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Identification of Substances in Gas Chromatography

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Methods for the qualitative analysis of substances separated chromatographically have been examined. Particular attention has been paid to methods which have been intensively developed in recent years for identifying substances from their chromatographic characteristics without the use of a standard. The bibliography contains 265 references.

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I. INTRODUCTION

One of the central problems with which research workers have been concerned throughout all stages of the development of the gas chromatographic method is the identification of substances separated chromatographically. In almost all monographs on gas chromatography, chapters have been devoted to qualitative analysis, and this question has also been dealt with in a number of review articles. In most of the latter, attention has been concentrated chiefly on one aspect of the problem. Monographs and reviews on this subject do not deal with recent work. In the most detailed review devoted to the contribution of gas chromatography to identification [1], published material up to only 1969 was reviewed. The most significant progress in this field, however, which has made it possible to reach conclusions regarding the structure of a substance from its gas chromatographic behaviour and to predict the chromatographic behaviour of a substance from its structure and physicochemical properties, has been made in recent years.

The present review deals with data on qualitative gas chromatographic analysis published up to and including 1974. Since zone identification based on additional operations with the components of mixtures before and after gas chromatographic separation has been dealt with in sufficient detail in reviews and monographs, for example in Ref. 2, the present review was restricted to an examination of methods which use only gas chromatographic data for identification. In addition to a discussion of methods of identification using standards, particular attention has been paid to the latest achievements in the development of correlation methods and methods based on predictive retention calculations, not involving the use of standards.

II. METHODS OF IDENTIFICATION USING STANDARDS

In these methods, the qualitative analysis of a mixture is carried out by comparing the chromatogram of the specimen being studied with the chromatograms of standard substances or with tabulated data. The identity criterion is the coincidence of the retention data of the substance being analysed and the standard, since under identical and correctly chosen experimental conditions, the retention values should be physicochemical constants of the substances, characterising their distribution in the gas–sorbent system [3-5].

In the first version, which is very frequently used in practice, the identification is carried out by comparing the retention values, measured under identical conditions, of the components of the mixture being analysed and standard substances, the presence of which in the material being studied is assumed. It is concluded that a substance is present in a mixture when the retention times coincide (for the analysis of standard directly before or after the chromatographic study of the specimen) or from the increase in the corresponding peak on the chromatogram (in the case where the assumed standard substance is added to the mixture being studied) [3]. The probability of correct identification depends on the number of substances eluted close to one another and on the accuracy of the measurement of the retention volume, and was characterised quantitatively by Klein and Tyler [4] by the magnitude of the "peak density" (the ratio of the total number of peaks to the total number of possible separations in a given interval). The reliability of the identification is increased if the chromatographic separation is carried out on two stationary phases of different polarity [3-5], since components having identical solubilities in one stationary phase in most cases have different solubilities in another. According to Brown [6] it is best to use a combination of non-polar, electron-donor, and electron-acceptor phases. Super-selective sorbents are effective for this purpose.

If the analysis is carried out in parallel on several columns operating under identical conditions, it is possible to obtain the so-called chromatographic spectra of substances. This method was first proposed by Klouwen and Ter Helde [7], who showed for the case of aliphatic compounds and monocyclic and bicyclic terpenes that each class of substance is characterised by a strictly definite form of the curves representing the retention on five stationary phases. Chromatographic spectra have been used for the qualitative analysis of organic substances by a number of workers [8-11]. Franc and Michajlova [8,9] showed that if the same specimen volatiliser and the same detector are used, the chromatographic spectra, like optical spectra, are specific for each individual substance. The possibilities for the identification of the components of mixtures are extended considerably by switching four columns with different stationary phases in pairs in the same apparatus; in this way, eight different versions of the analysis are carried out [11].

The method of standards is widely used in laboratories, but it requires on a priori knowledge of the possible composition of the mixture being analysed and the availability of standard substances for comparison.

In the second version, the components of a mixture are identified by comparing their retention data with data previously obtained by other workers and summarised in tables. Primary gas chromatographic data—retention

times t_R or retention volumes V_R—cannot be used, since they depend on the conditions of their determination. To eliminate this influence, either absolute or relative retention values are used.

Absolute retention characteristics—the specific retention volumes V_g and the distribution coefficients K [12-14] (reference tables [15-19])—are sufficiently reliable criteria for identification if they are accurately determined [20]. This last feature is responsible for the fact that these characteristics are not very widely used, since the accurate reproduction of the conditions of analysis, particularly the quantity of stationary phase in the column, is an extremely tedious task. For the identification of substances, it is preferable to use relative retention characteristics [3]. When the analysis is carried out at the appropriate temperature using the column and standard substance given in the literature, the retention times or volumes related to the corresponding values for the standard are free from the influence of the other conditions of the experiment and can be used to identify the components of the mixture being separated. The relative retention characteristics are given in general form by the equation [21]

$$R^{rel} = p\left(k + \frac{R_x - R_1}{R_2 - R_1}\right), \quad (1)$$

where R_X, R_1, and R_2 are the reduced retention values for the substance being studied and two standard substances respectively; and p and k are constants characteristic of the chosen system of coordinates. In the simplest case when $p = 1$, and $k = R_1 = 0$, the relative retention volume V_R^{rel} (or retention time t_R^{rel}) are obtained.

The relative retention volumes of representatives of the principal classes of organic substance have been tabulated [15-18,22-29]. Of particular interest are the tables of Schupp and Lewis [16], in which retention data are collected for 209 stationary phases and 26 carriers at different temperatures. An edition of tables of retention values has been planned in the USSR Committee of Standards.

An unsatisfactory feature of the method is that a large number of varied compounds are used as standard substances. In spite of an IUPAC recommendation [30], in which it was proposed that the choice of standards be restricted to several substances readily available in pure form (n-butane, 2,2,4-trimethylpentane, benzene, *p*-xylene, naphthalene, butan-2-one, cyclohexanol, and cyclohexanone), different research workers continue to determine V_R relative to any substance which they regard as convenient.

In 1960, Smith [31] proposed that a single substance—"theoretical nonane"—be used as standard. The retention values of "theoretical nonane" are obtained from an analysis of a mixture of n-hydrocarbons by extrapolating the linear relationship between the logarithms of the retention times and the number of carbon atoms in the molecules. To determine the retention relative to "theoretical nonane" R_{X9}, any alkane is added to the mixture being studied, and the retention volume relative to it is calculated. The above linear relationship is then used to determine the retention volume of the hydrocarbon used relative to n-nonane, and the two quantities obtained are multiplied. If the use of an n-alkane is difficult for any reason (analysis on columns containing polar sorbents), the use of the retention value relative to "theoretical n-pentanol", defined analogously, is proposed [31].

The "theoretical nonane" system was further developed by Smith and Evans [32-36]. For high column temperatures, an analytical method was proposed instead of graphical extrapolation [35]. Other retention values can also be recalculated to R_{X9} units, so long as V_R for four n-hydrocarbons are known [34]. The possibility of using a system of secondary standards [36] and of predicting retention values for compounds from the molecular formulas has also been examined [37-39]. The accuracy of the determination of the R_{X9} values, however, depends on how far the primary standard is separated from n-nonane.

A more general solution of the problem of the choice of standards was proposed by Kovats', who recommended the determination of relative retention data using the homologous series of n-alkanes as standards [40,41]. The choice of this series is most natural, since the n-alkanes represent as it were a "zero structure", on the basis of which it is possible to reproduce the structure of all organic substances. Kovats called the new parameter the "retention index". The data are expressed on a logarithmic scale; the retention indices are determined from Eqn.(1) for $p = 100$, $k = n$, $R_1 = \lg R_n$, $R_2 = \lg R_{n+1}$, $R_X = \lg R_X$ (n and $n + 1$ are the numbers of carbon atoms of the n-alkanes diluted immediately before and after the substance being determined). Since for n-alkanes, $\lg R$ is a linear function of the number of carbon atoms in the molecule, the denominator in Eqn.(1) is replaced by b — the slope of the straight line obtained by plotting $\lg R$ against n (b is determined for n-alkanes having $n \geq 6$).

Kovats' system of retention indices is now generally accepted. According to the Recommendation of The Data Sub-Committee For The Publication Of Retention Data [42], and the well-founded opinion of a number of research workers [20,43-53], it provides the most convenient and promising method of characterising retention in gas chromatography. When the retention times are measured accurately, and the temperature of the column is maintained to within 0.1°, [54,55] the retention indices have a high reproducibility, which reaches $\pm(0.03-0.05)$ units [52,56]; the reproducibility of the indices in different laboratories often lies in a range of ± 1 unit [51,52]. A detailed review [57] has been devoted to the problem of applying Kovats' indices in gas chromatography.

In addition to its indisputable advantages, Kovats' system of indices also has some unsatisfactory features. These include the comparatively tedious calculations and the fact that the n-alkanes are not always the most convenient reference substances. Thus in analysis on polar stationary phases, the characterisation of low-boiling polar substances requires the use of high-boiling n-alkanes, because of the weak retention of the latter on polar phases. The simultaneous analysis of high- and low-boiling substances under identical conditions is inaccurate.

The subsequent improvement of Kovats' system of indices has taken place in two directions: 1) simplifcation and an increase in the speed of the calculations, and 2) the use of other series of standard substances instead of n-alkanes and the development of systems similar to Kovats' system. Graphical methods have been proposed in order to increase the speed of calculations [58-60]. The accuracy of the values obtained is low, however. In place of Kovats' logarithmic index, an arithmetic index (also linear) was introduced ($p = 100$, $k = n$, $R_1 = R_n$, $R_2 = R_{n+1}$). [61-65] The problem of calculations is now being solved by the use of computers and special programs for calculating retention indices [66-69].

To avoid the difficulties in the identification of polar and high-boiling substances in Kovats' system, some workers propose that the use of n-alkanes as standards be

replaced by the use of other homologous series: androstane and cholestane for the characterisation of the gas chromatographic retention of steroids (the "steroid number" of Vanden Heuvel and Horning)[70,71]; linear polyphenyls for polyphenyl compounds (the "phenyl number" of Habgood and Harris)[72]; polyacenes for condensed aromatic and heterocyclic systems[73]; dimethylsiloxanes for methylpolysiloxanes ("dimethylsiloxane number")[74-76]; n-alcohols[77]; n-propyl esters[78]; and methyl n-alkyl ketones[79]. For the analysis of lipids, the methyl esters of saturated[80-82] or monounsaturated[83,84] normal acids have been recommended as standards ("equivalent chain length system"). Thus there is a danger of an increase in the number of proposed series of standards, and the problem of standardising retention data may arise again.

The above systems of standards are mainly applicable only for the characterisation of definite groups of substances, and often show poor agreement with one another[85]. For the recalculation of data to Kovats' system, if the indices of the standards I_1 and I_2 are known, the following equation can be used[86]:

$$I = (I_2 - I_1)\frac{\lg R_x - \lg R_1}{\lg R_2 - \lg R_1} + I_1. \qquad (2)$$

The logical conclusion of improvements to the system of retention indices is the introduction of a generalised retention index I_a,[87] which provides for the use, as fixed points, of any homologous series of substances with functional group X_a. The change from one scale of standards to another is brought about using the equation

$$I_a = I_b - I_b(a) + 100\,n(a), \qquad (3)$$

where I_a and I_b are the retention indices of the substances on the scales of the standards a and b respectively; and $I_b(a)$ is the retention index of the substance a with number of carbon atoms $n(a)$ on the scale of standards b.

Systems of expressing gas chromatographic data with an altered scale, such as the "carbon numbers"[80,81], the "methylene unit"[88,89], and the "standardised retention energies"[90,91] must be regarded merely as particular cases of Kovats' system; their adequacy has been demonstrated[92].

There are at present several systematic reference tables of retention indices[19,40,93]. The reference tables of McReynolds[19] are particularly extensive, and give the retention indices of substances on 26 stationary phases for rigorously standardised conditions. In addition to the quantities mentioned, Walraven and Berezkin[21] proposed another two quantities—the relative index ($p = 1$, $k = 100\,n$, $R_1 = 0$, $R_2 = R_n$) and the retention exponent ($p = 100$, $k = 1$, $R_1 = R_A$, $R_2 = R_B$).

The relative retention values are characterised by approximately equal accuracy (equivalent quadratic deviations 0.50–0.75%). For systems with two standards, the increase in the error resulting from the error of the measurement of the retention of the second standard is compensated by the significant of the correlation coefficients. The retention indices give more accurate results than the relative retention volumes only when the substance being analysed and both n-alkanes are introduced simultaneously on to the column[21]. The retention times of the n-alkanes should be measured as accurately as possible, since it has been shown from Erdey's equation[94,95] that these measurements introduce the greatest errors into the value of the retention index.

What has been said above applies chiefly to the accuracy of determinations in a given laboratory. The accuracy and the reproducibility of relative retention values in different laboratories are much lower. One of the chief reasons for the poor reproducibility of retention data between laboratories is the adsorption of substances at gas–liquid and liquid–solid carrier interfaces. The adsorption properties of these interfaces depend on the conditions of preparation of the sorbent[96,97].

To obtain constants which are independent of the conditions of the experiment and the method of preparing the sorbent, it is necessary to take account of the adsorption on the surfaces between the phases and to determine the relative retention values using the equations proposed by Berezkin and coworkers[98]:

$$\frac{V_N}{V_{N_{st}}} = \frac{K_L}{K_{L_{st}}} + \lambda\frac{1}{v_{L_S}};$$

$$\lambda_1 = \frac{(K_{GL}K_{L_{st}} - K_{GL}\cdot K_L)S_{L_S} + (K_S - K_{S_{st}})K_L K_{L_{st}} S_{S_S}}{K^2_{L_{st}}}, \qquad (4)$$

where V_N and $V_{N_{st}}$ are the pure retention volumes of the substance and the standard respectively; K_L and $K_{L_{st}}$ the distribution coefficients of the substance and the standard between the gaseous phase and the stationary liquid phase; K_{GL} and $K_{GL_{st}}$ the distribution coefficients of the substance and the standard in the system formed by the gas and the surface of the stationary liquid phase; K_S and $K_{S_{st}}$ the distribution coefficients of the substance and the standard in the stationary liquid phase–solid carrier system; v_{L_S} the volume of the stationary liquid phase corresponding to 1 g of carrier; S_{L_S} the area of the surface of separation between the gas and the stationary liquid phase, corresponding to 1 g of carrier; and S_{S_S} the specific surface of the solid carrier. If the substance chosen as standard is one for which the retention in the column is determined chiefly by solution, $K_{GL_{st}} = K_{S_{st}} = 0$ and Eqn.(4) is simplified.

The following equation has been proposed for the retention indices[98]:

$$I = 100n + 100\frac{\lg K_L - \lg K_{L_n}}{\lg K_{L_{n+1}} - \lg K_{L_n}} + \frac{43\lambda_2}{\lg K_{L_{n+1}} - \lg K_{L_n}}\cdot\frac{1}{v_{L_S}}, \qquad (5)$$

where $\lambda_2 = \lambda_1 K_{L_n}/K_L$; and K_{L_n} and $K_{L_{n+1}}$ are the distribution coefficients of the n-alkanes with n and $n+1$ carbon atoms between the gaseous and liquid phases. An analogous equation was proposed for the case where capillary columns are used[99].

Allowance for adsorption factors is necessary to obtain reliable results in qualitative analysis using tabulated retention values. This is particularly important in cases where the polarities of the substances being analysed and the stationary phases differ considerably.

III. METHODS OF IDENTIFICATION WITHOUT THE USE OF STANDARDS

From the initial development of gas chromatography, the inconvenience and disadvantage of the use of standard substances have directed research workers to the search for other methods of identification. Considerable progress in this field has been achieved by studying the relationship of the molecular characteristics and structures of substances to their gas chromatographic behaviour, with generalisation and transfer of the observed relationships to other series of compounds. The methods to be examined do not involve the use of standards in the

sense that they do not require the availability of the assumed components of the unknown mixture or the corresponding tabulated data.

The chief methods of identification without the use of standards are as follows: 1) the use of linear correlations between the physicochemical characteristics of substances and the retention values; and 2) calculation to predict retention by summation of the contributions made to it by the individual structural elements of a molecule.

1. Linear Correlations between the Retention Values of Substances and their Molecular Characteristics

An extremely widespread method for the qualitative analysis of substances is the method of homologue identification, in which use is made of linear correlations between the retention of substances and the size of their molecules. This method is based on the linear dependence of the logarithm of the distribution coefficient of the molecules of the substance being studied on the free energy of their reaction with stationary phases. The logarithm of the distribution coefficient of a substance $CH_3(CH_2)X$ is given by [87]

$$\ln K = -\frac{N\Delta G(CH_2)}{RT} - \left[\frac{\Delta G(CH_3)}{RT} + \frac{\Delta G(X)}{RT} + \ln\frac{M_L}{RTd_L}\right], \qquad (6)$$

where $\Delta G(CH_2)$, $\Delta G(CH_3)$, and $\Delta G(X)$ are the standard molar Gibbs free energies of sorption for the transfer of the pure sorbate between states of unit fugacity (gaseous phase) and infinite dilution in the sorbent (stationary phase) for the groups CH_2, CH_3, and X respectively; M_L the molecular weight of the stationary phase; N the number of methylene groups in the molecule of the substance; T the absolute temperature of the experiment, K; R the universal gas constant; and d_L the density of the stationary phase. Since homologues differ from one another only in the values of N, the existence of a linear correlation between $\ln K$ and N in homologous series is obvious.

In the qualitative analysis of homologues, use is made of a logarithmic relationship of the general form:

$$\lg R = a \cdot n + b, \qquad (7)$$

where R is the corrected retention time or volume, or specific or relative retention volumes (the equation remains applicable if the retention index is taken instead of $\lg R$); a a constant characterising the energy of the interaction of the CH_2 group with the sorbent; b a constant characterising the energy of the interaction of the functional groups with the sorbent†; and n the number of carbon atoms in the molecule.

Attention was first drawn to the existence of this correlation by James and Martin[3] for the case of carboxylic acids. The linear relationship naturally still holds if in Eqn. (7) the number of carbon atoms n is replaced by the number of CH_2 groups [101-103] or the molecular weight [104,105]. The retention index of the higher members of homologous series increase by 100 units for every CH_2 group [40,93,106]. The correlation was subsequently confirmed by many workers for various homologous series (the literature has been reviewed[1]).

† Hoshikawa, Kuriyama, and Yamabe[100] give the detailed significance of the constants for the case where the retention is expressed in the form of Kovats' logarithmic indices.

The linearity of the correlation is observed most accurately in the case of non-polar stationary phases, where a decisive factor in the interaction is the dispersion forces, which increase with increase in the size of the molecule. Some deviations from linearity are observed for the first members of the homologous series, particularly on polar stationary phases. Thus the increment in the retention indices, corresponding to one $-CH_2$ group, is rigorously equal to 100 for hydrocarbons only beginning from the seventh member of the series[107]. On polar stationary phases, this increment is lowered, as a consequence of the increase in the contribution to the total energy of the interaction from the partial excess free energy of mixing, which changes in the opposite direction to the molar free energy of condensation[108].

The distortion of the linearity of Eqn. (7) is also influenced slightly by the odd or even character of the number of carbon atoms; the magnitude of this influence can be taken into account[109].

The linear correlation between the free energy of solution and the molecular characteristics is universal, and can be extended to the dependence of the free energy on the number of other atoms or repeating structural units in the molecules of the substances in homologous series—silicon [110], sulphur [111], nitrogen, and oxygen [112,113] atoms, benzene rings [114], $-CH_2-CH_2-NH$ groups [112,113], double bonds [115,116], etc. The relationships between the retention values and the numbers of atoms or groups of the same kind in molecules are justified from the viewpoint of set theory, since both variables take denumerable sets of rational values[117]. Mathematically, these relationships are expressed in the most general form by linear-fractional equations (as revealed in the deviation from linearity of the correlation observed for more accurate measurements over a sufficiently wide range of values [107,118]), which are readily transformed into linear equations. The straight lines obtained for individual classes of substances form a pencil of lines.

Methods related to the group being considered are those based on the correlation between the energy of intermolecular interaction and the molar volume or polarisability of the substance. The energy of the dispersion interaction of an atom i of a substance with a stationary phase U_i can be calculated from the equation[119]

$$U_i = 0.9\pi h\nu \frac{\alpha\rho}{(r + r_f)^3}, \qquad (8)$$

where ν is an average frequency characterising the atom i and the stationary phase; α the polarisability of the atom i of the substance being analysed; ρ the density of the polarisability of the stationary phase; and r and r_f the average van der Waals radii of the atoms of the substances being analysed and the functional groups of the stationary phase respectively.

Since the volume of a molecule is proportional to the cube of its van der Waals radius, and the ratio of the polarisability to the molecular volume is in turn a function of the coefficient of refraction, the energy of the intermolecular interaction, and hence the retention value of the substance in the stationary phase, show a correlation with such physicochemical characteristics of the molecules as the parachor, density, coefficient of refraction, molar refraction, dipole moment, etc.

In fact, a number of authors have demonstrated and used for qualitative analysis the relationship between the retention parameters on the one hand and the dipole moments [120,121], density [122,123], coefficient of refraction or

molar refraction[124,125,126], the parachor[127], heat of formation[128], and other molecular characteristics[122] on the other. The existence of correlations with other physicochemical characteristics which take denumerable sets of rational values is to be expected.

For example, one group of identification methods is based on the relationship between the retention values and the saturated vapour pressures or boiling points of substances. Since there is a logarithmic relationship between V_g and the saturated vapour pressure p^0,[129,130] a correlation should also be expected between the boiling points $t_{b.p.}$ and the logarithms of the retention values of substances. This correlation cannot be strictly linear, since the dependence of the boiling points on the numbers of carbon atoms in a homologous series is non-linear, but the relationship for I or $\lg V_g$ is close to linear. The correlation is closer to linearity, the greater the similarity in the nature of the forces of intermolecular attraction which are responsible for the interaction between the molecules of the pure substance and between the molecules of the substance and the molecules of the stationary phase[131]. This requirement is satisfied most frequently when the substances being analysed and the stationary phase are similar in character. The relationship

$$\lg R = a(t_{b.p.} + b) \qquad (9)$$

is most frequently used in analyses on non-polar stationary phases, but the linearity is also preserved on polar columns[132,133]. In general, the linearity of the correlation is improved if a term including the activity coefficients of the substances being separated is included in Eqn.(9).[134]

In addition to the correlation (9), other equations including the boiling point have been proposed. Thus Zhukhovitskii and coworkers[135] and Sen[136] proposed the use of the independent parameter $T_{b.p.}/T_{col}$ for the identification of substances. The linear relationship between V_R and $T_{b.p.}/T_{col}$ makes it possible not only to determine the boiling point but also to estimate, from the slope of the straight line, the series to which a given substance belongs[137]. Another dimensionless parameter for the identification of related compounds, independent of the temperature of the analysis and the stationary phase, has been introduced[138]:

$$\varphi_T = \frac{\lg V^0_{R_i} - \lg V^0_{R_1}}{\lg V^0_{R_2} - \lg V^0_{R_1}} = \frac{T_{b.p._i} - T_{b.p._1}}{T_{b.p._2} - T_{b.p._1}}; \qquad (10)$$

where $V^0_{R_i}$, $V^0_{R_1}$, and $V^0_{R_2}$ are the corrected retention volumes; and $T_{b.p.i}$, $T_{b.p.1}$, and $T_{b.p.2}$ the boiling points of the unknown substance and two known substances respectively. A series of empirical equations for determining boiling points from retention data has been proposed by Japanese workers[139-142].

Bach and coworkers[143], from the dependence of t_R on the vapour pressures of substances, introduced the "retention boiling point" to supplement Kovats' system of retention indices. For correctly chosen operating conditions, this boiling point is fairly close to the true boiling point. All the above correlations make it possible to use the retention value to determine approximately the boiling point of a substance and hence to use tables of the boiling points of substances for identification.

Some authors ascribe considerable importance to the dependence of the retention values on the temperature of analysis T. The relationship between $\lg V$ and the reciprocal of the absolute temperature is linear[12]

$$\lg V = A + B/T. \qquad (11)$$

An analogous relationship holds for the relative retention characteristics[144]. It was later found that the correlation between I and $\lg V$ or I [145,148] is given more accurately by an equation which is analogous to the Antoine equation, describing the temperature dependence of the saturated vapour pressure of a substance:

$$\lg V_g \text{ or } \lg I = A' + \frac{B'}{T + C'}. \qquad (12)$$

In the temperature range characteristic of gas chromatography, the almost linear part of the hyperbola is used[144,146]. The coefficient A is directly related to the entropy, and the constants B [in Eqn.(12)] and also B' and C' are related to the enthalpy of solution. Since the thermodynamic functions of solution are characteristic for each substance and are different for different homologous series, the correlations (11) and (12) can be widely used for the identification of substances. The $\lg R - 1/T$ straight lines for the members of a given homologous series intersect at a characteristic point, the position of which is independent of the nature of the stationary phase[149].

Various non-linear equations characterising the temperature dependence of the retention indices have also been proposed[150,151]. The fruitful application of this method for the qualitative analysis of compounds of different classes has been demonstrated by a number of workers[12,103,126,149,150,152-155].

A characteristic parameter for the identification of substances is the temperature coefficient of the retention indices dI/dT. The values of this coefficient are different for groups of substances having different degrees of saturation or branching and also for cyclic compounds[156-158]. Saha and Mitra[159-161] showed that dI/dT for each series of hydrocarbons is constant and decreases in the order: aromatic hydrocarbons > cyclo-alkanes > tetra- and trialkylalkanes > di- and monoalkylalkanes. The temperature coefficients of the retention indices are linearly related to the mean square radii of the molecules of isomeric alkanes[162]. A thermodynamic treatment of the temperature coefficients of the retention indices has been given by Hammers and de Ligny[163].

Thus a number of correlations have been proposed for the gas chromatographic identification of separated substances using a single column. They have been widely used up to the present, but since the constants of the correlation equations are empirical, the validity of the correlations for individual classes of substance must be proved experimentally. To construct the corresponding curves, it is necessary to have at least three representatives of a series. After the construction of the correlation graphs, the identification of homologues does not present serious difficulty.

In addition to correlations between the physicochemical characteristics of substances and the retention values on a single stationary phase, corresponding correlations determined on two or several columns of different polarity are widely used in qualitative analysis. The values of $\lg R$ obtained on several columns show a correlation with one another. The graphs for substances belonging to different homologous series lie in different regions of the corresponding diagrams. Thus the values of $\lg R$ obtained on two columns of different polarity for each homologous series of substances lie on straight lines parallel to one another[164]. If R is plotted directly on the graph instead of $\lg R$, the homologues lie on straight lines having a characteristic slope. A correlation of this kind was

first used for the identification of primary, secondary, and tertiary alkylamines[165]. The method was subsequently widely recommended for the identification of organic substances of different classes[4,29,111,164,166-170]. Since many pairs of columns, for series of substances, give straight lines which are situated extremely close of one another on the graph, the identification requires a careful choice of sorbents[169,170].

A significant discovery was the detection[171] of the "roofing tile effect", that is that the values of $\lg V_R$ or I for isomeric compounds, obtained on two columns of different polarity, lie on parallel lines, forming "roofing tile groups" in accordance with the number of primary, secondary, tertiary, and quaternary carbon atoms in the molecules. This effect makes it possible to use gas chromatographic retention data on two columns to determine the fine structure of organic molecules. Moreover, the difference in the retention indices on two columns having sorbents with different polarities gives information on the nature of the functional groups[40,45].

Brown[6] proposed the measurement of the retention of substances on three columns, containing stationary phases with different electronic characteristics—non-polar, electron-donor, electron-acceptor. If the data are expressed as retention fractions ("affinity fractions") and plotted on a triangular diagram, each substance is represented by a point, according to its donor-acceptor properties. The points corresponding to substances in a given homologous series lie on straight lines, which are directed towards the apex corresponding to the non-polar column. This method has been used to identify steroids[172], ethers, nitriles, and aldehydes[173], alcohols and esters[174,175], aromatic hydrocarbons and ketones[175], and nitrogen-containing bases[176,177]. Brown's method can also be used to estimate the donor–acceptor properties of stationary phases[172] and to determine the optimum composition of binary stationary phases[178].

Ladon and Sandler[179] put forward an equation for determining the number of carbon atoms in a substance being analysed from its retention times on three carefully selected phases; the coefficients of the equations were found by regression analysis. The correlation is based on the use of one or several columns, depending on the complexity of the problem. Correlations using several columns are employed more frequently for the group analysis of substances.

2. Calculations for Predicting Retention Values

The subsequent development of the method using the correlation between gas chromatographic data and the structures of substances has involved the development of the so-called predictive calculation, in which the retention values on a given column or pair of columns are predicted from an assumed structural formula, and the qualitative analysis is carried out by comparing the calculated value with the experimental value for the component of the mixture being studied. Calculations for predicting retention form the subject of a large number of original papers and several reviews[47,180-182].

a) Calculation of the retention values from the physicochemical properties of the sorbates and stationary phases

The retention of a substance in a chromatographic column is determined by the free energy of the intermolecular interaction in the sorbent–sorbate system; it is therefore possible to predict retention values from empirical relationships between this energy and the physicochemical characteristics of the substances being analysed and the stationary phases.

The distribution coefficient and specific retention volume are inversely proportional to the product of the saturated vapour pressure of the substance being analysed at the temperature of the column and the activity coefficient[183]; a knowledge of these quantities makes it possible to predict the retention. The empirical calculation of activity coefficients from the general theory of solutions has been described[184]. This calculation is tedious, however, and makes it possible to estimate the activity coefficient only approximately. It is more convenient to use the relative values based on the following equation[185]:

$$\frac{\lg V_{R_2}}{\lg V_{R_1}} = \lg\left(\frac{p_1^0}{p_2^0}\right) + \lg\left(\frac{\gamma_1^0}{\gamma_2^0}\right), \qquad (13)$$

where γ_1^0 and γ_2^0 are the activity coefficients of substances 1 and 2 dissolved in the stationary phase. If the substances belong to the same series, $\gamma_1^0 = \gamma_2^0$ and Eqn.(13) is simplified[186].

The retention index of hydrocarbons on hydrocarbon stationary phases is given by[187]:

$$I = 100\,\frac{\lg (p_n^0 \cdot V_{\mathrm{mol}_n}/p_x^0 V_{\mathrm{mol}_x})}{\lg (p_n^0 \cdot V_{\mathrm{mol}_n} p_{n+1}^0 V_{\mathrm{mol}_{n+1}})}, \qquad (14)$$

where p_x^0, p_n^0, and p_{n+1}^0 are the saturated vapour pressures of the substance being studied and n-alkanes containing n and $n+1$ carbon atoms; and V_{mol_x}, V_{mol_n}, and $V_{\mathrm{mol}_{n+1}}$ the molar volumes of the substance and n-alkanes containing n and $n+1$ carbon atoms.

Several equations have been proposed for the theoretical calculation of the heats (or free energies) of solution. Sakharov[119] showed that the heat of formation ΔH_S of a solution at infinite dilution is made up of the energy of interaction of the sorbate with the sorbent (equal to the difference in the energies of the dispersion interaction of the atoms of the substance with the stationary phase, U_i, and the dispersion interaction of the atoms of the substance with the molecules of the stationary phase which might have occupied the space blocked by the other atoms of the molecules of the substance, E_i) and the energy of formation, in the stationary phase, of cavities having shapes and sizes corresponding to those of the sorbate molecule (this energy is proportional to the surface area of the molecule of the substance S and the surface tension of the solvent σ):

$$\Delta H_s = -\sigma S + \Sigma U_i - \Sigma E_i. \qquad (15)$$

The value of U_i for spherical molecules is determined from Eqn.(8), and ΣE_i, if the polarisability densities of the stationary phase and the sorbate are similar, can be replaced by twice the energy of the dispersion interaction between the atoms of the molecule of the sorbate $2E_S$ (that is by the magnitude of the steric effect)[119]. The method has been used successfully to calculate the retention of acyclic saturated[119], unsaturated[124], and aromatic[118] hydrocarbons, and also amino-substituted pyridines, quinolines, and thiophenes[188] on non-polar or weakly polar stationary phases.

Various modifications of the general Eqn.(15) have been proposed, with more accurate allowance for the energy of formation of a hole in the case of planar molecules of the stationary phase[189] or with an expression for

the energy of the London dispersion interaction [190-192]. These equations [190-192], together with the interaction of non-polar substances, have also been used to estimate the interaction of polar sorbates with non-polar stationary phases. The identification of substances reduces to the theoretical calculation of the heats of solution and comparison of the results with the experimental values found from the temperature dependence of $\lg V_R$.

The proportion of polar interactions in a column is also characterised by the dielectric constant of the stationary phase ϵ. A method has been proposed for predicting the retention of a substance on any stationary phase, based on the linear relationship between $\lg V_g$ and $1/\epsilon$. [193] If the substance being analysed and the stationary phases are polar, the retention volumes in the general case can be written as the sum [194]:

$$\lg V_R = \lg V_R^A + pP, \qquad (16)$$

where V_R^A is the retention volume of the substance on the non-polar stationary phase, p the polarity of the substance being analysed, and P the polarity of the stationary phase.

The value of V_R^A can be calculated from the above equations, or determined experimentally; the polarities p and P can also either be estimated from the dipole moments, dielectric constants, or other physical quantities, or found experimentally from gas chromatographic data.

A procedure for predicting the retention from the gas chromatographic characteristics of sorbates and stationary phases was developed by Rohrschneider [195-199], who used a so-called linear combination of forms of interaction, based on the additivity of the free energy of solution [197]:

$$\Delta G = \Delta G_A + \Delta G_B + \ldots + \Delta G_Z, \qquad (17)$$

where ΔG is the total free energy of solution; and $\Delta G_A \ldots \Delta G_Z$ the proportions of the free energy of solution corresponding to the different forms of intermolecular interaction from A to Z. The proportions of the free energy of solution represent the product of a factor characterising the ability of the stationary phase to undergo interaction of a definite type and a factor characterising the ability of the substance to undergo the same type of interaction.

Initially, Rohrschneider took account of only the dispersion interaction with the π-electrons of the aromatic ring, donor–acceptor interaction with the formation of a hydrogen bond, and the orientation of dipoles [195,196]. Subsequently, the calculation was improved by taking account of electron-acceptor and proton-donor interactions [197-199]. The retention of a substance, in the form of the relative retention volumes or times, is obtained by taking account of six types of interaction, or in the form of I or ΔI by taking account of five types of interaction [195,198]. For any substance on an arbitrary stationary phase

$$\Delta I = ax + by + cz + du + es, \qquad (18)$$

where ΔI is the difference in the retention indices on polar and non-polar stationary phases; a, b, c, d, e, are constants characterising the substance being separated; and x, y, z, u, and s are constants characterising the stationary phases. The constants x, y, z, u, and s are determined from the difference in the retention indices, on the column being studied and on squalane, of substances characterising the types of interaction listed above (benzene, ethanol, butan-2-one, nitromethane, and pyridine) [198, 199], and the constants a, b, c, d, and e from the difference in the retention indices of the substance being studied on a non-polar sorbent and on stationary phases characterising the principal types of intermolecular interaction [199].

The subsequent development of Rohrschneider's method has involved an increase in the number of standard substances for characterising stationary phases and sorbates in order to make more detailed allowance for the interactions [200], and also a decrease in the number of standard substances by combining standards characterising similar types of interaction [201-203]. Appropriate mathematical methods have been developed for each of these approaches. Weiner and Howery [204,205] showed by factorial analysis that for an adequate description of a sorbate–sorbent system it is sufficient to have eight terms in an equation of type (18) to the five types of interaction it is necessary to add the Lewis acidity, the Lewis basicity, and the entropy [206]. Lowry and coworkers [207], using the "nearest neighbour" method, showed that satisfactory results in the prediction of retention can be obtained using four functional tests characterising the principal types of interaction.

The above methods are semi-empirical, and require a fairly large expenditure of time for the determination of the corresponding constants. In addition, the values found are not completely unambiguous.

b) Calculation of retention values from structural element increments

An extremely fruitful approach in qualitative analysis by predictive calculations is the development of methods based on the additivity of the enthalpies and free energies of solution of a substance in stationary phases. The interaction of any substance with a sorbent, determining its retention, represents the sum of the interactions of the separate parts of the molecule. By determining the increments in the retention values for all the structural elements of a molecule, it is possible to predict the chromatographic behaviour of the molecule as a whole. Since the enthalpy of solution is linearly related to $\lg V_R$, [12] additivity of the increments can be expected only if the retention data are expressed on a logarithmic scale. The identification of homologues from linear correlations, based on this principle, was examined in the previous section.

The additivity of the increments in retention values characteristic of the structural elements of molecules was first demonstrated on the basis of Kovats' system of retention indices [40,93,106,208]. In addition to the fact that the contribution of the $-CH_2-$ group to the retention value is constant, which formed the basis of the linear correlation methods examined above, it was established that the introduction of a given group of atoms into the molecules of compounds having analogous structures changes the value of the retention indices by the same amount. Assuming that the dispersion interactions of parts of molecules with different stationary phases are equal, Kovats proposed that the specific interactions of the molecules with a sorbent be characterised by increments ΔI, calculated from the difference in the values of the retention indices of the substances on polar and non-polar stationary phases. The increments ΔI consist of a principal term taking account of the influence of the "characteristic zone" (functional group, double bond, ring, etc.), and corrections taking account of the influence of the surroundings of this zone. Unknown compounds are identified by comparing the experimentally determined value with the values of ΔI calculated from several assumed structural formulae.

In 1962, Swoboda [209] suggested that the chromatographic behaviour of substances could be characterised more effectively by subtracting from their retention indices the

retention indices of the n-alkanes making up the main framework of the molecule. Since the difference obtained characterises the contribution of the functional groups to the retention, Swoboda called it the "functional retention index".

These ideas were later developed by Schomburg [47,52,210-217], who suggested that the difference between the retention indices of the substance and the alkane having an analogous carbon framework (the homomorph) be called the homomorphic factor H.[211] The homomorphic factors are extremely sensitive to changes in the geometry of a molecule—branching, the position of a double bond, and configuration—whereas the values of ΔI are not very characteristic in this respect [212,213]. The difference in the homomorphic factors on polar and non-polar columns ΔH, characterises the influence of the specific forces of intermolecular interaction [47,213]. The values of H, ΔI, and ΔH are additive, but the additivity breaks down if two characteristic structural elements are in close proximity. In these cases, Schomburg proposes the introduction of a correction in the form of increments of second order [215,216], which, like the corrections of Kovats and Wehrli [40,93,208], take account of the interaction of groups and the steric and other effects of the environment. The applicability of the principle of additivity of the increments in the retention indices for predicting the chromatographic behaviour of substances [210-217] has been confirmed by a number of workers for various classes of compound [103,218-224].

Since I and ΔI depend on temperature, they must be compared for identical temperatures, or recalculated [147]. A number of authors [147,225,226] have suggested that ΔI values be related to 0 K. At the absolute zero, when the thermal energy of a substance is equal to zero, the factors corresponding to the interaction between substances and stationary phases are more rigorous characteristics, depending only on the structural characteristics of the substances.

If the retention indices are expressed on the molecular weight scale (so-called effective molecular weights), substances in homologous series can be identified using the constancy and additivity of the increments in the molecular weights ΔM_e (the difference between the true and effective molecular weights) [37,39], as in the case of ΔI. Finally, instead of using ΔI, ΔH, and ΔM_e, retention values can be predicted by using directly the increments in the partial molar standard enthalpy $\Delta\bar{H}^0_S$ and entropy $\Delta\bar{S}^0_S$ of solution, characteristic of the individual structural elements of molecules [227]. They are less dependent on temperature than the increments ΔI, ΔH, and ΔM_e, and this makes it possible to calculate V_g over a wide temperature range, using the values of $\Delta\bar{H}^0_S$ and $\Delta\bar{S}^0_S$ measured at a given temperature.

Most of the works cited demonstrate that ΔI, ΔH, and ΔM_e are constant in homologous series, but more accurate measurements of these quantities over a sufficiently wide range show that they depend slightly on the number of carbon atoms in the group. The dependence is described effectively by the equation of a linear-fractional function

$$\Delta I = \frac{n}{an+b}, \qquad (19)$$

which can be transformed into the straight line equation [117]

$$Y = an + b \quad \text{for} \quad Y = n/\Delta I.$$

The principle of additivity of ΔI, H, ΔH, and ΔM_e, and its use for the identification of substances, are also justified by set theory.

The identification of substances by predicting retention from molecular structure is also possible using logarithmic interpolation. This method was developed by Evans and Smith [32], who showed that the retention time $t_{R_{1,2}}$ of unsymmetrical compounds of the type RXR′ can be determined if the retention times $t_{R_{1,1}}$ and $t_{R_{2,2}}$ for the symmetrical substances RXR and R′XR′ respectively are known. The equation which they proposed,

$$\lg t_{R_{1,2}} = \frac{1}{2}(\lg t_{R_{1,1}} + \lg t_{R_{2,2}}) \qquad (20)$$

is applicable if the active group X is not sterically shielded and is not included in a conjugated system of multiple bonds, and if the other parts of the molecule R and R′ are not highly polar.

The linear-fractional dependence of $\lg V_R$ on the molar refraction of the stationary phase has been made the basis of a method for predicting retention for substances of a given homologous series on any stationary phase if the values of V_R for this series on two stationary phases are known [228].

A general approach to the problem of predicting retention by calculation based on the additivity of the contributions of structural elements was developed by Berezkin [229-233], who showed that all the above relationships are particular cases of the general relationship [229,230]

$$\lg R = \sum_{i,j}^{k} n_{ij} P_{ij}, \qquad (21)$$

where P_{ij} is the contribution of a given structural element to $\lg R$; and n_{ij} the number of structural elements in the molecule of the substance. The structural elements on which the calculation is based may be either atoms or bonds, since the accuracy of the calculations depends not on the fundamental differences between the atoms and the bonds, but on the detail with which they are classified [234,235]. As the structural elements for the calculations, Berezkin took the bonds, with allowance for the first-order environment. If allowance is made for a larger environment, it is possible in principle to obtain more accurate results, but the error in the determination of the experimental data makes this calculation inappropriate. It is more justified and convenient in practice to carry out the predictive calculation of t_R^{rel} from an equation which contains an additional constant P_0, which depends on the choice of standard substance [233]:

$$\lg t_R^{rel} = P_0 + \sum_{i,j}^{k} n_{ij} P_{ij}. \qquad (22)$$

Relative or absolute values of R have been calculated for alkanes [229,230], alkenes [232], esters [230], amines [233], alcohols, ketones, sulphides, and various oxygen- and nitrogen-containing heterocyclic compounds [236].

Berezkin's approach has been made the basis of a predictive calculation of the retention indices of substances [237]. The influence of the environment is taken into account [237] not as different versions of the bonds [232] but as a separate component Π:

$$I = \sum_{i,j} I_{ij}^{(1)} + \Pi, \qquad (23)$$

where $I_{ij}^{(1)}$ represents the contributions of the individual bonds and structural elements to the retention indices of

the mono-functional compounds, and $\Pi = \sum_{ij}\pi_{ij}$ is the contribution of the interaction, which takes maximum values for 1,2-substitution.

It has also been shown that it is necessary and possible to take account of the inductive effect, which is estimated in the form of the coefficients of a multiple regression equation [238]. The dependence of the contributions of the structural elements and their sensitivity to the inductive effect on the nature of the structural elements and on the dielectric constant of the stationary phase has been studied [239,240].

In a series of papers [241-249] devoted to the predictive calculation of retention indices from the additivity of the contributions of the structural elements of molecules, the latter were dealt with in even more detail. The retention index of a substance was represented as the sum of three components [241-243]:

$$I = I_a + I_b + I_i = I_M + I_i, \qquad (24)$$

where I_a, I_b, and I_i represent respectively the contributions made to the retention index by the atoms, the bonds, and the interaction between the substance and the stationary phase. The atomic component of the retention index I_a is found as the sum of the indices of all the atoms of the molecule, which in turn are approximately equal to the atomic weight of the element divided by 10. [242,243] The component I_b is equal to the sum of the contributions from all the bonds of the molecule; the contributions of the bonds are determined with allowance for the immediate environment, by iteration. These two terms make up the part of the retention index which is characteristic of the given substance and independent of the nature of the stationary phase and temperature. This part of the retention index, called the molecular component I_M, can be calculated from the structural formula of a substance.

The interaction of a substance with a stationary phase, and its dependence on the temperature of the analysis, are taken into account by the component I_i. Experimental data [243] show that for homologous series of substances on squalane, $I_i = 4.97\,yI$ (y is a coefficient characteristic of a given class of substance; for example, for alkanes, $y = 0.15$ [241]). For other stationary phases, it is suggested that the component of the interaction I_i (or the interaction factor $F_i = I_M/I$) be further divided into two parts: I_{ia}, the contribution of the average interaction, and I_{ii}, the contribution of the individual interaction [242,244]. I_{ia} characterises the dispersion interactions, and I_{ii} the specific interactions between the molecules of the substance being analysed and the stationary phase. $I_{ia} = 0.7455.I$, [244] but I_{ii} must be determined by the methods of Rohrschneider [197-199,244] or McReynolds [200,245,246] (on a non-polar sorbent, $I_{ii} = 0$, $I_i = I_{ia} = 0.7455.I$ [249]). The method is also applicable when corrected retention volumes are used instead of the retention index [248].

The predictive calculation system developed by Takacs represents a theoretical approach to the separate determination of all the factors making up the retention index. This approach makes it possible to understand more deeply the nature of the retention of substances in chromatography and to distinguish the factors responsible for the gas chromatographic behaviour of substances in specific examples of analysis. Although the method is undoubtedly of considerable value, the determination of such important components of the retention index as I_b and I_{ii} is still semi-empirical. Moreover, the method for determining I_b is not given, so that the calculation is not reproducible [250], particularly for cyclic compounds. For practical purposes, it is much more convenient to use the method of calculation proposed by Berezkin, which, although it does not contain the details of P_{ij}, makes it possible to use definite experimental material to find unambiguous values of the contributions of the structural elements for the predictive calculation of the retention of other substances.

Thus the methods of incremental calculation provide theoretically justified and extremely promising methods for the qualitative gas chromatographic analysis of organic substances. Their use facilitates to a considerable extent the solution of problems arising when gas chromatography is used as an analytical method.

c) Prediction of retention values from a molecular-statistical calculation

The most general solution of the problem of predicting retention values by calculation is the theoretical molecular-statistical calculation of the specific retention volumes and Henry coefficients. This quantitative approach is being successfully developed in the USSR by Kiselev, Poshkus, and Afreimovich [251-259] for the gas-adsorption chromatographic characteristics obtained at sufficiently high temperatures with the assumption that the intramolecular vibrations of the adsorbent remain unchanged on adsorption [257]. Henry's coefficient K_1 (the specific retention volume for zero degree of covering of the surface of the adsorbent V_ρ) for three-dimensional quasi-rigid molecules is given by the following equation [256, 259]:

$$(V_\rho)\,K_1 = \frac{1}{8\pi^2 S}\int \{\exp[-\Phi(x, y, z, \vartheta, \varphi, \psi)/kT] - 1\}\sin\vartheta\, dx\, dy\, dz\, d\vartheta\, d\varphi\, d\psi, \qquad (25)$$

where S is the surface area of the adsorbent; Φ the potential energy of the adsorbate–adsorbent intermolecular interaction, which depends on the coordinates of the centre of mass of the molecule x, y, z and the angles of its orientation relative to the surface of the adsorbent θ, φ, ψ; and k the Boltzmann constant.

The potential energy of the intermolecular interaction is determined as the sum of the energies of the paired interactions over all interacting atoms, expressed in terms of the atom–atom potential functions of intermolecular interaction $\varphi_{C\ldots A}$ (or the atom–group potential functions in the case of the study of complex molecules). The atom–atom potential functions are calculated using the familiar semi-empirical equations for the Buckingham–Korner or Lennard-Jones potentials; the constants of the equations are calculated by the method of Kirkwood and Miller [260,261]. This method has been used to calculate the Henry coefficients for the noble gases and nitrogen for adsorption on graphitised thermal carbon black [251,253,258] and various cationic forms of zeolite A. [262,263] The molecular-statistical calculation of the Henry coefficients for adsorption on graphitised thermal carbon black was carried out for the C_1–C_6 n-alkanes [255-259]; the effective atom–atom potentials of the intermolecular interaction $\varphi_{C\ldots C}$ and $\varphi_{C\ldots H}$ were calculated using a special constant factor [256,259]. Using the effective potential functions of the atom–atom interaction and taking account of the differences in the adsorption of the rotational isomers of the n-alkanes, the authors cited obtained the values of V_ρ, K_1, and $\lg K_1$, and the dependence of the latter on the reciprocal of the absolute temperature, in good agreement

with experimental data. In the case unsaturated and aromatic hydrocarbons, it was necessary to introduce into the potential functions $\varphi_{C\ldots C}$ additional factors taking account of the stronger interaction between the graphitised carbon black and carbon in other valency states (compared with the n-alkanes and cycloparaffins). In principle, by taking account of the differences in the valency states of carbon in molecules, it is possible to calculate the Henry coefficients or retention volumes for any hydrocarbons on graphite.

Molecular-statistical calculations have also been carried out for the adsorption of neopentane by NaX zeolite[264] and the adsorption of ethane by the zeolites NaX and NaY.[265]

The molecular-statistical calculation of retention values using semi-empirical potential functions is at present the most well-founded theoretical approach to the solution of the problems of qualitative analysis in gas chromatography. The chief disadvantage of the method is the tedious character of the calculations, and also the semi-empirical character of various constants in the equations used; the calculation of these constants requires many assumptions. This disadvantage can be overcome, however, using modern computing techniques. Unfortunately, at the present time the possibilities provided by molecular-statistical calculations are restricted to several examples of gas-adsorption chromatography on the fairly uniform surfaces of crystalline adsorbents. Since the structure of liquids has not yet been sufficiently fully studied, molecular-statistical calculations in gas-liquid chromatography represent a task for the future.

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