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Method for the Determination of the Average Structural Characteristics of Different Organic Substances

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Abstract—A method was developed for the calculation of the structural and chemical characteristics of organic substances of natural origin and their conversion products based on elemental analysis data and the quantity of oxygen bound to carbon with double bonds. The adequacy of this method for calculating structural and chemical characteristics was tested with the use of humic acids as an example. The applicability of the proposed method to any organic compounds of natural origin was demonstrated.

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Studies on the structure and properties of organic substances of natural origin (coal, oil, peat, oil shale, etc.), which are different mixtures of individual compounds, are always associated with a number of the difficulties caused by the heterogeneity of their composition. Along with currently available experimental physicochemical methods, an additional tool based on the fundamental concepts of the structure of matter—the calculation of structural and chemical characteristics of a typical structural unit—can be used for the acquisition of data on the structure of these substances.

It is well known that the structure and composition of the organic matter of caustobioliths depend on the degree of metamorphism of these combustible natural materials. The organic matter of coals and peats is a mixture of structurally irregular biopolymers, which consists of a set of compounds with different structures, properties, and molecular weights. Extraction with different solvents is a universally recognized method of studying the structure of the organic matter of caustobioliths. However, the products of extraction consist of structurally different molecules; therefore, it is necessary to group them according to specific signs. One of these groups of compounds, which are usually isolated by alkaline extraction, includes humic acids insoluble in aqueous solutions at pH < 2. Other groups include insoluble humin and fulvic acids, which are soluble in aqueous solutions of any acidity [1–4].

Because of their structural features, humic substances have unique biochemical and ecological properties, and they easily undergo target-oriented chemical modification [5–7]. They find wide applications in different branches of national economy (agriculture, pharmacology, and stock raising); they are used as sorbents. A study of the structure and properties of humic substances with the application of contemporary experimental and theoretical methods is a problem of increasing current interest. A question sharply arises as to whether there is a quantitative interrelationship between these parameters. However, studies in this area are associated with the following difficulties: the experimentally determined physicochemical indices of humic substances as a groups of compounds, such as elemental analysis, molecular weight, spectral-analysis data, etc., are average values in contrast to of the characteristics of individual compounds. Structural models are often developed in order to understand the structure peculiarities of humic substances [3, 9]. Although these models are speculative, they play an important role in the development of the chemistry of these substances.

Is in this work, we describe a method for constructing the average models of humic substances based on elemental analysis and ^{13}C NMR-spectroscopic analysis data. The essence of this method consists in the application of an algorithm for calculating structural parameters per unit mass of humic substances based on experimental data and fundamental concepts of the structures of matter. The construction of the algorithm of calculation consists of several stages.

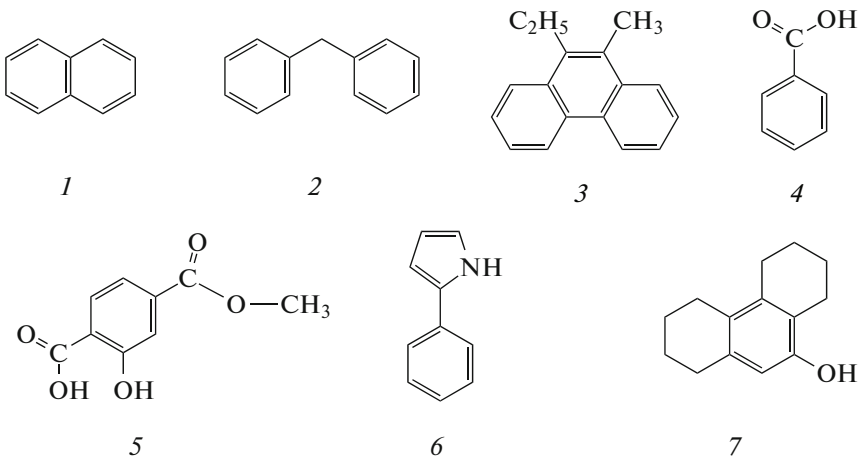

Fig. 1. Model substances used for the approval of the calculation method: (*1*) naphthalene; (*2*) diphenylmethane; (*3*) 9-methyl-10-ethylphenanthrene; (*4*) benzoic acid; (*5*) 4-monomethyl ester of 2-hydroxy-1,4-benzenedicarboxylic acid; (*6*) 2-phenylpyrrole; and (*7*) 1,2,3,4,5,6,7,8-octahydro-9-hydroxyphenanthrene.

Using the experimental data of elemental analysis and the rounded values of atomic masses, we obtain

$$C + H + N + O + S = 100. \quad (1)$$

If $x = C/12$, $y = H/1$, $m = N/14$, $n = O/16$, and $z = S/32$, the molecular weight M for the empirical formula $C_xH_yN_mO_nS_z$ is the following [7]:

$$12x + y + 14m + 16n + 32z = M. \quad (2)$$

Formula (1) is converted to (2) with the aid of the coefficient $\Omega = 100/M$ [7].

We introduce the following parameters, which characterize the presence of two types of carbon and hydrogen atoms, into the unit mass an organic substance with the empirical formula $C_xH_yN_mO_nS_z$:

$$C = \sum C_{ar} + \sum C_{al},$$

$$H = \sum H_{ar} + \sum H_{al},$$

where $\sum C_{ar}$ and $\sum C_{al}$ are the sums of carbon atoms in the sp^2 and sp^3 hybrid states, respectively, regardless of functional groups in which they are located; $\sum H_{ar}$ and $\sum H_{al}$ are the sums of hydrogen atoms chemically bound to C_{ar} and C_{al} carbon atoms, respectively. Hydrogen atoms bound to heteroatoms (O–H, N–H, and S–H) are also included in $\sum H_{al}$.

For any organic compound, the following formula is valid [7]:

$$N_b = \frac{1}{2}\sum \omega_i n_i, \quad (3)$$

where N_b is the number of all σ and π chemical bonds in the molecule (bond/mol), ω_i is valence, and n_i is the number of moles of ith atom (g-atom/mol).

From formula (3), it follows that

$$N_b = \frac{1}{2}(4n_C + n_H + 3n_N + 2n_O + 2n_S). \quad (4)$$

It is well known that any molecule can be represented in the form of a graph, in which the atoms are apexes and σ bonds are edges, and γ is the number of rings in the graph. There is the following relationship between the above parameters:

$$N_\sigma = N_{at} + (\gamma - 1), \quad (5)$$

where N_σ is the number of all σ bonds, N_{at} is the number of atoms, γ is the total number of rings in the molecule (for example, benzene, naphthene, heterocontaining, and nonaromatic rings).

Table 1. Results of the calculation of the structural parameters of model substances

Parameter	Model compound						
	1	*2*	*3*	*4*	*5*	*6*	*7*
x, mol	10	13	17	7	9	10	14
y, mol	8	12	16	6	8	9	18
m, mol	0	0	0	0	0	1	0
n, mol	0	0	0	2	5	0	1
z, mol	0	0	0	0	0	0	0
X_{ar}, mol	10	12	14	8	10	10	6
N_b, bond/ mol	24	32	42	19	27	26	38
M, mol	128	168	220	122	196	143	202
N_{at}, atom/ mol	18	25	33	15	22	20	33
δ	12	14	18	8	10	12	10
γ – 1, ring/ mol	1	1	2	0	0	1	2
N_σ, σ bond/ mol	19	26	35	15	22	21	35

Table 2. Results of the elemental analysis of humic acids [8, 9]

Element	C	H	N	O	S
Peat humic acids					
Elemental analysis, wt % on a *daf* basis	59.1	5.0	3.0	32.4	0.5
mol	4.93	5.0	0.21	2.02	0.02
Lignite humic acids					
Elemental analysis, wt % on a *daf* basis	69.3	4.4	1.6	24.4	0.3
mol	5.77	4.40	0.11	1.52	0.01

For the completeness of linear equations, we also use the following equation for the determination of the structure nonsaturation parameter: $\delta = C/6 - H + N/14$ [7].

Because $C = 12x$, $H = y$, and $N = 14m$,

$$\delta = 2x - y + m. \quad (6)$$

For calculating the number of π bonds, the parameter x_{ar} should be considered:

$$x_{ar} = \sum C_{ar} + \sum O_{\pi}, \quad (7)$$

where O_{π} is the total quantity of oxygen atoms in carboxyl, ketone, and quinoid groups, which form the C=O double bond with carbon atoms.

The following system of linear equations was obtained after minor conversions:

$$\begin{aligned} 2x + \frac{1}{2}y + \frac{3}{2}m + n + z &= N_b, \\ 12x + y + 14m + 16n + 32z &= M, \\ z + y + m + n + z &= N_{at}, \\ x - \frac{1}{2}y + \frac{1}{2}m - \frac{1}{2}x_{ar} &= \gamma - 1, \\ 2x - y + m &= \delta, \\ 2x + \frac{1}{2}y + \frac{3}{2}m + n + z - \frac{1}{2}x_{ar} &= N_{\sigma}. \end{aligned} \quad (8)$$

The system of linear equations obtained can be represented in a matrix form convenient for practical application as follows:

$$\begin{pmatrix} 2 & 0.5 & 1.5 & 1 & 1 & 0 \\ 12 & 1 & 14 & 16 & 32 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 \\ 2 & -1 & 1 & 0 & 0 & 0 \\ 1 & -0.5 & 0.5 & 0 & 0 & -0.5 \\ 2 & 0.5 & 1.5 & 1 & 1 & -0.5 \end{pmatrix} \begin{pmatrix} x \\ y \\ m \\ n \\ z \\ x_{ar} \end{pmatrix} = \begin{pmatrix} N_b \\ M \\ N_{at} \\ \delta \\ \gamma - 1 \\ N_{\sigma} \end{pmatrix} \quad (9)$$

In Eq. (9), the matrix of coefficients is constant and singular; it does not have a reciprocal matrix and can be used only for the calculation of the vector of structural parameters. The vector of initial data, whose components are the empirical formula data x, y, m, n, and z converted to the average molecular weight M, and x_{ar} according to Eq. (7) are determined according to the ^{13}C NMR-spectroscopic data and based on the concentrations of carboxyl, ketone, and quinoid groups determined by structural group analysis. The elements and vectors of structural parameters are calculated.

The calculation method proposed was tested with structurally different model substances, which are shown in Fig. 1.

Table 1 summarizes the results of the calculation of the structural parameters of model substances. An analysis of these data showed that the calculation method proposed adequately describes the structural parameters of the model substances of different structures; therefore, it can be successfully used for calculating the structural parameters of typical molecules of any natural organic compounds, including humic substances. Both the average molecular weight deter-

Table 3. Dependence of the structural parameters of humic acids on the amount of matter (mol) of aromatic carbon x_{ar}

Structural parameter*)	Peat humic acids				Lignite humic acids			
X_{ar}, mol	2	2.5	3	3.5	2	2.5	3	3.5
N_b, bond/ mol	14.71	–	–	–	15.43	–	–	–
M, mol	100	–	–	–	100	–	–	–
N_{at}, atom/ mol	12.18	–	–	–	11.81	–	–	–
δ	5.07	5.07	5.07	5.07	7.25	–	–	–
γ – 1, ring/ mol	1.53	1.28	1.03	0.78	2.62	2.37	2.12	1.87
N_{σ}, σ bond/ mol	13.71	13.46	13.21	12.96	14.43	14.18	13.97	13.68

*) A mole is taken to be 100 g.

Table 4. Experimental data on the elemental analysis of coal humic acids and the aromatic carbon content [3]

Humic acid	Concentration						
	% on a *daf* basis					% on a total C basis	
	C	H	N	O	S	C_{ar}	C_{ar}=O
1	67.0	4.1	0.7	25.8	2.5	57.8	17.4
2	66.4	4.5	1.0	27.1	1.0	56.0	16
3	59.8	3.9	1.3	34.1	1.0	65.9	20.6
4	63.0	2.5	1.8	31.7	1.0	71.9	19.3

mined experimentally and a mass unit calculated, for example, per 100 g of substance, can be used for the calculation. The latter approach is more reasonable for comparative analysis because the experimental determination of average molecular weight is associated with some difficulties [1], especially because an average value can be converted to that calculated per unit weigh with the aid of the coefficient $\Omega = M/100$.

Table 2 summarizes the results of the elemental analysis of peat and lignite humic acids [8, 9].

For determining the adequacy of the calculation method, the number of oxygen-containing double bonds X_{ar} was varied in a wide range. Table 3 summarizes the results of calculations. An analysis of these data showed that the variation of the parameter X_{ar} influences only the hypothetical number of rings γ and the number of σ bonds. The numbers of rings and σ bonds decreased with the value of X_{ar}. Note that, in the general case, there is the dependence of structural and chemical indices of the average structural unit of humic acids on the elemental composition, which is confirmed by the data given in Table 3. Consequently, the models consistent with the parameters N_b, M, N_{at}, δ, γ – 1, and N_σ specified in Table 3 rather than hypothetical models should be used as structural models.

The comparison of the structural parameters of humic acids with different carbon contents is of interest. For this purpose, we used the experimental data given in Table 4 for the elemental composition and the aromatic carbon content C_{ar} [3]. In the calculation of the structural parameters, it was taken that $M = 100$ amu.

Table 5 summarizes the initial data for calculation determined from the data of Table 4.

Table 6 gives the results of the calculations of the structural parameters of coal humic acids on a 100-g basis.

Figure 2 shows the relationships between the structural parameters of humic acids obtained based on the data given in Table 6. The classification of humic acids in the coordinates is represented in Fig. 2a. It is evident that humic acid preparations 3 and 4 had the smallest and greatest values of the structure nonsaturation parameter δ, respectively. Consequently, the structure of humic acid 4 is more metamorphized; in this case, this fact indicates an increase in the degree of aromaticity. With an increase in the total number of bonds N_b, the parameter N_σ, which denotes the number of σ bonds, linearly increases (Fig. 2b). The number of σ bonds N_σ also increases with the number of rings γ (Fig. 2c). In this case, the value of γ linearly depends on the total number of bonds N_b (Fig. 2d).

Thus, we proposed a method for the calculation of structural and chemical characteristics and relationships between them based on element analysis and ^{13}C NMR-spectroscopic data on the concentrations of C_{ar} as the constituents of different functional groups and tested this method with the use of humic acids as an example. On the one hand, the set of these parameters characterizes the structure peculiarities of humic acids, and, on the other hand, it gives strict limitations

Table 5. Initial data for the calculation of the structural parameters of coal humic acids

Humic acid	Content, mol					
	n_C	n_H	n_N	n_O	n_S	X_{ar}
1	5.58	4.1	0.05	1.61	0.08	4.20
2	5.53	4.5	0.07	1.69	0.03	3.98
3	4.98	3.9	0.09	2.13	0.03	4.31
4	5.25	2.5	0.13	1.98	0.03	4.79

Table 6. Results of the calculation of the structural parameters of coal humic acids

Structural parameter*)	Humic acids			
	1	*2*	*3*	*4*
N_b, bond/ mol	14.97	15.13	14.20	13.95
M, 100 g	100.08	99.84	99.96	99.96
N_{at}, atom/ mol	11.42	11.87	11.13	9.89
δ	7.11	6.63	6.15	8.13
γ – 1, ring/ mol	1.45	1.32	0.92	1.67
N_σ, σ bond/ mol	12.87	13.45	12.05	11.56
N_{at}/n_{at}	2.05	2.15	2.23	1.88

*) A mole is taken to be 100 g.

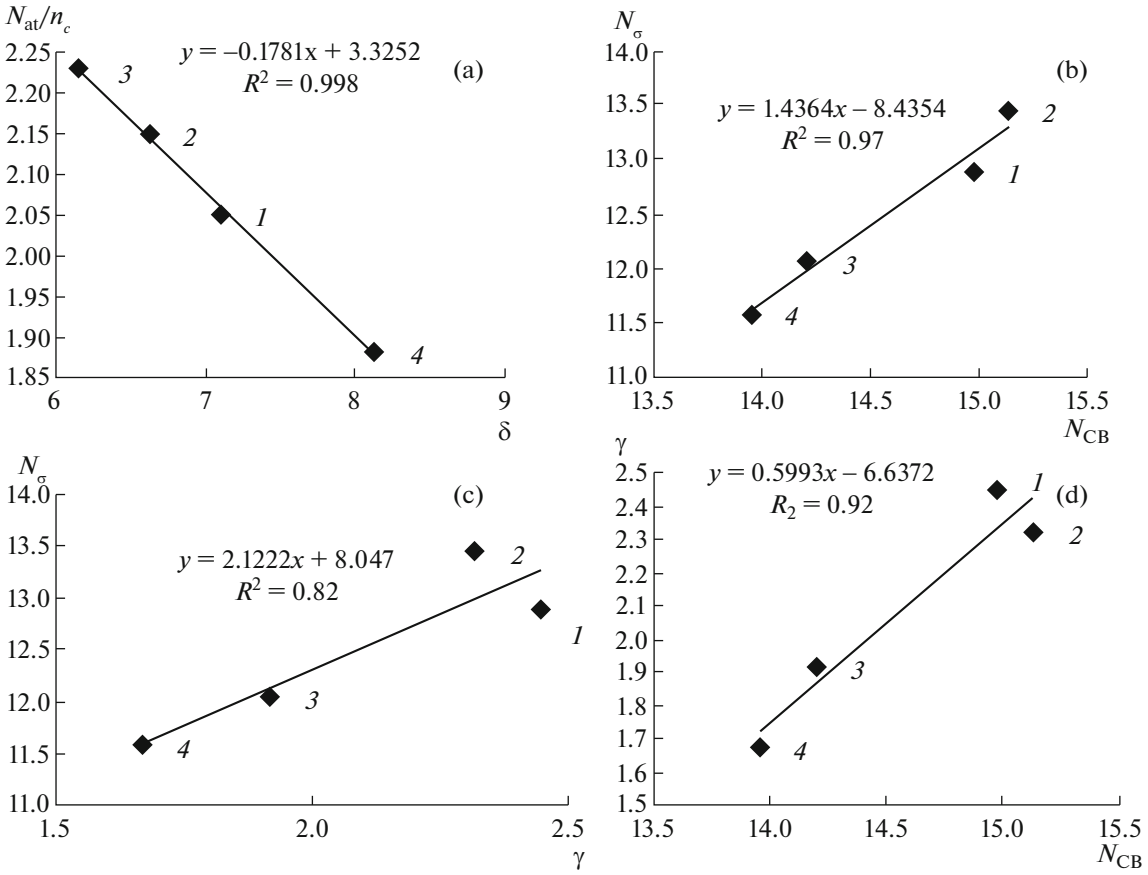

Fig. 2. Relationships between the structural parameters of coal humic acids: (a) the dependence of the N_{at}/n_C atomic ratios on the structural parameter δ; (b) the dependence of the number of σ *bonds* N_σ on the total number of common bonds N_b; (c) the dependence of the number of σ *bonds* N_σ on the total number of rings γ; and (d) the dependence of the total number of rings γ on the number of common bonds N_b.

in the construction of an average structural model. The method can be applied to any other organic substances of complex structure, mixtures, and structurally irregular biopolymers, including those of natural origin.

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