

A NEW ITERATIVE METHOD OF CONSTRUCTION OF THE HAMMETT ACIDITY FUNCTION

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A new iterative algorithm has been devised for construction of the H acidity function. The procedure is based on gradual transformation of the dependence of $\log I$ vs acid concentration into the dependence of H vs acid concentration, and it involves four steps. In the first step a continuous acidity function is obtained by taking the average of $\log I$ values for the same acid concentrations. The second step of the algorithm is smoothing out of the acidity function by means of smoothing the H value by weighted moving average. In the third step, the mean distances between the $\log I$ values and the corresponding values of the smoothed acidity function H are calculated for the given indicator, and in the fourth step these distances are used together with $\log I$ values for calculating a new acidity function. The procedure designed was converted into a programme in the Delphi 2 language for PC Pentium and was successfully validated on literature data.

Key words: Acidity functions; Acidity function construction; Dissociation constants; Weak acids and bases.

Despite some weaknesses, since the time of its appearance¹⁻³ the concept of the Hammett acidity function has proved useful⁴⁻⁶. The main idea consists in involving the manifestations of non-ideality of medium^{4,5} connected with changes in composition^{7,8} into a single acidity function H . This function is defined by a simple relationship,

$$\log I = \text{p}K - H, \quad (1)$$

where $\log I$ is the logarithm of concentration ratio of protonated and nonprotonated forms of a weak base (indicator), and $\text{p}K$ is negative logarithm of dissociation constant of this indicator. The main drawback of the original Hammett approach is the dependence on the indicator type, solvent, and the acid or base used⁴⁻⁶. Due to that there exist a number of acidity functions⁶ out of which, of course, only a few are used practically⁵. In this context, the H_0 acidity function can be denoted as standard: it was constructed for sulfuric acid with primary aromatic amines used as the indicators^{1,6,9}. Besides, the construction of acidity function based on Eq. (1) brings some mathematical-statistical

problems resulting in obtaining various final acidity functions from the same set of starting data.

The attempts at removing the dependence on indicator led to suggestion of more general dependences – “universal” acidity functions – which adopt the principle of similarity given by a certain mathematical expression. An older approach by Bunnett and Olsen¹⁰ starts from the presumption of similarity of any acidity function with the H_0 acidity function. Then the relation between $\log I$ and acidity function is expressed by Eq. (2).

$$\log I - \log [H^+] = pK + (\phi - 1) (H_0 + \log [H^+]) , \quad (2)$$

where $\log [H^+]$ is the proton concentration calculated from the concentration of the acid used and $(\phi - 1)$ is the coefficient of proportionality. Further generalization is represented by the definitions of general acidity function^{11–17} in the form of Eq. (3)

$$\log I - \log [H^+] = pK + n_{is} M_c , \quad (3)$$

or similarly^{18–20} in the form (4),

$$\log I - \log [H^+] = pK + m^* X , \quad (4)$$

where M_c and X are the functions of analytical concentration of acid which describe the correction for non-ideality of medium, and n_{is} and m^* are sensitivity coefficients. Although relations (2) through (4) appear to be elegant approaches, they have, on the other hand, also some drawbacks. The first is the extent of similarity between the non-ideality of behaviour of a particular indicator with the “universal” acidity function. Other objections are statistical. At lower concentration of the protonating acid, when the expression at the left-hand side of the equation is almost constant, it is first of all the experimental errors (a small difference of big numbers) which correlate with M_c or X . At higher concentrations, on the other hand, the pK value is obtained as an intercept from a long-range extrapolation. Both effects are, irrespective of the concentration, increased by the fact that, despite the presence of the difference at the left-hand sides of the equations, the resulting error is a sum of experimental errors of both the experimental values (random variable).

The consequence of drawbacks of both Hammett’s classical concept and “universal” acidity function concept is relatively distinct differences between the dissociation constant values determined by various methods^{13,21–25}. It is certainly possible to speculate

which of the values are more correct. In our opinion it seems the most suitable to construct the Hammett acidity function for a given series of indicators according to Eq. (1). This method of determination of dissociation constants does not introduce into calculation any external (maybe uncertain) parameters existing in (probably approximate) correlation relationships. In addition, it is possible to statistically verify some presumptions on which the construction of acidity function is based. Therefore, the relations (2) through (4) are only suitable in the cases where there is no series of suitable indicators available, the above-mentioned statistical objections, nevertheless, being still valid.

Of course, even the determination of dissociation constants by means of construction of the Hammett acidity function according to relation (1) has its particular pitfalls. The dominant step of this method is mutual shifting of the curves $\log I$ vs acid concentration c with the aim of producing mathematically the optimum (constantly increasing) dependence of H vs c . This procedure has an *a priori* requirement of identical course of the $\log I$ vs c dependence in the region of common concentrations of acid or base. Usually it is presumed that the curves are parallel in this interval, *i.e.* mutually linearly dependent with slope 1. From the physico-chemical viewpoint this means that the ratio of activity coefficients of the protonated and nonprotonated forms is constant for all the indicators in the series used. This condition need not be fulfilled if the selection of indicators is not suitable or the experimental error is rather large, and this problem is usually solved^{24,26} by introducing the slope m into Eq. (1) to give Eq. (5).

$$\log I = \text{p}K - mH \quad (5)$$

Equation (5) in the regression form is an only apparent analogy of Eqs (2) through (4) since it does not exhibit the above-mentioned statistical drawbacks at low concentrations of the protonating acid. The presumption of slope 1 ($m = 1$) can be statistically tested. A slope different from 1 need not necessarily be a hindrance, provided the correlation between $\log I$ and H is sufficiently close.

Several methods have been suggested^{21,24} for constructing the Hammett acidity function. The condition of their application is the mathematically optimum resultant curve in relation to the presumptions introduced, an easy calculation being also desirable. The aim of the present communication is to suggest such algorithm and compare the results obtained with suitable examples taken from literature.

DESCRIPTION OF THE ALGORITHM SUGGESTED

The suggested algorithm for construction of acidity function starts from the definition equation (1). The procedure is iterative, hence relatively simple and easily programmable. The basic idea is gradual improving of the initial estimate of the acidity function

constructed which would lead to the optimum result in the form of a smooth, constantly increasing curve.

The first iteration step is construction of estimate of acidity function H in the form of a continuous curve formed from the values $H = \log I$ in dependence on a series of acid concentrations c . The $\log I$ values for various indicators at the same acid concentrations are averaged. The saw-tooth curve obtained (Fig. 1) is transformed to the target acidity function in the course of the iteration process.

The second iteration step of the algorithm is smoothing out the acidity function by smoothing the H_i value for the i -th concentration c_i using Eq. (6).

$$(H_i)^{\text{new}} = \frac{p_{i-1}H_{i-1}(c_{i+1} - c_i) + p_iH_i(c_{i+1} - c_{i-1}) + p_{i+1}H_{i+1}(c_i - c_{i-1})}{p_{i-1}(c_{i+1} - c_i) + p_i(c_{i+1} - c_{i-1}) + p_{i+1}(c_i - c_{i-1})}, \quad (6)$$

where p are numbers of $\log I$ values used for a given acid concentration c in the calculation of H value. In principle, relation (6) is a weighted moving average.

The third iteration step is calculation of mean distance between $(\log I)_{ij}$ values for the j -th indicator (identical with $\text{p}K_j$) and the corresponding i -th values of smoothed acidity function H_i for q_j experimental points using Eq. (7).

$$\text{p}K_j = \sum_i [(\log I)_{ij} - H_i] / q_j \quad (7)$$

The $\text{p}K_j$ values are used in the fourth, last iteration step to calculate the H_{ij} values for all the experimental values $k = 1, 2, \dots, q_j$ for the j -th indicator using Eq. (8),

$$(H_{ij})^{\text{new}} = (\log I)_{ij} - \text{p}K_j, \quad (8)$$

wherefrom the H_i value is obtained by taking the average over all the contributing indicators j .

Repeating of the 2nd through 4th steps up to a self-consistency expressed by the termination criterion (9)

$$|\sum_j \text{p}K_j^{\text{new}} / \sum_j \text{p}K_j^{\text{old}} - 1| < \varepsilon \quad (9)$$

(a suitable ε value is about $5 \cdot 10^{-5}$) gives a smooth $H(c)$ curve, which can be called a "relative acidity function". This curve has a shape identical with the physico-chemically relevant acidity function, however, it is shifted by a certain value in the axis of ordinate. The magnitude of this shift must be calculated as a mean difference between

known (*i.e.*, in other ways determined) pK values of standard(s) and the pK values calculated for the same indicators from the relative acidity function using Eq. (7). By adding this correction to the relative acidity function we obtain the resulting H acidity function. Using this function and a standard procedure, we then can calculate from Eq. (7) also the physico-chemically relevant pK values of all the indicators used. The residual variance s_{pK}^2 of these point estimates for the j -th indicator are obtained from Eq. (10), and the standard deviations s_{pK} by extracting their square root.

$$s_{pK}^2 = \sum_i [(\log I_{ij} - H_i - pK_j)^2 / (q_j - 1)] \quad (10)$$

The algorithm described was transformed into a programme using the Delphi 2 language and the calculations were carried out on a personal computer with a Pentium processor.

RESULTS AND DISCUSSION

Validation of Algorithm Suggested by Means of Construction of Acidity Function

The correctness of the procedure suggested was tested on a selection of data measured with the standard system of substituted anilines and sulfuric acid at 25 °C (ref.²⁷, 12 indicators). The calculation course according to the above-described algorithm is clearly demonstrated by the H vs c curve after seven iterations (Fig. 1) and after 275 iterations (according to the termination criterion (9), $\varepsilon = 5 \cdot 10^{-5}$, Fig. 2, curve 1). As it can be seen from Fig. 1, the acidity function constructed assumes the characteristic

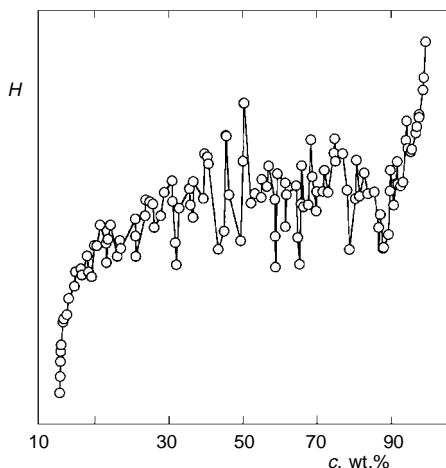


FIG. 1

Dependence of the acidity function constructed on concentration c of sulfuric acid (wt.%) for literature data²⁷ after 7 iterations; the scale on axis of ordinate changes in the course of transformation of $\log I$ scale into H scale and, therefore, is not given

shape after a few iterations already. Figure 2 compares the acidity curve constructed (curve 1) with that constructed by the authors of the paper quoted (curve 2), 4-nitro-aniline ($pK_a = 1.00$ in water at 25 °C) being the standard for both the curves. The comparison shows that the largest differences between the two curves are in the region of lower concentration of acid, whereas at higher concentrations the curves coincide upon a slight shift. The differences found can possibly be due to the small number of the indicators covering the region of low acid concentrations near the distinct curvature of the acidity function, whereas the opposite is true at higher concentrations. Comparisons^{13,27} of values of the H_0 acidity function published by various authors show that the differences at low concentrations of sulfuric acid vary within 10^{-1} unit, varying within as high as 10^0 unit at the highest concentrations. As the differences found by us are distinctly smaller, the results obtained by the algorithm suggested can be considered comparable with those obtained by earlier procedures.

Validation of Algorithm Suggested through Calculation of pK

Acidity functions are usually constructed with the aim to determine values of dissociation constants of weak acids and bases in the given medium. A comparison of the pK values obtained by different procedures can represent another way of verification of correctness of the procedure used. As the algorithm described starts from Eq. (1), which is a special case of Eq. (5) for $m = 1$, this presumption has been tested simultaneously. In order to verify the algorithm suggested, we selected sets of data from literature covering both various types of indicators and various media.

The results obtained for dissociation of substituted anilines in sulfuric acid at 25 °C (ref.²⁷) are presented in Table I. Firstly, on the basis of the results we can see that the

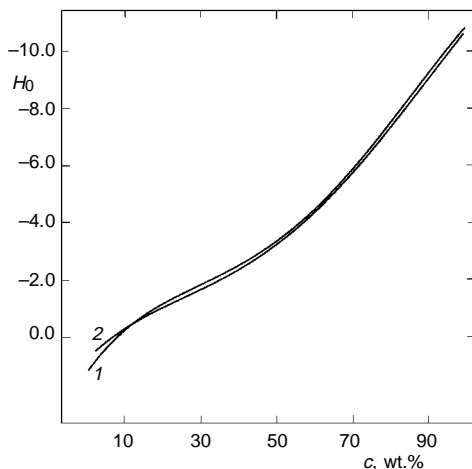


FIG. 2
Comparison of dependences of the H_0 acidity function obtained by the algorithm suggested (curve 1) and H_0 acidity function from ref.²⁷ (curve 2) on concentration c (wt.%) of sulfuric acid

standard deviations of pK are very low, not exceeding the value of 0.1 usually given. The pK values calculated by us and those given in literature²⁷ basically agree, the greatest difference not exceeding 0.25 units. On the other hand, distinctly different are pK values¹³ obtained from Eq. (3). The difference of almost 2 units already casts doubt on the correctness of prediction using the universal acidity function, and it obviously results from the extrapolation at a long range. The slopes m of the dependence $\log I$ vs H (Eq. (5)) show statistically significant difference from 1 in a number of cases, which indicates the lack of fulfilment of the requirement of constant ratio of activity coefficients of the protonated and nonprotonated forms of indicator. On the other hand, the residual standard deviations of these relationships do not exceed the value of 0.05 of $\log I$ unit, which is obviously within the limits of the experimental accuracy.

Secondly, comparison of the pK values calculated by two methods based on Eq. (1) forms another example. The input data were obtained by measuring the dissociation of substituted diphenylamines in aqueous sulfuric acid²¹. The results obtained now and those obtained by the algorithm earlier suggested (Table II) show excellent agreement, the standard deviations s_{pK} being distinctly lower when compared with the older algorithm. Like in the previous case, we can see deviations from the pK values obtained with the help of universal functions, the values thus obtained appearing less correct²¹. Although again most of the slopes m in Eq. (5) show statistically significant difference

TABLE I
Numbers of experimental points q , pK values, their standard deviations s_{pK} , slopes m in Eq. (5) obtained with algorithm suggested and comparison with literature data

Indicator	q	pK	s_{pK}	m	pK , ref. ²⁷	pK , ref. ¹³
4-Nitroaniline	15	1.000	0.050	0.961 ^a	1.00	1.00
2-Nitroaniline	11	-0.345	0.041	0.955 ^a	-0.30	-0.34
4-Chloro-2-nitroaniline	9	-1.122	0.025	1.007	-1.06	-1.14
2,5-Dichloro-4-nitroaniline	9	-1.855	0.070	0.926 ^a	-1.75	-1.72
2-Chloro-6-nitroaniline	7	-2.481	0.046	1.033	-2.38	-2.49
2,6-Dichloro-4-nitroaniline	11	-3.378	0.038	0.970 ^a	-3.27	-2.98
2,4-Dinitroaniline	11	-4.407	0.034	0.972 ^a	-4.27	-4.09
2,6-Dinitroaniline	9	-5.556	0.017	1.009	-5.39	-4.97
2-Bromo-4,6-dinitroaniline	11	-6.846	0.037	0.978	-6.69	-6.20
3-Methyl-3,4,6-trinitroaniline	11	-8.489	0.040	0.974	-8.33	-8.09
3-Bromo-2,4,6-trinitroaniline	10	-9.543	0.046	1.047 ^a	-9.34	-9.18
2,4,6-Trinitroaniline	11	-10.264	0.066	0.941 ^a	-10.03	-8.15

^a The value statistically significantly different from 1 at the significance level of $\alpha = 0.05$.

TABLE II

Numbers of experimental points q , pK values, their standard deviations s_{pK} , slopes m in Eq. (5) obtained with algorithm suggested and comparison with literature data referred to 4-nitroaniline as standard²⁷

Indicator	q	pK	s_{pK}	m	pK^a , ref. ²¹	pK^b , ref. ²¹
4-Nitroaniline	15	1.000	0.034	1.030 ^c		
4-Ethoxydiphenylamine	21	1.269	0.083	1.113 ^c	1.350	1.478
4-Methoxydiphenylamine	18	1.338	0.035	0.971 ^c	1.355	1.413
4-Methyldiphenylamine	24	1.106	0.040	0.988	1.123	1.208
3-Methyldiphenylamine	24	0.873	0.043	0.954 ^c	0.872	0.976
Diphenylamine	23	0.624	0.030	0.995	0.643	0.769
3-Methoxydiphenylamine	24	0.443	0.051	0.953 ^c	0.429	0.318
4-Chlorodiphenylamine	23	0.127	0.022	1.050 ^c	0.090	-0.070
3-Chlorodiphenylamine	20	-0.358	0.049	1.068 ^c	-0.332	-0.412
3-Bromodiphenylamine	22	-0.117	0.022	0.967 ^c	-0.242	-0.238
3-Nitrodiphenylamine	15	-1.241	0.032	1.038 ^c	-1.270	-1.276
4-Nitrodiphenylamine	10	-2.693	0.028	1.005	-2.634	-2.237

^a Calculation according to the algorithm suggested in the paper quoted. ^b Calculation using the universal acidity function X . ^c The value statistically significantly different from 1 at the significance level of $\alpha = 0.05$.

TABLE III

Numbers of experimental points q , pK values, their standard deviations s_{pK} , slopes m in Eq. (5) obtained with algorithm suggested and comparison with literature data

Indicator	q	pK	s_{pK}	m	pK , ref. ²⁸	pK , ref. ¹³
Pyrrole-2-carboxamide	9	-1.230	0.027	1.026 ^a	-1.23	-1.15
4-Methoxybenzamide	12	-1.436	0.031	0.994	-1.44	-1.22
3,4,5-Trimethoxybenzamide	10	-1.820	0.037	1.005	-1.82	-1.62
3-Nitrobenzamide	11	-2.462	0.025	0.982	-2.42	-2.05
3,5-Dinitro-4-methylbenzamide	10	-2.718	0.028	0.992	-2.69	-2.27
2,3,6-Trichlorobenzamide	9	-3.364	0.038	1.041	-3.30	-2.59
2,4-Dichloro-3,5-dinitrobenzamide	11	-3.779	0.041	0.957 ^a	-3.73	-2.98
2,4,6-Trinitrobenzamide	9	-4.141	0.053	1.073 ^a	-4.08	-3.55

^a The value statistically significantly different from 1 at the significance level of $\alpha = 0.05$.

from 1, the residual standard deviations do not exceed 0.05 log I units in this case either.

Other examples of application of the algorithm suggested to indicators of other types confirm the above-mentioned conclusions. The agreement between our results and the data given for a series of amides in original literature²⁸ (Table III) can be considered excellent, which cannot be claimed in the case of values obtained by means of universal acidity function. The measurements of dissociation of substituted indoles in sulfuric acid²⁹ revealed certain anomalies, however, these anomalies did not appear (but for few exceptions) in the pK values calculated by us (Table IV). The differences in pK values of 5-nitroindole are obviously due to both lower accuracy of measurement²⁹ and unsuitable intervals in the log I scale. The consequences of the anomalies mentioned are marked with the application of universal acidity function, *i.e.* about 3 units in the pK scale. The last example chosen is special in that the indicators used (alkylcarbenium ions³⁰ in sulfuric acid) cover practically the whole scale of concentrations of the protonating acid. Comparing our results with those in original literature³⁰ (Table V) we can see, that the results of the two methods differ by a value slightly exceeding one pK unit, whereas the comparison with the values obtained by applying the universal acidity function exhibits a difference of almost 7 units of pK scale. Such a difference in results obtained from different methods applied to the same set of data is obviously alarming

TABLE IV
Numbers of experimental points q , pK values, their standard deviations s_{pK} , slopes m in Eq. (5) obtained with algorithm suggested and comparison with literature data

Indicator	q	pK	s_{pK}	m	pK , ref. ²⁷	pK , ref. ¹³
1,2-Dimethylindole	6	0.262	0.035	1.065	0.30	0.25
2-Methylindole	5	-0.319	0.009	0.983	-0.28	-0.27
1,2,3-Trimethylindole	6	-0.678	0.019	1.031	-0.66	-0.62
Indole-3-acetic acid	5	-6.069	0.030	0.965	-6.13	-4.92
5-Nitroindole	7	-7.051	0.072	0.956	-7.40	-4.25
2,3-Dimethylindole	9	-1.513	0.021	0.989	-1.49	-1.48
1-Methylindole	8	-2.365	0.034	1.036	-2.32	-2.38
Tryptamine	8	-6.256	0.064	1.102 ^a	-6.31	-5.54
Indole	12	-3.500	0.161	0.752 ^a	-3.50	-2.78
1,2-Dimethyl-5-nitroindole	6	-2.996	0.068	1.040	-2.94	-2.77
3-Methylindole	9	-4.489	0.058	1.028	-4.55	-4.03
1,3-Dimethylindole	14	-3.323	0.100	1.155	-3.30	-3.59

^a The value statistically significantly different from 1 at the significance level of $\alpha = 0.05$.

TABLE V

Numbers of experimental points q , pK values, their standard deviations s_{pK} , slopes m in Eq. (5) obtained with algorithm suggested and comparison with literature data

Indicator	q	pK	s_{pK}	m	$pK_{\text{ref.}}^{30}$	$pK_{\text{ref.}}^{13}$
4,4',4''-Trimethoxytriphenylmethanol	13	0.820	0.024	0.987	0.82	0.67
4,4'-Dimethoxytriphenylmethanol	12	-1.266	0.038	0.964 ^a	-1.24	-1.20
4-Methoxytriphenylmethanol	9	-3.351	0.069	1.083 ^a	-3.40	-3.22
2,2',2''-Trimethyltriphenylmethanol	7	-3.323	0.058	0.910 ^a	-3.40	-2.84
4,4',4''-Trimethyltriphenylmethanol	8	-3.528	0.055	1.062 ^a	-3.56	-3.31
4-Methyltriphenylmethanol	6	-5.070	0.044	1.056	-5.24	-4.34
4,4'-Dimethoxydiphenylmethanol	8	-5.504	0.117	1.110 ^a	-5.71	-4.73
3,3',3''-Trimethyltriphenylmethanol	6	-6.095	0.150	1.242 ^a	-6.35	-5.95
4,4',4''-Triisopropyltriphenylmethanol	6	-6.280	0.156	1.251 ^a	-6.54	-5.87
Triphenylmethanol	5	-6.344	0.111	1.210 ^a	-6.63	-5.96
4,4',4''-Trichlorotriphenylmethanol	5	-7.173	0.150	1.216	-7.74	-6.32
4-Nitrotriphenylmethanol	5	-8.472	0.052	1.021	-9.15	-7.37
2-Phenylborneol	6	-8.983	0.100	1.087	-9.75	-7.45
3,3',3''-Trichlorotriphenylmethanol	5	-10.097	0.101	1.131 ^a	-11.03	-8.85
4,4'-Dinitrotriphenylchloromethane	5	-11.774	0.118	1.107	-12.90	-10.33
4,4',4''-Trinitrotriphenylmethanol	5	-15.155	0.053	1.019	-16.27	-10.87
9-Methylfluoren-9-ol	5	-15.442	0.058	1.044	-16.60	-10.19
2,4,6-Trimethylbenzyl alcohol	8	-16.231	0.043	1.044	-17.38	-10.53
4- <i>tert</i> -Butyltriphenylchloromethane	6	-5.952	0.021	0.984	-6.10	-4.72
4,4'-Di- <i>tert</i> -butyltriphenylchloromethane	6	-6.329	0.034	0.988	-6.60	-4.27
4,4',4''-Tri- <i>tert</i> -butyltriphenylmethanol	5	-6.153	0.068	1.107	-6.50	-4.35
Dimesitylmethanol	6	-6.261	0.092	1.131 ^a	-6.60	-4.77
4,4'-Dimethyldiphenylmethanol	4	-9.481	0.059	1.120 ^a	-10.40	-7.89
2,2'-Dimethyldiphenylmethanol	5	-11.318	0.080	1.024	-12.45	-9.47
4,4'-Di- <i>tert</i> -butyldiphenylmethanol	4	-12.059	0.103	1.204 ^a	-13.20	-10.72
Diphenylmethanol	4	-12.184	0.037	1.036	-13.30	
4,4'-Dichlorodiphenylmethanol	5	-12.811	0.054	1.079 ^a	-13.96	-8.89
Fluoren-9-ol	3	-12.817	0.036	0.872	-14.00	-6.07

^a The value statistically significantly different from 1 at the significance level of $\alpha = 0.05$.

and raises the question of which of those results are more correct. With regard to the arguments given in the introduction to this paper we consider the results obtained from the acidity function constructed on the given series of indicators to be more correct.

In conclusion it can be stated that the results obtained by means of the algorithm suggested have shown a good agreement with those obtained by classical or other procedures, and hence we consider the method suggested for construction of acidity function to be validated.

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