Chromatographic and NMR Study of High Boiling Oils

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Summary
This paper presents an analytical system for the rapid and effective analytical control of hydrocarbon oil fractions. Three instrumental analytical methods were used:
(1) semipreparative liquid adsorption chromatography (LC)
(2) high-performance liquid chromatography (HPLC)
(3) nuclear magnetic resonance spectroscopy (NMR).
These methods were successfully applied for the determination of aliphatic, naphthenic and aromatic compounds in oils used in the preparation of motor oils.

Introduction
The choice of a suitable method for the rapid and accurate analytical control of the hydrocarbon oil fractions is a significant factor in the technological process. In this field instrumental analysis is gaining in importance in replacing the current methods used for the determination of chemical composition.

Dedicated to Professor J. F. K. Huber on the occasion of his 60th birthday.

Liquid chromatography is a prominent separation method giving rapid and effective separation without too many limitations. A very important problem in liquid chromatography is the proper choice of the detector. UV detector is unsuitable for the analysis of the saturated fractions. Therefore, the combination of refractive index (RI) and UV detectors has been used for such determinations.

Some researches studied the group analysis of higher-boiling fractions by HPLC using the RI detector [1, 2] which is suitable for the measurement of saturated, unsaturated and aromatic hydrocarbons. The oil fractions (60-215°C) were separated on silica gel with n-pentane, n-hexane and Fluorinert FC-78 as the mobile phase. A model mixture of aromatic hydrocarbons was used for the calibration. Relationships used for the determination of saturated, olefinic and aromatic hydrocarbons are detailed in the quoted papers [1, 2].

The aromatic oil fractions (220-385°C) were analyzed [3] using a UV detector (at 254nm). The column was packed with alumina and n-pentane was used as the mobile phase. The obtained chromatograms were compared with the chromatograms of model mixtures.

Combination of two columns has been recommended by Charlet et al. [4]. Reversed-phase chromatography has also been used for the separation of the aromatic fractions [5-10].

High-performance columns (particle diameter: 5-10μm) were used for the separation of aromatic hydrocarbons [11-15]. Silica gel and alumina were applied as the adsorbents. In some of the publications the use of gradient elution has also been recommended. Chemically bonded phases were also found to be suitable for the separation of aromatics [16-18], with water-containing mobile phases.

Miller et al. [19] presented the results of structural group type separation of gasolines by HPLC using a perfluorocarbon mobile phase and refractive index detection. They also investigated the problem of calibration and the possibility of using infrared detection. The problem of calibration and the difference in response factors were studied
in detail. Quantitative analysis of hydrocarbons by structural group type in gasolines and distillates was also presented [20].

A number of researches were interested in the NMR analysis of some oil samples and interpreted the $^1$H and $^{13}$C spectra of many petroleum distillation fractions [21-28]. NMR and mass spectrometry were also combined with gel chromatography in the separation of high-boiling fractions [29]. Aromatic hydrocarbons were also quantitatively determined in lower and middle oil fractions [30-33].

The aim of our work was the characterization of the higher-boiling distillation fractions using liquid chromatography and nuclear magnetic resonance spectrometry. In our study we have tried to develop a rapid method for the analytical control of the quality of fractions used for the preparation of motor oils.

Experimental

Apparatus

A Packard Model 8200 high-performance liquid chromatograph with a UV detector (254, 280nm) in combination with the Model 1107 RI detector (Laboratory Data Control, England) were used in our work. A FX-100 NMR spectrometer (JEOL, Japan) operating at a magnetic field of 2.3T, with observation frequency for $^1$H and $^{13}$C spectra (99.54 and 25MHz) was also used. The $^1$H spectra were obtained in 8K data points in the frequency range of 1000Hz.

Three columns were used in our work: a 250 x 2.6mm analytical (metal) column packed with 10μm silica gel (Laboratory přístroje, Praha, Czechoslovakia), a 150 x 3.2mm analytical (glass) column packed with 5μm reversed-phase Separon C-18 (Laboratory přístroje, Praha, Czechoslovakia), and a 500 x 12mm semipreparative (glass) column packed with 100μm silica gel Silpearl (Labora, Praha, Czechoslovakia). Normal hexane served as the mobile phase in adsorption chromatography while a water-methanol mixture 30:70 was used in reversed-phase chromatography.

Chemicals

All oil samples were obtained from Slovnaft Bratislava, Czechoslovakia.

All organic solvents were of analytical-reagent grade and were dried over magnesium perchlorate and redistilled. CDCl$_3$ was used for the NMR analysis.

<table>
<thead>
<tr>
<th>Oil no.</th>
<th>Viscosity (cSt)</th>
<th>Flash temperature °C</th>
<th>Freezing temperature °C</th>
<th>Distillation temperature °C</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>50°C</td>
<td>100°C</td>
<td>0°C</td>
</tr>
<tr>
<td>1</td>
<td>17.8</td>
<td>4.68</td>
<td></td>
<td>204</td>
</tr>
<tr>
<td>2</td>
<td>25.7</td>
<td>6.01</td>
<td></td>
<td>218</td>
</tr>
<tr>
<td>3</td>
<td>58.8</td>
<td>10.30</td>
<td></td>
<td>238</td>
</tr>
<tr>
<td>4</td>
<td>94.0</td>
<td>14.20</td>
<td></td>
<td>266</td>
</tr>
</tbody>
</table>

Procedures

The semipreparative column was packed with 20g Silpearl in n-hexane. Silpearl was activated 3 hours at 150°C.

The oil samples were injected into the column in the concentration of 0.4g oil per 2cm$^3$ n-hexane and eluted gradually with 75cm$^3$ n-hexane (fraction A), 75cm$^3$ CHCl$_3$ (fraction B) and 80cm$^3$ 1:1 methanol-benzene (fraction C). The flow rate was 1cm$^3$/min. All fractions were evaporated and dissolved in CDCl$_3$ (for NMR analysis) or in n-hexane (for HPLC analysis).

Before the analysis the HPLC column packed with silica gel was activated in nitrogen for about 60 minutes at 180°C. After the activation the column was washed with n-hexane for about 30 minutes.

Results and Discussion

Semipreparative liquid adsorption chromatography gives the possibility of separating the higher-boiling oils into three main fractions:

Fraction A: aliphatic and naphthenic compounds;
Fraction B: aromatic compounds;
Fraction C: polar-aromatic compounds.

All three fractions were analyzed by HPLC and NMR. Table I lists the physical constants of the analyzed oils which are known not to contain any olefinic hydrocarbons. The relative amounts of the individual fractions separated on the semipreparative column are given in Table II. It is obvious that increasing the distillation temperature has caused a loss of the saturated hydrocarbon content (fraction A) while the concentration of the aromatic hydrocarbons has increased (fraction B).

The aromatic fractions were analyzed by high-performance liquid chromatography on the analytical columns using UV and RI detectors. The used standard aromatic hydrocarbons (benzene, naphthalene, anthracene, 1,2-benzanthracene and perylene) were dissolved in n-hexane or chloroform.

We have determined the optimum conditions for the separation of a model mixture. Typical chromatograms using UV and RI detectors are demonstrated in Figs. 1a and 1b respectively.

The aim of the HPLC separation was to verify the composition obtained on the semipreparative column (Table II). Further separation of the saturated or aromatic hydrocarbons is not necessary for our control analyses of the distillation fractions used for the preparation of motor oils. The analyzed samples do not contain any olefinic hydrocarbons.