QUANTITATIVE INTERPRETATION OF THE CHROMATOGRAMS
OF MULTICOMPONENT MIXTURES

A. I. Bogdanchikov and M. S. Vigdergauz

One of the factors which determine the accuracy of quantitative chromatographic analysis is the selection of the most reasonable method for calculating the concentration of the substances. In the case of the chromatograms of multicomponent mixtures, the generally adopted method is that of internal normalization of the areas of the peaks with, if necessary, the introduction of correction coefficients, \( K_1 \), taking account of the differing sensitivity of the detector to the components being determined [1-4].

However, with a quantitative analysis of chromatograms, based on the value of the area of the peaks, determined as the product of their height by their half-width, there often arise difficulties connected with the impossibility of measuring the width of poorly resolved peaks, and with the low degree of accuracy in the case of the peaks of weakly sorbed substances. In view of this, a method has been developed for the quantitative interpretation of chromatograms [5] by internal normalization of the products of the height of the peak, \( h \), by the retention time, \( t_R \), since the value of \( t_R \) can be measured with considerably greater accuracy than the half-width of a peak, \( \tau \).

The application of the above method is based on the well-known empirical relationship [6-10]

\[
\tau = a + bt_R,
\]

which holds for the analysis of substances with close structures (\( a \) and \( b \) are constants).

If the content of the \( i \)-th component is determined by the method of internal normalization as

\[
P_i = \frac{K_i h_i \tau_i}{\sum K_i h_i \tau_i},
\]

then, from (1) and (2), it follows that:

\[
P_i = \frac{K_i h_i (a + bt_R)}{\sum K_i h_i (a + bt_R)}. \tag{3}
\]

Fig. 1. Graph of the dependence of the half-width of the peak on the retention time for the component of the mixture being determined.

Fig. 2. Graph of the dependence of the width of a peak on the retention time of a component, at different pressures (in atm): 1) 1.54; 2) 1.36; 3) 1.18; 4) 1.12.
TABLE 1. Results of Analysis of a Synthetic Mixture

<table>
<thead>
<tr>
<th>Hydrocarbons</th>
<th>Comp. of ref. mixt., wt.%</th>
<th>Calculated results, wt.%</th>
<th>Absolute error, wt.%</th>
<th>Relative error, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>9.55</td>
<td>9.59</td>
<td>9.71</td>
<td>9.91</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>10.71</td>
<td>10.97</td>
<td>10.96</td>
<td>10.08</td>
</tr>
<tr>
<td>2,4-Dimethylpentane</td>
<td>10.79</td>
<td>11.58</td>
<td>11.24</td>
<td>11.46</td>
</tr>
<tr>
<td>3,3-Dimethylpentane</td>
<td>11.72</td>
<td>12.42</td>
<td>11.85</td>
<td>11.87</td>
</tr>
<tr>
<td>3-Methylhexane</td>
<td>11.57</td>
<td>11.82</td>
<td>11.72</td>
<td>11.73</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>11.64</td>
<td>12.31</td>
<td>12.14</td>
<td>12.18</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>13.78</td>
<td>13.30</td>
<td>13.48</td>
<td>13.44</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>8.92</td>
<td>8.57</td>
<td>8.93</td>
<td>8.85</td>
</tr>
<tr>
<td>n-Octane</td>
<td>11.02</td>
<td>10.44</td>
<td>10.97</td>
<td>10.48</td>
</tr>
</tbody>
</table>

Notes. I. 1) Composition of mixture calculated by the method of internal normalization of the products h¢t; 2) composition of mixture calculated by the method of internal normalization of the products h¢tR; 3) composition of mixture calculated by the method of internal normalization of h¢t'. II. Mean absolute error equal to 0.49, 0.28, and 0.38 wt.%; mean relative error equal to 4.38, 2.93, and 3.46%.

Thus, the method of internal normalization of the products h¢t using the equation

\[ P_i = \frac{K_{ih}ht_{Ri}}{\sum K_{ih}ht_{Ri}} \]  

(4)

can be used without the introduction of supplementary correction factors only with a \( a \approx 0 \). In the contrary case, the calculation must be made using the equation

\[ P_i = \frac{K_{ih}ht_{Ri}}{\sum K_{ih}ht_{Ri} - K_{2}ht_{Ri}} \]  

(5)

where

\[ K_{2} = \frac{a}{t_{R}^2} + b. \]

In other words, the results obtained using the method of internal normalization of the products h¢tR are free of supplementary errors only when the ratios \( t_{R}/t \) are equal for all the peaks in the chromatogram, which corresponds to equal efficiency of the column, calculated with respect to the parameters of the different peaks, since the number of theoretical plates is

\[ n = 5.55 \left( \frac{t_{R}}{t} \right)^2 \]  

(6)

Thus, the correction coefficient \( K_{2} = \sqrt{H} \), where \( H = L/n \) is the height equivalent to a theoretical plate; \( L \) is the length of the column.

In [11] averaged empirical corrections were proposed for groups of hydrocarbons, elutriated between adjacent normal paraffins.

Unfortunately, a whole series of investigators, using the chromatographic method to determine the composition of multicomponent mixtures, carry out the quantitative analysis of the chromatograms by normalization of the products h¢t without introducing the corrections \( K_2 \), although this can only be justified in the case of analysis of mixtures boiling within narrow temperature limits, when the efficiency is practically constant for all the peaks.

In view of this, a graphical method [6] is useful; this method is based on the use of the relationship (1), when, with respect to a fixed retention time, the calculated width of the peak is determined (Fig. 1, straight line 1), with a subsequent calculation using Eq. (2). The graph is plotted from experimental data for several well resolved peaks, with sufficient width for accurate measurement.

It can easily be shown that calculation using Eq. (4) corresponds to a graphical determination of the width of a peak, \( t' \), on the basis of straight line 2 (Fig. 1) connecting the origin of coordinates with the point \( (t_{R}, t'_{R}) \), which corresponds to some mean peak on the chromatogram. It follows from this that the a priori error in determination of the width of the peak from straight line 2 (compared to the result of a determination using straight line 1) will be

\[ \Delta t = t' - t = (m' - m) \left( t_{R} - t_{Rm} \right), \]  

(7)