption chromatography serves as a preparative approach to determining the hydrocarbon group-type composition. Developed in the 1970s for the analysis of petroleum bitumens and heavy petroleum distillates [46, 47], it was truly revolutionary at that time. The essence of the LAC method involves the preliminary separation of an ODS into maltenes and asphaltenes, followed by the further separation of the maltenes. Maltenes are then separated into hydrocarbon groups based on solubility and polarity [1–4, 6, 7, 9, 10, 14, 17, 18, 20].

The procedure using this method is quite labor-intensive. The isolation of asphaltenes from an ODS is typically achieved by precipitating them with an excess of low-molecular-weight *n*-alkanes (hereafter referred to as deasphalting)—*n*-pentane, *n*-hexane, or *n*-heptane—upon prolonged boiling. Precipitation occurs due to the mismatch in the size and type of molecules between the asphaltenes and the precipitant. After removing the precipitant, maltenes are separated into hydrocarbon groups using solvents (eluents) in a chromatographic column in increasing order of compound polarity: saturates, aromatics, and polar compounds. The separation boundaries in the chromatographic column are usually visually estimated using a refractometer or a source of ultraviolet (UV) radiation. The concentrations of the separated hydrocarbon groups are determined by gravimetry. Thus, the LAC method remains an absolute one and continues to be relevant nowadays.

The method has its advantages and disadvantages [4, 6, 7, 9, 10, 13, 15, 16, 19, 39]. Among its unquestionable advantages are its nondestructive nature, a possibility of preparing calibration samples for other chromatographic methods, and the simplicity of the equipment.

The main disadvantages include long time, high sample consumption, and materials and reagents expenditures. Sample preparation for analysis, involving the capture of volatile compounds and/or deasphalting, is necessary. The process is challenging to automate (e.g., by connecting eluent delivery system and/or detecto), and the reproducibility of the results is low.

High-performance liquid chromatography. The drawbacks of LAC prompted researchers to explore new methodological approaches to determining the hydrocarbon group-type composition of ODSs. The primary task was to select an instrumental method with high performance, sensitivity, and accuracy. The HPLC method satisfied these requirements [48–50] and became actively used to analyze ODSs with wide ranges of boiling temperatures. It also enabled the differentiation of aromatic compounds based on the number of aromatic rings, distinguishing between mono-, di-, tri-, and polyaromatic compounds [3, 6–8, 15, 16, 18, 27–29, 31–33, 35–38, 41].

The procedure for determining the hydrocarbon group-type composition of ODSs using the HPLC method is analogous to the one described above for LAC, but is less labor-intensive. At the initial stage, the deasphalting of a sample is conducted by briefly and periodically shaking it with a precipitant without boiling. Typically, *n*-hexane is used as the precipitant for asphaltenes. At the second stage, the obtained solution of maltenes is introduced into a chromatograph to determine three hydrocarbon groups: saturates, aromatics, and polar compounds.

In conventional normal-phase chromatography, silica gel with attached amino-, cyano-, or diol groups are commonly employed as polar stationary phase [7, 8, 10, 18, 41, 50], and the nonpolar mobile phase consists of a single solvent, which also serves as a precipitant at the deasphalting stage. During the analysis, the elution direction is switched from direct to reverse. Signals from saturates are recorded during direct elution, while signals from aromatic hydrocarbons are detected during reverse elution. Polar compounds are retained in the column in both modes, and their concentration in the sample is determined by calculations [48]. To remove polar compounds for column regeneration, the column is washed with dichloromethane.

The use of multiple stationary phases with different polarities enables the elution of polar compounds, yielding a detectable signal [6, 8, 10, 41, 43, 50]. The detection of saturated compounds is primarily carried out using a refractometer. Despite its relative versatility, the sensitivity of this detector is limited [7]. In contrast, an ultraviolet (UV) spectroscopic detector offers high sensitivity but is limited in its applicability to nonfluorescent aromatic hydrocarbons and nonpolar compounds. The UV detector ensures a wide range of responses, making it challenging to establish a clear correlation between the recorded signal and the concentration of a specific group [7, 41]. A combination of two detectors mitigates the drawbacks of each one, contributing to an improved determination of hydrocarbon groups. Saturated hydrocarbons are detected using a refractometer, while aromatic and polar compounds are detected using a UV detector [3, 6, 8, 15, 16, 41]. Like any relative method, HPLC requires the determination of a calibration dependence. Calibration samples are usually employed, prepared from individual hydrocarbons or hydrocarbon groups, isolated by LAC from samples of a known composition of petroleum feedstocks [8, 15, 16, 48, 50].

The HPLC method possesses undeniable advantages over the LAC method. It is characterized by low time consumption; minimal sample, materials and reagents usage; an ability to analyze low-boiling samples; compatibility with various detectors; the capability to determine subgroups of aromatic hydrocarbons (mono-, di-, tri-, polyaromatics); and higher reproducibility.

However, the method has some drawbacks [7, 8, 15, 16]. Among them, we note the inability to analyze asphaltene-containing ODSs due to the irreversible adsorption of asphaltenes on the column stationary phase [6–8, 10, 15, 16, 27–33, 35–38, 48], the need in determining a calibration dependence [18, 27–33, 35–38, 41, 48, 50], and the complexity of the equipment (including the lack of a universal method for hydrocarbon group detection [1, 18, 41]).

Using HPLC for determining the hydrocarbon group-type composition represents a scientific breakthrough. The method steadily evolves towards the modernization of chromatographic separation units, involving the selection of new stationary phases and the improvement of HPLC column systems. According to numerous studies, it is considered a potentially superior analytical method for determining the hydrocarbon group-type composition of petroleum products [41]. According to the findings of [20], the HPLC method has surpassed the LAC method in terms of its widespread application.

Thin-layer chromatography with flame ionization detection emerged during the development of planar chromatography in the late 1960s to early 1970s. The separation and determination of components in complex organic matrices were proposed on the surface of thin cylindrical rods (quartz or glass-ceramic) with subsequent flame ionization detection [7, 13, 17, 21, 51, 52]. The cylindrical shape of the rods enabled avoiding edge effects that could disrupt the movement of the solvent front, and their small size required less sample, materials and reagents consumption [51, 53, 54]. The flame ionization detector distinguished itself with its versatility, high sensitivity, and broad linear dynamic range. This led to the development of the well-known and currently the only commercially available semi-automated thin-layer chromatography system with flame ionization detection, Iatroscan. The system includes a chromatographic separation unit (quartz rods, quartz rod holder, solvent containers), a UV lamp panel for detecting the solvent front height, a flame ionization detector, a data collection unit, and an automatic sample applicator (optional). This system has immense potential applications in various scientific, industrial, and medical fields, and notably occupies a special place among the primary methods for determining the hydrocarbon group-type composition in ODSs [4, 7, 8, 10, 13–17, 20, 21, 51–55].

The basis of the TLC–FID method using the Iatroscan system involves the chromatographic separation of hydrocarbons on the surface of quarts rods Chromarods into four groups. The Chromarods are uniformly coated along their entire length with a thin, a homogeneous, and a porous layer made of a mixture of low-melting glass and an adsorbent (silica or alumina). The small particle size distribution of the stationary phase ensures a high resolving power of the system [17, 53]. The separation of hydrocarbon groups occurs step-by-step in the ascending flow of the mobile phase by changing the solvent in the order of increasing polarity [55]. At each stage, the Chromarods with the applied sample are maintained to rise to different heights of solvent front progression. As chromatographic separation is performed manually, the TLC–FID procedure is less sophisticated in terms of procedural simplicity compared to the HPLC procedure.

Detection occurs through the combustion and ionization of the separated hydrocarbon groups in the space as the Chromarods pass through the hydrogen flame of the FID burner. The ions generated, with varying charges, create currents between the burner and the detector. The measured ionic currents are directly proportional to the concentration of hydrocarbon groups in the sample [7, 14, 17, 51–53, 55].

Compared to LAC, the TLC–FID method has the following advantages: lower time costs; smaller sample, materials and reagents consumption; a possibility of reusing the stationary phase multiple times; presence of an automatic detection stage; and higher reproducibility.

The TLC–FID method surpasses the HPLC method in higher performance [13, 17, 52, 54], an ability to analyze asphaltene-containing ODSs [4, 7, 8, 10, 13–17, 21, 54–56], and the absence of a need in a calibration dependence procedure.

The disadvantages of the method include its inability to analyze low-boiling samples, difficulties in separating resins and asphaltenes, the destructive nature of the method, and the complexity of the equipment. The advantages mentioned earlier, such as the ability to analyze asphaltene-containing ODSs and the absence of a calibration dependence procedure, can also be considered drawbacks of this method.

The absence of a preliminary deasphalting stage for a petroleum sample leads to the redistribution of the most polar groups of the compounds (resins and asphaltenes) during chromatographic separation. As a result, the TLC–FID method does not ensure the separation of compounds into classical SARA groups.

In practice, a single calibration coefficient equal to unity is indeed used for each hydrocarbon group. Because of this, the results are approximate, as confirmed by various studies [7, 8, 10, 11, 13, 15–17, 20, 51, 53, 55]. Attempts to determine a calibration dependence are complicated by the lack of commercially available universal calibration samples. Currently, each researcher prepares calibration samples independently for analysis of specific ODS from individual compounds or hydrocarbon groups isolated by LAC.

The TLC-PID method is gaining popularity in the petrochemical industry for routine analyses [51, 52].

Characteristics of the main chromatographic methods are compared in Table 1. Despite low operational costs, LAC is characterized by high time and sample, materials and reagents consumption. Typically, several working days, tens of grams of a sample, hundreds of grams of the stationary phase, and several liters of solvents are required to determine the hydrocarbon group-type composition of an ODS by the LAC method. However, instrumental methods allow for the analysis of petroleum products within a few hours using less than 1 g of a sample, tens of grams of the stationary phase, and no more than 1 L of solvents. For the TLC-PID method, the costs are minimal. The high operational expenses of instrumental methods are associated with the high cost of the equipment used.

The labor intensity of LAC is explained by the fact that each stage of analysis (preliminary capture of volatile compounds and/or deasphalting, separation of maltenes into hydrocarbon groups using solvents, gravimetric determination of the concentration of the isolated groups) is performed manually. In this method, only sample and solvents dosing, as well as detection, can be automated. The determination of the hydrocarbon group-type composition of ODSs by HPLC implies minimal operator involvement. In TLC–FID, only the stage of chromatographic separation is not automated.

All the considered methods can be applied to analyzing asphaltene-containing ODSs. In LAC and HPLC, preliminary deasphalting of samples is necessary. The HPLC method is the only technique capable of analyzing volatile samples.

Taking into account that the contribution of random errors to the analysis results depends on the number of manipulations (stages) performed by an operator during the analysis, the highest reproducibility of the results should be characteristic of the instrumental HPLC method, while the lowest should be observed for the preparative LAC method.

STANDARD PROCEDURES FOR DETERMINING THE HYDROCARBON GROUP-TYPE COMPOSITION OF OIL DISPERSED SYSTEMS

Standard procedures of liquid adsorption chromatography. Within the LAC method, the following standard analysis procedures have been developed: ASTM D2007 [23] and ASTM D4124 (equivalent to GOST 32269-2013) [24, 26].

The ASTM D2007 procedure is designed to analyze ODSs with a boiling point (T_{bp}) not lower than 260°C, containing no more than 0.1 wt % of asphaltenes. Samples with higher asphaltene concentrations require preliminary deasphalting. Asphaltenes are precipitated by a tenfold excess of *n*-pentane. During the analysis, the concentration of three groups of hydrocarbons is determined: saturated hydrocarbons, aromatic hydrocarbons, and polar compounds. In other words, within this standard procedure, the determined hydrocarbon groups correspond to the classical SARA groups.

Chromatographic separation is carried out using a two-section percolation column. The upper section is loaded with clay of a required adsorption activity, while the lower section contains a 1 : 4 mixture of clay and silica. During the first elution with *n*-pentane, saturated hydrocarbons are eluted, which are not adsorbed by any of the stationary phases used, and aromatic hydrocarbons, which are adsorbed on the surface of silica, are displaced to the lower section of the column. At the second elution stage, polar compounds adsorbed on the clay are eluted from the previously detached upper section of the column using a 50 : 50 toluene–acetone mixture. In some cases, aromatic hydrocarbons are desorbed from the surface of silica in the lower section of the column using hot toluene.

Table 1. Comparative characteristics of the main chromatographic methods for determining the hydrocarbon group-type composition of oil dispersed systems

Method	Expenses				Execution		Nature of the samples		Reproducibility
	time	sample weight	consumption of materials and reagents	operational*	simplicity of the procedure	possibility of automation	asphaltene-containing	highly volatile	
LAC	High (2–5 days)	Large (1–10 g)	Large (adsorbent 50–200 g, solvents 0.5–2 L)	Low (glass column)	Complex	±**	±***	–	Low
HPLC	Average (2–5 h)	Average (0.5–1 g)	Average (column****, solvents 0.5–1 L)	High (chromatograph)	Simple	+	±***	+	High
TLC–FID	Low (1–3 h)	Small (0.05–0.2 g)	Small (quartz rods****, solvents 0.35–0.5 L)	High (Iatroscan TLC-FID system)	Medium	+	+	–	Average

* Complexity and cost of the equipment used.
** Can be automated by connecting a dosing pump for supplying eluents and/or a detector.
*** A procedure for preliminary deasphalting of the sample is required.
**** Reusable.

The concentration of the separated saturated hydrocarbons and polar compounds is determined gravimetrically after the preliminary preparation of the eluates and the evaporation of the solvents from them. The concentration of aromatic hydrocarbons is determined by two methods. The first method (the simplest) is a calculation method: by subtracting the concentration of saturated hydrocarbons, polar compounds, and asphaltenes (if present) from 100 wt %. The second method (applied during extraction) is gravimetric [7, 17, 23].

The standard procedure ASTM D4124 enables the determination of the hydrocarbon group-type composition in petroleum bitumens and also in high-boiling petroleum products with low asphaltene concentrations: vacuum gas oils, lubricating oils, and cycle stocks products. Preliminary asphaltene precipitation is a mandatory step, conducted using a 100-fold excess of isooctane, although previously *n*-heptane was used [25]. This procedure (unlike the ASTM D2007 procedure) determines the concentration of the following hydrocarbon groups: saturated hydrocarbons, naphthenic aromatic hydrocarbons, and polar aromatic compounds.

For chromatographic separation, a single-section column equipped with a water jacket is used, connected to a metering pump for supplying the sample solution and eluents and to a UV source for fixing the boundaries of the eluate hydrocarbon groups. The column is packed with activated alumina. The three-stage elution of hydrocarbon groups is carried out in order of increasing solvent polarity. To separate saturated hydrocarbons, *n*-heptane and toluene are successively passed through; for naphthenic aromatic hydrocarbons, toluene and a 1 : 1 toluene–methanol mixture; for polar aromatic compounds, trichloroethylene is used. The separation of hydrocarbon groups is monitored visually or using a UV source. In the visual control, it is considered that saturated hydrocarbons form a colorless (light) eluate, naphthenic aromatic hydrocarbons are yellow, and polar aromatic compounds are dark and opaque. The concentration of separated hydrocarbon groups is determined gravimetrically after removing solvents from the obtained eluates.

Thus, standard procedures are aimed at analyzing only high-boiling ODSs. This is accompanied by a potential loss of volatile components during prolonged multi-stage separation.

Standard procedures of high-performance liquid chromatography. The spectrum of possibilities offered by HPLC has led to the development of several standard procedures for determining the hydrocarbon group-type composition of petroleum samples: ASTM D6379 (analogues are IP 436, GOST R 54268-2010, and GOST 33912-2016) [28, 33, 36, 37], ASTM D6591 (and analogue is IP 548) [29, 35], EN 12916 (analogues are IP 391 and GOST EN 12916-2017) [27, 32, 38], and ASTM D7419 (an analogue is IP 368) [30, 31]. None of the mentioned procedures enable the determination of the hydrocarbon group-type composition of ODSs in the classical sense, i.e., the determination of all four SARA groups simultaneously. The first three procedures are focused on the determination of aromatic hydrocarbons (their types). They are based on conventional HPLC: the use of a polar stationary phase (silica with attached amino or amino/cyano groups) and a nonpolar mobile phase (*n*-heptane).

The ASTM D6379 procedure is applied to the analysis of aviation fuels and petroleum distillates with boiling points in the range 50–300°C to determine the concentration of aromatic hydrocarbons, specifically mono- and bicyclic hydrocarbons. The ASTM D6591 and EN 12916 procedures offer a possibility of determining aromatic hydrocarbons, including not only mono- and bicyclic but also tri- and polycyclic hydrocarbons. In this case, the test samples are diesel fuels and petroleum distillates with T_{bp} ranging from 150 to 400°C.

The limitations of these standard procedures are determined by the nature and physical characteristics of the test ODS: the procedures are not suitable for the analysis of high-boiling petroleum products ($T_{\text{bp}} >$ 400°C) enriched with high-polar polycondensed compounds.

ASTM D7419 is the only standard procedure within the HPLC framework designed for determining the hydrocarbon group-type composition of additives-free lube basestocks, i.e., high-boiling petroleum fractions close in boiling points to heavy petroleum distillates. This procedure is intended for the determination of saturated and aromatic hydrocarbons (along with polar compounds if their concentration does not exceed 1 wt %). In this case, chromatographic separation is carried out using two columns packed with stationary phases of different polarities: one with silica with attached cyano groups (more polar) and the other with regular silica (less polar). The prepared sample, upon injection, interacts first with the more polar stationary phase. *n*-Heptane is used as the mobile phase. Saturated hydrocarbons are eluted with *n*-heptane in the forward direction, without interacting with either of the stationary phases. Meanwhile, aromatic hydrocarbons and polar compounds are adsorbed on the stationary phase. Their elution is performed in the reverse direction. A refractometric detector is used for the detection and quantitative determination of hydrocarbon groups. In some cases, a UV detector can also be used to monitor the overlap of the recorded signals from saturated hydrocarbons and total aromatic compounds, which include polar compounds alongside aromatic hydrocarbons.

The concentration of hydrocarbon groups is determined automatically, considering calibration coefficients. A calibration dependence is obtained using individual compounds of specific purity (with the concentration of the main substance not less than

97 wt %): hexadecane for determining saturated hydrocarbons and octadecylbenzene for determining aromatic hydrocarbons.

Standard procedure of thin-layer chromatography with flame-ionization detection. To determine the hydrocarbon group-type composition in petroleum feedstocks and products using TLC–FID, the only standard procedure IP 469 [34] has been developed. This procedure is employed for the analysis of petroleum feedstocks and products with boiling points of not lowers than 300°C, such as vacuum gas oils, lubricating oil basestocks oils, aromatic extracts (process oils), residual fuels, feedstocks, and components from both atmospheric and vacuum processing, as well as bitumens. The stage of preliminary deasphalting is not used.

The procedure enables the determination of the concentration of four groups of compounds: saturated hydrocarbons (paraffins and naphthenes), aromatic hydrocarbons, polar compounds I, and polar compounds II. Saturated hydrocarbons include nonaromatic acyclic and cyclic hydrocarbons (paraffins and naphthenes). Aromatic hydrocarbons refer to compounds containing one or more aromatic rings, including some sulfur-containing compounds of the thiophene or sulfide type, some nitrogen-containing compounds (e.g., benzocarbazoles), and oxygen-containing compounds (e.g., benzofurans). Polar compounds I are low-molecular-weight polar compounds containing N, S, and O heteroatoms (e.g., benzquinolines, carboxylic acids, phenols, metalloporphyrins). Polar compounds II are high-molecular-weight polyfunctional polar compounds, similar but not identical to asphaltenes, insoluble in heptane, and determined by the standard IP 143 procedure [57]. These compound groups are not equivalent to the classical SARA-groups classification.

An analysis begins with the activation of quartz rods held in a special frame by burning them in the hydrogen flame of the PID burner. The three-stage chromatographic separation is carried out after applying an aliquot portion of a sample solution in dichloromethane to the rods. At the first stage, the quartz rods with the applied sample are kept in *n*-heptane until the solvent front advances to a height of 100 ± 5 mm from the starting line. At the second stage, they are kept in a mixture of *n*-heptane and toluene (1 : 4) until the solvent front advances to a height of 50 ± 5 mm from the starting line. At the third stage, they are kept in a mixture of dichloromethane and methanol (19 : 1) until the solvent front advances to a height of 20 ± 5 mm from the starting line. Thus, the spatial separation of compound groups occurs in the order of increasing polarity.

The concentration of compound groups is determined after recording and processing the chromatogram obtained with the PID. No calibration curve is set, and a unified calibration coefficient is assumed equal to unity. The concentration of each compound group are presented with normalization to 100 wt %.

A comparative characteristic of standard procedures for determining the hydrocarbon group-type composition of ODS products is presented in Table 2. The test samples in the standard LAC and TLC–FID procedures were petroleum feedstocks and high-boiling petroleum products enriched with highly polar polycondensed structures. Standard HPLC procedures were primarily developed for the analysis of fuels or petroleum distillates with trace amounts of resins and asphaltenes.

The most labor-intensive and time-consuming sample preparation procedure (deasphalting) is characteristic of standard LAC procedures. In other cases, minimal operator involvement is required, usually involving the preparation of a sample solution in a suitable solvent.

In all standard LAC and TLC–FID procedures, concentrations of four compound groups can be determined. However, the only standard LAC procedure (ASTM D2007) determines precisely the SARA groups. In standard HPLC procedures, the number of the determined Hydrocarbon groups is limited; they are primarily used to find the concentration of either aromatic hydrocarbons or saturated and aromatic hydrocarbons.

According to the standard LAC and TLC–FID procedures, hydrocarbon groups are separated on a nonpolar stationary phase using various solvents of different polarities. Standard HPLC procedures use a different approach. Here, the stationary phase is a polar adsorbent, and the mobile phase is a single nonpolar solvent.

The concentration of compound groups in standard LAC procedures is determined gravimetrically after their separation and isolation. The construction of a calibration dependence procedure is a mandatory step in the standard HPLC procedures. At the same time, in the standard TLC–FID procedure, the calibration dependence procedure is overlooked, and a single calibration coefficient of unity is set.

MODIFICATION OF STANDARD PROCEDURES FOR DETERMINING THE HYDROCARBON GROUP-TYPE COMPOSITION OF OIL DISPERSED SYSTEMS

Many researchers note the incomparability of the results in determining the hydrocarbon group-type composition obtained by different analytical methods [4, 6, 8–11, 14–18, 20, 21, 39, 45]. To achieve a correlation between the analysis results and enable their correct comparative assessment, various modifications to the existing standard procedures have been proposed.

Modification of standard liquid adsorption chromatography procedures. Standard LAC procedures are

Table 2. Comparative characteristics of standard procedures for determining the hydrocarbon group-type composition of oil dispersed systems

Method	Procedure	Objects	Sample preparation	Determined groups of compounds	Stationary phase	Mobile phase	Determination method
LAC	ASTM D 2007	ODS ($T_{bp} > 260°C$)	(1) Deasphalting with *n*-pentane; (2) loading maltenes into the column	Saturated hydrocarbons, aromatic hydrocarbons, polar hydrocarbons, asphaltenes	I, Clay; II, clay–silica (1 : 4)	*n*-Pentane, toluene–acetone (1 : 1), toluene (extractant)	Gravimetry
	ASTM D 4124	Petroleum bitumens, vacuum gas oils, lubricating oils, cycle stocks	(1) Deasphalting with isooctane; (2) loading maltenes into the column	Saturated hydrocarbons, naphthenic aromatic hydrocarbons, polar aromatic hydrocarbons, asphaltenes	Alumina	*n*-Heptane, toluene, toluene–methanol (1 : 1), trichloroethylene	Gravimetry
HPLC	ASTM D 6379	Aviation kerosines, petroleum distillates (T_{bp} 50–300°C)	(1) Dissolution in *n*-heptane; (2) filtering of insoluble substances (if any)	Aromatic hydrocarbons (mono- and bi-)	Silica with attached amino or amino/cyano groups	*n*-Heptane	Calibration
	ASTM D 6591	Diesel fuels, petroleum distillates (T_{bp} 150–400°C)	(1) Dissolution in *n*-heptane; (2) filtering of insoluble substances (if any)	Aromatic hydrocarbons (mono-, bi-, tri+-)	Silica with attached amino or amino/cyano groups	*n*-Heptane	Calibration
	EN 12916	Diesel fuels (FAME up to 30 vol %), paraffinic diesel fuels (FAME up to 7 vol %), petroleum distillates (T_{bp} 150–400°C)	(1) Dissolution in *n*-heptane; (2) filtering of insoluble substances (if any)	Aromatic hydrocarbons (mono-, bi-, tri+-)	Silica with attached amino or amino/cyano groups	*n*-Heptane	Calibration
	ASTM Lube basestocks	Lube basestocks free of additives	(1) Dissolution in *n*-heptane	Saturated hydrocarbons, aromatic hydrocarbons (together with polar ones)	I, Silica with attached cyano groups; II, silica	*n*-Heptane	Calibration
TLC–FID	IP 469	ODS ($T_{bp} > 300°C$), vacuum gas oils, lubricating oil basestocks, aromatic extracts (process oils), residual fuels, feedstocks and components from both atmospheric and vacuum processing, bitumens	(1) Dissolution in dichloromethane	Saturated hydrocarbons, aromatic hydrocarbons, polars I, polars II	Silica applied to quartz rods (Chromarods)	*n*-Heptane, *n*-heptane–toluene (1 : 4), dichloromethane–methanol (19 : 1)	Without calibration (calibration coefficient = 1)

FAME, fatty acid methyl esters.

the most flexible in terms of modifications [4, 6, 7, 9, 10, 14–16, 18, 19, 39, 40, 42, 56] due to the peculiarities of the method (Table 1). The key directions of their modification include changes to the deasphalting procedure, conditions of the chromatographic separation of ODS components, and instrumental setup.

The preliminary precipitation of asphaltenes is often carried out using an alternative method—according to ASTM D6560 (or analogue, IP 143) [57, 58] or ASTM D3279 [59]. In this case, the chromatographic separation of maltenes is performed according to standard LAC procedures [4, 6, 9, 10, 14, 18, 19].

The essence of the key changes in the conditions of the chromatographic separation of ODS lies in varying the stationary and mobile phases, i.e. adsorbents and solvents. Special attention is given to the physical properties of the selected adsorbent, as these properties affect the separation of the maltenes part of the sample [9]. The pore size, particle size, and surface pH may differ even for the same type of stationary phase. The use of adsorbents with different characteristics can critically affect not only the reproducibility of the obtained results but also the feasibility of the chromatographic separation itself.

Variation in the composition of the mobile phase primarily involves replacing solvents used in standard procedures for the deasphalting and/or elution of saturated hydrocarbons with a single *n*-alkane: *n*-hexane or *n*-heptane instead of *n*-pentane (according to ASTM D2007) and *iso*-octane, *n*-heptane, or toluene (according to ASTM D4124) [11, 14–16, 39, 56]. Alternative solvents for the elution of aromatic hydrocarbons and polar compounds are less commonly used [9, 14, 18, 39, 42, 56]. The aim of replacing the mobile phase is to improve the quality of the group separation, create comparable chromatographic separation conditions (compared to other methods), and shorten the solvent removal procedure.

Modification of the instrumental setup is aimed at reducing time, sample, materials and reagents consumption, and also at incorporating instrumental detection and determination of the concentration of hydrocarbon groups. To reduce the mentioned costs, it was proposed to use a miniature chromatographic column [9] or a solid-phase extraction cartridge [14], a pump for sample and mobile phase supply, solvent distillation systems (for regeneration), and valves for controlling flow directions [18].

Detectors can be used not only to detect the boundaries of the eluate of hydrocarbon groups (as in ASTM D4124), but also to determine their concentrations. For example, an optical method was proposed instead of gravimetry to determine the concentration of hydrocarbon groups: saturated hydrocarbons were quantified using a refractometric detector, and aromatic hydrocarbons and polar compounds were determined using a UV detector [9].

Modification of standard high-performance liquid chromatography procedures. Due to the limitations of standard HPLC procedures (related to the nature of the test substances and the number of determined hydrocarbon groups) priority is given to modifications aimed at introducing a mandatory deasphalting stage (manual or automatic) and ensuring the ability to determine polar compounds.

The HPLC determination of four compound groups can be achieved using a chromatographic separation unit consisting of several columns with different stationary phases and more than one solvent [6, 10, 15, 16, 41, 43, 48–50]. Sample consumption, elution circuit, the detectors used, the procedure for determining calibration dependence, and other parameters are usually comparable to the recommendations of standard procedures.

In [15, 16], procedures for the analysis of medium-viscosity oils were proposed to determine four compound groups using a system of two chromatographic columns (silica with attached amino groups) and multiple mobile phases. Sample preparation for analysis involves its preliminary manual deasphalting with an excess of *n*-hexane. Saturated and aromatic hydrocarbons are eluted in the forward direction with *n*-hexane. Their concentrations are determined using refractometric and UV detectors, respectively. Polar compounds are separated in the reverse direction with a mixture of *n*-hexane and dichloromethane, and their concentration is determined gravimetrically.

In addition to *n*-hexane for eluting saturated and aromatic hydrocarbons, the use of *n*-heptane or cyclohexane was recommended, and for eluted polar compounds, dichloromethane, chloroform, or acetone is most suitable [7, 10, 15, 16, 41, 60].

Some procedures for the analysis of ODSs are based on a combination of adsorption and partition chromatography [6, 10, 43]. A particular feature of these procedures is the automation of SARA groups determination using HPLC.

Bissada et al. [10] focused on determining concentrations of compound groups in petroleum feedstocks. Chromatographic separation was conducted using a system of two columns packed with silica with attached cyano groups and pure silica. Saturated hydrocarbons were eluted with *n*-hexane without adsorption on any stationary phase. The retained remaining compound groups in the respective columns were sequentially eluted. Polar compounds were eluted with a mixture of *n*-hexane and chloroform (47 : 3); asphaltenes, with a mixture of methanol, acetone, and chloroform (3 : 3 : 14); and aromatic hydrocarbons, with chloroform. The concentration of hydrocarbon groups could be determined gravimetrically after solvent removal or using an evaporative light scattering detector.

Karevan et al. [6] analyzed bitumen and heavy oil using a chromatographic separation unit consisting of four columns: a guard column, a polytetrafluoroethylene column (for retaining asphaltenes), a column with silica with attached cyano groups (for retaining polar compounds), and a column with silica (for retaining aromatic hydrocarbons). Saturated hydrocarbons were eluted with *n*-pentane without adsorption on any stationary phase. The retained remaining compound groups in the respective columns were sequentially eluted with toluene. A UV detector was used to determine their concentration.

Youtcheff [43] used a system of four columns for separating bitumen and heavy oil into SARA groups (with additional fractionation of asphaltenes by the degree of condensation): a polytetrafluoroethylene column (for retaining asphaltenes), glass bead columns (for retaining polar compounds), columns with silica with attached aminopropyl groups (for retaining polar compounds), and columns with silica (for retaining aromatic hydrocarbons). Saturated hydrocarbons were eluted with *n*-heptane without adsorption on any stationary phase. The retained remaining compound groups in the respective columns were sequentially eluted. Asphaltenes of different degrees of condensation were eluted with cyclohexane, toluene, and a mixture of dichloromethane and methanol (49 : 1). Aromatic hydrocarbons were eluted with toluene; polar compounds were eluted with a mixture of dichloromethane and methanol (49 : 1). The concentration of SARA groups was determined using a UV detector or an evaporative light scattering detector.

Modification of the standard thin layer chromatography with flame ionization detection procedure. The main directions of the modification of the standard TLC–FID procedure involve several key aspects, including changes in sample preparation procedures, chromatographic separation conditions for ODSs, and the determination of calibration dependence procedure.

The modification in the sample preparation procedure involves a decrease in the sample weighed portion taken to prepare a solution applied to the adsorbent layer surface. According to IP 469, the ODS concentration in this solution is 20 mg/mL, with a recommended concentration range of 10–20 mg/mL [4, 8, 13–17, 21, 45, 52, 54, 55]. In [44], a decrease in the concentration of the test solution to 5 mg/mL (for bitumen) and 2 mg/mL (for asphaltenes isolates) was proposed. This approach helps to prevent potential local overloading of the adsorbent during the analysis of ODSs with elevated asphaltenes concentrations [17, 44, 54]. It was assumed that highly polar molecules (such as asphaltenes) can block the existing channels in the adsorbent layer by precipitating and aggregating within them, hindering the complete adsorption of the sample. Preventing such overloading contributes to the registration of representative chromatograms with peaks close to Gaussian in shape, improved resolution, and reduced baseline drift. This undoubtedly influences on the accuracy of the results.

The modification of the conditions of the chromatographic separation of ODSs involves the variation of solvents used as the mobile phase, change of the elution circuit, and modification of the surface of the adsorbent layer. Different solvents or their mixtures were employed as mobile phases, distinct from those used in the standard IP 469 procedure [4, 8, 13–17, 21, 44, 45, 54–56]. These included *n*-hexane (for the separation of saturated hydrocarbons), toluene, its mixtures with *n*-alkanes, or a mixture of *n*-hexane with dichloromethane (for the separation of aromatic hydrocarbons), and a mixture of dichloromethane with methanol in a different ratio (for the separation of polar compounds).

The variation of solvents is typically aimed at creating similar elution conditions, contributing to obtaining comparable results through different methods. It was suggested to select eluents based on the principle of the equivalence of solvent parameters and the hydrocarbon groups extracted using these solvents or their mixtures [14, 18, 19]. In [17], it was emphasized that the use of individual solvents instead of their mixtures ensures results with higher reproducibility.

Changing the elution circuit from direct to reverse involves altering the sequence of solvents in which quartz rods with the applied sample are held. According to IP 469, the sequence of solvents corresponds to the order of increasing polarity. With a reverse elution circuit, the order is inverted. The goal of changing the elution circuit is to improve the quality of the chromatographic separation and enhance the accuracy of the results.

In [17, 44], direct and reverse elution approaches were compared using analyses of high-boiling neutral base oils, aromatic extracts, and vacuum residues, and also of products of their oxidation. Barman [17] noted a partial overlap of the recorded peaks of saturated and aromatic hydrocarbons (with an overestimation of results for this group) and baseline drift in the region of aromatic and polar hydrocarbons in using the direct elution scheme. The observed baseline drift indicates the incomplete separation of the corresponding groups. The replacement of the elution scheme with a reverse one helped to eliminate these drawbacks.

Wojewódka et al. [44] reported the distortion of chromatographic peak shapes, poor separation quality, and low reproducibility of the results in using the direct elution circuit. The distortion of peak shapes was attributed to the mechanical transport of asphaltenes microcrystals through the adsorbent layer, which precipitated in the adsorbent layer at the initial separation stage in using a nonpolar solvent. The poor quality of peak separation and the low reproducibility of the results were explained by the ability of the precipitated asphaltenes and other polar compounds to occlude saturates and aromatic hydrocarbons. Occlusion hinders the migration of these hydrocarbon groups through the adsorbent layer. The inversion of the elution circuit mitigates these effects.

The surface of the adsorbent layer is typically modified by the chemical treatment of quartz rods with iodine vapor or solutions of acids (nitric, boric, oxalic) or salts (copper sulfate, silver nitrate) [45, 51–53]. Despite the reduction in the service life of the adsorbent layer due to such manipulations, an increased sensitivity and selectivity of the TLC–FID method were achieved.

As noted earlier, the standard IP 469 procedure does not include the determination of a calibration dependence procedure. A universal calibration coefficient equal to unity is used for all compound groups. However, the sensitivity of FID for different groups of compounds and even for individual components within the same group is not uniform. In this regard, attempts were made to set a calibration dependence using individual compounds of certain purity [51–54] or hydrocarbon groups separated by the LAC method [4, 13, 52–54, 56]. Universal calibration standards for the TLC–FID method have not been developed yet.

CONCLUSIONS

The study of the hydrocarbon group-type composition (determination of the concentration of saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes—the so-called SARA groups) is of practical significance. Knowledge of the ratio of different groups of compounds in an ODS is essential for assessing its quality and stability and selecting appropriate processing methods.

The hydrocarbon group-type composition is conventionally determined using chromatographic methods: the absolute LAC method and the relative HPLC and TLC–FID methods. While the LAC method has a relatively simple instrumentation, it is characterized by high time consumption; substantial sample, material, and reagent consumption; labor intensity; difficulties in automation; and low reproducibility. Instrumental methods like HPLC and TLC–FID, which require high operational costs, exhibit opposite characteristics in terms of the mentioned factors.

Standard analysis procedures were developed for each of the mentioned methods. Despite their diversity, only the LAC method, specifically ASTM D2007, is used to determine the SARA groups. The specifics of the standard HPLC and TLC–FID procedures directly affect the composition of the determined groups of compounds. This leads to incomparability in the results of determining the hydrocarbon group-type of ODSs.

To achieve a correlation between the results obtained by different analytical methods and their correct comparative assessment, researchers apply modifications to standard procedures. The main directions of modification for all three methods include changing the procedures for preparing ODS for analysis and varying the conditions of it chromatographic separation. Attempts were made to automate some stages of analysis within the LAC method, while particular attention was given to implementing and refining the procedure for determining calibration dependence in the TLC–FID method.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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