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The use of molecular-statistical methods for the calculation of thermodynamic characteristics of adsorption for identification of organic compounds by gas chromatography – mass spectrometry

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Abstract. The current state of research on the theoretical description of adsorption in the Henry region by semiempirical molecular-statistical procedures, as applied to identification of organic compounds in complex mixtures, is considered. Various approaches to correcting the atom – atom potential parameters used to determine thermodynamic characteristics of adsorption are compared. Examples of calculations involved in the chromatographic and chromatography – mass spectrometric identification of model and real organic compounds including isomers are given. The bibliography includes 89 references.

I. Introduction

Identification of organic compounds in mixtures is one of the most complicated problems of physical organic chemistry. The main difficulty arising in the work with mixtures is that simultaneous solution of two problems is required: the mixture should be separated into components and the components should be identified. At present, the most informative and reliable method for identification of organic compounds is the chromatography – mass spectrometry (GC-MS) technique.[1] Modern instruments make it possible to analyse volatile compounds in the gas chromatography – mass spectrometry mode (GC-MS) and nonvolatile compounds, in the liquid chromatography – mass-spectrometry mode (LC-MS).[2] The use of different ionisation techniques allows one to produce stable molecular ions, to vary fragmentation and to detect both positive and negative ions.[2, 3] In recent years, the range of masses that can be determined has markedly extended due to application of new ionisation techniques.[4] A significant advantage of mass spectrometry is the possibility to determine the masses of molecular and fragment ions in the high-resolution mode with an accuracy of millionths of atomic mass units. Thus, it is possible to determine almost unambiguously the elemental compositions of molecules.[5] The only limitation that holds up extensive use of high-resolution mass spectrometers for identification of substances is their high cost, which is 5 – 10 times as high as the cost of instruments for routine analysis.[6] Chromatography – IR spectroscopy or chromatography – NMR spectroscopy could be possible alternatives to the GC-MS;[7] however, the development of these techniques is held up by relatively low sensitivity of IR spectroscopy and insufficient speed of operation of NMR spectrometers.

Even a highly potent method such as high-resolution mass spectrometry does not allow reliable identificaion of isomers in complex mixtures. This is due to the fact that differences in the fragmentation can hardly be attributed unambiguously to the structure of a particular isomer. Therefore, the use of chromatographic data for identification of substances becomes very important.[8] The procedures for chromatographic identification of compounds based on the use of reference compounds, specific detectors, preliminary chemical reactions,[9] chromatographic spectra [10] and dependences of retention indices on various molecular characteristics [11] have been developed fairly comprehensively and we do not consider them here. However, all these methods are much inferior to the GC-MS technique in labouriousness, information content and reliability.

When discussing the GC-MS identification, one should note that the methods of structure determination based on mass-spectrometry data can be classified into three groups.

(1) Library search which consists in comparing the spectrum of an unknown compound with the spectra deposited in databases or libraries and selecting those spectra that fit best the spectrum of the compound under study.[12]

(2) Methods for representing the compound structure on the basis of fragmentation rules.[13]

(3) Methods for substance identification consisting in determination of structural features by statistical analysis.[14]

Successful utilisation of mass spectrometry and determination of the structures of organic compounds requires the use of empirical rules and regularities elucidated in the studies of large numbers of compounds belonging to different structural classes,[13, 15] the presence of vast libraries of standard mass spectra (up to 300 thousand) of compounds, the use of high-end software for image recognition which resort to data of other spectroscopic methods [16] (not only experimental but also obtained by calculations [17]) for structure determination and advanced computing machinery. The use of GC-MS provides not only mass-spectroscopic but also chromatographic information, namely, the retention indices for various stationary phases. These values are sufficiently accurate because a mass spectrometer is a highly selective detector and chromatographic peaks are usually much better resolved in ionic mass chromatograms than in chromatograms recorded with other detectors.

Combination of chromatographic identification techniques with GC-MS to identify isomers in complex mixtures is usually resorted to in investigations carried out along two lines, namely, identification based on semiempirical molecular-statistical calcu-

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lations of retention values [18] and identification using retention indices calculated theoretically.[19]

Retention index is a qualitative characteristic of a molecule correlated with physicochemical parameters, for example, with the molecule polarisability or with the melting or boiling point of the substance.[8, 11, 19] Numerous equations have now been found to relate retention parameters (calculated as retention indices) to various physicochemical properties of molecules, in particular, isomer molecules.[20] Commonly, these equations make use of so-called increments which characterise separate fragments of a molecule that can be joined to form a new molecule. The main drawback of this approach is that assembling the increments gives an approximate geometrical structure rather than the real molecule. Therefore, fine intramolecular effects, especially those characteristic of isomers, can be taken into account only by introducing special corrections, which are rather arbitrary.[21] Generally, this situation resembles the situation faced by an attempt to obtain precise values for molecular polarisability in terms of additive schemes — one too many corrections are needed to reach high accuracy. One more drawback of this method is the necessity of experimental determination of increments on the basis of a broad range of reference molecules.[22] Extensive databases of experimental retention indices have now been composed; they can be efficiently used to identify separate classes of organic molecules.[23, 24] Such bases are also supplemented by theoretically calculated indices; however, these have not yet found wide use.

Using the semiempirical molecular-statistical theory of adsorption, one can calculate the thermodynamic characteristics of adsorption (TCA) including the retention values for organic molecules of various classes. The theory is based on the use of atom–atom potentials (AAPs) for the interaction between the sorbent and sorbate atoms. An important advantage of this theory is the fact that the calculations of retention indices are based on the real structures of molecules, determined from electron diffraction data or constructed with allowance for the regularities of variation of bond angles and bond lengths. In the case of isomers, the TCA calculations alone based on real data on the molecular structure permit reliable identification of compounds.

II. Semiempirical molecular-statistical theory of adsorption

1. Scope of molecular-statistical calculations

To date, molecular-statistical calculations of TCA have been carried out for a broad range of adsorbents and adsorbates. The calculations of TCA for inert gases, simple polar molecules and hydrocarbons on zeolites of various types [25] and on porous crystalline silica (silicalite) have been reported.[26–28] The molecular-statistical calculations have been developed most thoroughly for systems comprising graphitised thermal carbon black (GTCB) and hydrocarbons or their derivatives.[29] Graphitised thermal black is a good model sorbent because it has a homogeneous planar surface the geometry and the chemical properties of which have been studied in sufficient detail. Vast experimental information on the adsorption of organic compounds of various classes on the GTCB surface has been accumulated.[29, 30] The main reason why the molecular-statistical calculations for the adsorption on GTCB surface are being developed and improved is the fact that this process is exceptionally sensitive to the structure of adsorbed molecules. This creates conditions for the separation of geometric isomers.[30–32] In most cases, a combination of the molecular-statistical calculations and GC-MS data provides unambiguous identification of individual isomers in complex mixtures.[18, 32]

2. The procedure of molecular-statistical calculations

Kiselev and Poshkus [29, 30] developed a semiempirical molecular-statistical method for the calculation of thermodynamic characteristics of the physical adsorption of gases on GTCB at very low surface coverages. Within the framework of this method, the Henry constant (K_1) for the adsorption of quasi-rigid molecules is calculated using the equation

$$K_1 = \frac{1}{4\pi}\int\int\left(\frac{2\pi kT}{\Phi_z''}\right)^{1/2}\exp\left(-\frac{\Phi_0}{kT}\right)\sin\Theta\,\mathrm{d}\Theta\,\mathrm{d}\psi, \qquad (1)$$

where Φ_0 and Φ_z'' are the potential function Φ values for the interaction between the adsorbate and adsorbent molecules in a potential minimum and its second derivative with respect to the distance z from the center of gravity of the molecule to the adsorbent surface; Θ and ψ are Euler angles, which define the orientation of the molecule relative to the adsorbent surface. The Φ_z'' and Φ_0 values and the equilibrium distance z_0 depend on Θ and ψ. The potential function Φ is presented as the sum of the AAPs for the interaction of each atom of the adsorbed molecule (A) with each carbon atom of GTCB (C_{GTCB}).

$$\Phi = \sum_{A}\sum_{C_{GTCB}} \varphi_{A\ldots C_{GTCB}}. \qquad (2)$$

The $\varphi_{A\ldots C_{GTCB}}$ potential is written in the Buckingham–Corner form (6, 8, exp)

$$\varphi_{A\ldots C_{GTS}} = -C_6 r^{-6} - C_8 r^{-8} + B\exp(-qr), \qquad (3)$$

where C_6, C_8 are the parameters of the dipole–dipole and dipole–quadrupole dispersion interaction potentials; r is the interatomic distance; B and q are parameters of the repulsion potential. The C_8 and C_6 values are estimated using approximate quantum-mechanical formulae. The parameter C_6 is found using the Kirkwood–Müller relation

$$C_6 = -6m_e c^2\,\frac{\alpha_a\alpha_b}{(\alpha_a/\chi_a)+(\alpha_b/\chi_b)}, \qquad (4)$$

where m_e is the mass of an electron; c is the velocity of light; α_a, α_b are polarisabilities of atoms a and b; χ_a and χ_b are diamagnetic susceptibilities of atoms a and b.

The parameter C_8 is estimated using the formula

$$C_8 = \frac{45h^2}{32\pi^2 m_e}\alpha_a\alpha_b\left[\frac{1}{2}\left(\frac{\alpha_b/\chi_b}{\alpha_a/\chi_a}+1\right)^{-1}+\frac{1}{2}\left(\frac{\alpha_a/\chi_a}{\alpha_b/\chi_b}+1\right)^{-1}\right], \qquad (5)$$

where h is Planck's constant. The repulsion parameter B is expressed in terms of the equilibrium interatomic distance r_0 and other AAP parameters using the equilibrium condition for all the attraction and repulsion forces for $r = r_0$

$$\left(\frac{\mathrm{d}\varphi}{\mathrm{d}r}\right)_{r=r_0} = 0, \qquad (6)$$

$$B = \frac{6C_6\exp(qr_0)}{qr_0^7}\left(1+\frac{4C_8}{3C_6 r_0^2}\right). \qquad (7)$$

The parameter q is taken to be 35.7 nm^{-1}. The equilibrium distance r_0 is normally estimated using crystal parameters or data on the interaction of atoms of the adsorbate molecule with GTCB. In particular, the value $r_0 = 0.382$ nm was accepted for C...C_{GTCB} (this value was obtained from data on the graphite lattice properties) and $r_0 = 0.341$ nm was taken for H...C_{GTCB}. The summation of φ over the GTCB carbon atoms above the graphite basis plane is done using the Crowell approximation.[30] The potential function Φ_i for the interaction of an i-th atom of the molecule with the graphite basis plane is calculated from the equation

$$\Phi_i = -C_{6,i}\frac{\pi\vartheta}{2d^4}\xi\left[\frac{z_i}{d},4\right]-C_{8,i}\frac{\pi\vartheta}{3d^6}\xi\left[\frac{z_i}{d},6\right]+ \qquad (8)$$

$$+\frac{2B_i\pi\vartheta}{q^2}(qz_i+1)\mathrm{e}^{-qz},$$

where $\vartheta = 0.382 \times 10^{-3}$ nm^{-2} is the number of carbon atoms per unit area of the graphite basis plane; d is the interplanar spacing in graphite equal to 0.356 nm; ξ is the Riemann zeta function; z_i is the distance from the i-th atom to the plane passing through the centres of atoms of the outermost atomic layer of graphite. Relation (8) takes into account the contribution of only the outermost atomic layer of graphite to the repulsion energy.

The differential molar changes of the intrinsic energy ΔU_1 and entropy ΔS_1 upon adsorption are calculated using the relations

$$\Delta U_1 = RT^2 \frac{\mathrm{d} \ln K_1}{\mathrm{d}T}, \tag{9}$$

$$\frac{\Delta S_1}{R} = \ln K_1 + T\frac{\mathrm{d} \ln K_1}{\mathrm{d}T} - 1. \tag{10}$$

A special program is used to calculate the TCA.[33] The parameter C_6 is first estimated from Eqn (4). However, the K_1 and ΔU_1 values found using the C_6 value determined in this way differ markedly from the corresponding experimental data.[29] Therefore, the AAPs for the interaction of atoms in the adsorbate molecule with GTCB ($\varphi_{\mathrm{H...C_{GTCB}}}$ and $\varphi_{\mathrm{C...C_{GTCB}}}$ for each atom of the molecule in different valence states) are further corrected using relations (4)–(11) and the experimental K_1 values for one or two simple representatives of the class of hydrocarbons under consideration. The $\varphi_{\mathrm{H...C_{GTCB}}}$ and $\varphi_{\mathrm{C}(sp^3)\mathrm{...C_{GTCB}}}$ values are corrected assuming that the parameters C_8/C_6, r_0 and q, estimated in terms of the properties of the adsorbate and the adsorbent taken separately, differ only slightly from the exact values and that the following equality holds:

$$\frac{C_{6,\mathrm{C...C}}}{C_{6,\mathrm{C...H}}} = \frac{C^{\mathrm{KM}}_{6,\mathrm{C...C}}}{C^{\mathrm{KM}}_{6,\mathrm{C...H}}}, \tag{11}$$

where $C_{6,\mathrm{C...C}}$ and $C_{6,\mathrm{C...H}}$ are the values of parameters that satisfy experimental data; $C^{\mathrm{KM}}_{6,\mathrm{C...C}}$ and $C^{\mathrm{KM}}_{6,\mathrm{C...H}}$ are the C_6 values estimated using the Kirkwood–Müller formula. If these assumptions are valid, the corrected potential functions φ are related to the rough functions φ^* in the following way:

$$\varphi = \beta\varphi^*, \tag{12}$$

$$\Phi = \sum_{\mathrm{A}} \sum_{\mathrm{C_{GTCB}}} \varphi = \beta \sum_{\mathrm{A}} \sum_{\mathrm{C_{GTCB}}} \varphi^* = \beta\Phi^*, \tag{13}$$

where

$$\beta = \frac{C_{6,\mathrm{C...C}}}{C^{\mathrm{KM}}_{6,\mathrm{C...C}}} = \frac{C_{6,\mathrm{C...H}}}{C^{\mathrm{KM}}_{6,\mathrm{C...H}}}. \tag{14}$$

The β coefficient is usually determined by comparing the K_1 values calculated on the basis of Φ^* with those found experimentally. The equations for the interaction potentials of atoms in alkanes with GTCB corrected in this way (kJ mol^{-1}) have the form

$$\varphi_{\mathrm{C}(sp^3)\mathrm{...C_{GTCB}}} = -1.386 \times 10^{-3}\, r^{-6} - 2.148 \times 10^{-5} r^{-8} + 1.89 \times 10^5 \exp(-35.7r), \tag{15}$$

$$\varphi_{\mathrm{H...C_{GTCB}}} = -0.498 \times 10^{-3}\, r^{-6} - 0.950 \times 10^{-5}\, r^{-8} + 3.60 \times 10^4 \exp(-35.7r). \tag{16}$$

The K_1 and ΔU_1 values calculated using these potentials for alkanes with known molecular structures are close to experimental results. Assuming that the $\varphi_{\mathrm{H...C_{GTCB}}}$ potential of the hydrogen atom in a hydrocarbon molecule does not depend on the valence state of the car20. atom and that the r_0 and q parameters are identical for carbon in any valence state, it was found that

$$\varphi_{\mathrm{C}(sp^2)\mathrm{...C_{GTCB}}} = \delta\varphi_{\mathrm{C}(sp^3)\mathrm{...C_{GTCB}}}, \tag{17}$$

where δ is the parameter depending on the valence state of the carbon atom.

Using the experimental K_1 values, it was found for ethylene that

$$\varphi_{\mathrm{C}(sp^2)\mathrm{...C_{GTCB}}} = -1.48 \times 10^{-3} r^{-6} - 2.30 \times 10^{-5}\, r^{-8} + 2.026 \times 10^5 \exp(-35.7r). \tag{18}$$

Relying on the K_1 values determined experimentally for acetylene adsorption, the potential $\varphi_{\mathrm{C}(sp)\mathrm{...C_{GTCB}}}$ can also be calculated. These potentials were used to calculate the TCA for a large number of hydrocarbons: alkanes,[34] cycloalkanes,[29,35] alkenes, alkynes [36] and aromatic hydrocarbons [37] on the GTCB surface. In the case of hydrocarbons with known molecular structures, the TCA values found in this way coincide with the corresponding experimental values to within the error of determination.

The above-described procedure was used to determine the AAPs for the interaction of the carbon atoms in graphite with oxygen in two valence states (in ethers and ketones) [38] and to calculate the TCA for a number of oxygen-containing organic compounds on the GTCB surface.[39]

Guiochon and coworkers [40,41] also used the molecular-statistical method for calculation of the TCA for various hydrocarbons and their chlorinated derivatives; however, these calculations were performed using uncorrected AAPs, therefore, the calculated and experimental TCA markedly differ. When calculating Φ for complex conjugated molecules, researchers attempted to take into account the anisotropy of graphite polarisability.[42] For chloro-derivatives of aromatic hydrocarbons, it was found that the order of elution of isomers out of the column is better described by a model that does not take into account the electrostatic interaction of the adsorbate molecule with the adsorbent surface.[41]

Apart from the organic compounds mentioned above, adsorption of noble gases [29,30] and nitrogen-,[43] sulfur- and selenium-containing [44] compounds on the GTCB surface has also been studied. Some of the AAP parameters known to date are listed in Table 1. Satisfactory agreement of the experimental results with the theoretical results obtained using these parameters is attained in those cases where the mutual influence of atoms in the adsorbed molecule is insignificant. When the mutual influence of atoms is substantial, corrections should be applied to the AAPs. In some

Table 1. Parameters of the AAPs for the interaction of various atoms with the GTCB carbon atom.

Element	AAP parameter [a]			β
	C_6	C_8	B	
Hydrogen	−0.5672	−0.06403	1618.0	–
Fluorine	−0.9775	−0.07000	2903.800	0.85
Carbon				
sp^3	−1.5750	−0.14530	8491.0	–
sp^2	−1.6853	−0.15547	9085.370	–
Chlorine				
see [b]	−4.2180	−0.38000	31189.489	0.95
ortho	−4.0848	−0.36800	30204.558	0.92
ortho-ortho	−3.9516	−0.35600	29219.626	0.89
Oxygen				
ketone	−1.1194	−0.11005	3250.015	–
ether	−1.7519	−0.17223	5086.273	1.565
Sulfur	−3.8672	−0.45069	26759.806	–
Bromine				
see [b]	−5.0740	−0.45060	37501.136	0.76
ortho	−4.9404	−0.43878	36514.270	0.74
Nitrogen	−1.6318	−0.26445	6194.358	–

[a] C_6 is expressed in kJ m^6 mol^{-1}, C_8 is in kJ m^8 mol^{-1}, and B is in kJ mol^{-1}. [b] An atom not interacting with the neighbouring atoms in the molecule.

cases, the calculations are hampered by the absence of precise structural parameters for sorbate molecules.[45]

Thus, fairly good agreement between the calculated and experimental TCA values for compounds with known molecular structures is attained if corrected AAP values are used to calculate the potential function of intermolecular interactions.

However, for some molecules, TCA cannot be predicted with a satisfactory accuracy. For example, during identification of isomers in mixtures, the sequence of isomer emergence from the column with GTCB predicted by calculations does not coincide in some cases with the experimental one. This is due to the difference between the AAP parameters for atoms incorporated in the molecule in question and the parameters corrected using the reference molecules. The difference is caused by the change in the nearest environment or valence state of the atom, manifested as a change in polarisability. Therefore, to identify separate isomers in complex mixtures and to determine reliable TCA (especially, the Henry constants), one must find the precise values for the AAP parameters.

3. Correction methods for the parameters of the atom – atom potentials

Several methods for correcting the AAP parameters have been developed to date.

a. Traditional method

The approach proposed by the developers of the semiempirical molecular-statistical theory of adsorption [29] can be considered to be the first of the known methods for correcting the AAP parameters. This approach is based on determination of individual AAPs (using reference molecules) for atoms forming the molecule under study, including chemically identical atoms in different valence states. In terms of the semiempirical molecular-statistical theory,[29] the AAP parameters are determined from approximate quantum-mechanical formulae (see above) using some characteristics of adsorbate and adsorbent atoms, *e.g.*, polarisability, diamagnetic susceptibility and equilibrium distances. The atom – atom potentials determined for the interaction of atoms of the adsorbate molecule with the adsorbent (GTCB) carbon atoms are corrected using the comparison of the theoretical and experimental Henry constants K_1 for the adsorption of a representative of the class of compound studied. The correction is carried out using so-called reference molecules, whose adsorption has been studied most comprehensively. The obtained AAPs are assumed to be transferable, *i.e.*, they allow correct prediction of the TCA for any molecule that contains the corresponding atoms. This \0procedure was used to determine and correct the AAP parameters for the adsorption of alkanes, alkenes, alkynes and aromatic hydrocarbons on GTCB; methane and ethane, ethylene, acetylene, and benzene, respectively, served as the reference molecules. In these calculations, three AAPs for carbon atoms corresponding to the sp^3, sp^2 and sp^1 hybridisation states were found; they differ only by the correction factors, which are equal to 1.00, 1.07, and 1.27, respectively. Two AAPs for the oxygen atoms in ethers and ketones were found in the same way; they differ by the correction factors, which are 0.72 and 0.92, respectively.[38] The AAPs for sulfur, selenium,[44] fluorine,[46] chlorine,[47] and bromine [48] were determined. The corresponding correction factors are equal to 0.87, 0.89, 0.85, 0.95 and 0.76, respectively. Actually, this approach is similar to the calculation of polarisabilities, diamagnetic susceptibilities, and the dipole moments of molecules in terms of additive schemes.[49] The AAPs determined in this way were used to predict the TCA for a number of hydrocarbons and their derivatives, which are in good agreement with experimental data.[36, 38, 46] However, for many molecules [both relatively simple ones such as *ortho*-halobenzenes,[50] perhydroanthracenes, perhydrophenanthrenes,[51] heterocyclic nitrogen-containing compounds,[52, 53] and fairly complex molecules such as molecules with abnormal geometric parameters (strained molecules), with bulky substituents, with several heteroatoms, and their unusual combinations], the TCA could not be correctly predicted.

The main drawbacks of the above method are as follows. For each valence state (and, in the general case, for each type of the atom nearest environment), one must know a separate AAP, which has to be corrected on the basis of experimental data for reference molecules. However, the number of these AAPs may become too large (especially for carbon, oxygen and nitrogen atoms), which would complicate the calculation. In addition, this procedure does not take into account the changes in the AAPs caused by the influence of atoms not bound by valence bonds.

b. Taking into account the dependence of the atom – atom potentials on the bond angles

The method proposed by Arkhipova [54] takes into account the effect of the change in the geometric parameters of a molecule on the carbon atom hybridisation and, correspondingly, on the AAP parameters. A pattern of dependence of AAP parameters on the deviation of the bond angles formed by carbon atoms from the ideal values corresponding to the sp^3, sp^2 and sp^1 hybridisation states has been proposed. Using this dependence, one can determine more precisely the AAP values for atoms that form non-ideal bond angles. The results obtained by this method for a series of strained molecules (for example, cyclopropane derivatives and some bicyclic compounds) are in good agreement with experimental data. An example illustrating the efficiency of this method is the correct (experimentally confirmed) prediction of the order of elution of C_8H_{12} isomers, cyclobutadiene and bicyclo[3,3,0]oct-1,5-ene, from a column with GTCB, which could not be determined without applying corrections.

However, this method also suffers from serious drawbacks: first, it is applicable only to molecules with a known geometry because corrections are based on structure differences; second, determining a correction requires the knowledge of, at least, two boundary potentials, because the correction provides some intermediate value of the AAP parameters; third, this method cannot be used to correct the AAP parameters that change under the influence of non-bonded atoms, which does not distort the geometric structure of the molecules. Other 'AAP parameter – atom property' relationships have also been constructed; the atom properties used in these relationships are, in particular, the polarisability, the effective charge, the shielding constant, and the hybridisation state. The methods based on these dependences suffer from the above drawbacks.[55]

c. Variation of the parameters of atom – atom potentials

The variation of the AAP parameters is done in order to minimise the discrepancy between the experimental and calculated data for all molecules of the group chosen for the investigation; this can be done, for example, by the regularisation technique.[56] A single parameter can also be varied. For example, in the calculation of AAP for a series of bromobenzene molecules, the role of this parameter was played by the equilibrium distance between the GTCB carbon atom and the bromine atom.[48]

However, this method allows one to attain the optimal agreement between the experimental and theoretical results only for the considered group of molecules. The transfer of parameters corrected for a given group of molecules to other (even 'related') molecules usually results in a deviation between the experimental and calculated values for new molecules. For example, the AAP values corrected by varying the GTCB carbon – halogen equilibrium distance are in good agreement with experimental data only for the molecules of halobenzenes containing no halogen atoms in *ortho*-positions.[48] Otherwise, to describe experimental data with a satisfactory accuracy, additional corrections taking into account the mutual influence of atoms (corrections for *ortho*-effects) should be applied when calculating the AAPs.

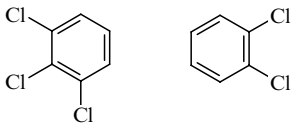
d. The use of corrected initial data for the calculation of atom – atom potentials

It is known [57] that the mutual influence of atoms can change their polarisabilities. In calculations of the TCA, these changes are taken into account either by applying additional corrections to the equations for AAP [48] or by using corrected polarisabilities. In our opinion, the use of corrected polarisabilities is most efficient for calculating the TCA of perhalogenated compounds, first of all, freons, for which isostructural fragments can hardly be chosen (or there are too many of them). The adsorption heats [58] of such compounds are described satisfactorily, within the experimental error, without introducing any corrections; however, for predicting the Henry constants, the correction of the AAPs is necessary. The method in which corrected initial data (first of all, polarisabilities and diamagnetic susceptibilities) are used in the calculation of the AAP parameters is of undisputed interest also due to the fact that a vast experimental base has now been accumulated and detailed additive schemes for polarisability calculations for molecules of diverse compounds,[59] especially perhalogenated ones, have now been developed.

A shortcoming of this method is the need to measure the polarisabilities, which requires a substantial amount of the material. In addition, one should borne in mind the relatively low accuracy of the polarisability values calculated according to additive schemes,[60, 61] which can lead to greater errors in the calculations of the TCA.

e. The introduction of corrections for *ortho*-effects

Changes in the AAP parameters are due to the mutual influence of atoms, in particular, when they occupy *ortho*-positions.[61] By varying these parameters, one can attain the correspondence between experimental and theoretical data for an *ortho*-substituted molecule with known experimental TCA. The corrected AAPs can be used for the calculation of TCA for other molecules with atoms in *ortho*-positions. The applicability of this approach (the introduction of corrections for the *ortho*-effect) was demonstrated in relation to halobenzenes.[48] Actually, this method for correcting the AAPs is similar to the method using reference molecules (and, correspondingly, the drawbacks are also the same) but applies to a more limited group of molecules. In some cases, additional corrections are required to bring the theoretical results in correspondence with the experiment, for example, *ortho – ortho*-effect corrections.[62] As an example, one can consider 1,2-dichlorobenzene and 1,2,3-trichlorobenzene molecules in which corrections for the *ortho*- and *ortho – ortho*-effects are required.



Probably, it is expedient to apply such corrections to molecules that possess specific properties, for example, to adamantane in which 1-substituents are subject to the 'cage effect', which is also involved in adsorption.

The term 'cage effect' implies the overlap of the electronic orbitals of the carbon atoms at the 1-positions which are not bound by valence bonds. This overlap brings about a substantial difference between the properties of 1- and 2-substituted isomers, which is manifested, in particular, in the chromatographic separation on phases having different polarity. The allowance made for the cage effect for chloro- [63] and amino-substituted adamantane isomers [64] permitted the prediction of the correct order of isomer elution from a column packed with GTCB, whereas traditional calculations [65] did not provide a correct prediction. The overlap of the orbitals of the bridgehead carbon atoms and their influence on the substituent (amino group) polarisability is illustrated by Fig. 1.

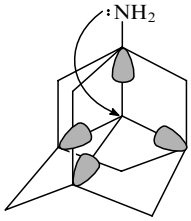


Figure 1. Cage effect in the 1-aminoadamantane molecule.

f. The method of isostructural fragments

The method of isostructural fragments [66] (IF) is based on the use of AAPs corrected for some single molecule or its fragment in the calculations made for other molecules containing the same fragment. For a molecule containing the isostructural fragment, the AAPs are corrected by processing the theoretical and experimental values by the least-squares calculations, their agreement being attained by varying the correction factor. In doing this, the AAPs for atoms of one sort are changed, in order to decrease the total number of AAPs used in calculations. The IF is chosen on the basis of comparison of the geometrical structures of molecules of the group under interest; in particular, the specially obtained electron diffraction data, the known regularities of the change in the bond angles and bond lengths in groups of related molecules, or the results of quantum-chemical calculations can be compared. Usually, molecules with a geometrical structure (or its fragment) common to the given class of molecules are chosen as the IF. For example, in the case of cyclopropane derivatives, this is the cyclopropane molecule, and for *ortho*-substituted chlorobenzenes and naphthalenes, this is the 1,2-dichlorobenzene molecule.

In fact, the IF method allows one to overcome the limitations of the atom – atom approximation and takes into account the mutual influence of atoms and groups of atoms including the change in the polarisabilities and geometric parameters of the interacting fragments.

g. The method of variation of the molecular geometry

An important benefit of the semiempirical molecular-statistical theory of adsorption is the use of structural parameters of molecules in the TCA calculations. However, this benefit is simultaneously a drawback, because exact parameters of the molecular structure have been determined for a limited range of substances and, normally, they are lacking for most of isomers. An alternative to all the methods of AAP correction considered above is the method of variation of the geometric parameters of the molecule. This procedure has been used to predict the retention values for perhydroanthracenes and perhydrophenanthrenes.[51] By using this variation, the researchers predicted the order of isomer elution from a GTCB column that coincided with the experimental results. However, the geometry variation, especially for molecules with an unknown structure, is legitimate only in the case of quantitative comparison of theoretical and experimental data, and, naturally, it is impossible to estimate the variation of the AAP parameters in terms of this method.

4. Comparison of various methods for the correction of the atom – atom potential parameters

Among the methods for correcting the AAP parameters considered above, the following are most important: the method based on the use of corrected initial data (first of all, polarisability); the introduction of *ortho*-effect corrections and the IF method. The Henry constants calculated using the AAP parameters corrected by these methods for a number of molecules have been compared.[66, 67] The results of comparative analysis confirm the good prospects of the IF method.

For a number of chlorobenzenes with different degrees of substitution, the Henry constants were calculated using the AAP values corrected by various methods and the results were com-

pared. The chlorobenzene molecules were chosen as the model series because they represent groups of isomers, and the sequence of elution of isomers from a GTCB column is an important criterion of the reliability of calculations. In addition, both experimental and calculated TCA determined by various methods are available for molecules of this series (Table 2).[41,47,48,68] Of all possible TCA that can be calculated using the semiempirical molecular-statistical adsorption theory, the Henry constants were chosen as the characteristics most sensitive to variations of the AAP parameters and the geometrical structures of molecules. It was shown[48,50] that even for molecules containing no strained fragments or *ortho*-arranged atoms, the experimental and theoretical values of the Henry constants can be brought in correspondence by correcting the AAP only in terms of the procedure of reference molecules. Therefore, corrections were applied to the already corrected potential, which was 5% smaller than the initial one.

In the calculations in terms of the IF method, known AAPs tested in the calculations of TCA for chlorobenzenes were used as the basic parameters. The IF chosen were 1,2-di- and 1,2,3-trichlorobenzenes. Relying on the experimental data for these molecules (the Henry constants and their differences for isomers closest in retention values), researchers obtained corrections for the AAPs to describe the interaction between the chlorine atom and the graphite carbon atom. In any case, the molecular-statistical calculations were carried out as described above (see Section II.2). The geometric parameters of molecules were found either from electron diffraction data or by combining the known parameters for other molecules of the given group.

However, the introduction of corrections by some procedures does not always provide the best correspondence between the experimental and calculated data. For example, the use of the method of reference molecules, the method of correcting the polarisability values and the geometry variation give rise to inconsistency between the experimental and calculated orders of isomer elution out of a GTCB column, and for some isomers, the experimental and theoretical $\ln K_1$ values differ appreciably (see Table 2). The best results are provided by the IF method and by applying the *ortho*-effect corrections.

The IF method appears to be more versatile and reliable because its application rules out the uncertainty related to the geometrical structures of molecules. Naturally, it is suitable for refining the parameters of AAPs not only for the molecules considered above. In our opinion, this method is especially advantageous for calculating the TCA of complex (in particular, isomeric) molecules containing heteroatoms and strained fragments.

Table 2. Values $\ln K_1$ ($cm^3\,m^{-2}$) for the adsorption of chlorobenzenes on GTCB at 473 K obtained experimentally and calculated using the AAPs corrected by various methods.[50]

Molecule	Experiment	Calculations				
		1	*2*	*3*	*4*	*5*
Chlorobenzene	−0.44	−0.44	−0.44	−0.44	−0.44	−0.44
1,3-Dichlorobenzene	0.93	0.98	0.98	0.98	0.98	0.98
1,2-Dichlorobenzene	1.01	1.15	1.10	1.01	1.01	1.08
1,4-Dichlorobenzene	1.06	1.06	1.06	1.06	1.06	1.06
1,3,5-Trichloro benzene	2.23	2.25	2.25	2.25	2.25	2.25
1,2,4-Trichloro-benzene	2.41	2.59	2.54	2.44	2.44	2.50
1,2,3-Trichloro-benzene	2.42	2.82	2.74	2.52	2.52	2.60
1,2,3,5-Tetrachloro-benzene	3.86	4.19	4.11	3.86	3.88	3.40
1,2,4,5-Tetrachloro-benzene	3.89	4.23	4.12	3.92	3.92	4.02
1,2,3,4-Tetrachloro-benzene	4.24	4.47	4.37	4.03	4.06	3.58

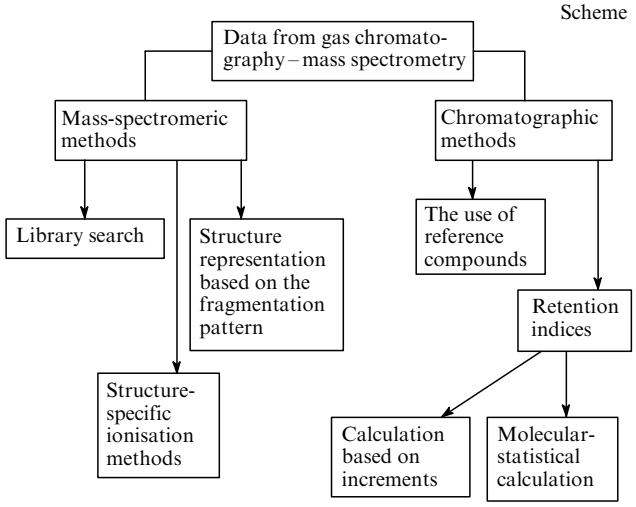
Notes. The correction of the AAPs by method *1* was carried out using the reference 1,4-dichlorobenzene molecule;[48] the correction by method *2* was based on the experimental polarisability value determined in Ref. 60 for the chlorine atoms in 1,2-dichlorobenzene (in the calculations of $\ln K_1$ for other chlorobenzenes, these corrected AAP values were used only for *ortho*-arranged chlorine atoms); in method *3*, the corrections for the *ortho*- and *ortho*–*ortho*-effects were taken from Refs 48, 50; in the case of method *4*, 1,2-di- and 1,2,3-trichlorobenzenes were chosen as the isostructural fragments; the corrections for the AAPs based on the experimental Henry constants or the differences between the retention of neighbouring isomers is 0.92 for the fragment containing two chlorine atoms in *ortho*-positions and 0.91 for the fragment containing three atoms of this type; in the correction by method *5*, the molecular geometry was varied assuming that *ortho*-chlorine atoms cause a deflection of the carbon–chlorine bond from the benzene ring plane; for the first five chlorobenzene molecules, the angles of deflection of the carbon–chlorine bonds from the benzene ring plane were taken from Ref. 48, while for other isomers, the transferability of the angles was assumed, in particular, in calculations of the Henry constant for 1,2,3-trichlorobenzene, a value of 78 was taken, as for 1,2,4-trichlorobenzene, while in the case of 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes, this value was 128, as for the 1,2,4,5-substituted isomer.

5. Combination of the gas chromatography – mass-spectrometry data with semiempirical molecular-statistical calculations

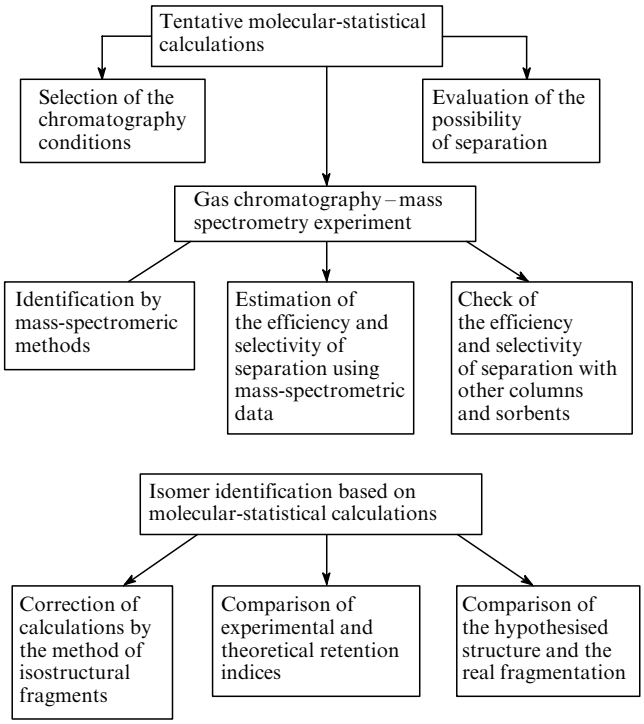
When calculating retention indices, in particular, Kovac indices, an approximate rather than real structure of the molecule is actually used.[8,10] Therefore, in those cases where corrections for definite effects have not been applied, identical values are usually obtained for isomers. The corrections are not transferable: usually, they are applicable only to the group of molecules for which they have been determined. When the retention indices are calculated within the framework of the semiempirical molecular-statistical adsorption theory, the real structure of the molecule is used.[18,30] To increase the efficiency of GC-MS identification, one should take into account the retention indices calculated in terms of this theory. Scheme 1 represents the pattern of usual GC-MS identification,[1,5] while Scheme 2 shows the identification procedure based on the molecular-statistical calculations.[67]

The first stage consists in molecular-statistical calculations performed to estimate tentatively the possible efficiency of the chromatographic column. The tentative calculations help to answer the key question of whether the isomers under consideration can be separated by chromatography using a GTCB column. Adsorption of a broad range of substances on this sorbent has now been studied, but their number, of course, is not

Scheme 1



Scheme 2



commensurate with the number of known organic compounds; therefore, the tentative calculation of the TCA is a necessary item in the research. In addition, these calculations permit one to optimise the conditions of the chromatographic experiment planned, to choose the temperature, the carrier gas velocity, the adsorbent weight and the column length.

The next stage is the GC-MS study in which individual isomers are to be separated and identified on the basis of differences in the mass spectra or, if the spectra are identical, it is necessary to confirm that the substances being analysed belong to the group of isomers in question. The efficiency and selectivity of the chromatographic separation is evaluated on the basis of the observed overlapping mass spectra. The modern instrumentation and computer software for data processing allow this to be done in the mass chromatography and mass fragmentography modes. To verify the completeness of separation attained on a micropacked column with GTCB, it is expedient to record the chromatogram on a highly efficient capillary column most appropriate regarding the selectivity (in order to compare the results obtained with different columns).

The next stage is conduction of molecular-statistical calculations for isomers using corrections for the possible variations of the AAP parameters. In the simplest case, identification can be performed by comparing the sequence of isomer elution from a GTCB column observed experimentally with the calculated one. The experimental retention indices and those determined by molecular-statistical calculations can also be compared, which is generally preferred. In addition, the data on the molecular structure used in the calculations can be verified by examining fragmentation of the molecule, induced, for example, by an electron impact.

Comparison of Schemes 1 and 2 shows that the identification procedure resorting to molecular-statistical calculations provides more reliable results. It is evident that combination of the results obtained in terms of the molecular-statistical theory with the results of a mass-spectrometric experiment would allow one to increase the efficiency, reliability and the information contents of the method and, hence, to solve the problem of isomer identification at a new level.

Correlation equations that relate the Henry constant,[69] the second virial coefficient of the intermolecular interaction,[70] or the heat of adsorption[71] to some characteristics of the molecule are usually considered as alternatives to the molecular-statistical calculations. The critical temperature and pressure or both,[71] the molecular refraction,[72] the dipole moments and the boiling points[73] are used most often. An advantage of such calculations is the possibility of changing the sorbent[71,73] or specifying the degree of its inhomogeneity,[74] which helps to elucidate the applicability of a sorbent to the separation and analysis of a particular group of substances. Good correlation coefficients are usually obtained for series of related molecules;[69] however, the relationship between the molecular structure and the physicochemical characteristics of adsorption remains obscure. Therefore, these methods are suitable only as auxiliary ones in the identification of isomers.

An *ab initio* molecular-statistical method for calculation of the Henry constant has been developed.[75–80] The method makes use of the relationship between the structural characteristics of molecules and the energetic, geometric and topological[81–84] properties involved in the adsorption. Unlike the traditional semiempirical molecular-statistical theory, the main idea of this approach has been the refusal of the additivity principle for AAP. Instead, the view of generalised charge of the molecule was introduced and a law for summing these charges was postulated. This theory was used to calculate the TCA for various types of hydrocarbons on GTCB and to determine the Kovac indices on a nonpolar stationary liquid phase (squalane). The calculated values are in good agreement with experimental data. This calculation method appears rather promising; however, it belongs to quantum chemistry and requires a separate review to be described.

III. The use of theoretical methods for identification of compounds

Mixtures of isomers can be separated into groups in conformity with the known numbers of isomers present. The simplest situation arises when the mixture is known to contain all the possible isomers or when this can be determined from the results of a GC-MS experiment. When analysing mixtures of isomers with a 'rigid' structure on a GTCB column, one should merely calculate the order of elution and thus identify the isomers. Such procedure has been carried out for the components of a mixture of *endo*- and *exo*-tetrahydrobicyclopentadienes. The *endo*-isomer has lower TCA and, correspondingly, it is the first to come out of the GTCB column. In this case, the fact that the mass spectra of the isomers are identical does not hamper the analysis.[67]

The isomers of 1-methyl-1,2-dicyclopropylcyclopropane[32] are more complex objects for identification, as their molecules are capable of internal rotation. The internal rotation angles are unknown; therefore, these isomers can be identified only on the basis of calculations performed for all the possible values of these angles; the differences between the Henry constants were calculated and compared with the difference found in the experiment. Upon this comparison, it was found that the *cis*-isomer is the first to come out of the GTCB column. In this case, the molecular-statistical calculations represent the only possible method for identification because the mass spectra of the isomers are identical.

The isomer mixtures for which the composition can be suggested from a known chemical reaction pattern can reasonably be regarded as another group. The catalytic oxidative dimerisation of methyl-, fluoro- and chlorobenzenes normally furnishes mixtures of six isomers containing one substituent in each benzene ring. Using molecular-statistical calculations, all the isomers of dimethyl-[85] and dichlorobiphenyls[86] were identified based only on the order of their elution from a GTCB column. The molecular-ion mass chromatograms are presented in Fig. 2. The following calculated values of $\ln K_1$ ($cm^3\ m^{-2}$) were obtained for dichlorobiphenyls at 475 K and dimethylbiphenyls at 450 K:

Substituent position	2,2′	2,3′	2,4′	3,3′	3,4′	4,4′
Methyl	3.02	3.42	4.24	5.42	6.24	7.12
Chlorine	2.39	4.25	4.78	5.75	6.24	7.20

Despite the fact that only traces of 2,2′-substituted isomers were present, they were identified on the basis of mass spectra.[87]

In the case of difluorobiphenyls, the chromatogram exhibits only five peaks. To identify the isomers in conformity with Scheme 2, the Henry constants and the numbers of theoretical plates needed for the complete (n_1) and partial (n_2) resolution of each isomer pair were calculated. This gave the following results:

Isomer pair	2,2′ and 2,3′	2,3′ and 2,4′	2,4′ and 3,3′	3,3′ and 3,4′	3,4′ and 4,4′
n_1	22	1500	22	5100	3500
n_2	5	380	5	1300	900

For some isomers, only partial resolution is possible and this is confirmed by the chromatogram presented in Fig. 3 *a*. It can be seen that the mixture contains 2,2′-difluorobiphenyl, which is the first to be eluted. To verify this, a chromatogram on a capillary column was obtained; however, in this case, too, the isomers could not be completely resolved (Fig. 3 *b*). The isomers cannot be identified using a mass spectrometry because they exhibit identical mass spectra. Therefore, comparison of the calculated and experimental retention values is the only way to confirm the presence of all isomers in the mixture. The results of calculations confirming that a mixture of difluorobiphenyls also contains all six isomers have been reported.[87]

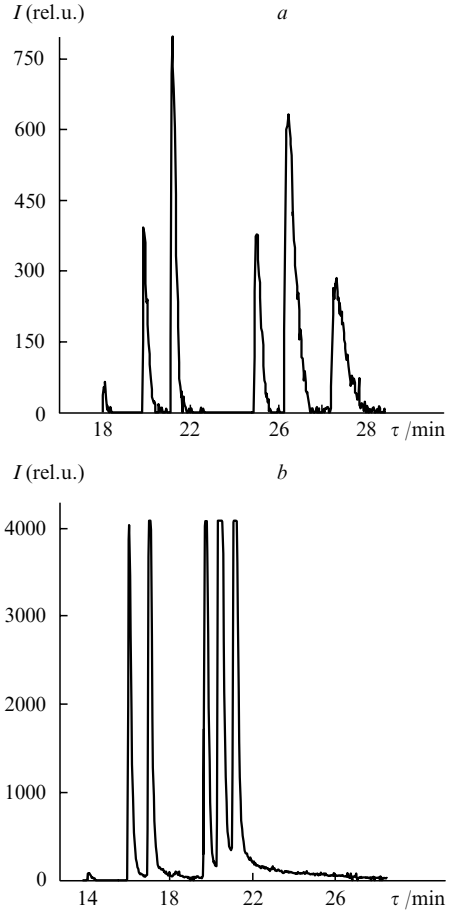


Figure 2. Molecular ion mass chromatograms of dimethylbiphenyl (*a*) and dichlorobiphenyl (*b*), m/z = 182 and 222(224), respectively.[85,86]

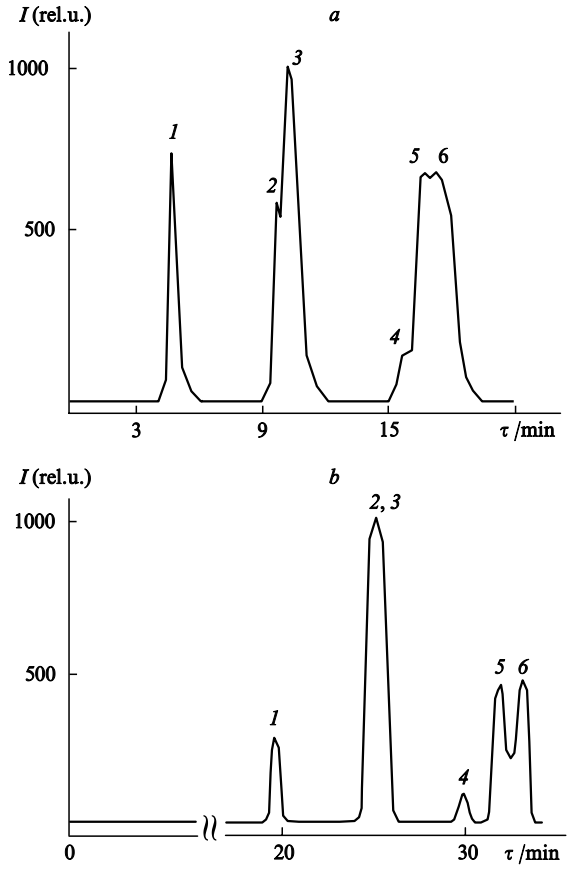


Figure 3. Chromatograms of a difluorobiphenyl isomer mixture obtained on a micropacked column with GTCB (*a*) and a capillary column (*b*).[87] Isomer (position of the substituent): (*1*) 2,2′; (*2*) 2,3′; (*3*) 2,4′; (*4*) 3,3′; (*5*) 3,4′; (*6*) 4,4′.

The advantages of calculations using the AAPs corrected by the IF method can be demonstrated in relation to the identification of trace impurities formed upon the catalytic oxidative dimerisation of chlorobenzene.[66,88] The isostructural fragments used are presented in Fig. 4. The results of identification of the major components, dichlorobiphenyls, are presented above. The formation of trichlorobiphenyls can easily be confirmed on the basis of mass-spectrometry data; however, it is impossible to identify individual isomers, as their mass spectra are identical. Figure 5 shows the mass chromatograms of the molecular ions of tri- and dichlorobiphenyls with m/z = 256 and 226, respectively. It can be seen that the trichlorobiphenyls come out of the column with GTCB between two groups of dichlorobiphenyls.

All the dichlorobiphenyls have been identified (see above), and their Henry constants can be used as the reference values in the identification of trichlorobiphenyl isomers. The results of calculations of the Henry constants for *ortho*-substituted tri- and dichlorobiphenyls are listed in Table 3. In this case, there is no need to carry out calculations for all the isomeric trichlorobiphenyls, because only *ortho*-substituted isomers have retention times

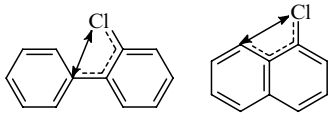


Figure 4. Isostructural fragments (marked by dashed lines) in molecules used for correction of the AAP parameters in calculations of the Henry constants of chlorobiphenyls.

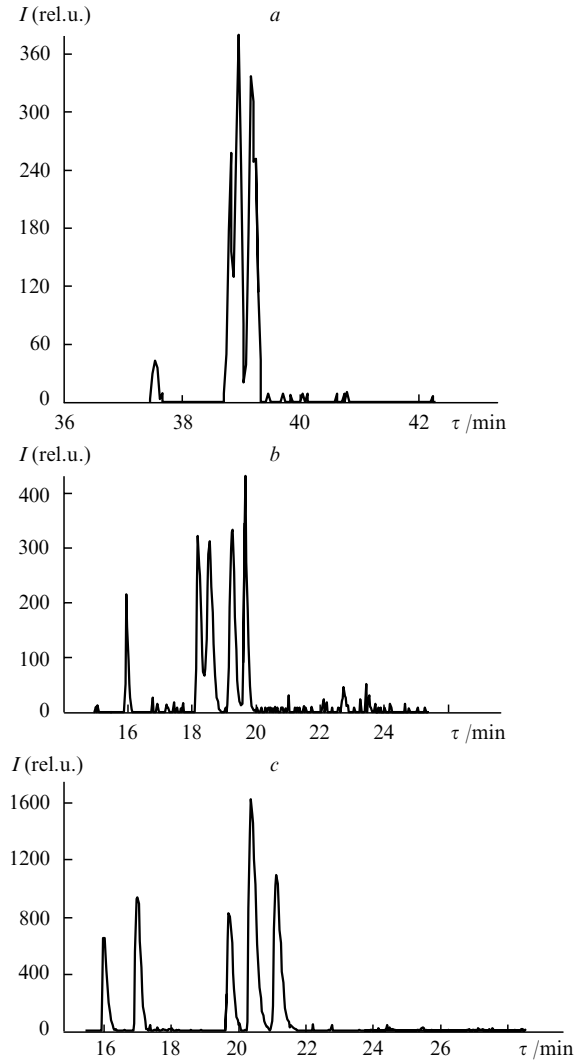


Figure 5. Characteristic-ion mass chromatograms of di- and trichlorobiphenyls obtained from the chromatograms for total ion currents in the separation of a chlorobiphenyl mixture on a capillary (*a*) and micropacked (*b*, *c*) columns.[66] The characteristic ion has $m/z = 256$ (*a*, *b*), 226 (*c*).

comparable with the retention times of dichlorobiphenyls. It can be seen from Table 3 that the elution of 3,3′-dichlorobiphenyl from the GTCB column is preceded by the elution of 2,4,6-, 2,6,4′- and 2,3,6-trichlorobiphenyls. The isomer whose retention time is close to that of 2,3′-dichlorobiphenyl is 2,3,2′-trichlorobiphenyl, while the compound with a retention time similar to that of 3,3′-dichlorobiphenyl is 2,5,4′-trichlorobiphenyl. It is noteworthy that the efficiency of separation of these isomers achieved on a microcolumn packed with GTCB is higher than that on a capillary column with a slightly polar liquid stationary phase. This outcome is attributable to the high 'sensitivity' of the GTCB surface to the structural differences between the adsorbed molecules. In view of the large difference between the Henry constants for tri- and dichlorobiphenyls (see Table 3), one can state that in this case, complete separation of the mixture has been attained and each chromatographic peak really corresponds to a single isomer.

In the case of nonsymmetrical molecules, for example, 2,3,2′-trichlorobiphenyl, two conformers can exist differing by the internal rotation angles. Since the structure of the adsorbed molecule is unknown, the calculations were carried out for the two possible conformations, *syn* and *anti*.

The catalytic oxidative dimerisation of toluene [85] was found to give, in addition to dimethylbiphenyls, impurities with a molecular mass of 196. The chromatograms obtained using a GTCB column (Fig. 6) show that the retention time of these compounds is close to the retention time of 2,4-dimethylbiphenyl. On the basis of analysis of the regular features of retention on GTCB, one can state that compounds with higher molecular masses can have

Table 3. Henry constants calculated for tri- and dichlorobiphenyls at 500 K and the internal rotation angles (*a*) used for the calculations.[66]

Molecule	α /deg	$\ln K_1$ ($cm^3\ m^{-2}$)
2,6,2′-Trichlorobiphenyl	65	2.88
2,3′-Dichlorobiphenyl		
syn	53	3.34
anti	127	2.91
2,3,2′-Trichlorobiphenyl		
syn	60	3.38
anti	120	2.97
2,5,2′-Trichlorobiphenyl		
syn	60	3.15
anti	120	3.48
2,6,3′-Trichlorobiphenyl	60	3.62
2,4,2′-Trichlorobiphenyl		
syn	60	3.70
anti	120	3.30
2,4′-Dichlorobiphenyl	53	3.94
2,4,6-Trichlorobiphenyl	60	4.15
2,6,4′-Trichlorobiphenyl	60	4.32
2,3,6-Trichlorobiphenyl	60	4.57
3,3′-Dichlorobiphenyl		
syn	38	4.85
anti	142	4.50
2,5,4′-Trichlorobiphenyl	53	4.87

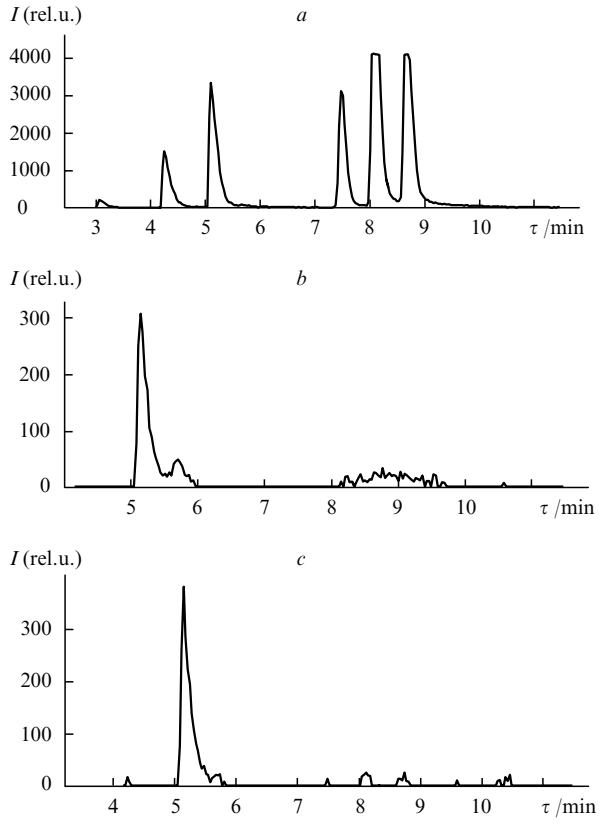


Figure 6. Characteristic-ion mass chromatograms of dimethylbiphenyls (*a*) and impurities (*b*, *c*) obtained on a micropacked GTCB column.[88] The characteristic ion has $m/z = 182$ (*a*), 196 (*b*), 104 (*c*).

shorter retention times only when their molecules are nonplanar, in particular, for large internal rotation angles. A dimethylbiphenylmethane or *ortho*-substituted trimethylbiphenyl structure can be proposed for these compounds. In this case, identification of the impurities using mass spectra confirmed the validity of the assumption. Analysis of the recorded mass spectra provides the conclusion that the isomer whose spectrum contains a large peak with $m/z = 104$ (Fig. 7 *a*) corresponds to the group of dimethylbiphenylmethanes. The mass spectrum of the other compound (Fig. 7 *b*) resembles most closely the spectrum of trimethylbiphenyl but this assignment can hardly be confirmed on the basis of library search, as the published data are scarce. In order to identify this compound, molecular-statistical calculations of $\ln K_1$ ($cm^3\ m^{-2}$) were carried out for all possible trimethylbiphenyl isomers containing at least one methyl group in the *ortho*-position relative to the bond connecting the benzene rings. The results of these calculations are presented below.

Substituent position	$\ln K_1$	Substituent position	$\ln K_1$
2,3,2′	3.32	2,5,4′	3.53
2,3,3′	8.16	2,6,2′	3.67
2,3,4′	10.14	2,4′	4.24
2,4,2′	3.93	2,6,3′	4.29
2,4,4′	10.1	3,3′	5.42
2,5,2′	3.64	2,6,4′	4.86
2,5,3′	7.24		

Yet another example of utilisation of the method in question for compound identification is analysis of an industrial mixture of chlorobiphenyls for the most toxic, 'dioxin-like' isomers.[66, 67, 89] The results of chromatographic separation of this mixture on micropacked and capillary columns showed that the degree of separation obtained on a micropacked column for a mixture containing tri- and tetrachlorobiphenyls is adequate for the molecular-statistical identification of isomers by comparison with characteristic-ion mass chromatograms of tri- and tetrachlorobiphenyls (Fig. 8). The results of calculation of the Henry constants for tetrachlorobiphenyl isomers were compared with this constant for 4,4′-dichlorobiphenyl, present in the mixture and used as the standard. This comparison made it possible to find out that the retention times of all tetrachlorobiphenyls present in the mixture are shorter than that of the 4,4′-substituted isomer, whereas the retention time of the 'dioxin-like' 3,4,3′,4′-tetrachlorobiphenyl is longer. Thus, the mixture under study does not contain the most toxic *ortho*-unsubstituted isomers.

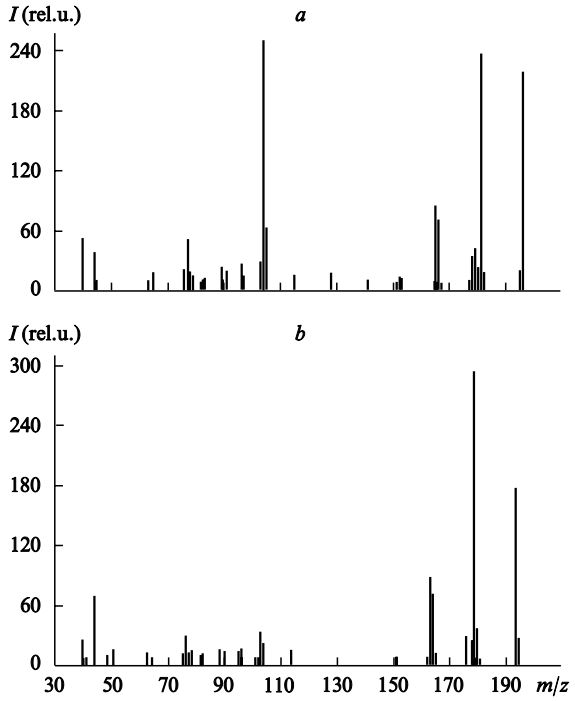


Figure 7. Mass spectra of various impurities with identical molecular ions detected in the reaction mixture resulting from catalytic dimerisation of toluene.[67, 88]

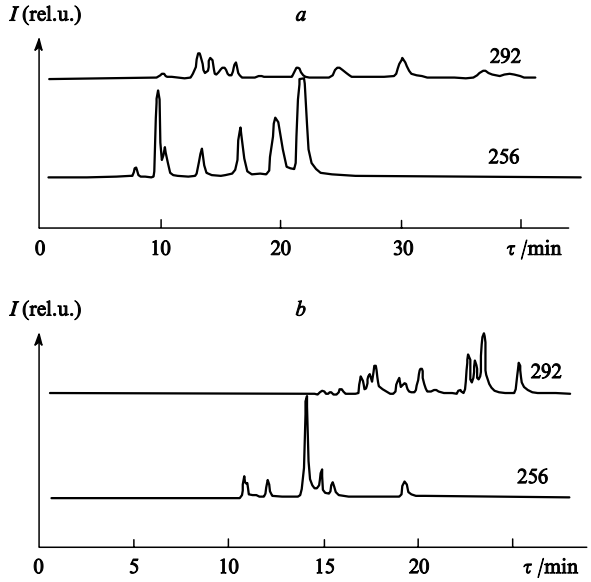


Figure 8. Molecular-ion mass chromatograms of trichloro- ($m/z = 256$) and tetrachlorobiphenyls ($m/z = 292$) obtained on a micropacked GTCB column (*a*) and on a capillary column (*b*).[67, 89]

* * *

The gas chromatography – mass spectrometry method considered in this review, which was used for mixture identification, appears to be the only reliable method known to date suitable to identify the belonging of isomers to a particular class of compound. Naturally, the examples cited do not cover all the possible fields of GC-MS application but they demonstrate that in combination with molecular-statistical calculations, this method provides the most reliable results. When discussing the semiempirical molecular-statistical theory, one should note one substantial limitation, namely, that the theory is applicable only to adsorption on the GTCB surface. Nevertheless, the experience accumulated for decades demonstrates high potency of this theory in complex situations, which often arise during chromatographic identification of organic compounds.

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