METHODS OF ASSESSING THE QUALITY OF FUELS AND OILS

ROLE OF THE SOLID CARRIER IN THE ANALYSIS OF IMPURITIES∗

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The shape of the principal component's zone is of great importance in the quantitative chromatographic analysis of impurities. The unsymmetrical peak of the principal component, with an elongated tail, masks the impurities eluted after this component and impedes their quantitative determination. It is therefore desirable to reduce to a minimum the width and asymmetry of the principal component's peak.

It is usually assumed that asymmetry is due to nonlinear isothermal adsorption of the substances being chromatographically analyzed on the interface of the liquid phase and the solid carrier.

Kusy [1] has shown that irreversible adsorption of the analyzed compounds on this interface leads sometimes to considerable errors in the quantitative analysis of polar components when we use sorbents with nonpolar liquid phases.

It may be noted that neither Kusy nor any other author (as far as we know) has dealt with the effect of the solid carrier on the quantitative analysis of impurities.

The present paper deals with the effect of the solid carrier on the quantitative analysis of impurities, and various ways of modifying this effect.

Since the effect should only be very pronounced in the case of a nonpolar liquid phase, all the experiments were performed on carriers impregnated with 10% of the nonpolar phase—Apiezon N, made by the British firm A.E.I., Ltd.

The initial carrier used in this work was Sferokhrom-1, made by the Gor'dii Experimental Base of VNII NP.

The experimental work was performed in a KhV-1 chromatograph (for mixtures with 1% impurities) or a Tsvet-1 chromatograph (where the impurity concentration was 5 × 10⁻³%). The chromatographic columns (200 × 0.4 cm) were packed with 10% of Apiezon N on the solid carrier. The experiments were performed at 90°C. The velocity of the carrier gas (helium) was 50 ml/min. The volume of the sample was 2-5 μl. Below we give the characteristics of the initial solid carrier (carrier III), taken from a paper by Pakhomov et al. [2].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, g/cm³</td>
<td>0.57</td>
</tr>
<tr>
<td>Grain size, mm</td>
<td>0.16-0.25</td>
</tr>
<tr>
<td>Specific surface, m⁴/g</td>
<td>1.46</td>
</tr>
<tr>
<td>Mechanical strength, %</td>
<td>1.75</td>
</tr>
<tr>
<td>Catalytic activity (rel. to conversion of cyclohexanol), %</td>
<td>5.2</td>
</tr>
<tr>
<td>pH</td>
<td>8.8</td>
</tr>
</tbody>
</table>

The carrier's surface was processed at 250°C for several hours in nitrogen, saturated at room temperature with dimethyldichlorosilane vapor (carrier II). Modification of the carrier's surface with triethylene glycol (1%) was performed by depositing a liquid phase (carrier I). Triethylene glycol was deposited on the solid carrier from an acetone solution, and Apiezon from a solution in n-hexane, in which triethylene glycol is virtually insoluble.

Since in practice the impurity concentration varies very markedly, we took as the models standard mixtures of polar and nonpolar components with different impurity concentrations (cf. Table 1).

Table 2 gives the results of the quantitative analysis of mixtures A and B in relative units \( \eta = S_I/S_N \) (\( S_I \) and \( S_N \) are the relative areas of the i-th component and n-nonane, respectively).

∗L. V. Sitnikov took part in the experiments.

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TABLE 1. Characteristics of the Standard Mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Principal component</th>
<th>Impurities</th>
<th>Impurity concentration, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Heptane</td>
<td>Toluene, methyl ethyl ketone, n-amyl alcohol, and n-nonane</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>Methanol</td>
<td>The same</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>Cyclohexane</td>
<td>Toluene, methyl ethyl ketone, n-amyl alcohol, n-1-hexanol, and n-nonane</td>
<td>5 \times 10^{-3}</td>
</tr>
</tbody>
</table>

TABLE 2. Results of Quantitative Analysis of Mixtures A and B

<table>
<thead>
<tr>
<th>Mixture components</th>
<th>Relative content of impurities (internal standard - nonane)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>carrier I</td>
</tr>
<tr>
<td>Mixture</td>
<td>mixture A</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.12</td>
</tr>
<tr>
<td>n-Amyl alcohol</td>
<td>0.76</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>1.09</td>
</tr>
</tbody>
</table>

It will be seen from Table 2 that, irrespective of the mixture analyzed, on all the sorbents toluene (the component of low polarity) gives virtually the same results. In the case of the more polar component, methyl ethyl ketone, we observe a characteristic decrease in \( \eta \) as we pass from the modified to the unmodified carrier. For example, in the analysis of mixture A the value of \( \eta \) decreases by 18.3% as we go from carrier I to II, and by 28.4% as we go to III. This is evidently due to practically irreversible adsorption of methyl ethyl ketone on the solid carrier's surface. For carriers II and III, in the analysis of mixture B, in which the principal polar component (methanol) is eluted before methyl ethyl ketone, the value of \( \eta \) for the latter is higher than in the case of mixture A (principal component - heptane).

The most polar compound of the impurities analyzed, n-amyl alcohol, is eluted quantitatively only on carrier I (at the same concentration in mixtures A and B). The analytic data show that its content in mixture B is higher than in A, evidently owing to the modifying influence of the principal polar component.

The relative retentions of the polar impurities also vary with the carrier's modification. Thus in the case of modified carriers the relatively retained volume for methyl ethyl ketone (standard - nonane) is only one third of that on a sorbent with an unmodified carrier. For components of low polarity (toluene) this value is practically constant.

Table 3 gives the results of the quantitative analysis of mixture C, containing \( 3 \times 10^{-3} \% \) impurities. It will be seen that the relative content of toluene is again virtually constant on sorbents prepared from all three carriers. However, the observed methyl ethyl ketone concentration decreases by 21% as we go from carrier I to carrier II, and its determination becomes impossible in the case of carrier III. The more polar compound, the alcohol (n-1-hexanol), is eluted only on a sorbent with solid carrier I.

n-Amyl alcohol could not be determined because it is masked by the peak of the principal substance (cyclohexane).

Therefore with decreasing impurity concentration the effect of the solid carrier on quantitative analysis is intensified.