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# Inverse gas chromatography and other chromatographic techniques in the examination of engine oils

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#### Abstract

The emerging market of engine oils consists of a number of products from different viscosity and quality classes. Determination of the base oil used in manufacturing of the final product (engine oil) as well as estimation of mutual miscibility of oils and their solubility could be crucial problems. Inverse gas chromatography and other chromatographic techniques are presented as an interesting and fruitful extension of normalised standard analytical methods used in the oil industry.

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### 1. Introduction

Utilisation of appropriate exploitation materials in modern engines (engine oils, lubricating oils, fuel oils, cooling liquids) is of the same importance as more and more sophisticated and excellent construction of the engines. Every modern engine oil has to meet different requirements. It should cause a decrease of the friction between the moving parts of the engine; a decrease in the amount of sediments (coke, carbon deposit); the removal of the products of combustion; a decrease of the fuel consumption and the inhibition of corrosion.

Car producers demand a high quality of engine oils. All such products should be characterised by high values of viscosity index, low value of kinematic viscosity at 100 °C, low value of volatility at 250 °C (NOACK, % loss) and low pour point.

Mixing the base oil with the viscosity modifier and the packet of additives produces the engine oil. The achievement of all these requirements is difficult or even impossible for engine oils produced with the use of mineral base oils. Therefore, one may note the increasing role of, so-called, synthetic base oils. These are products of chemical processes: polymerisation, polycondensation, chemical synthesis and catalytic hydrocracking. The products from these processes are products having defined structure and desired physicochemical properties [1-12]. A comparison of the basic physicochemical properties of several base oils is presented in Tables 1 and 2. The structure of selected base oils is presented in Fig. 1. Ester base oils exhibit more advantageous physicochemical properties than base oils from processes of polymerisation and polycondensation [poly-α-alkenes (PAOs)] or such petrochemical processes as catalytic reforming, fluid catalytic cracking [HC

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Table 1 Physicochemical parameters for mineral and synthetic base oils having similar values of viscosity at 100 °C [12,13]

|                             |       | •     | -    | -    |      |
|-----------------------------|-------|-------|------|------|------|
| Parameter                   | 200SN | PAO-6 | VHVI | UHVI | HC-6 |
| Viscosity<br>at 40 °C, cSt  | 40.8  | 30.9  | 24.1 | 25.9 | 33.4 |
| Viscosity<br>at 100 °C, cSt | 6.31  | 5.98  | 5.14 | 5.49 | 5.96 |
| Viscosity index             | 102   | 143   | 149  | 156  | 124  |
| Pour point, °C              | -6    | -64   | -15  | -9   | -12  |
| Flash point, °C             | 212   | 235   | 230  | 226  | _    |

VHVI: Very high viscosity index; UHVI: Ultra high viscosity index; HC-6: Hydrocracking.

(hydrocracking), VHVI (very high viscosity index) and UHVI (ultra high viscosity index) oils]. However, their application is still limited due to relatively high price in comparison to, e.g., PAOs and their ability to dissolve seals and rubber connections. Addition of ester base oil to PAO significantly increased the rheological properties of the final mixture [13].

Depending on the type of base oil used commercial engine oils belong to:

- (i) synthetic oils (viscosity class SAE 0W and 5W);
- (ii) semisynthetic oils (viscosity class SAE 10W);
- (iii) mineral oils (viscosity class 15W and higher).

Choice of engine oil should be based on producer recommendations, age of the car, price of engine oil and conditions of use (climate, ground conditions). Biodegradability of synthetic oils is higher in com-

Table 2 Physicochemical parameters for ester synthetic base oils [9]



Fig. 1. Some types of synthetic oils [4].

parison to that of mineral ones [14–16]. Therefore, one may call the engine oils produced from the synthetic base ecologically friendly. Repartition of the commercial engine oils to different viscosity classes is based on SAE J300 and the following parameters are taken into account: (i) low temperature viscosity: cracking (cP) max. at different temperatures [°C], pumping (cP) max. with no yield stress at different temperatures [°C], (ii) high temperature viscosity: low shear rate kinematic (cSt) at 100 °C, high shear rate (cP) at 150 °C. Quality classification (API) separates engine oils in two groups: **S** (Service) for use in spark ignited engines and **C** (Commercial) for use in compression ignited engines.

| Parameter                   | Diesters     | Phthalates   | Trimellitates | C <sub>36</sub> Dimerates | Polyols   | Polyoleates |
|-----------------------------|--------------|--------------|---------------|---------------------------|-----------|-------------|
| Viscosity<br>at 40 °C, cSt  | 6–46         | 29–94        | 47-336        | 13–20                     | 14–35     | 46-100      |
| Viscosity<br>at 100 °C, cSt | 2-8          | 4–9          | 7–22          | 90-185                    | 3-6       | 10-15       |
| Viscosity index             | 90-170       | 40-90        | 60-120        | 120-150                   | 120-130   | 130-180     |
| Pour point, °C              | -70 to $-40$ | -50 to $-30$ | -55 to -25    | -50 to $-5$               | -60 to -9 | -40 to $+8$ |
| Flash point, °C             | 200-260      | 200-270      | 270-300       | 240-310                   | 250-310   | 220-280     |

A variety of base oils are used in the production of engine oils. Similarities and differences between the commercial oils can be effectively examined with several chromatographic techniques: high-temperature gas chromatography (HT-GC), column chromatography and thin-layer chromatography with flameionisation detection (TLC–FID). One important problem is estimation of mutual miscibility and solubility of oils from different viscosity and quality classes. Inverse gas chromatography (IGC) seems to be the appropriate tool to challenge the problem. The advantages of the use of all chromatographic methods mentioned above are discussed in this paper.

#### 1.1. Inverse gas chromatography

Inverse gas chromatography is a method for the physicochemical characterisation of any material which can be placed in a chromatographic column. The term *inverse* indicates that the examined material is placed in a chromatographic column. Carefully selected test solutes are injected into the flow of carrier gas and transported over the surface of the examined material. Retention data, collected during IGC experiments for the series of test solutes, are further used in calculation of parameters characterising the examined material.

The Flory–Huggins interaction parameter is calculated according to the following equation used in our earlier investigations [17,18]:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15R}{p_1^{o}V_g M_1}\right) - \frac{p_1^{o}}{RT} \cdot (B_{11} - V_1^{o}) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^{o}}{V_2^{o}}\right)$$
(1)

1 denotes the solute and 2 denotes the examined material (oil, ester, PAO),  $M_1$  is the molecular mass of the solute,  $p_1^o$  is the saturated vapour pressure of the solute,  $B_{11}$  is the second virial coefficient of the solute,  $V_1^o$  is the molar volume,  $\rho_1$  is the density, *R* is the gas constant.

Values of the Flory–Huggins interaction parameter may be used in the estimation of mutual miscibility of the examined material (here—engine oil) and the test solute. Two species (oil and test solute) are miscible if  $\chi_{12}^{\infty} \ll 0$ . For  $\chi_{12}^{\infty} \approx 0$  one may expect limited mutual solubility of test solute and examined chemical substance.

Having the set of  $\chi^{\infty}_{(1,2)i}$  and  $\delta_{1i}$  values for the respective test solutes, one may calculate the slope of the linear relationship: left-hand-side (LHS<sub>i</sub> versus  $\delta_{1i}$ ):

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(1,2)i}^\infty}{V_1^o} = \frac{2\delta_2}{RT} \delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^o}\right)$$
(2)

The slope is proportional to the solubility parameter of the examined material, i.e.  $\delta_2$  [19–23]. This material may be used in the estimation of mutual solubility of two substances. These are mutually soluble if the difference in values of solubility parameter is lower than approximately 2 (MJ/ m<sup>3</sup>)<sup>1/2</sup>. This criterion is generally accepted in the polymer industry as well as in the examination of heavy oil residues, e.g. slack waxes.

# 1.2. SIMulated DIStillation

SIMDIS is a useful method in the examination of oil products, at a temperature range from 36 to 750 °C. One of the applications is the simulated distillation of crude petroleum. The sample is injected directly into the evaporator with programmed temperature (PTV). The injector temperature is always above oven analysis temperature. Results are given in tables or as a chromatogram. The characteristic points are: IBP (initial boiling point) boiling temperature of 0.5% of probe mass; FBP (final boiling point) boiling temperature of 99.5% of probe mass [24,25].

# 1.3. TLC-FID

This technique is the result of coupling highperformance thin-layer chromatography (TLC) and highly sensitive flame ionisation detection (FID). It is most often used for the determination of group composition of vacuum distillates, lubrication oils and asphalts. Its advantages are short time of analysis and small amount of sample in comparison to e.g. traditional column chromatography [26–28].

# *1.4. Column chromatography (adsorption–elution chromatography)*

The oldest chromatographic technique is still useful in the examination of different heavy petroleum fractions. The separated fraction may be further used in additional analysis by e.g. spectroscopic methods. This chromatographic technique offers the use of large groups of adsorbents, types and volumes of eluents as well as the possibility of the choice of the ratio of adsorbent to sample weight. All these advantages allow the separation of the examined mixture in the required number of fractions.

The aim of present paper was the presentation of possibilities inherent in the application of various chromatographic techniques in characterising base oils, intermediates and final products—engine oils.

#### 2. Experimental

# 2.1. Materials

We have examined a series of engine oils belonging to different viscosity (SAE J300) and quality (API) classes (Table 3).

The examined oils were characterised by the following standard physicochemical parameters: (i) kinematic viscosity at 40 °C and at 100 °C (ASTM D-445); (ii) viscosity index (ASTM D-2270); (iii) density at 20 °C (ASTM D-4502); (iv) refraction index at 20 °C (ASTM D-1218); (v) average molecular mass (ASTM D-2503); (vi) total basic number (ASTM D-2896).

Table 3 Viscosity and quality classification of examined engine oils

| Engine oil          | Viscosity class<br>SAE | Quality class<br>API |
|---------------------|------------------------|----------------------|
| Valvoline syn Power | 5W/40                  | SJ/CF                |
| Lotos Syntetic      | 5W/40                  | SJ/CF                |
| Lotos Semisyntetic  | 10W/40                 | SG/CD                |
| Aquila Semisyntetic | 10W/40                 | SG/CD                |
| Helius Mineral      | 15W/40                 | SG/CD                |
| Visco 2000          | 15W/40                 | SJ/CF                |
| Quaker State HDX    | 15W/40                 | CD/SH                |

#### 2.2. SIMDIS experiments

Conditions from Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 700 °C by Gas Chromatography (on the base of ASTM D-6352) were: (i) column-capillary, aluminium clad fused-silica 5  $m \times 0.53$  mm I.D., film thickness 0.1 µm of a 100% dimethylopolysiloxane stationary phase; (ii) flow conditions-helium at 18 ml/min; (iii) injection temperature-oven track mode; (iv) FID, air 400 ml/min, hydrogen 32 ml/min, make-up gas, helium at 24 ml/min, temperature: 450 °C; (v) oven program-initial oven temperature 50 °C, initial hold 0 min, program rate 10 °C/min, final oven temperature 400 °C, final hold 6 min, equilibration time 5 min; (vi) sample dilution 1% (w/w) in carbon disulphide; (vii) instrument-gas chromatograph equipped with temperature programmable vapourising injector.

### 2.3. Inverse gas chromatography

The examined engine oils were placed into the chromatographic column as the liquid stationary phases. Conditions of IGC experiments were as follows: support—Chromosorb P AW DMCS (80–100 mesh); content of liquid stationary phase (20%, w/w); apparatus—Hewlett-Packard 5730A gas chromatograph with FID; 2 m×2 mm I.D. stainless-steel column; column temperature—80 °C, 100 °C, 120 °C, 140 °C and 160 °C; sampler temperature—200 °C; detector temperature—250 °C; carrier gas—argon at the flow-rate 20 ml/min; conditioning at 160 °C (ASTM D-5480), overnight; injection volumes—0.1  $\mu$ l.

The following compounds were used as the test solutes:  $C_5-C_{11}$  *n*-alkanes, toluene, xylene, *n*-propylbenzene, *n*-alkanols (methanol-*n*-hexanol-1), acetone, butanone-2, nitromethane, chloroform, methylene chloride, 1,2-dichloroethane, 1,4-dioxane, oxolane and diethyl ether.

Saturated vapour pressures were calculated from Antoine's equation using data published in Refs. [29–31]. Values of second virial coefficient  $B_{11}$  were calculated according to procedures presented in papers [32,33] using data from Refs. [34,35]. IGC parameters  $\chi_{12}^{\infty}$  and  $\delta_2$  were calculated from Eqs. (1) and (2), respectively.

# 2.4. TLC-FID

Thin-layer chromatograms were obtained with the use of TLC–FID analyser Jatroscan MK-5. Stationary phase—Chromarod SIII (silica gel coated on the glass rod); mobile phase—*n*-hexane, toluene; development path: *n*-hexane—10 cm, for toluene—5 cm.

### 3. Results and discussion

Basic physicochemical properties of the examined oils are presented in Table 4. Values of density, refraction index increase while viscosity index decrease in following order:

Table 4

Basic physicochemical characteristics of examined engine oils

oil from 5W class  $\rightarrow$  oil from 10W class  $\rightarrow$  oil from 1-5W class

This could be used for the distinction of oils. Observed direction of changes is expected and caused by increasing content of aromatic and polar fractions. Values of other standard parameters are similar for oils from different viscosity classes.

Differences between examined oils from various viscosity classes are easily visible on SIMDIS chromatograms (Figs. 2–4). Oils from 5W class were produced with the use of poly- $\alpha$ -alkene (PAO-6) as the base oil (Fig. 2). Oils from 10W viscosity class were obtained from different base oils. A mixture of PAO-6 and mineral oil was probably used in the preparation of Lotos Semisyntetic. One can easily find similarities between the chromatograms for

| Property  | Engine oil             |                     |                       |                        |                     |                   |                     |  |  |
|---|------------------------|---------------------|-----------------------|------------------------|---------------------|-------------------|---------------------|--|--|
|   | Valvoline<br>syn Power | Lotos<br>Syntetic   | Lotos<br>Semisyntetic | Aquila<br>Semisyntetic | Helius<br>Mineral   | Visco<br>2000     | Quaker State<br>HDX |  |  |
| Kinematic<br>viscosity<br>(mm <sup>2</sup> /s) at<br>40 °C  | 89.01±0.05             | 88.2±0.05           | 94.48±0.05            | 95.88±0.05             | 102.48±0.06         | 104.81±0.06       | 107.64±0.06         |  |  |
| Kinematic<br>viscosity<br>(mm <sup>2</sup> /s) at<br>100 °C | 14.37±0.01             | 14.27±0.01          | 14.11±0.01            | 14.45±0.01             | 14.17±0.01          | 14.13±0.01        | 14.34±0.01          |  |  |
| Viscosity<br>index  | 168                    | 166                 | 153                   | 156                    | 141                 | 136               | 136                 |  |  |
| Density<br>(g/cm <sup>3</sup> )<br>at 20 °C                 | $0.8458 \pm 0.0001$    | 0.8587±<br>0.0001   | $0.8692 \pm 0.0001$   | $0.8717 \pm 0.0001$    | 0.8812±<br>0.0001   | 0.8806±<br>0.0001 | 0.8809±<br>0.0001   |  |  |
| Refraction<br>index at<br>20 °C                             | $1.4595 \pm 0.0001$    | $1.4605 \pm 0.0001$ | 1.4720±<br>0.0001     | 1.4718±<br>0.0001      | $1.4765 \pm 0.0001$ | 1.4764±<br>0.0001 | 1.4750±<br>0.0001   |  |  |
| Average<br>molecular<br>mass                                | 8.50±0.21              | 12.1±0.30           | 10.06±0.25            | 7.8±0.19               | 11.02±0.27          | 10.16±0.25        | 10.02±0.25          |  |  |
| Total basic<br>number<br>(mg KOH/g)                         | 618±12                 | 576±11              | 474±9                 | 463±9                  | 448±9               | 449±9             | 480±10              |  |  |





Fig. 2. SIMDIS chromatograms for base oil PAO-6 and two oils from SW viscosity class.

Fig. 3. SIMDIS chromatograms for base oil HC-6/PAO-6 and two oils from 10W viscosity class.



Fig. 4. SIMDIS chromatograms for mineral base oil 200 SN and three oils from 15W viscosity class.

Lotos Semisyntetic and 200SN/PAO-6 mixture (Fig. 3). The chromatogram of Aquila Semisyntetic is similar to the chromatogram of the mineral oil 200SN (Fig. 4). Therefore, one can deduce that this base oil was used for the preparation of Aquila Semisyntetic engine oil. The mineral oil used for production of the engine oil from 10W class has been probably deeply refined to acquire properties of HVI oil. The use of 200SN base oil for the preparation of 15W viscosity class oils is evidenced by the similarity of their SIMDIS chromatograms. However, one should note how difficult it is to distinguish the chromatogram of Aquila Semisyntetic oil (10W class) and chromatograms of all oils from class 15W. One cannot use these chromatograms to select the examined oils according to viscosity classes.

Interesting conclusions may be drawn from the analysis of values of physicochemical parameters determined by IGC. Values of the Flory-Huggins interaction parameter determined for different engine oils with the use of *n*-alkanes and aromatic compounds as test solutes are always negative,  $\chi_{12}^{\infty} \ll 0$ (Table 5). This means that examined oils and test solutes are mutually miscible. Values found with the use of polar test solutes, e.g. for *n*-alkanols/engine oil systems, indicate no or very limited miscibility of the components. Comparing values of the Flory-Huggins parameter for the same test solute and different oils one may indirectly deduce the miscibility of examined oils . In our case such comparison assures us that all oils mentioned in this paper are mutually miscible. However, two engine oils, Valvoline syn Power and Lotos Syntetic, produced with the use of PAO-6 as the base oil exhibit somewhat different properties (Fig. 5). Higher  $\chi_{12}^{\infty}$ values (n-alkanes and aromatic hydrocarbons as test solutes) and lower  $\chi_{12}^{\infty}$  values for alkanols were found for Valvoline syn Power. This means that this oil was produced with the use of a packet of additives having stronger polar character than in the case of Lotos Syntetic.

Discussing and comparing properties of different engine oils with the use of the Flory-Huggins interaction parameter one has to indicate the test solute used in the IGC experiment. We compare parameters determined for different "systems". It is much more comfortable to use values of parameter describing solely the character of the examined

| Table 5                 |                          |           |                          |          |          |          |      |         |    |       |    |
|-------------------------|--------------------------|-----------|--------------------------|----------|----------|----------|------|---------|----|-------|----|
| Values of Flory-Huggins | interaction <sub>1</sub> | parameter | $\chi_{12}^{\infty}$ for | examined | oils and | selected | test | solutes | at | 120 ° | °C |

| Property                     | Engine oil             |                   |                       |                        |                   |               |                     |  |  |
|------------------------------|------------------------|-------------------|-----------------------|------------------------|-------------------|---------------|---------------------|--|--|
|                              | Valvoline<br>syn Power | Lotos<br>Syntetic | Lotos<br>Semisyntetic | Aquila<br>Semisyntetic | Helius<br>Mineral | Visco<br>2000 | Quaker State<br>HDX |  |  |
| n-Hexane                     | -0.8945                | -1.1065           | -0.9654               | -0.8818                | -0.8215           | -0.8958       | -0.9832             |  |  |
| <i>n</i> -Heptane            | -0.9845                | -1.2067           | -0.9982               | -0.9909                | -0.9145           | -1.0219       | -0.0234             |  |  |
| <i>n</i> -Octane             | -0.9538                | -1.2456           | -0.9812               | -1.0349                | -0.9117           | -1.0223       | -0.9577             |  |  |
| n-Nonane                     | -0.9218                | -1.2760           | -0.9941               | -1.0705                | -0.9085           | -1.0222       | -0.8947             |  |  |
| n-Decane                     | -0.9675                | -1.1268           | -0.9345               | -1.0918                | -0.9297           | -1.0289       | -0.8797             |  |  |
| n-Undecane                   | -0.9792                | -1.1240           | -0.8823               | -1.1195                | -0.9445           | -0.9527       | -0.8862             |  |  |
| Benzene                      | -0.7678                | -0.9795           | -0.8612               | -0.8541                | -0.7525           | -0.8382       | -0.8654             |  |  |
| Toluene                      | -0.7984                | -1.0143           | -0.8618               | -0.9298                | -0.8138           | -0.9138       | -0.88317            |  |  |
| Ethylbenzene                 | -0.8162                | -1.0159           | -0.8360               | -0.9678                | -0.8296           | -0.9637       | -0.8659             |  |  |
| <i>m</i> -Xylene             | -0.8240                | -1.0105           | -0.8596               | -0.9839                | -0.8535           | -0.9941       | -0.8139             |  |  |
| <i>n</i> -Propyl-<br>benzene | -0.8422                | -1.0494           | -0.8605               | -1.0014                | -0.8609           | -0.9823       | -0.8031             |  |  |
| Methanol                     | 0.2972                 | 0.7294            | 0.5999                | 0.7860                 | 0.6799            | 0.6199        | 0.8122              |  |  |
| Ethanol                      | 0.3664                 | 0.5781            | 0.4397                | 0.5433                 | 0.5581            | 0.3474        | 0.6193              |  |  |
| Propanol-1                   | 0.0006                 | 0.2089            | 0.4141                | 0.5243                 | 0.5346            | 0.3160        | 0.3916              |  |  |
| Butanol-1                    | 0.3303                 | 0.2017            | 0.4558                | 0.4015                 | 0.1873            | 0.1517        | 0.2805              |  |  |



Fig. 5. Values of the Flory–Huggins interaction parameter  $\chi_{12}^{\infty}$  (120 °C) for Valvoline syn Power, Lotos Syntetic and PAO-6.

material. Mutual miscibility of engine oils may be also deduced from the comparison of values of solubility parameter  $\delta_2$  (Table 6). These values indicate that all examined oils are miscible within the temperature range of IGC experiments, e.g. 80–160 °C.

Values of the solubility parameter are always higher for Valvoline syn Power than for Lotos Syntetic. However, the content of aromatic fraction in Valvoline syn Power is low (8.1%) in comparison to Lotos Syntetic (12.9%) (Table 7). Despite this the polarity of the first oil (expressed by  $\chi_{12}^{\infty}$  and  $\delta_2$ values) is higher. This supports the statement that probably the packet of additives used in the preparation of the first oil exhibited much more polar

Table 6 Values of the solubility parameter ( $\delta_2$ ) for examined engine oils [(MJ/m<sup>3</sup>)<sup>1/2</sup>]

| Engine oil          | Temperature [°C] |                    |                    |                  |                  |
|---------------------|------------------|--------------------|--------------------|------------------|------------------|
|                     | 80               | 100                | 120                | 140              | 160              |
| Valvoline syn Power | 16.38±0.22       | 16.27±0.15         | 16.27±0.13         | 16.64±0.09       | 16.44±0.03       |
| Lotos Syntetic      | $15.66 \pm 0.10$ | $15.72 \pm 0.07$   | $15.98 \pm 0.06$   | $16.28 \pm 0.04$ | 16.26±0.04       |
| Lotos Semisyntetic  | $15.77 \pm 0.14$ | $15.72 \pm 0.09$   | $16.09 \pm 0.07$   | $16.63 \pm 0.07$ | $17.28 \pm 0.10$ |
| Aquila Semisyntetic | $15.42 \pm 0.14$ | $15.45 \pm 0.09$   | $15.80 \pm 0.06$   | $16.24 \pm 0.07$ | $16.66 \pm 0.07$ |
| Helius Mineral      | 16.17±0.21       | 16.28±0.13         | $15.99 \pm 0.07$   | $16.63 \pm 0.08$ | $15.81 \pm 0.03$ |
| Visco 2000          | $16.46 \pm 0.18$ | $16.31 \pm 0.12$   | $16.18 \pm 0.07$   | $16.49 \pm 0.07$ | $15.83 \pm 0.02$ |
| Quaker State HDX    | $14.94 \pm 0.09$ | $15.37 {\pm} 0.08$ | $15.86 {\pm} 0.06$ | $16.43 \pm 0.05$ | $15.88 \pm 0.03$ |

| Engine oil          | Non-aromatic fract  | ion              | Aromatic fraction   |                  |  |
|---------------------|---------------------|------------------|---------------------|------------------|--|
|                     | Content<br>(%, w/w) | Refractive index | Content<br>(%, w/w) | Refractive index |  |
| Valvoline syn Power | 91.9                | 1.4560           | 8.1                 | 1.4990           |  |
| Lotos Syntetic      | 87.1                | 1.4555           | 12.9                | 1.4840           |  |
| Lotos Semisyntetic  | 81.1                | 1.4650           | 18.9                | 1.4960           |  |
| Aquila Semisyntetic | 84.7                | 1.4655           | 15.3                | 1.4955           |  |
| Helius Mineral      | 88.4                | 1.4735           | 11.6                | 1.4828           |  |
| Visco 2000          | 82.4                | 1.4705           | 17.6                | 1.5040           |  |
| Quaker State HDX    | 73.1                | 1.4670           | 26.9                | 1.4980           |  |

Table 7 Non-aromatic and aromatic fractions in examined engine oils—their content<sup>a</sup> and values of refractive index<sup>b</sup>

<sup>a</sup> Determined according to ASTM D-2549.

<sup>b</sup> Determined according to ASTM D-1218.

character. Additionally, the value of refractive index for the aromatic fraction from Valvoline syn Power is higher than for the aromatic fraction from Lotos Syntetic. This also indicates a higher polarity of additives from Valvoline syn Power.

Two additional remarks: (i) values of refractive index for non-aromatic fractions from Valvoline syn Power and Lotos Syntetic are higher than for non-aromatic fractions from their base oil—PAO-6 ( $n_D^{20}$  = 1.4530); (ii) content of non-aromatic fraction in Helius Mineral and Visco 2000 is higher than in their base oil 200SN (78% m/m). These effects are probably caused by the co-elution with the non-

aromatic fraction of the components of the packet of additives exhibiting low affinity to adsorbent (silica gel) and/or having large molecules. These could be polymeric species used in the packet of additives as viscosity modifiers. The presence of such components was evidenced by TLC–FID (Fig. 6). Components being eluted (under analysis conditions) at the location (retention time approximately 0.45 min) characteristic for polar species were found on chromatograms of non-aromatic fractions from Lotos Syntetic (6.2%, w/w) and Helius Mineral (7.6%, w/w). A similar content of such species was also detected for other non-aromatic fractions from ex-



Fig. 6. TLC-FID chromatograms of non-aromatic fractions separated from different engine oils: A=Lotos Semisyntetic; B=Valvoline syn Power; C=Quaker State HDX.

amined engine oils. These could be viscosity modifiers as their similar content results in values of viscosity index of engine oils higher by 30-35 units in comparison with the base oils used in their production. The only exception is the non-aromatic fraction separated from Quaker State HDX oil. The content of polar species–viscosity modifiers is lower and equal to 4.6% (w/w). This probably results from the use of a base oil having higher viscosity index than other base oils applied in the production of the remaining oils from the same viscosity class.

#### 4. Conclusions

All discussed chromatographic techniques may be successfully used in the characterisation of engine oils. Standard physicochemical parameters (density, kinematic viscosity, total basic number, refraction index, viscosity index) are useful in the division of the oils to different viscosity classes. The base oil used in the production of a given engine oil may be identified with the use of SIMDIS analysis. Polarity (ability for non-specific and specific interactions) of engine oils may be described with the use of Flory-Huggins  $\chi_{12}^{\infty}$  and solubility  $\delta_2$  parameters. The applicability of the inverse gas chromatography in the examination of the engine oils is evident. The values of Flory–Huggins interaction parameter  $\chi_{12}^{\infty}$ found for all the examined oils and the test solutes representing the same type of intermolecular interactions are similar. This means that the examined oils are mutually miscible. Moreover, the difference between the values of solubility parameter  $\delta_2$  for each pair of examined oils is much lower than 2  $(MJ/m^3)^{1/2}$ . This means that one may call these oils mutually soluble. It is obvious that the properties of the final product (engine oil) are influenced by the chemical components present in the packets of additives. It has been also shown that the relative polarity (activity) of the packet of additives may be deduced from values of the above parameters and the content of non-aromatic and aromatic fractions. Column chromatography and TLC-FID techniques are useful in separation of fractions mentioned above.

However, it should be noted that we cannot predict the potential interactions (reactions leading to

the precipitation of sediments) of the components of the packets of additives from different oils.

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