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GC/MS application in the structural group analysis of basic lubricant oils. Part I – State of knowledge

Introduction

The terms 'basic oils' and 'base oils' are used interchangeably in many cases, regardless of whether we talk about refined hydrocarbon components obtained from original distillates or about mixtures of several refined distillates produced in order to obtain lubricant oil of appropriate properties which is further improved by addition of suitable non-hydrocarbon components – additives. In presented paper, for clarity, the term '**basic oils**' covers oil distillation fractions subjected to appropriate technological processes, consisting mainly of hydrocarbons of varying structures. The combination of selected basic oils results in producing **base oil** of required viscosity whose properties are further improved and modified by introducing appropriate groups of additives. Among them, there are mainly viscosity modifiers which influence the rheological properties of lubricant oil and also various groups of additives preventing wear and scuffing and improving friction properties. Depending on the purpose of lubricant oil, important are also additives like detergents and dispersants which increase the ability of oil to suspend solid contamination which occur while the engine is working; antioxidants, use to prevent hydrocarbon oil components against the reactions with oxygen present in the air and many other types other additives which optimize the functional properties of lubricant oil.

The chemical composition of crude oil fractions from oil distillation is very complex, but the basic type of compounds occurring in them are hydrocarbons. According to information provided by Spaight [1] concerning crude oil composition, such saturated hydrocarbons can be mentioned as n-paraffin, isoparaffin and other branched structures, cycloalkanes (naphthalene), and among them, condensed cyclanes, such as steranes, or hopanes and other alicyclic

structures. Unsaturated hydrocarbons practically do not exist in oil fractions, and their appearance usually points to thermal cracking of oil components during processing. Another group of compounds which define the oil fractions are such aromatic hydrocarbons as benzene homologues, in other words aromatic monocyclic compounds, arenes with condensed rings starting with naphthalene, and also aromatic – naphthalene structures, frequently alkyl substituted. Apparently in original oil distillates there are also compounds containing heteroatoms, but on account of their adverse effect on the quality of basic oils they are removed during refining.

Hydrocarbon components, present in base and basic oils give the lubricant oil specific properties which finally cause quality differences in ready to use lubricant oils. The possible reason for such properties of refined basic oils is their group composition, or rather the presence of particular hydrocarbon structures which affect the sensitivity of basic oil to introduction of specific additives [e.g. 2]. Very useful for the explanation of this effect may be some information about structural group composition of hydrocarbons which create the basis for lubricant oil composition, hence the search for tools to enable this kind of analysis which started already at the moment of broad application range of lubricants, particularly in attempts to optimize their quality upgrading methods.

The significance of the problem may be best shown in a draft of activities conducted to determine the structures occurring in oil fractions, used as the base for lubricating agents presented below.

It should be noted that in the analysis of higher boiling point oil fractions (oil fractions) the determination of

individual components is practically omitted, rather the content of specific hydrocarbon groups is determined, as in the majority of cases the properties of basic oils only slightly depend on the specific component. An exception may be for instance polycyclic aromatic hydrocarbons whose presence gives the oils a carcinogenic character. Another reason inducing further examination of structures present in heavy distillates is the explanation of differentiation of their effects from introduced additives, and by the same, working out the possibilities of optimization of specific additives selection to achieve a proper quality product, using the basic oils already possessed.

At the beginning of the 20th century, in times of increasing importance of petroleum-based lubricants, the methods of chemical determination of aromatic hydrocarbon content were used for that reason, taking advantage of the possibility of their removal, e.g. by sulfonation [3, 4]. A curiosity may be the fact that at present, the principle of such marking is used by ASTM D 483:1947 standard [5] for evaluation of the amount of non-aromatic substances, explicitly stating that on account of the fact that the relation between unsulfonating residue and the real composition of the oil is not known, this method is not suitable for determination the content of aromates, olefins, or both components and it is used in evaluation of possibilities of the degree of oil refinement.

As an indicator of lubricating oil quality, still used today, aniline point was determined [6]. The fact was used here that the components of aromatic oil fractions depict good solubility in aniline, saturated naphthene structures much lower, and paraffin hydrocarbons are generally badly soluble in this amine. However, this is not the measurement which enables specific determination of the amount of any of the hydrocarbon groups, but rather a test which allows to describe specific properties of the product.

The invention and implementation of new methods of instrumental analysis, mainly in the area of spectral analysis [7], were an impulse to search for new research techniques which would make it possible to obtain more detailed information about the structures of oil distillate components. The UV methods of analysis were used then to evaluate the degree of condensation present in these fractions of aromatic polycyclic hydrocarbons [e.g. 8], also IR analytic methods were developed which found much wider application in examination of lighter fractions, and also other than hydrocarbon components of oil fractions. A variant of the n-d-M method was elaborated which uses for determination of the number of aromatic carbons the measurements of maximum intensity of peaks of aromatic

structures in the infrared [9]. This method was developed on the basis of results obtained, proposed by van Westen et al. [10] computational method taking advantage of determined values of refraction of light coefficient, density and particle mass, broadly discussed in the monograph, among other things [11].

In the fifties, examination of oil fractions was undertaken using the Raman analysis technique (measurement of radiation of inelastic scattering of photons) [e.g. 12], which used intensive sources of monochromatic radiation as excitation source. Today, laser sources are used [13], including those which allow to eliminate fluorescence of many compounds, excited about the high energy radiation, disrupting the measurement. This analytical technique produces excellent effects in structural research, supplementing the results obtained by IR analytic methods, particularly in case of testing non-polar groups, such as C=C, C-C, C≡C, C-S or S-S, showed the small intensity in the infrared region. However, it should be noted that described in literature applications of Raman spectroscopy concern mainly the fuel fractions, and presently this technique is used for measurements of the size of particles in the area of nanotechnology [14].

Parallel to the methods of physical and chemical examination which allow to identify specific organic compound structures, there are developed techniques of separation of particular compound groups of similar properties. The analysis, with the use of the method of column chromatography of hydrocarbons originated from petroleum was started in the first half of the 19th century. In 1928 API began their research project concerning distribution, identification and determination of components of commercial oil fractions [15]. Using fluid chromatography for testing fuel fractions (petrol, heavy oil) enables fast evaluation of the content of basic hydrocarbon groups (the method with fluorescent indicator [16]). The techniques of gas chromatography permit full identification of components of petrol fractions [17], on the other hand, examination of heavy fraction composition does not produce expected results. Only the introduction of mass spectrometry made it possible to further examine the types of hydrocarbon structures present in middle distillates (approximately 200 to 350°C), which is reflected in the standard ASTM D 2425 [18]. This technique allowed also to achieve important information on the types of structures in oil distillates (of middle particle mass 226 to 450 Da), but only in the case of fractions which do not contain aromatic hydrocarbons [19].

With oil distillates (~350–550°C), the application of partition chromatography makes it possible to separate

from the mineral oil matrix in a rather simple method [20] a series of fractions of different polarity, described as paraffin and naphthene fraction, a series of aromatic fractions and polar “resins”.

Other normalized procedures allow to determine the content of saturated and aromatic hydrocarbons and polar compounds in fractions distilling above 260°C using the Attapulgit clay as sorbent, mainly for oils used in rubber industry [21], and even for asphalts of petroleum origin [22], resolute the examined sample, after earlier removal of asphaltenes, into fractions of saturated, naphthene – aromatic hydrocarbons and polar aromatics. This method may also be used for analysis of heavy residual oils. Most of the analytical methods mentioned here, including computational method [10], are used in research conducted in INiG, and the achievement of accreditation of such methods as [16, 23] confirms the proficiency of the analytical laboratory in this field.

Use of gas chromatography to investigation of components in oil fraction

Chromatography [29], according to definition by IUPAC (International Union of Pure and Applied Chemistry) is a physical method of separation of mixture components which are divided into two phases, one of which is a stationary phase (motionless), and the other phase – mobile (movable), moving in specific directions. Liquid chromatography is a technique in which the mobile phase in a continuous way flows through the chromatographic packing, and the sample is introduced to the system as a specified dose. In case of gas chromatography (GC), gas is the movable phase. The GC technique, besides numerous advantages has a few serious disadvantage of which the most important is limited application range of volatile samples in analytic conditions, the lack of possibilities to directly analyze the thermally unstable samples, serious difficulties during laboratory separation of the sample, and also the necessity to use other techniques (mostly spectral) for identification of separated sample.

The development of gas chromatography can be dated for the 1950s, and it can be cited as curiosity that in the first international symposium devoted to chromatography in the gas phase, organized by the British Institute of Petroleum in 1956, some presented papers concerning the analysis of refining gases, solvents, or aromatic compounds were performed on chromatographs of own construction. It should be mentioned that in the Institute of Petroleum Technology in the Automation and Electronics Laboratory in the sixties a gas chromatograph was also constructed by Józef Sikora, which was still working there in the seventies.

Extraction methods are used mostly in industry (e.g. sulfolan used in extraction of aromatic hydrocarbons from petrols – in the 1960s Shell [24], developed by UOP – [25], or furfural in extraction of oil fractions [26]). Nonetheless, it should be mentioned that the procedures of determination carcinogenic, polycyclic aromatic hydrocarbons based on extraction, which allows the examined compounds can be significantly concentrated, are also used in conducted analytical examinations, both as an effect of implementation and accreditation of standard PN-EN 12916 [27, 28] as in developed, own analytical procedures.

Summing up, it should be noted that there is a need for more profound research into the composition of oil fractions used as basic oils. As prospective analytical techniques, the following can be indicated: high performance liquid chromatography (HPLC), gas chromatography – particularly when is used in high temperature ranges, and mass spectrometry as an effective identification tool.

The application of gas chromatography for direct analysis of heavy fraction components from petroleum distillation encounters, as mentioned before, a few limitations [1]. First of all, the number of possible components in fraction of specified distillation temperature range rapidly grows together with increasing of their molecular mass, and at worse, it is accompanied by decreasing of differences in physical and chemical properties of isomer compounds. This phenomenon is the source of considerable difficulties, and sometimes simply the lack of possibility to separate and identify a single compound from heavy oil distillates by means of discussed technique. In general, increasing the molecular mass of separated substances is associated with their longer stay in the chromatographic column, and increasing the temperature to reduce the analysis time increases the possibility of thermal breakdown of examined substance. Therefore, individual components usually are not determined in heavy oil fractions, but they are characterized with regard to the content of specific hydrocarbon groups, i.e. paraffins, naphthenes and arenes. It practically means a chance to find out statistical distribution of particular structural elements in the oil fraction, regardless of the fact in what connection a specific structural element is.

The development of GC technique contributed to it's wider application, although there is relatively little literature relating to analysis of substances whose distillation end point is over 350°C. An exception is the examination of distillation characteristics for crude oils, compiled also as

normalized analytical procedure [30]. An essential problem in analyzing this kind of medium is the possibility of incomplete elution from the column of introduced substances and for this reason it is recommended to use the internal standard. The examination of heavier distillation fractions can make use of substances of boiling temperature lower than the lower limit of examined fraction distillation temperature, most often the n-paraffins C₁₀–C₁₂ are used, which are eluted before the main sample.

Usually 538°C is assumed as the upper limit of distillation, but the application of Dexil 300 column enables determination of final boiling temperature to 600°C, which extends the range of hydrocarbon analysis.

The example of n-paraffin chromatogram, obtained during the chromatograph calibration for procedure of determination the distillation curve according to standard PN-EN 15199 [31] was shown in fig. 1.

The application of two-dimensional gas chromatography for analysis of lubricating oils became the subject of patent [32]. The essential part of the invention was the use of a system of two chromatographic columns of varying polarity. The first one, non-polar, serves to distribute the examined mixture into particular connection groups (the first dimension), which are in turn distributed in the other column (the second dimension) with polar, or semipolar distribution phase. Appropriate time intervals between analyses conducted in the other column are ensured by a cryogenic trap cooled by liquid nitrogen. A model chromatogram obtained by GC-GC technique was shown in fig. 2.

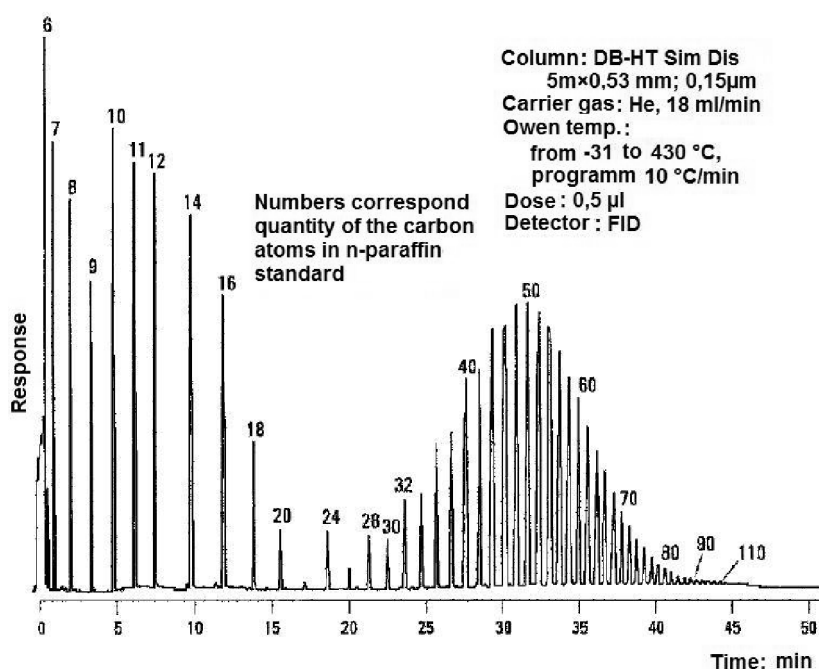


Fig. 1. n-Paraffin standard (Polywax) chromatogram obtained in INiG in calibration high temperature chromatograph

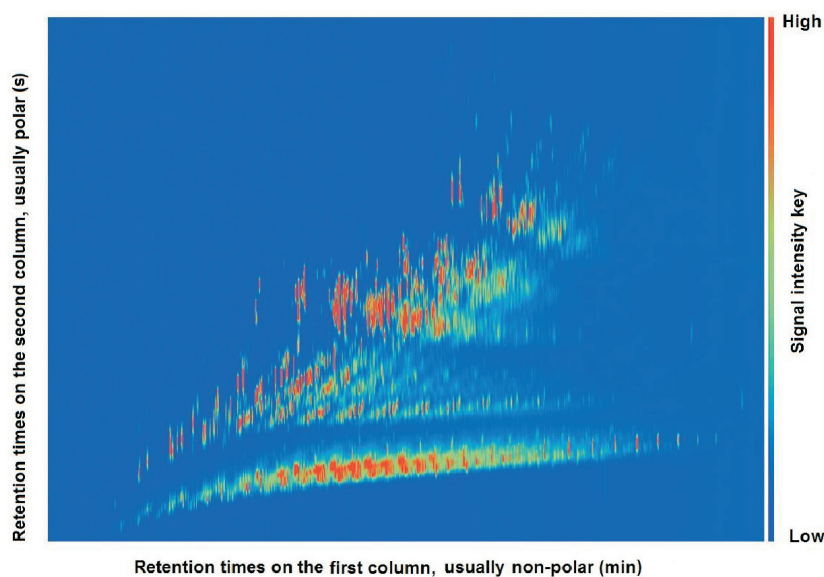


Fig. 2. Example of two-dimensional chromatogram of hydrocarbon oil according to [33]

Use of mass spectrometry in examination of oil fraction components structure

Mass spectrometry is an invaluable identification technique. It is characterized by high repeatability of quantitative results, already the difference of one unit in atomic mass unit is recorded by the mass detector. It allows to distinction the observed ion, which makes it possible in some conditions to assign it to a specific compound group, and in case of high resolution mass spectrometry, a precise molecular formula can be ascribed to practically every arising ion.

One of the methods of obtaining ions from analyzed substance in gaseous phase is exposure it to a electron beam of specific energy. The beam of electrons is generated in the ion source by appropriate filament, similarly as in the electron lamp (fig. 3.)

The energy of electron beam is defined by the difference of potentials between the filament and the housing of the ion source. Ionization energy usually equals to 70 eV.

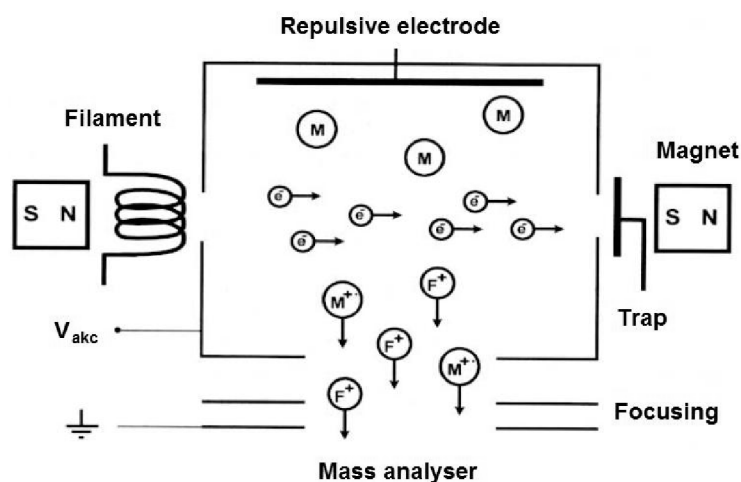


Fig. 3. Diagram of obtaining ions beam formed during fragmenting a molecule (M) in the ion source; (e^-) corresponds to electrons; (M^+) to molecular ions; (F^+) to fragmentation ions; the accelerating voltage was marked as V_{akc}

The magnetic field focuses the beam of electrons passing through the ion source chamber to the trap. A molecule in the gaseous phase, after hitting an electron of energy 70 eV, may lose its electron, receiving a positive charge and becoming a charged ion, called a molecular ion M^+ . In the process, an unpaired electron appears in the molecule which, depending on its structure, may fill various orbitals, so there may occur various excited states which, depending on their energy may cause particular bonds cleavage, creating fragmentary ions and neutral molecules. The 70 eV beam supplies considerable amount of energy to the molecule, which leads to its significant fragmentation. Produced ions are then accelerated and removed from the source by electric field created by a difference of potentials between the source and grounded electrode, while the repulsive electrode helps to stabilize the direction of the field inside the ion source.

Depending on the stability of the ion in the excited state, its lifetime, the fragmentary ions may be created not only in the ion source, but also during the ion movement to the detector. Also, the so-called metastable ions can be observed. For goals associated with evaluation of particle masses, the most desirable are signals of molecular peaks, although during structure identification of specific substance a valuable information can be obtained from fragmentation ions. The mass spectra usually

contains signals from all formed ions of various values m/z (where z is a ion charge). The intensity of observed signal is a function of the number of ions reaching the detector, and indirectly it is connected with probability of a particular path of fragmentation of excited molecule. Result of this the mass spectra obtained for molecules of similar structure have a similar formation and are relatively complex because of the presence of considerable number of fragmentation ions. In order to obtain a mass spectra with limited number of fragmentary ions, the amount of energy supplied to the molecule during ionization should be reduced. Therefore, a beam of electrons is used with reduced energy, even 10 eV, or other ionization methods (chemical ionization) are applied.

The mass spectrometry technique based on direct introduce of sample to the ion source is widely applied in fuel analysis, and in general – distillates of final boiling point – to about 350°C. The first papers relating to this kind of determination were already published in 1955 at the 4th Petroleum Congress in Rome [34]. To enable the inserting of low volatile samples of oil fractions, a modified, heated system of the sample inserting was used and it was determined that the temperature of the injector between 325–370°C practically responds to an optimum between thermal cracking of the sample and conditions of its evaporation which make it possible to obtain an sufficient quantity of vapors introduced to the ion source. Using the method of analysis of molecular peaks distribution, the authors presented the distribution of hydrocarbons in lubricating oils of medium viscosity, giving information about content of the alkylobenzene type compounds and mono- and dicyclo-naphthenes. They also presented the list of characteristic fragmentation ions for various hydrocarbon groups.

Subsequent papers devoted to group analysis of hydrocarbon mixtures appeared by the end of the sixties [e.g. 35]

Table 1. Characteristic fragmentation ions (m/z) [34]

Hydrocarbons	m/z
Alkanes	70, 71, 84, 85, 99, 113
Uncondensed cyclopentanes	69, 83, 97, 111, 125, 139
Uncondensed cyclohexanes	83, 97, 111, 125, 139, 153
Condensed cycloalkanes	67, 81, 95, 109, 121, 122, 123, 135, 136, 137, 149, 150, 151
Monoaromatic compounds	77, 78, 90, 91, 92, 104, 105, 106, 117, 118, 119, 129, 130, 131, 132, 133, 143, 144, 145, 146
Naphthalenes	128, 141, 142, 155, 156

and on that basis normalized analytical procedures were developed, accordingly some ASTM standards [18, 19, 36].

It can be said that the problem of hydrocarbon analysis of lubricating oil matrix, due to indicated above limitations, still arouses interest. For instance in the paper [37] by Nagamatsu Noritoshi available only as an abstract were discussed the results of research into optimization of ionization methods of a lubricating oil sample during MS analysis. It has been stated that the most advantageous ionization method is field-ionization and field-desorption.

Further development of mass spectrometry is closely connected with achievements in separation techniques, first of all gas and liquid chromatography.

Typical diagram of a mass spectrometer operating together with gas chromatograph was shown in fig. 4.

In the scope of oil fraction examination an interesting position is contribution to discussion on classification

the synthetic oil [38] presented at the conference NPRA in 1999. The composition of saturated fraction of Group III paraffin-free oil was analyzed, using the GC-MS technique. The examination of high boiling products was also described in the paper [39] connected with identification of heavy oil which contaminated the sea and the Spanish coast during the disaster of the Prestige-Nassau ship. Comparative studies of the composition of two heavy oils were performed, and the GC-MS technique was used to examine and compare the composition of aromatic compounds and biomarkers in both examined products.

Obtaining quantitative information on alkylated, aromatic polycyclic hydrocarbons present in heavy diesel oil, during the examination of its environmental effect became possible due to a variation of two-dimensional technique GC-GC/MS [40]. In the first column phase DB-1701 was applied, on which cuts were made, and in the other,

phase HP-5 used in aromatics distribution. An example of obtained chromatogram was presented in Fig. 5.

The application of GC-MS technique in examination of petroleum age was described in the paper [41] discussing the evaluation results of petroleum from the Pannonia basin in Serbia. Evaluated were the changes in biomarkers content, both saturated and alkylarenes. Hydrocarbons identification research on petroleum and distillates using the GC-MS technique were also described in the paper [42] oriented mainly to examination of biomarkers and other particular compound groups, such as diamondoids (adamantanes and diadamantanes), steroids, terpenes, sesquiterpenes, hopanes and others.

A very interesting proposition relating to the analysis of basic oils was presented in the paper by Peng-gao Duan et al. [43]. The method of Laser Induced Acoustic Desorption connected with chemical ionization with ion $CIMn(H_2O)^+$ gives a single ion $CIMn-M^+$ from each component (M) of base oil. It allows to determine

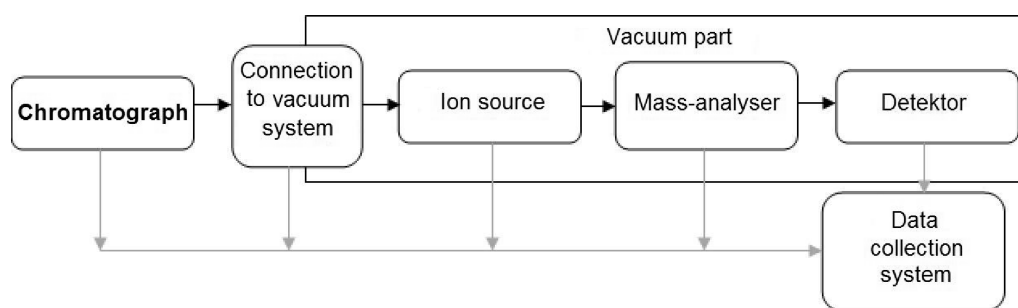


Fig. 4. Diagram of gas chromatograph linked with mass detector (GC-MS)

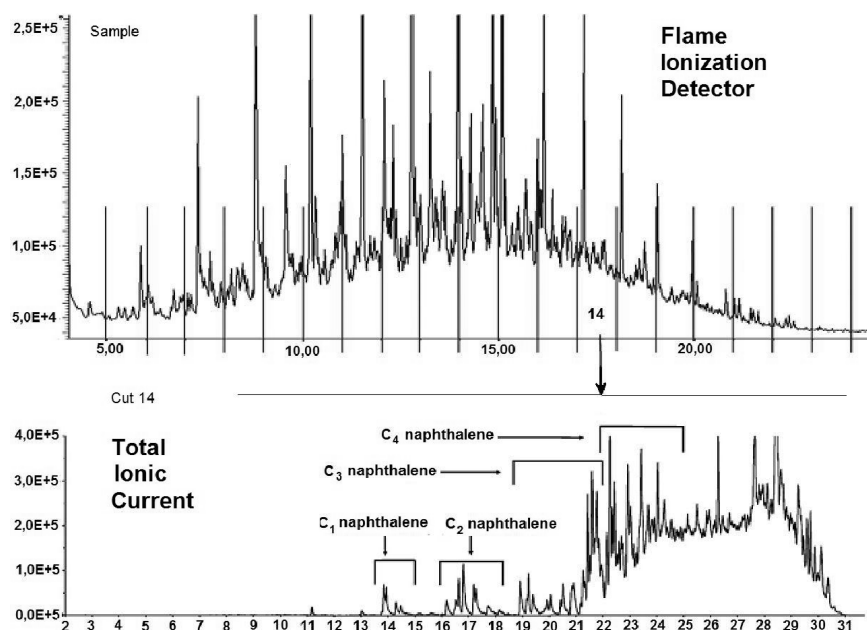


Fig. 5. Chromatogram of heavy diesel oil with cut lines. In the lower part, distribution of alkyl naphthalenes present in 14th section of chromatogram was shown, obtained by means of GC-MS technique of measurement of total ionic current (TIC) [40]

its particle mass, and usually fragmentation of arising ions is not observed.

Summing up, it can be stated that the growing interest in finding the substances which are the basis of lubricants applied nowadays is still increasing and it is limited only by the availability and labour consumption of analytical methods used. No findings have been discovered in literature which take advantage of the GC-MS system in examination of hydrocarbons contained in basic lubricant oils in excitation by an electron ionization (EI), although in the recent years, the sensitivity of used detectors substantially increased, which makes it possible to undertake attempts to detect substances of very low partial vapour pressure in separation conditions, particularly that techniques of examination of distillation characteristics of petroleum and received from it heavy fractions [30] are known and normalized.

The materials presented above indicate that the most promising techniques which help to determine the character of basic oil components are two-dimensional chromatography, and LIAD mass spectrometry based on the formation of molecular ions by chemical ionization technique. The

method of two-dimensional chromatography consisting in the introduction of additional chromatographic analysis (the second dimension) on the column of different polarity for more complete identification of substances with similar boiling points (this is the way that the distribution occurs on the non-polar column) is, with relation to the assumptions similar to contemporary gas chromatography with mass detector which enables spectrometric analysis of each planned section of examined sample chromatogram. This creates the possibility to produce a two-dimensional image of ionic distribution of specific mass numbers (m/z) in relation to the retention time of substances separated chromatographically. In case of using a non-polar column the retention times are a function of boiling points of components eluted from the column.

In the next part of this paper will be presented the results of research on possibilities of the qualitative differentiation of *n*-paraffin, isoparaffin and naphthene hydrocarbons in selected basic oils and non-polar fraction (paraffinic and naphthenic) separated from such oils by the classic elution chromatography.

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