GAS CHROMATOGRAPHIC METHOD OF IDENTIFYING COMPONENTS
OF COMPLEX MIXTURES

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For the chromatographic identification of components, use is generally made of tables of retention volumes (V_g), of the dependence of the retention on some physical property (boiling point, dielectric constant), or of the behavior of $\log V_g$ on two or three stationary phases. These methods are effective for the analysis of relatively simple mixtures.

In order to identify the components of complex mixtures it is expedient to use functions of the retention volume which depend only on the composition of the material analyzed and not on the type of solvent. It can be shown that such functions exist. Between the values of $\log V_g$ of substances of similar composition to the different solvents there are linear relationships of the type:

$$\log V_{g_i} = A \log V_{g_{stand.}} + B,$$
(1)

where A and B are coefficients determined by the composition of the substance; $V_{g_{stand.}}$ is the retention volume

of the substance chosen as the standard. On choosing a new standard substance from a group of substances of similar composition Eq. (1) will change in a linear manner. At the same time is known [1] that the binary ratios must remain constant.

A method is proposed below for the identification of complex mixtures, based on the use of binary ratios of the following form:

$$\frac{\lg V_{g_i} - \lg V_{g_1}}{\lg V_{g_2} - \lg V_{g_1}},$$

where V_{g_i}, V_{g_1}, V_{g_2} are the retention volumes of substances i, 1, 2, measured on the same solvent. If substance 1 and 2 belong to the same class of compounds, the above ratio must have the solvent-independent constant value [2]:

$$\frac{\lg V_{g_i} - \lg V_{g_1}}{\lg V_{g_2} - \lg V_{g_1}} = \varphi = \text{const.}$$
(2)

Substances	Hydrocarbon class			
	paraffinic	olefinic	cycloparaffinic	diolefinic
Standard	2,3-di-methyl-butane	pentene-1	cyclopentane	isoprene
	n-heptane	heptene-1	methyl cyclo-hexane	1,3-pentadiene (cis)
Test	n-hexane	2-methyl-pentene-2	cyclohexane	1,3-pentadiene (trans)

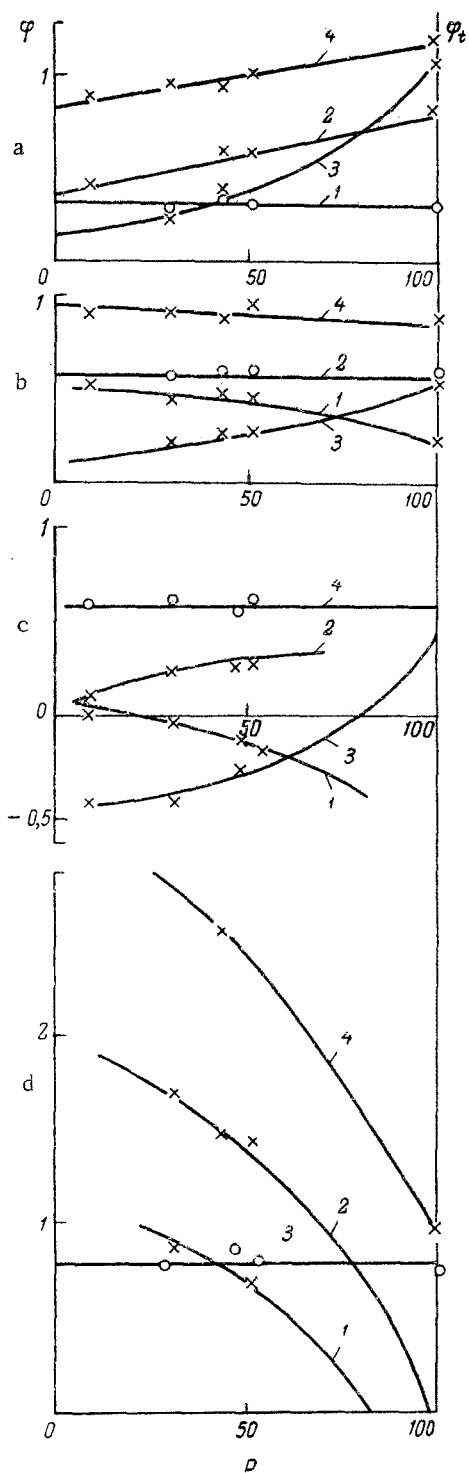To test Eq. (2), the hydrocarbons listed in the table were selected.

Fig. 1. The variation of φ with solvent polarity for the hydrocarbons: a) paraffins; b) olefins; c) cycloparaffins; d) diolefins; 1) n-hexane; 2) 2-methylpentene-2; 3) isoprene; 4) cyclohexane. (φ_t—cf. [4].)

In order to characterize the properties of the liquid phases, their relative polarities were determined [3], giving the following values:

Liquid phases	Polarity P (rel. units)
Apiezon	7
Benzyl benzoate	28.1
7,8-Benzoquinoline I	45.5
Tricresyl phosphate	51.5
$\beta\beta'$-Dicyandiethyl ether	100.0

Figure 1a, b, c, d shows the way in which φ varies with solvent polarity for paraffins, olefins, cycloparaffins, and diolefinic hydrocarbons.

From Fig. 1 it is seen that the function φ remains constant for all the solvents, i.e., straight lines parallel to the abscissa are obtained for paraffinic (Fig. 1a), olefinic (Fig. 1b), cycloparaffinic (Fig. 1c), and diolefinic (Fig. 1d) hydrocarbons if the standard substances belong to the same class as substance i. If substance i differs structurally from standard substances 1 and 2, then φ is not a linear function of P. The nature of the curves depends on the properties of the hydrocarbons.

For example, on the graph for diolefinic hydrocarbons the line for n-hexane, a saturated hydrocarbon, has the greatest curvature; at the same time it has zero dipole moment and a minimal dielectric constant of 1.8924 [4].

A lower curvature is obtained for cyclohexane, which also has no dipole moment but has a greater dielectric constant (2.044). 2-Methylpentene-2, and olefinic hydrocarbon having a polarizable π-bond, gives a line of even lower curvature. In conformity with this a minimal curvature is given by the most polarizable hydrocarbon, isoprene, which has two double bonds (dipole moment 0.38). This sequence of curvatures also applies to the other graphs (diolefins > olefins > cycloparaffins > paraffins). In accordance with this the curves corresponding to the more polar compounds compared with substance i are curved upwards from the abscissa, while the less polar are curved downwards. It is advisable to choose as standards substances having appreciably different boiling points.

The proposed function is associated with a linear dependence between log V_g for substances of a given class (substances of normal structure and isomers) in two solvents [5]:

$$\lg V_{g_i}^{I} = A^1 \lg V_{g_i}^{II} + B^1, \tag{3}$$

where A^1, B^1 are constant coefficients for a given group of substances.

If substances 1, 2 are normal paraffins Eq. (2) will be proportional to Kovats' index [6]. If the substance is an isoparaffin, then on the basis of Eq. (2) its retention index will have a constant value in different solvents, as noted previously as an empirical fact [6].

Thus the proposed function includes previously known behavior, but being more general has a number of advantages for determining the components of complex mixtures. The main advantages are the following:

1. The function φ does not depend on the nature of the solvent for different classes of compounds.
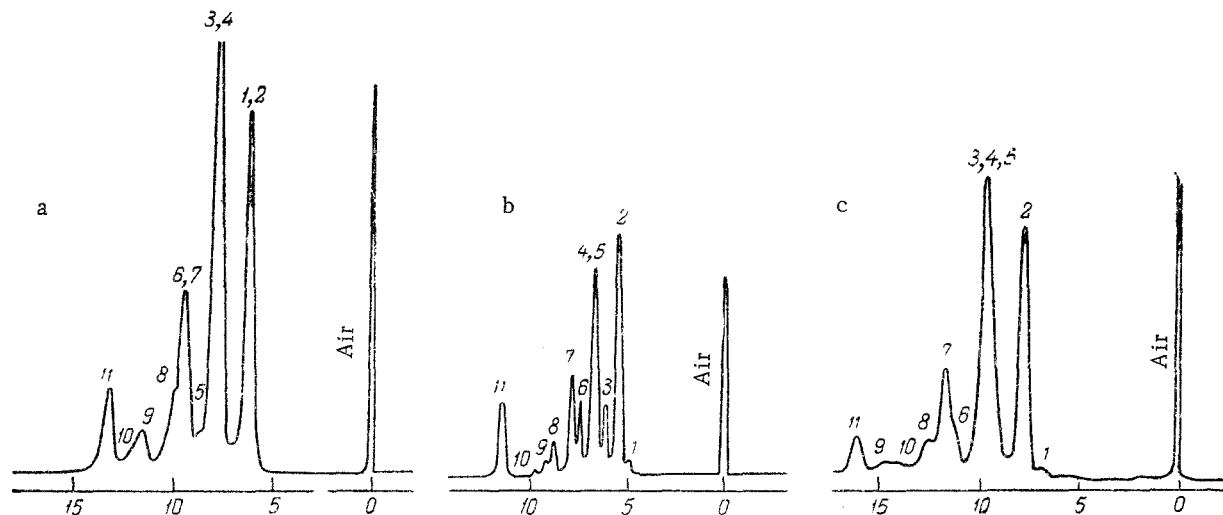
Fig. 2. Chromatograms of fraction 1 after preparative separation of the gasoline fraction at 80-100°C. Liquid phases: a) tricresyl phosphate; b) 7,8-benzoquinoline; c) benzyl benzoate. Hydrocarbons: 1) 2,3-dimethylbutene-3; 2) 2-methylhexane; 3) 3,3-dimethypentent-1; 4) 3-trimethylhexane; 5) methylcyclopentane; 6) 2,4-dimethylpentent-1; 7) 2,4-dimethylpentene-2; 8) methylhexene-1; 9) 4-methylhexene-1; 10) n-heptane; 11) 2-methylhexene-1.

2. The function φ can be used to determine the class of compounds to which an identified component belongs.

3. In carrying out identifications it is possible to use experimental and literature retention volume data for the same components in other solvents.

4. It is known that the logarithms of the retention volumes of substances with identical functional groups depend linearly on the boiling points. In this connection the applicable equation is

$$\frac{\lg V_{g_i} - \lg V_{g_1}}{\lg V_{g_2} - \lg V_{g_1}} = \frac{T_i - T_1}{T_2 - T_1} = \varphi_T, \tag{4}$$

where T_i, T_1 and T_2 are the boiling points of substances i, 1, and 2, respectively.

If an auxiliary ordinate is imposed on Figs. 1a, b, c, d, and values of φ_t plotted on it, the points fall on a good straight line parallel to the abscissa. In this connection Eq. (4) can also be used to identify individual components.

5. The function φ is independent of the temperature at which an analysis is carried out, for substances of similar chemical structure.

From the temperature dependence of the logarithm of the retention volumes and the boiling points it is easy to show that

$$\frac{T_i - T_1}{T_2 - T_1} = \text{const} \tag{5}$$

6. Finally, a significant advantage of function φ is the possibility of using retention volumes determined at any temperature, thus widening its range of application.

The function φ was used in conjunction with other methods to identify the components of the gasoline fraction from a high temperature catalytic cracking unit.

The gasoline fraction boiling between 80-100°C was separated on a preparative column into three fractions, each of which was then chromatographed on three different liquid phases: benzylbenzoate (BB), 7,8-benzoquinoline (7,8-BQ), and tricresyl phosphate (TCP). Figure 2 shows chromatograms of fraction 1, obtained after preparative chromatographic separation; this fraction consists of C_7 hydrocarbons. The peaks on the chromatograms were identified from the graphical dependence of $\log V_g$ on the dimensionless number z, the ratio of the boiling point of of the component to the experimental temperature [7]. However, it was necessary to verify the identification of some uncertain components by comparing their retention volumes with the retention volumes of individual hydrocarbons. In the absence of the latter, the method described was used.

As an example we cite the interpretation of peak nine, which we have identified as 4-methylhexane-1. In order to verify its identification, the function φ was evaluated for the standard substances pentene-1 and heptene-1. The following values of were found: 0.933 on BB, 0.915 on 7,8-BQ, and 0.907 on TCP. The calculated value of the b.p. for 4-methylhexene-1 was 87.9°C, compared with the handbook value of 87.3°C for this hydrocarbon. Other components also were checked in this way.

CONCLUSIONS

The new functions φ and φ_t are proposed which enable the components of complex mixtures separated chromatographically to be identified with great accuracy.

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