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Optimized conditions for hydrocarbon group type analysis of base oils by thin-layer chromatography–flame ionisation detection

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Abstract

The results of research on the optimization of the thin-layer chromatography–flame ionisation detection for the determination of group composition of natural base oils, including separation of the aromatics into subgroups, are presented. Neutral base oils obtained in several steps of refining from vacuum distillation petroleum fractions are the most difficult to analyze by hydrocarbon group type analysis (HGTA) because of the high content of aliphatic fragments in their molecules. Factors affecting the accuracy and precision of the results were identified. The paper presents the analytical procedure, including two different calibration methods, as well as the results of studies on the reproducibility of HGTA of typical base oils of different viscosity classes under the optimized conditions. The same conditions were found suitable for HGTA of other high-boiling petroleum fractions by TLC with flame ionisation detection. The paper also introduces a new procedure for reproducible determination of polar fractions in base oils utilizing solid-phase extraction columns, and presents a corrected procedure for the determination of saturated compounds and aromatics (mono-, bi- and polycyclic) in base oils by column liquid chromatography.
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1. Introduction

Hydrocarbon group type analysis (HGTA) of petroleum heavy fractions means the determination of the following classes of compounds:

(1) Saturated compounds (S), including paraffinic and naphthenic hydrocarbons, as well as unsaturated olefins, whose contents is usually characterized indirectly by the bromine number of the fraction;

(2) Aromatic compounds (A), including hydrocarbons with one, two, three or more aromatic rings; sometimes further divided into subgroups based on the number of aromatic rings in the molecule (A1, A2, A3, etc.); this fraction contains also some sulphur compounds of low polarity.

(3) Resins (R), including polar substances containing elements other than C and H in the molecule (nitrogen, sulphur and oxygen in particular)

(4) Asphaltenes (A), including polar substances insoluble in *n*-pentane or *n*-heptane; practically absent in base oils.

Group composition of high-boiling petroleum

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products, especially the content of bi- and polycyclic aromatic hydrocarbons and resins, determine their suitability as a raw material for a given petroleum product. Data gathered through HGTA are used to determine the choice of technology used for further processing of the material, allow the evaluation of its thermal and oxidative stability, as well as the environmental hazards associated with it. Besides, group composition distinguishing between the different groups of aromatic hydrocarbons constitutes a fingerprint of a low volatility petroleum product.

Group type analysis of heavy petroleum fractions refined to various degrees (including base oils) is usually carried out in its simplest form, without distinguishing between the different aromatic fractions. Such methods are commonly referred to as SARA type analysis, from the first letters of the names of the four fractions listed above. Sample fractionation is usually performed by preparative liquid chromatography in glass columns with stepwise eluent changes and with gravimetric final determination. The column is filled with freshly activated adsorbents before each analysis, including silica gel, neutral or calcinated alumina or Acapulco clay. The most commonly used method is ASTM D-2007 [1]. A similar method described in the Polish Standard PN-72/C-04025 [2] is used in Poland. This method allows the determination of content of saturated compounds, aromatics (subdivided into A1, A2 and A3+ fractions) and resins. The ASTM D-4124 method is used for group analysis of vacuum residue and asphalt [3].

HGTA results obtained by these and other similar methods based on column liquid chromatography are typically not identical to each other, yet they are usually close and generally considered accurate, i.e. reflecting the true contents of the particular hydrocarbon groups in the material examined. Consequently, they should be considered as reference methods when working on alternative techniques.

The preparative LC based methods are time- and labour-intensive. Besides, they require the use of large volumes of organic solvents. These solvents are often harmful, as for example in the PN-72/C-04025 method, where benzene is used. In addition, both our experience gathered over many years of use of such methods, and the literature, indicate that the reproducibility of these methods is poor.

Several modern HGTA techniques were developed based on preparative LC with the use of mechanical pumps and 12-mm ID steel columns [4], or medium-pressure glass columns and fraction collectors [5]. Even though these methods are based on the same principles as ASTM D-2007 and PN-72/C-04025, the reproducibility of the results is improved. On the other hand, they are still labour-intensive and require large amounts of solvents. Thus far, all attempts to replace these cumbersome group type analysis methods with HPLC analysis failed due to inability to develop proper separation and calibration conditions, especially for group separation of aromatics in base oils.

The results of research described in the literature [6–33] indicate that thin-layer chromatography combined with flame ionisation detection (TLC–FID) is a much better choice for HGTA of heavy petroleum fractions. In this technique, group separation is carried out on quartz rods covered with specially prepared, activated silica gel, using different eluents in sequence. Following the elution, the rod is dried and introduced gradually to the hydrogen flame of a FID system. The TLC–FID method is especially popular in group type analysis of fats and detergents [7,8,32], but it is also recommended for HGTA of heavy petroleum fractions [8–33], including base oils and bitumen, in the SARA convention.

Some papers are worth a special mention. Barman [13] compared the results of HGTA of base oils by the TLC–FID and ASTM D-2007 methods and demonstrated insufficient group separation when using the latter. Sharma et al. [20] compared the results of TLC–FID and ASTM D-4124 methods for group type analysis of vacuum residues obtained from different crude oils. Bahrati and co-workers [28,29] used the PLC fractions for TLC–FID calibration. Finally, Cebolla et al. [23,26,27] described meticulous studies on the calibration of the TLC–FID method for HGTA of different petroleum and coal liquefaction products.

The goal of this work was to develop optimal conditions for HGTA by TLC–FID of heavy petroleum fractions, especially refined base oils, including group analysis of the aromatics. Good reproducibility of the results and agreement with the PN-72/C-04025 or ASTM D-2007 methods were adopted as the optimization criteria.

2. Experimental

2.1. Materials

2.1.1. Samples

The samples used in the study included various batches of SAE 10, SAE 30 and brightstock (BS) base oils, as well as vacuum distillates and products of their furfural extraction or solvent deparaffination, manufactured in the Gdańsk Refinery (Gdańsk, Poland) from Russian Blend crude oil. Solutions in *n*-hexane or dichloromethane (5–30 mg/ml) were used in the experiments.

2.1.2. Solvents and eluents

HPLC-grade *n*-hexane, toluene and dichloromethane (Merck, Darmstadt, Germany), as well as reagent-grade benzene and anhydrous reagent-grade ethanol (POCh, Gliwice, Poland) were used. With the exception of anhydrous ethanol, the solvents were dried with molecular sieve 5A activated for 8 h at 350 °C. Eluents and components of eluent mixtures were stored in tightly sealed flasks over molecular sieve 5A.

2.1.3. Reference materials for calibration

Saturated, as well as mono-, bi- and polyaromatic fractions obtained from base oils by column liquid chromatography according to Polish Standard PN-72/C-04025 with modified elution volumes (see Procedures section), as well as resin fractions obtained by solid-phase extraction (SPE), were used in the study. Silica gel and alumina were used as packings in column LC, according to the PN-72/C-04025 standard.

2.2. Instruments and equipment

Alufolien silica gel 60 F_{254} TLC and HPTLC plates, LiChrolut Si (500 mg) SPE cartridges and SPE manifold were purchased from Merck. The Chromarod-S III rods were manufactured by Iatron Labs. (Tokyo, Japan). TLC chambers for the Chromarod-S III TLC rods, SES 3200/IS-01 autosampler, TK-8 rod dryer and the Iatroscan MK–5 instrument were purchased from Iatron. Hydrogen generator Packard 9400 was obtained from Alltech (Deerfield, Il, USA). The A/D converter and peak integration software were from Elkor (Gdańsk, Poland).

2.3. Procedures

2.3.1. Fractionation of base oils and other petroleum heavy fractions to produce calibration standards by unpublished modified PN-72/C-04025 standard

Fractions produced according to the PN-72/C-04025 standard were analyzed for purity by TLC. Based on these analyses, the conditions listed in the standard were modified to obtain better separation of the hydrocarbon groups. Saturated compounds and mono-, bi- and polyaromatic fractions obtained under the modified conditions were subsequently used for the calibration of the TLC–FID method. The fractionation was carried out in an preparative LC glass column (1125 mm×12 mm I.D.), equipped with a glass frit at the bottom and a water jacket (32 mm O.D.). The bottom half of the column was packed with alumina (50 g), while the upper with silica gel (50 g). The sorbents were activated according to the PN-72/C-04025 standard by heating at 180 °C for 8 h. The remaining procedure looked as follows.

2.3.2. Column conditioning

A 70-ml volume of *n*-hexane, until the upper hexane meniscus reached the top of the packing in the column; sample introduction: ~5 g of oil dissolved in 10 ml of *n*-hexane was carefully and uniformly introduced to the top of the column packing. When the upper meniscus of the oil solution reached the top of the packing layer, another 30 ml of *n*-hexane was added and its meniscus was allowed to reach the top of the packing bed. This procedure aimed at uniform introduction of the sample to the uppermost layer of the silica-gel packing.

2.3.3. Elution

The following eluents were used in sequence: 100 ml *n*-hexane, 100 ml *n*-hexane–benzene (95:5, v/v), 100 ml *n*-hexane–benzene (80:20, v/v), 100 ml *n*-hexane–benzene (50:50, v/v), 100 ml benzene, 150 ml benzene–ethanol (50:50, v/v).

2.3.4. Fraction collection

A 120-ml volume of saturated hydrocarbons,

50 ml monocyclic aromatic hydrocarbons, 30 ml bicyclic aromatic hydrocarbons, 300–400 ml polycyclic aromatic hydrocarbons (depending on the results of TLC analysis of the fractional composition; fraction collection was finished when resin spot appeared on the TLC plate); 50–150 ml resins (from the moment resin spot appeared on the TLC plate to the end of elution of the visible band from the column).

2.3.5. TLC control of the fractions from preparative LC separation

The purity of the fractions was verified by TLC using *n*-hexane as the eluent. The Alufolien silica gel 60 F_{254} TLC plates were not activated before the analysis. The HPTLC plates were activated for 3 h at 150 °C. A 2-μl volume of each fraction was spotted on a 10-cm long plate. After the solvent evaporated, elution with *n*-hexane was carried out until the solvent front reached the 9-cm mark. The plate was examined under UV light ($\lambda = 254$ nm). A nonshiny, white, very weakly fluorescent spot visible in daylight on a dried plate was interpreted as saturates (saturated hydrocarbons, naphthenes, olefins and possibly highly alkylated monoaromatics of very low polarity). Light violet fluorescence visible under UV light for spots with R_F greater than ~0.5 was caused by monocyclic aromatic hydrocarbons (A1). Intense blue fluorescence observed for spots with R_F between 0.35 and 0.5 was attributed to bicyclic aromatic hydrocarbons (A2), and that observed for spots with $0.07 < R_F < 0.35$ to polycyclic aromatic hydrocarbons (A3+). Spots revealing violet-brown fluorescence under UV light with R_F below 0.07 were interpreted as resins (R) (polar substances).

2.3.6. Independent determination of resin contents in base oils

The method used (as of yet unpublished) was developed at the Gdańsk University of Technology. Of all the methods tested so far in our laboratory, it is characterized by the best precision of resin content determination in base oils. The resin fraction for calibration of the TLC–FID method was obtained by SPE. A sample of ~2.5 g of oil dissolved in 8 ml of hexane was introduced into a dry SPE cartridge packed with silica gel (500 mg). After elution of saturated compounds and aromatics with 30 ml of hexane, the resins remaining in the cartridge were eluted with 3 ml of acetone into a preweighed flask. The solvent was evaporated to constant mass and the resins that remained in the flask were weighed with an accuracy of 0.00001 g.

2.3.7. Quantitative calibration of the TLC–FID method

2.3.7.1. External standard method

Calibration of the TLC–FID method was performed using base oils obtained by mixing known amounts of pure SAR fractions produced by column liquid chromatography according to the modified PN 72/C 04025 method (saturated compounds and aromatics) and by SPE in the case of resins. The resin fraction obtained by the modified PN 72/C 04025 method was found to contain some polycyclic aromatic hydrocarbons, as evidenced by fluorescence observed at $\lambda = 254$ nm for this fraction on the TLC chromatograms after a single elution with *n*-hexane, therefore resin fractions obtained with the SPE method were used for calibration of this group.

Individual fractions of saturated compounds, aromatics and resins from two production batches of each of the base oils were mixed together in known proportions to produce base oils of known group composition, similar to the actual products. Appropriate amounts of such oils were then dissolved in *n*-hexane to produce standard solutions ranging in concentration from 5 to 30 mg oil/ml *n*-hexane. Each standard solution was subjected to group type analysis by TLC–FID under optimal conditions described later. Peak areas obtained for the particular hydrocarbon groups were recorded and used to determine the calibration curves.

2.3.7.2. Normalization method with correction factors based on saturated compound content

A correction factor of 1 was assumed for saturates (first peak on the TLC–FID chromatograms) and used to calculate the correction factors for the remaining hydrocarbon groups (remaining peaks on the chromatograms of the standard solutions). Correction factors obtained in this way were used to calculate percent content of the individual fractions in the unknown samples of base oils.

2.3.8. Optimized procedure for HGTA of base oils and other heavy petroleum fractions by TLC–FID

2.3.8.1. Eluent preparation

Fresh eluent solutions stored in tightly sealed flasks over molecular sieve 5A activated for at least 3 h at 450 °C should be poured into the developing chambers an hour before the planned separation. Eluents prepared in this way are sufficiently dry, and the time is sufficient to saturate the chambers with vapours of the eluent. The purity and elution properties of the eluent should be controlled each time by including an additional Chromarod III in the frame with no sample spotted on it (blank determination).

2.3.8.2. Activation of chromarods

All rods to be used for HGTA and an additional rod for blank determination should be placed in the frame and activated by running them twice through hydrogen flame (35 s for the first run and 50 s for the second run). Activated rods should be placed immediately in a desiccator.

2.3.9. Sample preparation, spotting and development—optimized procedure

A 1-μl volume of the solutions of the examined oils in *n*-hexane prepared at a concentration of ~35 mg/ml for SAE 10 and ~20 mg/ml for SAE 30 and BS 90 should be spotted on the Chromarods using an autosampler. Similar concentrations should be used for other materials of similar viscosities. Care should be taken not to expose the rods to the laboratory atmosphere for times longer than necessary to spot the samples.

After spotting the sample and before the first and every subsequent developing stage, the rods should be dried for 2 min at 70 °C in a dryer and placed in a desiccator for 10 min. They should be then conditioned for 5 min in a closed developing chamber over appropriate mobile phase and developed in the following order: *n*-hexane (to 10 cm), *n*-hexane–toluene (90:10, v/v) (until the solvent front reaches a distance of 5–6 cm, ~2 mm below the visible boundary of the saturates fraction), toluene (until the solvent front reaches a distance of 4.5 cm). If the presence of asphaltenes in the sample is suspected, the rods should additionally be developed with a dichloromethane–ethanol (95:5, v/v) (until the solvent front reaches a distance of 2.5 cm). After developing, the rods should be dried for 3 min at 70 °C in the dryer and placed in a desiccator for 5 min.

2.3.9.1. Detection, peak area integration and calculation of group composition

Hydrocarbon group detection is carried out by passing each rod over 35 s through the hydrogen flame of the TLC–FID detector, with digital acquisition and processing of the detector signal. Group composition of the sample is determined based on peak areas using either external standard method, or, in a simpler version, normalization with correction factors.

3. Results and discussion

3.1. Optimization of the conditions of HGTA of base oils by TLC–FID using Chromarod S III, general description of the experiments and selected results

Initial experiments aimed at determining the elution distances or elution times of the different analyte groups at each stage of HGTA of base oils. The effect of experimental parameters on the accuracy and precision of the results was also examined. The goal was to achieve the best possible separation between the analyte groups (saturated compounds, A1, A2 and A3+ aromatic compounds and resins) in a reproducible fashion. A large number of experiments were performed; a detailed description of all of them would exceed the frameworks of this paper. In summary, the experiments made it possible to identify the effect of a large number of variables on the reproducibility of HGTA, which, in turn, allowed us to prepare the optimized procedure, described in Procedures.

First group type analyses of base oils by TLC–FID were carried out in our laboratory under the conditions described in the literature [8–32], using similar eluents and conditions. The authors recommend elution of the samples deposited on the rods with two or more eluents of increasing or decreasing elution strength. The elution distances are predetermined based on the time of each succeeding elution

or sometimes on the distance of eluents migration along the rod. With the exception of the method of Karlsen and Larter [10], such procedures should yield group separation into four fractions: saturated compounds, aromatics, resins and asphaltenes. In practice, we found that group separation of base oils, particularly in the aromatic hydrocarbon range, was incomplete, or the quantitative results were not sufficiently reproducible under these conditions.

One important observation we made was that the migration distance of the solvent front in the second elution stage (separation of aromatics with *n*-hexane–toluene, 90:10, v/v) should be varied depending on the amount of saturated compounds in the sample. The saturates spot is located near the top of the rod following elution with *n*-hexane in the first stage. We found that optimally, the solvent front of the *n*-hexane–toluene mixture should not overlap the saturates spot, easily noticeable on a dry rod as a matte white zone, different than the slightly greyish, analyte-free sorbent. In practice, elution with the *n*-hexane–toluene mixture should be stopped when the solvent front reaches ~2 mm below the saturates spot.

We also found among some earlier statements in the literature [13,20,23,26–29] that even the best separation conditions will not lead to reproducible separations if the entire analytical procedure is not strictly defined and observed. The following factors affect the reproducibility to the largest extent and should be strictly controlled

(1) constant, low amount of water in the eluent(s)

(2) constant and reproducible temperature of the dryer used to dry the rods after each elution

(3) constant and reproducible time between elutions

(4) constant conditioning time of the sample-spotted rods above each eluent.

It was also found that activation of the rods in hydrogen flame plays a very important role. It should be performed at least twice under reproducible conditions. Finally, the storage times of the activated rods in the laboratory atmosphere and in the developing chamber (above the eluent) should also be strictly controlled.

Another factor affecting the quality of group separation and reproducibility of the results is the concentration of the oil in the hexane solution spotted on the rod. In contrast to the findings reported in the literature [9,13], we found that it should be constant within 5 mg/ml for both the samples and the standards (see Table 1).

3.2. Identification of fractions separated by TLC–FID and by column liquid chromatography according to the modified PN-C/72-04125 method

Identification of the analyte groups contained in the individual zones on the Chromarod Si III rods at every stage of the elution process performed under optimized conditions was carried out using individual analyte fractions produced by column LC according to the modified PN-72/C-04125 standard. Such an approach was dictated by the fact that HGTA by column LC is generally considered the benchmark method in group type separations.

Each fraction produced by preparative LC was spotted on the Chromarods and subjected to the optimized elution procedure. Fig. 1 presents examples of the chromatograms obtained. The experiments revealed a problem with TLC–FID separation of the saturated compounds and the least polar, highly alkylated fraction of the monocyclic aromatic hydrocarbon group (A1) found in base oils. This fraction elutes from the preparative LC column right after the saturates and before the bulk of A1. Fig. 1 indicates that when this fraction was subjected to group separation by TLC–FID, it was contained partly in the saturates zone and partly in the A1 zone. Thus, it was impossible to determine unequivo-

Table 1
Effect of the concentration of SAE 30 base oil in hexane on the results of HGTA by TLC–FID; 1 μl of the solution spotted on the rod

Oil concentration (mg/ml)	16.12	24.64	Δ=8.52 mg/ml	29.49	24.64	Δ=4.81 mg/ml
Saturated compounds (%, w/w)	77.3	74.0	3.3>0.8*r*	73.3	74.0	0.7<0.8*r*
Aromatics (%, w/w)	22.2	25.5	3.3>0.9*r*	26.2	25.5	0.7<0.9*r*

r, difference between the contents of the particular group relative to method reproducibility; Δ, difference between the concentrations of the oil solutions.

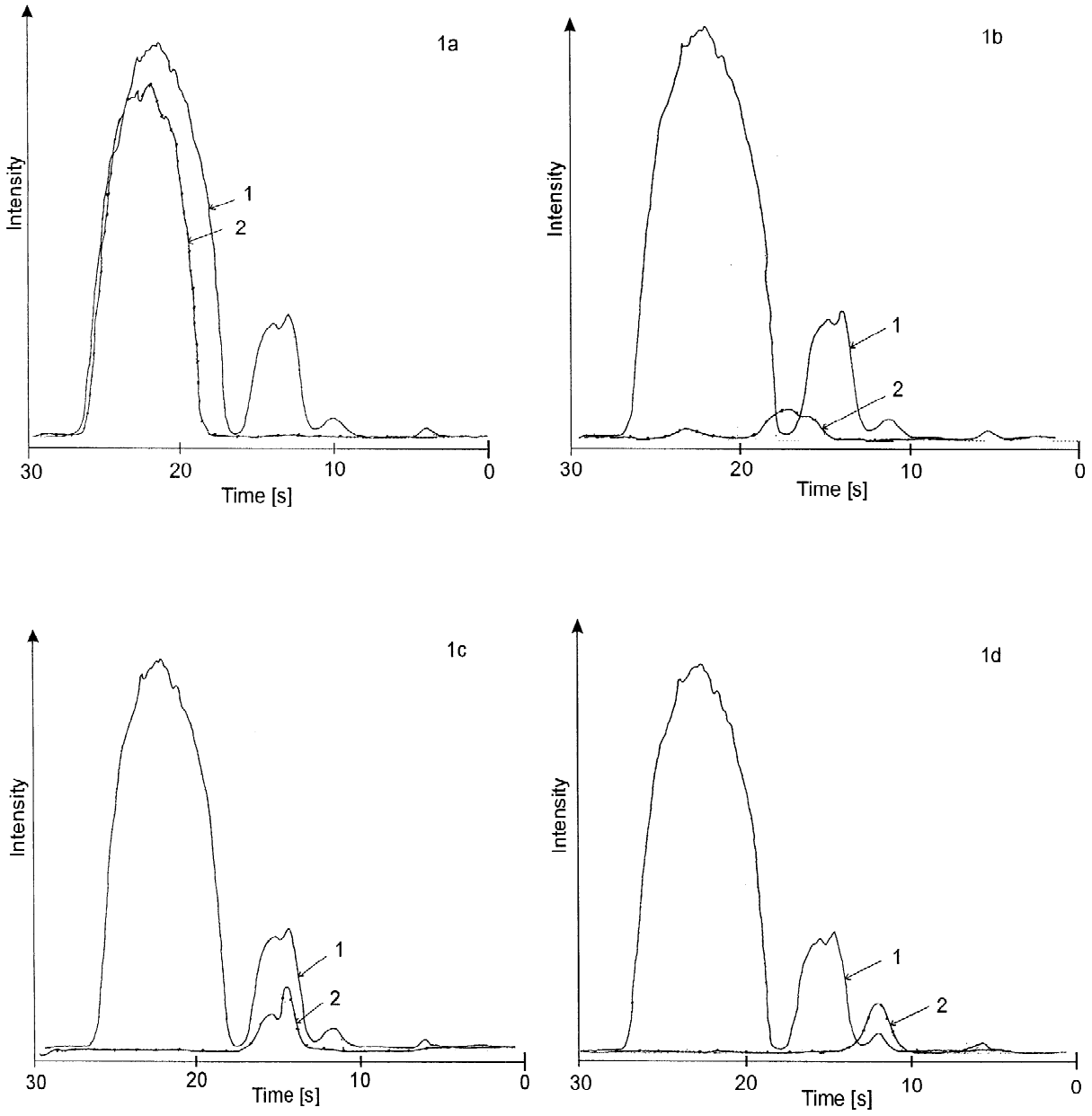

Fig. 1. Identification of TLC–FID peaks. The four chromatograms represent saturated compounds (a), monocyclic aromatic hydrocarbons (b), bicyclic aromatic hydrocarbons (c) and polycyclic aromatic hydrocarbons (d). 1 = TLC–FID chromatogram of SAE 30 base oil; 2 = fractions obtained according to the modified PN-72/C-04025 standard.

cally which of the TLC–FID peaks in HGTA of base oils contained this fraction. Further experiments demonstrated that when a known amount of this fraction was added to base oil subjected to HGTA by TLC–FID, only the first peak on the TLC–FID chromatogram increased. Thus, it can be concluded that the saturated compound fraction obtained in HGTA of base oils by TLC–FID contains also a

fraction of the least polar alkylated monocyclic aromatic hydrocarbons from base oils. Consequently, the following analyte groups can be assigned to the individual TLC–FID peaks obtained in the analysis of base oils:

Peak one (produced by elution with *n*-hexane): all of the saturated compounds (S) and the least polar, highly alkylated fraction of the monocyclic aromatic hydrocarbons group (A1), which is not sorbed strongly on silica due to sterical reasons;

Peak two: the more polar fraction of the monocyclic aromatic hydrocarbons group (A1) plus bicyclic aromatic hydrocarbons (A2);

Peak three: tricyclic and polycyclic aromatic hydrocarbons (A3+);

Peak four (practically not eluted, thus remaining at the beginning of the rod): resins (R) and asphaltenes (A) (if present in the oil).

In summary, it can be stated that in HGTA of highly refined base oils done by TLC–FID, some substances falling within the category of monocyclic aromatic hydrocarbons according to the modified PN-72/C-04025 standard (the least polar fraction of A1) elute on Si III rods in the saturates zone. This conclusion was further confirmed by the results of TLC separation of neutral base oils on activated TLC or HPTLC silica plates developed with *n*-hexane over a distance of 9 cm. The saturates zone (of whitish cast in daylight) slightly absorbed UV light at 254 nm and revealed weak fluorescence under 254 nm light, which indicates that some aromatics were present in this zone. We found experimentally that this problem can be eliminated by performing the TLC–FID group type analysis on Chromarods doped in the central part with Ag^{+} or Cu^{2+} ions forming a 1 cm wide zone, an approach similar to that used by Yamamoto [11] to separate alkenes from alkanes. The saturates content of SAE 30 base oils, determined by normalization using the doped rods, was from 10% (Ag^{+} ion) to 15% (Cu^{2+} ion) lower than for the Si III rods. It should be emphasized that this effect could not be due to olefins present in base oils, as their contents in highly refined base oils is generally lower than 0.5%. These results demonstrate that in the separation of base oils on Chromarod Si III, the first peak eluted with *n*-hexane contains not only saturated compounds, but also the less polar, highly alkylated monoaromatic compounds. However, it should be kept in mind that highly alkylated monoaromatics are thermally stable and have an overall beneficial effect on the performance of base oils, therefore their inclusion in the saturate compounds group is not a big problem from the practical point of view.

The procedure involving ion-doped Chromarods was neither as simple, nor as reproducible as the optimized procedure described in this paper. In addition, a doped rod could be used only up to 7 times before repeat doping was required, in contrast to Chromarod Si III rods which could be reused over 50 times.

3.3. Calibration of HGTA of base oils by TLC–FID

Two calibration methods described in the Experimental section were used: external standard and normalization with correction factors. The base oils and petroleum fractions examined did not contain asphaltenes, therefore neither conditions for their separation, nor the calibration factors for them were specified within the framework of this research.

3.3.1. (A) External calibration

It was found that the relationship between the abundance of a given hydrocarbon group and the peak area was linear. The following calibration curve equations and linear correlation coefficients were obtained for the different fractions and the samples analyzed where S is peak area, and r is the linear correlation coefficient:

Saturated compounds (S) and the least polar fraction of A1 (first peak on the TLC–FID chromatograms):

SAE 10: mass (μg) = $12.06S + 0.12$ $r = 0.986$
SAE 30: mass (μg) = $12.45S - 0.01$ $r = 0.997$
BS 90: mass (μg) = $12.71S - 0.11$ $r = 0.996$

Monocyclic aromatic hydrocarbons (A1, more polar fraction) and bicyclic aromatic hydrocarbons (A2) (second peak on the TLC–FID chromatograms):

SAE 10: mass (μg) = $8.80S + 0.35$ $r = 0.987$
SAE 30: mass (μg) = $9.11S + 0.67$ $r = 0.997$
BS 90: mass (μg) = $10.37S + 0.43$ $r = 0.999$

Tricyclic and polycyclic aromatic hydrocarbons (A3+) (third peak on the TLC–FID chromatograms):

SAE 10: mass (μg) = 8.20S + 0.14 r = 0.989
SAE 30: mass (μg) = 8.61S + 0.78 r = 0.996
BS 90: mass (μg) = 9.65S + 0.97 r = 0.999

Resins (R) (fourth peak on the TLC–FID chromatograms):

SAE 10: mass (μg) = 12.82S + 0.045 r = 0.995
SAE 30: mass (μg) = 13.32S + 0.073 r = 0.999
BS 90: mass (μg) = 13.51S + 0.035 r = 0.999

3.3.2. (B) Calibration by normalization with correction factors

The following correction factors were obtained for the aromatics and resins when a correction factor of 1.000 was assumed for the saturates:

SAE 10:	f_s = 1.000	SAE 30:	f_s = 1.000	BS 90:	f_s = 1.000
	f_a = 1.276		f_a = 1.201		f_a = 1.100
	f_p = 1.341		f_p = 1.275		f_p = 1.188
	f_r = 2.475		f_r = 1.825		f_r = 1.308

where f_s is the normalization correction factor for saturated compounds and the least polar fraction of monocyclic aromatic hydrocarbons (first peak on the TLC–FID chromatograms), assumed to be 1.000; f_a is the normalization correction factor for the more polar fraction of monocyclic aromatic hydrocarbons and bicyclic aromatic hydrocarbons (second peak on the TLC–FID chromatograms); f_p is the normalization correction factor for tricyclic and polycyclic aromatic hydrocarbons (third peak on the TLC–FID chromatograms) and f_r is the normalization correction factor for resins (fourth peak on the TLC–FID chromatograms).

Calibration based on pure hydrocarbon fractions obtained from base oils using liquid chromatography is extremely time- and labour-intensive. Consequently, it is difficult to verify the integrity of the calibration curve or to introduce modifications to the correction factors for the individual analyte groups, which may be necessary when a different raw material is used or when technological conditions change significantly. Straightforward normalization based on per cent contribution of the peak area of a given fraction to the total area of all peaks, with no correction factors, is a vastly simpler approach, often advocated in the literature on the application of the TLC–FID technique for HGTA of heavy petroleum fractions. However, the results presented in this paper indicate that such an approach can only be used to compare group composition of petroleum fractions of the same viscosity class. Normalization with no correction factors should not be used to determine the absolute amounts of the particular hydrocarbon groups (SARA) in petroleum fractions by TLC–FID.

The relatively large differences between the correction factors determined for the same hydrocarbon groups in base oils of different viscosity classes (SAE 10, SAE 30 and BS 90) and between the correction factors of the different groups in base oils of a given viscosity class are quite striking. These differences are markedly larger than those observed for the same substance classes in gas chromatography with FID detection (e.g. in simulated distillation). This seems to indicate that the efficiency of generation of ions from hydrocarbons present on the Chromarod during passage of the rod through the hydrogen flame is much lower than in GC. According to a convincing hypothesis of Cebolla et al. [23], this difference is caused by combustion of some of the sample material in the TLC–FID head. This hypothesis together with our experimental results indicate that the TLC–FID technique can be successfully used for HGTA of base oils and analogous heavy petroleum fractions provided that the determination is carried out under strictly standardized conditions similar to those described in this paper. Only in this case can the results be expected to be as reproducible as presented herein.

3.4. Reproducibility of HGTA of base oils by TLC–FID

Fig. 2 illustrates typical TLC–FID chromatograms of SAE 10, SAE 30 and BS base oils. Table 2 presents the results of HGTA of these oils from the same production batches and the calculated mean contents of the different hydrocarbon groups as determined from simultaneous analysis of nine rods in a frame. Table 2 also lists mean values and confidence intervals for hydrocarbon group composition determined for the above oils from several

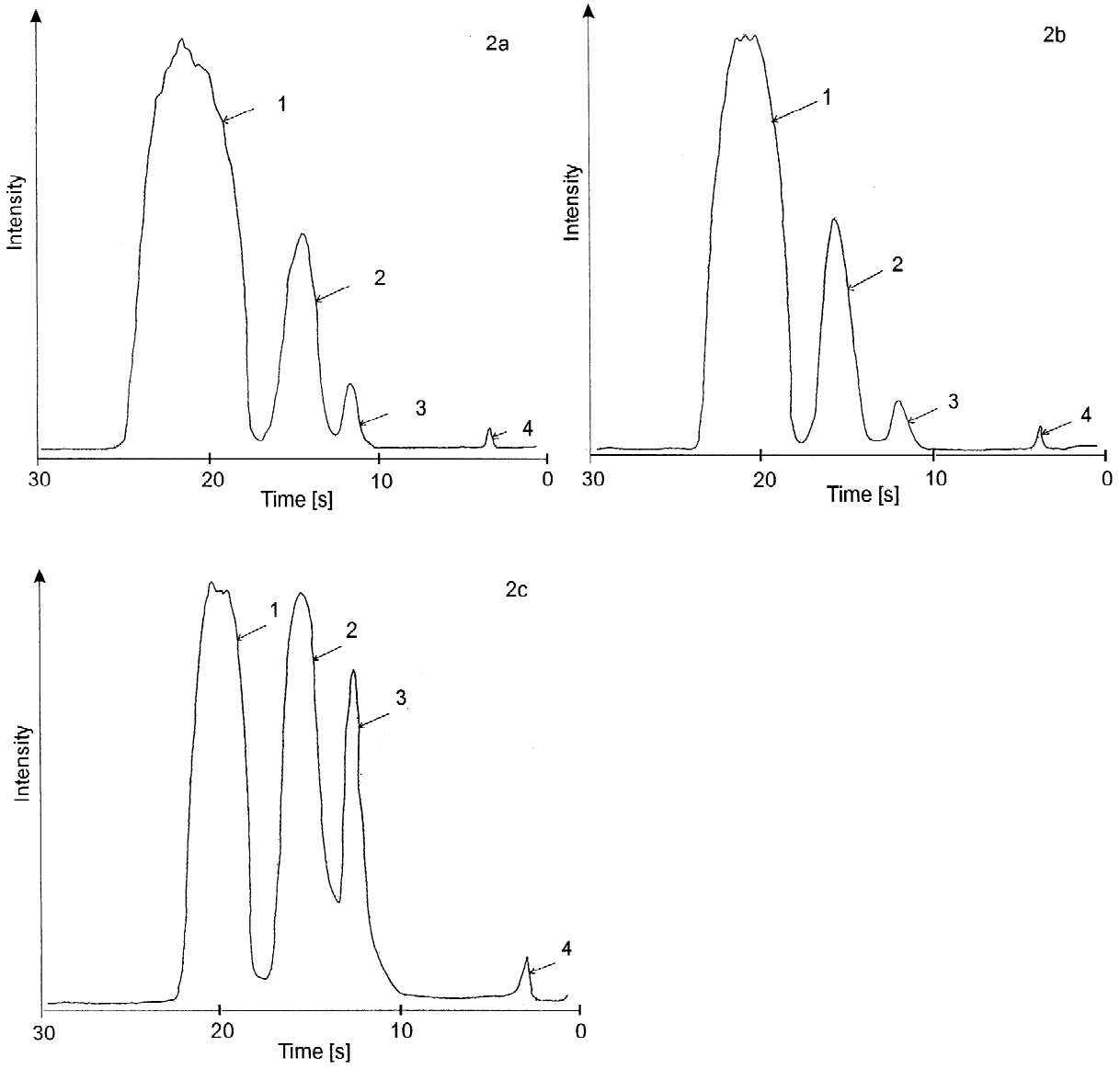

Fig. 2. Typical TLC–FID chromatograms obtained for base oils belonging to different viscosity classes under optimized conditions described in the Procedures section; (a) SAE 10, (b) SAE 30, (c) BS. 1 = Saturates and the least polar monocyclic aromatic hydrocarbons; 2 = polar monocyclic aromatic hydrocarbons and bicyclic aromatic hydrocarbons; 3 = polycyclic aromatic hydrocarbons; 4 = resins.

analyses performed in sequence (using different frames). Reproducibility of the determinations was calculated at the 95% probability level as 1/2 of the confidence interval.

Table 2 clearly shows that reproducibility of the determinations is much better when all rods are placed in the same frame compared to the case when replicate analyses are performed in sequence. This illustrates particularly well the strong effect external conditions have on the results of HGTA by TLC–FID. Consequently, it should be concluded that when group composition of different materials is com-

Table 2
Examples of the results of HGTA of three base oils belonging to different viscosity classes and confidence intervals of the results at 95% probability level when replicate analyses were performed simultaneously in a single frame or consecutively using different frames

Product	Group	Rod no.									Mean	Confidence interval* ±% value determined	Confidence interval** ±% value determined
		1	2	3	4	5	6	7	8	9			
SAE 10	Saturates	77.7	78.2	77.1	78.1	77.3	78.2	77.8	76.9	77.0	77.6	0.5	1.9
	Aromatics	19.6	19.0	20.1	18.6	19.8	18.1	19.6	20.2	19.8	19.4	2.8	6.7
	Polyaromatics	2.5	2.6	2.6	3.1	2.8	3.5	2.4	2.7	3.0	2.8	9.5	16.5
	Resins	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	8.7	30.3
SAE 30	Saturates	76.9	75.1	76.0	74.9	76.2	75.3	74.1	74.7	74.7	75.3	0.9	2.6
	Aromatics	18.6	20.7	19.1	20.4	19.2	20.2	21.1	22.3	19.9	20.1	4.3	12.4
	Polyaromatics	3.2	3.5	4.0	3.8	3.7	3.9	3.8	3.6	4.5	3.7	7.3	18.6
	Resins	1.1	0.7	0.9	0.3	0.9	0.6	1.0	0.6	0.9	0.9	12.6	36.9
BS 90	Saturates	45.8	45.7	46.5	45.9	46.4	47.9	45.9	47.8	47.2	46.6	1.4	3.9
	Aromatics	31.9	34.1	32.8	32.6	31.5	32.5	33.9	32.6	32.5	32.7	2.0	5.7
	Polyaromatics	19.5	17.6	18.5	18.7	19.3	18.7	17.9	18.4	19.1	18.9	2.6	6.8
	Resins	2.8	2.6	2.2	2.8	2.8	1.9	2.3	1.8	2.1	2.1	14.9	23.1

*, calculated based on 5 replicates for rods analyzed simultaneously in the same frame; **, calculated based on 5 replicates for rods analyzed consecutively in different frames.

pared, it is always more advantageous to perform all determinations simultaneously by spotting all samples on rods in the same frame.

The TLC–FID method can also be used for HGTA of asphalt and vacuum residue. However, in contrast to the findings reported among others in Refs. [8,10,20,30], optimized conditions for the analysis of these materials should be different because of poor solubility of asphaltenes (contained in high concentration in asphalt) in *n*-hexane. Elution should be carried out in this case with solvents of decreasing elution strength in sequence. Calibration of the method is even more complicated in this case than in HGTA of base oils.

4. Conclusions

The experience gained during more than 3 years of TLC–FID use in the Gdańsk Refinery for HGTA of more than 200 production batches of numerous base oils and other heavy petroleum fractions belonging to different viscosity classes indicate that the method developed is suitable for routine determination of group composition of base oils and other, less refined heavy fractions. Reproducible results can be obtained provided that the procedure described in this paper is strictly adhered to.

The method is relatively quick and solvent consumption is low. It takes ~2 h to complete HGTA of three to four different petroleum products analysed simultaneously using ten rods placed in a single frame. When the determination is carried out according to PN-72/C-04125 (ASTM D-2007) standard, it takes ~8 h to complete the analysis for a single product, with much worse reproducibility and sometimes plainly incorrect separation when the column is not correctly packed and eluent flow profile in the column is asymmetric.

Analyte detection and quantitation in TLC–FID is carried out automatically, which minimizes errors at this stage.

The TLC–FID method has also some disadvantages, including:

(1) strong effect of external conditions (ambient temperature, humidity, saturation of the developing chambers with eluent vapours, etc.) on reproducibility;

(2) relatively poor precision when a given fraction is present in low amounts (below 1–2.5%);

(3) coelution of the saturates and the least polar fraction of the monocyclic aromatic hydrocarbons

from base oils. It should be pointed out, though, that this is not a problem in HGTA of base oils because the least polar fraction of A1 is thermally stable and does not significantly affect the properties of the finished oil. Doping of the middle part of the Chromarod III with silver or copper salts results in the least polar fraction of A1 being included in the second peak.

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