

EVALUATION OF DATA PRETREATMENT METHODS IN TARGET TESTING FACTOR ANALYSIS APPLIED TO THE DETERMINATION OF PROTONATION PARAMETERS OF SOME HYDROXYBENZOIC ACIDS

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Abstract. The values of the basicity constant pK_{BH^+} , and of the solvation parameter, m^* , of three hydroxybenzoic acids (2,5-dihydroxybenzoic, 3,5-dihydroxybenzoic and 3,4,5-trihydroxybenzoic) were estimated by the target testing method of factor analysis, using the respective ultraviolet absorption spectra measured in aqueous sulphuric acid solutions. The results obtained have been compared with those calculated by the Davis–Geissman method. The following basicity parameter values have been obtained by the target testing of factor analysis:

2,5-dihydroxybenzoic acid: $pK_{BH^+} = -6.27 \pm 0.39$, $m^* = 0.84 \pm 0.10$;

3,5-dihydroxybenzoic acid: $pK_{BH^+} = -6.64 \pm 0.25$, $m^* = 0.82 \pm 0.15$;

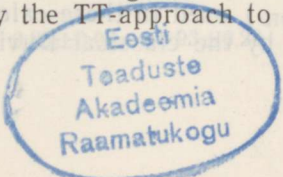
3,4,5-trihydroxybenzoic acid: $pK_{BH^+} = -5.65 \pm 0.10$, $m^* = 0.70 \pm 0.01$.

Key words: hydroxybenzoic acids, protonation, factor analysis, basicity.

INTRODUCTION

UV-absorption spectrophotometry is one of the most widely used experimental methods for determining the protonation parameters of weak organic bases. In a number of cases, however, including the protonation of carbonyl compounds, the changes in UV-spectra caused by the protonation of a base are superimposed by the medium effects, especially in concentrated mineral acids. To overcome these difficulties in calculating basicity constants, a number of correction methods have been suggested, the most recent of them having been developed with the use of factor analysis [1, 2]. These newly developed methods have the advantage of the simultaneous treatment of the whole set of spectral data, not only the respective major spectral features. In our previous work [3], we critically studied the application of two factor analytical methods (the target testing (TT) method and the principal component analysis) to the treatment of spectra with shifting UV-absorption bands. 2-Hydroxybenzoic acid in aqueous sulphuric acid solutions was chosen as a test base for this study [3]. As a result, the TT-method proved to be better for estimating the protonation parameter values for the weak bases studied.

Continuing the UV-spectrophotometric investigation of hydroxybenzoic acids (HBA), we decided to apply the TT-approach to a variety of base structures.



The mathematical background of the TT-method in factor analysis for application to the protonation of weak organic bases has been presented in [2].

The ionization ratio I for the base B has been calculated from the equation

$$I = \frac{C_{\text{BH}^+}}{C_{\text{B}}} = \frac{\varepsilon - \varepsilon_{\text{B}}}{\varepsilon_{\text{BH}^+} - \varepsilon}$$

where C_{B} and C_{BH^+} are the molar concentrations of the base B and its conjugated acid BH^+ ; ε_{B} , $\varepsilon_{\text{BH}^+}$ and ε are the molar extinction coefficients of B, BH^+ and the mixture of protonated and unprotonated forms of the base at the same wavelength.

To determine the values of the basicity constant, $\text{p}K_{\text{BH}^+}$, and of the solvation parameter, m^* , the Cox—Yates excess acidity method [4] has been used.

In complicated cases where the value of I (and consequently those of $\text{p}K_{\text{BH}^+}$ and m^*) depends on the wavelength chosen, the simultaneous treatment of the whole spectral band contour seems to be useful. The TT-method of factor analysis offers such an opportunity [2]. To increase the resolving power of the TT-method, one may use in calculations not only the raw ε values at different wavelengths and sulphuric acid concentrations, but also the data matrixes containing the differences $(\varepsilon - \varepsilon_{\text{B}})$ and $(\varepsilon - \varepsilon_{\text{BH}^+})$, where a constant component of the spectra (ε_{B} or $\varepsilon_{\text{BH}^+}$) has been subtracted [2].

EXPERIMENTAL

Reagents. All three samples of HBA were obtained in very limited amounts from Stockholm Technical University and were used without further purification. The melting points of HBA-s were controlled and found to be close to those reported in the literature.

Sulphuric acid, chemically pure grade, was used without additional purification. Sulphuric acid solutions containing HBA-s were prepared as before [5, 6].

The measurement of UV-spectra. This was done using spectrophotometry as in [5]. Dilution experiments after 15 min from the preparation of samples showed that no irreversible changes in the spectra of the bases dissolved in the concentrated sulphuric acid solution had occurred.

RESULTS

3,4,5-Trihydroxybenzoic acid (3,4,5-THB)

3,4,5-THB has two absorption bands in the UV-region studied: A (52 000—46 000 cm^{-1} , the number of wavelengths $\text{NW}=9$) and B (40 000—28 000 cm^{-1} , $\text{NW}=15$). The protonation of this base occurs mainly in 71—95% H_2SO_4 (the number of solutions $\text{NS}=29$).

The TT-treatment of the shifting band B gives coinciding results (see Table 1), no matter what the kind of data pretreatment (ε , $\varepsilon - \varepsilon_{\text{B}}$ or $\varepsilon - \varepsilon_{\text{BH}^+}$) used in these calculations. They are also close to the results obtained by the classical Davis—Geissman method [7], see Table 1.

Table 1

The values of pK_{BH^+} and m^* of 3,4,5-trihydroxybenzoic acid
(B , 40 000–28 000 cm^{-1})

Data pretreatment	pK_{BH^+}	m^*
ϵ	-5.60	0.69
$\epsilon - \epsilon_B$	-5.78	0.71
$\epsilon - \epsilon_{BH^+}$	-5.58	0.70
Davis—Geissman method [7]	-5.49 ± 0.17	0.69 ± 0.03

We also tried to use the absorption band 52 000–46 000 cm^{-1} to estimate the pK_{BH^+} and m^* values of 3,4,5-THB. This far UV-absorption band decreases constantly (even in diluted sulphuric acid solutions) with increasing sulphuric acid concentration without any shift. In this region, however, the dependencies of the molar extinction ϵ vs. % H_2SO_4 have no classical sigmoid shape, they are like a curve without platos corresponding to the ϵ_B and ϵ_{BH^+} values. All the attempts to calculate pK_{BH^+} and m^* in the far UV-region using the TT-method yielded too dispersed values and we decided not to choose the most reliable of them.

3,5-Dihydroxybenzoic acid (3,5-DHB)

Three different spectral regions A (51 000–46 600 cm^{-1} , $NW=10$), B (43 000–36 000 cm^{-1} , $NW=15$), and C (34 000–28 000 cm^{-1} , $NW=13$) were treated separately to estimate the pK_{BH^+} and m^* values of 3,5-DHB, see Table 2. The sulphuric acid concentrations of 71.7 to 95.8% were used ($NS=27$).

Firstly, the influence of the initial data on the results of calculations will be discussed. The line in Table 2 concerned with the ($\epsilon - \epsilon_{BH^+}$) pretreated data shows considerably more negative pK_{BH^+} values and the higher m^* values as compared to other pretreatments. As mentioned in a previous paper [5] 3,5-DHB is incompletely protonated even in the strongest H_2SO_4 solution used in the experiment (95.8% H_2SO_4). The ϵ value in this sulphuric acid solution is not exactly equal to that of ϵ_{BH^+} . But we subtracted the ϵ value in 95.8% H_2SO_4 preparing the ($\epsilon - \epsilon_{BH^+}$) data matrix for applying the TT-method. This may be the reason for the poor fit with the other pretreatments. The situation is similar for all three absorption bands, see Table 2.

Table 2

The values of pK_{BH^+} and m^* of 3,5-dihydroxybenzoic acid

Data pretreatment	A , 51 000–46 600 cm^{-1}		B , 43 000–36 000 cm^{-1}		C , 34 000–28 000 cm^{-1}	
	pK_{BH^+}	m^*	pK_{BH^+}	m^*	pK_{BH^+}	m^*
ϵ	-6.80	0.74	-7.10	0.84	-6.62	0.75
$\epsilon - \epsilon_B$	-6.36	0.69	-6.30	0.71	-6.65	0.76
$\epsilon - \epsilon_{BH^+}$	-8.40	0.99	-8.25	0.95	-7.90	0.95

Davis—
Geissman

method [7] -6.40 ± 0.17 0.73 ± 0.03 -7.23 ± 0.17 0.83 ± 0.03 -6.93 ± 0.20 0.78 ± 0.03

The choice of ϵ at 71% H_2SO_4 as the ϵ_B value is also arbitrary because it is evident that ϵ_B depends on sulphuric acid concentrations before the base protonates. But, in general, the results obtained for the first two data sets (ϵ and $\epsilon - \epsilon_B$) are in relatively good agreement for all three absorption bands and coincide with the $\text{p}K_{\text{BH}^+}$ and m^* values calculated using classical methods, see Table 2.

2,5-Dihydroxybenzoic acid (2,5-DHB)

The following absorption spectra regions of 2,5-DHB were used in the TT-treatment: A (51 000—45 600 cm^{-1} , $\text{NW}=12$), B (43 000—36 600 cm^{-1} , $\text{NW}=14$), and C (34 000—26 000 cm^{-1} , $\text{NW}=15$). Although the measurements of 2,5-DHB UV-absorption spectra were carried out in the sulphuric acid solutions containing $\leq 95\%$ H_2SO_4 , in TT-calculations only spectra within the range of 65.1—87.9% H_2SO_4 were applied. For this substance an unusual behaviour of the plot ϵ vs. % H_2SO_4 was described in [5]: at the sulphuric acid concentration of about 88% the dependence $\epsilon=f(\% \text{H}_2\text{SO}_4)$ shows an extremum. This means we do not know all the details of 2,5-DHB protonation in concentrated sulphuric acid solutions which finally cause such a behaviour of absorption spectra.

It should be pointed out that practically in all three spectral regions the TT-method gives more negative values of $\text{p}K_{\text{BH}^+}$ and higher values of m^* than those obtained by classical methods, see Table 3. There are no noticeable differences in the final results depending on the method of initial spectral data pretreatment.

Table 3
The values of $\text{p}K_{\text{BH}^+}$ and m^* of 2,5-dihydroxybenzoic acid

Data pretreatment	A, 51 000—46 600 cm^{-1}		B, 43 000—36 000 cm^{-1}		C, 34 000—28 000 cm^{-1}	
	$\text{p}K_{\text{BH}^+}$	m^*	$\text{p}K_{\text{BH}^+}$	m^*	$\text{p}K_{\text{BH}^+}$	m^*
ϵ	-6.45	0.86	-6.15	0.77	-6.79	0.88
$\epsilon - \epsilon_B$	-6.37	0.85	-6.06	0.72	-6.65	0.87
$\epsilon - \epsilon_{\text{BH}^+}$	-5.47	0.91	-6.25	0.84	-7.80	1.06
Davis— Geissman method [7]	-5.71 ± 0.23	0.74 ± 0.03	-5.77 ± 0.30	0.72 ± 0.05	-5.54 ± 0.20	0.72 ± 0.03

Table 4
The $\Delta \text{p}K_{\text{BH}^+}$ values for the estimation of the self-consistency of the calculations

Data pretreatment	2,5-Dihydroxybenzoic acid	3,5-Dihydroxybenzoic acid	2-Hydroxybenzoic acid [6]
ϵ	0.64	0.48	0.02
$\epsilon - \epsilon_B$	0.59	0.35	0.03
$\epsilon - \epsilon_{\text{BH}^+}$	0.78	2.33	0.04

Summarizing the application of data pretreatments over the three cases studied (3,5-DHB, 2,5-DHB and 2-hydroxybenzoic acid [6]), we should point out that independent and reliable pK_{BH^+} and m^* values for these bases are not available in the literature and therefore (for lack of more detailed information) we suggest focusing the attention on the inner self-consistency of the results obtained. This self-consistency may be estimated by differences in the pK_{BH^+} values calculated for different spectral regions (A, B and C for 3,5-DHB, 2,5-DHB and 2-hydroxybenzoic acid), see Table 4. From this Table it is evident that somewhat closer pK_{BH^+} values were obtained with the ϵ and $\epsilon - \epsilon_B$ involved in the TT-procedures. But we think that such a result depends on the kind of bases studied and the $\epsilon - \epsilon_{BH^+}$ case in data pretreatment should not be generally disregarded.

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MÖNINGATE HÜDROKSÜBENSOEHAPETE PROTONISATSIOONIPARAMEETRITE MÄÄRAMISE LÄHTEANDMETE EELTÖÖTLUSMENETLUSTE HINDAMINE FAKTORANALÜÜSI SIHTTEISENDUSTE MEETODI ABIL

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On arvatud kolme hüdroksübensoehappe (2,5-dihüdroksübensoe-, 3,5-dihüdroksübensoe- ja 3,4,5-trihüdroksübensoehappe) aluselise konstandi (pK_{BH^+}) ja solvatatsiooni parameetri (m^*) väärtused. Saadud tulemusi on võrreldud pK_{BH^+} ja m^* väärtustega, mis olid arvatud samade ainete puhul Davise—Geissmani meetodil. Arvutuste aluseks olid loetletud ainete UV-neeldumisspektrid, mis mõõdeti väävelhappe vesilahustes. Arvutused on tehtud faktoranalüüsi sihtteisenduse meetodit kasutades ja saadud järgmised tulemused:

2,5-dihüdroksübensoehape: $pK_{BH^+} = -6,27 \pm 0,39$, $m^* = 0,84 \pm 0,10$;

3,5-dihüdroksübensoehape: $pK_{BH^+} = -6,64 \pm 0,25$, $m^* = 0,82 \pm 0,15$;

3,4,5-trihüdroksübensoehape: $pK_{BH^+} = -5,65 \pm 0,10$, $m^* = 0,70 \pm 0,01$.

ОЦЕНКА МЕТОДОВ ПРЕДВАРИТЕЛЬНОЙ ОБРАБОТКИ ИСХОДНЫХ ДАННЫХ ПРИ ОПРЕДЕЛЕНИИ ПРОТОНИЗАЦИОННЫХ ПАРАМЕТРОВ НЕКОТОРЫХ ГИДРОКСИБЕНЗОЙНЫХ КИСЛОТ С ПРИМЕНЕНИЕМ ЦЕЛЕВЫХ ПРЕОБРАЗОВАНИЙ В ФАКТОРНОМ АНАЛИЗЕ

Марина КУДРЯШОВА, Юло ХАЛДНА

Методом целевого тестирования факторного анализа оценены константы основности (pK_{BH}^*) и величины сольватационных параметров (m^*) 2,5-дигидроксибензойной, 3,5-дигидроксибензойной и 3,4,5-тригидроксибензойной кислот на основе их УФ-спектров поглощения в водных растворах серной кислоты. Полученные величины сравнены с результатами, рассчитанными методом Девиса—Гейссмана. Значения, найденные методом факторного анализа, следующие:

- 2,5-дигидроксибензойная кислота: $pK_{BH}^* = -6,27 \pm 0,39$, $m^* = 0,84 \pm 0,10$;
 3,5-дигидроксибензойная кислота: $pK_{BH}^* = -6,64 \pm 0,25$, $m^* = 0,82 \pm 0,15$;
 3,4,5-тригидроксибензойная кислота: $pK_{BH}^* = -5,65 \pm 0,10$, $m^* = 0,70 \pm 0,01$.