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A STUDY OF THE INFLUENCE OF RELATIVE ACIDITY, NUMBER OF COMPONENTS AND NOISE LEVEL ON THE MULTIVARIATE pH-METRIC DETERMINATION OF WEAK ACIDS USING SIMULATED DATA

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Abstract

A systematic study has been conducted on the effect different factors including relative acidity, number of components and added noise on the simultaneous determination of weak acids by multivariate pH-metric titration. For this purpose, partial least squares (PLS) regression was applied on the simulated pH-metric titration data. Large numbers of acid mixture systems composed of different number of acids with varying acidity strengths were examined. The effect of added noise on the prediction ability of the PLS regression was also studied.

Key words: pH-metry, simultaneous determination, weak acids, relative acidity, components, noise, PLS

Introduction

Simultaneous determination of several analytes in a given sample is now an interesting area in chemometrics.[1-3] Multivariate calibration methods that are the basis of such determinations are applied to the second-order data. These data are taken from those instruments which generate a vector of signals per sample (e.g., spectrophotometric and voltammetric data).[4] Data taken from the potentiometric methods, which are first order (i.e., one signal per sample), can be converted to the second order one by a titration procedure. Application of multivariate calibration methods to the potentiometric titration data was introduced by Lindberg and Kowalski in 1988 for simultaneous determination of weak acids by using PLS regression.[5] They used the volume of titrant needed to reach a pre-selected pH as the response data and assumed a linear relationship between the added titrant volumes and analyte's concentration. After that, this PLS regression method has been applied to acid-base,[6,7] complexometric[8] and potentiometric precipitation titrations.[9] Previously, we used the artificial neural network calibration method for pH-metric acid-base titration of four organic acids.[10]

The results of multivariate calibration methods is affected by many factors. The accuracy of these methods is influenced by the selectivity of the analyte's signals.[11] As suggested by Lorber, selectivity in multivariate calibration methods is controlled by orthogonality between the component signals (i.e., the degree of overlapping between component spectra in spectrophotometric methods).[11]

Despite a large achievement in the field of multivariate potentiometric determination of several analytes, to the best of our knowledge, there is no literature report on the effects of different variables on the performance of these methods. In the present study, we have investigated the influence of number of components, relative acidity and added noise on such determinations. The systems used were different mixtures of weak acids with varying acidity and different number of acids. All the systems used were hypothetical and simulated pH-metric data were used.

Methods

Acids mixture systems.

For simplicity, we supposed that all the acids used are monoprotic. The system of acids used was categorized based on the number of acids in each system. Each system was divided to some subsystems based on the acidity strengths of the acids used in each system. These systems are indicated in Tables 1-3. The acidity constants of the hypothetical monoprotic acids are given in these tables. The subsystems where named as

Table 1. The acidity constants (pK_a) of the acids used in two-component systems.

Acid	pK_a							
	sys_{21}	sys_{22}	sys_{23}	sys_{24}	Sys_{25}	sys_{26}	sys_{27}	sys_{28}
acid 1	2.0	2.0	2.0	2.0	4.0	6.0	6.0	8.0
acid 2	3.0	2.7	2.3	3.5	5.0	6.7	7.0	8.3

Table 2. The acidity constants (pK_a) of the acids used in three-components system.

Acid	pK_a							
	sys_{31}	sys_{32}	sys_{33}	sys_{34}	sys_{35}	sys_{36}	sys_{37}	sys_{38}
acid 1	2.0	2.0	3.0	3.0	5.0	5.0	5.0	5.0
acid 2	2.7	3.0	4.0	4.7	6.0	5.7	5.3	6.7
acid 3	3.4	4.0	5.0	6.4	7.0	6.4	5.7	8.4

Table 3. The acidity constants (pK_a) of the acids used in four-component systems.

Acid	pK_a							
	Sys_{41}	sys_{42}	sys_{43}	Sys_{44}	sys_{45}	Sys_{46}	sys_{47}	sys_{48}
acid 1	2.0	2.0	2.0	2	4.0	4.0	4.0	6.0
acid 2	2.3	2.7	3.0	3.7	5.3	4.7	5.0	7.0
acid 3	2.7	3.4	4.0	5.4	6.7	5.4	6.0	8.0
acid 4	3.0	4.2	5.0	7.2	8.0	6.2	7.0	9.0

sys_{ij}, where *i* represent the number of components in the main system and *j* is the subsystem's number indicated in Tables 1-3.

Derivation of the simulated data.

Consider the titration of *V* ml of *n* weak acids (HA_i) with a strong base (BOH). The analytical concentrations of these acids are assumed as Ca_i. The charge balance equation in all steps of titration is:

$$[B^+] + [H^+] = [OH^-] + \Sigma\, [A^-]_i \tag{1}$$

The equilibrium concentration of A^- can be expressed by the following equations:

$$[A^-]_i = \alpha_i\, Ca_i \tag{2}$$

$$\alpha_i = K_a/([H^+] + K_a) \tag{3}$$

where α_i is the fraction of acid HA_i existed as A_i^-. The value of α_i, which can be evaluated by Equation (2), is only depend on the pH of solution and is calculated for each acid separately. By expressing of the concentration of B^+ as a function of the concentration (C_b) and volume of base added (V_b), the Equation (1) can be written as:

$$C_b\, V_b / V = [OH^-] – [H^+] + \Sigma\alpha_i\, Ca_i \tag{4}$$

From Equation (4), the volume of titrant needed to reach a given pH is calculated by the following equation:

$$V_b = ([OH^-] – [H^+] + \Sigma\alpha_i\, Ca_i)\, V / C_b \tag{5}$$

PLS modeling.

PLS regression was run on each system described below (sys_{ij}). For each case, two sets of standard solutions were considered. The calibration set solutions (25 solutions) were prepared according to five level (1.0, 2.5, 5.0, 7.5 and 10.0 mM) fractional factorial design as shown in Table 4.[12,13] Using such a design, maximum information for each acid can be obtained by using only a few number of standard solutions. In order to evaluate the performance of the PLS model on the systems used, 20 standard solutions were considered in the prediction set whose concentrations were selected randomly. The concentrations of the prediction samples are also shown in Table 4. The concentrations of all samples are in the milimolar range. Based on the number of components used, different columns of the Table 4 were considered, i.e., the first two columns of this table were used for the two components system, the first three columns for three components system and so on.

For each standard solution, the volume of titrant as the function of pH (in a 0.1 pH interval) was derived by using Equation (5). The starting pH value used was based on the initial pH of the standard solution, which had the highest value. The PLS regression was run on the calibration data set and the extracted data from this step were used to predict the concentration of acids in the prediction samples. Prediction residual error sum of squares (PRESS) was calculated from these data and the number of latent variables was selected based on Fisher's F-test.[2] Percent relative standard error (RSE)[14] for the prediction set and the correlation coefficient for prediction sets were calculated and used to evaluate the effect of variables defined previously on the prediction ability of the PLS model.

Results and discussion

In potentiometric titration methods, the selectivity arises from the difference between the shape of the titration curve and this is due to the difference in acidity constant of the components being titrated. Principally, if the difference between the pK_a of two acids is 3 or higher, distinct end points are observed. However, multivariate calibration methods can predict the end point of titration even if the ΔpK_a is lower than three.

It is reported that the concentration range in the calibration set and the type of mixture design also influence the results of multivariate calibration methods.[14] In order to neglect the effect of these variables, we used the same concentration matrix for all the systems studied. The concentrations are in the milimolar range. The compositions of calibration set mixtures were designed by five-level fractional factorial design[12,13] and the concentrations of prediction set standards were selected randomly. The concentration of aids used in the prediction set is shown in Table 4.

Table 4. Concentration of acids used in this study for the calibration and prediction sets.

Sample no.	Calibration set Concentrations (mM)				Prediction set Concentrations (mM)			
	acid 1	acid 2	acid 3	acid 4	acid 1	acid 2	acid 3	acid 4
1	5.0	5.0	5.0	5.0	9.5	0.6	8.4	5.0
2	5.0	1.0	2.5	1.0	2.3	3.5	0.2	9.0
3	1.0	2.5	1.0	10.0	6.1	8.1	6.8	8.2
4	2.5	1.0	10.0	10.0	4.8	0.1	3.8	6.4
5	1.0	10.0	10.0	5.0	8.9	1.4	8.3	8.2
6	1.0	1.0	5.0	2.5	7.6	2.0	5.0	6.6
7	1.0	5.0	2.5	10.0	4.6	2.0	7.1	3.4
8	5.0	2.5	10.0	2.5	0.2	6.0	4.3	2.9
9	2.5	10.0	2.5	7.5	8.2	2.7	3.0	3.4
10	10.0	2.5	7.5	7.5	4.5	2.0	1.9	5.3
11	2.5	7.5	7.5	5.0	6.1	0.2	1.9	7.3
12	7.5	7.5	5.0	10.0	7.9	7.5	6.8	3.1
13	7.5	5.0	10.0	7.5	9.2	4.4	3.0	8.4
14	5.0	10.0	7.5	10.0	7.4	9.3	5.4	5.7
15	10.0	7.5	10.0	1.0	1.8	4.7	1.5	3.7
16	7.5	10.0	1.0	1.0	4.1	4.2	7.0	7.0
17	10.0	1.0	1.0	5.0	9.3	8.5	3.8	5.5
18	1.0	1.0	5.0	7.5	9.2	5.2	8.6	4.4
19	1.0	5.0	7.5	1.0	4.1	2.0	8.5	6.9
20	5.0	7.5	10.0	7.5	8.9	6.7	5.9	6.2
21	7.5	1.0	7.5	2.5				
22	1.0	7.5	2.5	2.5				
23	7.5	1.0	2.5	5.0				
24	2.5	1.0	5.0	1.0				
25	2.5	5.0	1.0	2.5				

The results of application of PLS regression method on the pH-metric titration data of all the systems indicated in Tables 1-3 are summarized in Tables 5-7, respectively. The statistical values given in these Tables are the mean values over the number of acid components used in each Table (i.e., 2 acids in Table 5, 3 acids in Table 6 and 4 acids in Table 7). It must be noted that in almost all of the studied systems, the number of latent variables used in PLS modeling were greater than the number of components, and in the presence of added noise to the simulated data this number was increased. This means that the PLS method used more latent variables to extract useful information from the noisy data.

Table 5. The results of PLS regression for two-component systems.

System	Noise (%)	f	RSE (%)	r^2	System	Noise (%)	f	RSE (%)	r^2
Sys_{21}	0	3	0.25	1.0000	sys_{25}	0	3	1.60	0.9998
	1	4	1.84	0.9997		1	3	3.35	0.9992
	3	5	6.52	0.9982		3	4	6.69	0.9984
Sys_{22}	0	3	0.36	1.0000	sys_{26}	0	3	0.58	0.9999
	1	4	2.54	0.9991		1	4	2.37	0.9991
	3	6	8.52	0.9910		3	5	7.44	0.9982
Sys_{23}	0	2	1.30	0.9994	sys_{27}	0	3	0.91	0.9998
	1	3	3.04	0.9936		1	3	1.92	0.9991
	3	4	9.91	0.9910		3	4	4.22	0.9938
Sys_{24}	0	3	0.59	0.9999	sys_{28}	0	3	0.23	1.0000
	1	5	2.19	0.9984		1	5	3.24	0.9984
	3	6	5.48	0.9921		3	7	10.3	0.9826

Table 6. The results of PLS regression for three component system.

System	Noise (%)	f	RSE (%)	r^2	System	Noise (%)	f	RSE (%)	r^2
Sys_{31}	0	5	0.49	0.9999	sys_{35}	0	5	0.11	1.0000
	1	6	6.32	0.9962		1	5	0.77	0.9999
	3	7	10.2	0.9811		3	7	4.41	0.9994
Sys_{32}	0	4	0.56	0.9999	sys_{36}	0	4	0.57	0.9999
	1	5	3.27	0.9991		1	5	3.92	0.9978
	3	5	7.61	0.9916		3	7	8.65	0.9891
Sys_{33}	0	4	0.17	1.0000	sys_{37}	0	4	0.85	0.9996
	1	4	1.69	0.9998		1	6	10.5	0.9532
	3	6	5.61	0.9976		3	7	17.3	0.9024
Sys_{34}	0	5	0.18	1.0000	sys_{38}	0	5	0.14	1.0000
	1	5	0.52	0.9999		1	5	0.64	0.9999
	3	6	2.57	0.9987		3	5	1.74	0.9992

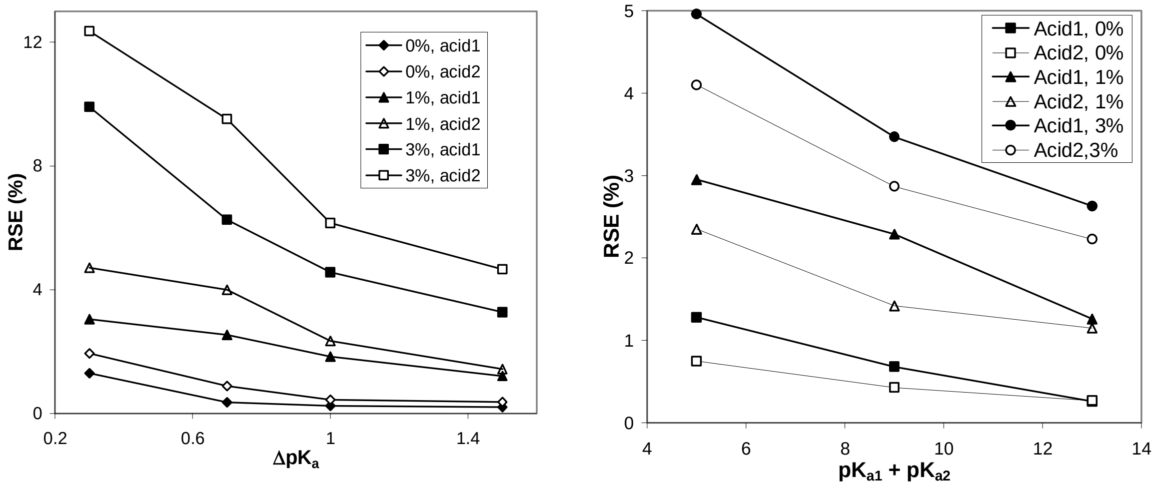
Two-component systems

Effect of relative acidity.

Table 1 represents the acidity constants (pK_a) of the acids employed and the corresponding results of PLS regression are given in Table 5. In systems sys_{21} and sys_{24}, the pK_a of one acid is 2.0 and those of the second one varied between 2.3-3.5. Figure 1a shows the plot of RSE against the difference in pK_a of the two acids studied (ΔpK_a). The error decreases when the ΔpK_a increases from 0.3 to 1.0. Meanwhile, further increase in ΔpK_a (upto 1.5) causes no significant improvement in the results.

Table 7. The result of PLS regression for four components system.

System	Noise (%)	F	RSE (%)	r^2	System	Noise (%)	f	RSE (%)	r^2
Sys_{41}	0	6	1.20	0.9998	sys_{45}	0	6	0.28	1.0000
	1	7	10.8	0.9768		1	7	3.84	0.9991
Sys_{42}	0	7	1.20	0.9995		3	8	8.69	0.9872
	1	8	5.42	0.9946	sys_{46}	0	5	0.93	0.9999
Sys_{43}	0	6	0.31	1.0000		1	5	3.41	0.9973
	1	7	0.82	0.9997		3	6	6.80	0.9904
	3	7	3.46	0.9991	sys_{47}	0	6	0.32	1.0000
Sys_{44}	0	5	0.50	1.0000		1	6	2.21	0.9991
	1	5	0.73	0.9998		3	7	6.90	0.9872
	3	6	4.48	0.9984	sys_{48}	0	6	0.25	1.0000
						1	6	2.65	0.9991
						3	7	5.61	0.9877



a b

Figure 1. Variation of RSE vs. ΔpK_a (a) and total acidity (b) for acids employed in two component systems using noise free data and data in the presence of one and three percent added noise.

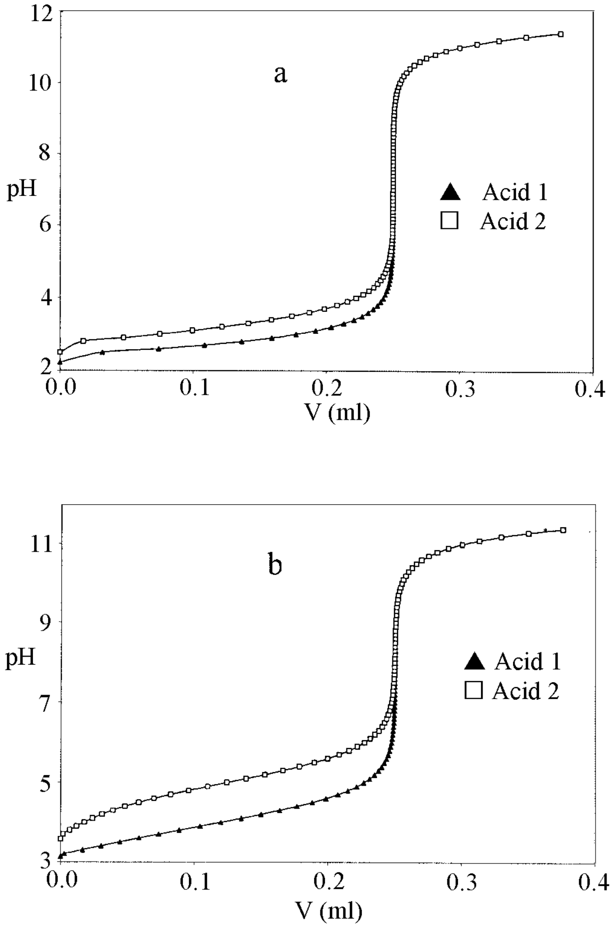


Figure 2. Theoretical curves for titration of 25 ml of 0.005 M individual acids with pK_as indicated in sys_{21} (a) and sys_{25} (b) with a 0.5 M solution of a strong base.

The total acidity of the components (i.e. $pK_{a1}+pK_{a2}$) was also found to influence the results of PLS method. The results are shown In Figure 1b. Here, the RSE is plotted vs. the total acidity when ΔpK_a is fixed at 1.0. As is obvious, the RSE decreases when the acids studied become weaker. This is due to the dependence of the shape of titration curve on the acidity strength of the acids. The shape of titration curves of two weak acids is more different from those of two strong acids. For example, the titration curves for the acids sys_{21} and sys_{25} in Table 1 are shown in Figures 2a and 2b, respectively. The difference in the shape of titration curves, especially at the beginning of the titration, for weaker acids causes the orthogonality between the signals of analytes to be increased and, therefore, the RSE becomes lower when the acids are weaker. The effect of total acidity on the RSE is influenced by the ΔpK_a of the acids used. It was found that the influence of total acidity RSE is larger when the ΔpK_a is smaller.

Effect of noise.

The effect of added root mean square noise (at 1 and 3 percent) on the resulting RSE values was investigated. Figure 1a shows the variation of RSE vs. ΔpK_a in the presence of noise. When the difference between the acidity of components increased, the effect of noise on the RSE is lowered. A 1% noise does not influence the model performance significantly when ΔpK_a is between 0.3-1.5. However, in the presence of 3% noise, the RSE becomes greater significantly when ΔpK_a is 0.7 or lower, while relatively better results is obtained at $\Delta pK_a > 1$.

The effect of noise on the plots of RSE vs. acidity are shown in Figure 2b. As is obvious, the effect of noise becomes more significant when total acidity decreased. This observation my also be related to the lesser selectivity when acids become stronger.

Three-component systems

Effect of relative acidity.

Table 2 represents the acidity constant (pK_a) of the acids used in three-component systems and the corresponding results of PLS regression are summarized in Table 6. Figure 3a are shown the variation of RSE vs. ΔpK_a for the systems sys_{32} and sys_{35} in which the acidity of the strongest acid (i.e., acid) is 2 and 5, respectively. As expected, the RSE decreases by increasing the ΔpK_a. Moreover, the errors are lower when the acidity of the strongest acid is 5 rather than 2. The prediction ability of the model for the acid number two (the acid with mildest acidity in each system) is lower than others especially, at smaller ΔpK_a values. In the case of weaker acids system, when ΔpK_a value is 1.0 or greater the results of PLS modeling for all acids are going to be close to each other.

The effect of total acidity on the prediction ability of the PLS on the three-component system is represented in Figure 3b. For all the acids, the errors become smaller when the total acidity decreased. This behavior is more considerable for acid number 2 (the acid with mildest acidity). It should be noted that this acid is titrated after the stronger acid (acid 1) and before the weaker ones (acid 3). Thus, its titration curve overlapped with those of the two other acids and this fact lowers the selectivity of the signal of this acid. However, if the acids used in a three component system are weak, the orthogonality between their titration curves increases and more selective signals are obtained.

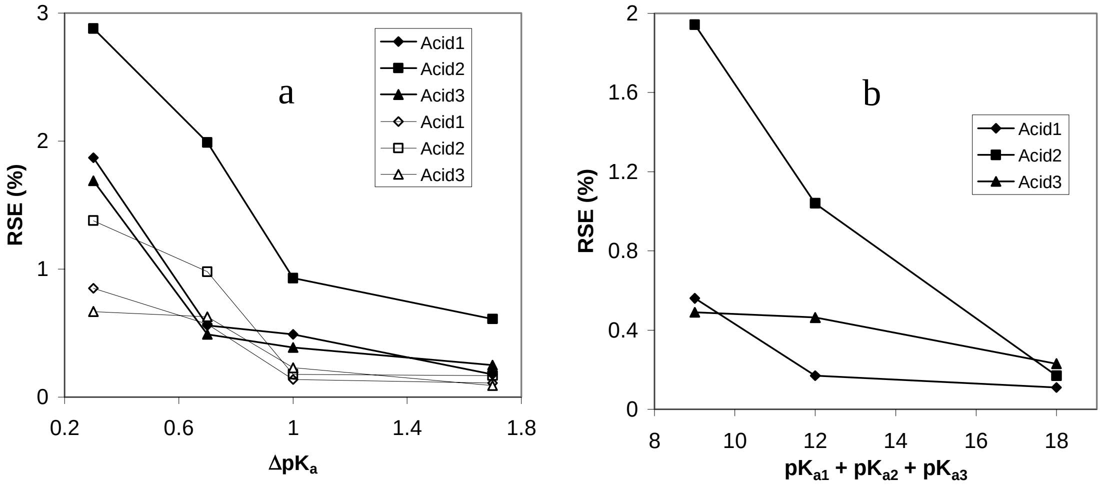


Figure 3. (a) Variation of RSE against ΔpK_a for acids 1 and 2 of the three component systems when the pK_a of the strongest acid is 2 (solid markers) and 5 (open markers). (b) Variation of RSE against total acidity when ΔpK_a is 1.

Effect of noise.

The influence of noise in the systems three component found to be stronger than that of the two-component systems. The plots of variation of RSE against the added noise for different cases are plotted in Figure 4. In this figure, only the results for acids number one and two are plotted. The result for the third one is relatively the same as acid number one. Figure 4a shows the results when the systems studied contain stronger acids (i.e., pK_a of the strongest acid is 2.0) while Figure 4b is representative for the systems containing weaker acids (i.e., pK_a of the strongest acid is 5). For the systems shown in Figure 4a, the prediction errors become very large in the presence of noise when ΔpK_a is 0.3 and, thus, the results are not included in this Figure. Increasing the ΔpK_a to 0.7 and 1.0 causes the error for acid number one to decrease to an acceptable value in the presence of 1% noise. However, the resulted error for acid number two is still high. Meanwhile, no good results obtained in the presence of 3% noise for both acids. However, when ΔpK_a increases to 1.7, an excellent result for acid one and a good result for acid two are obtained in the presence of 1% noise, and even in the presence of 3% noise, a very good result is obtained for acid number one and the result for acid number 2 is acceptable.

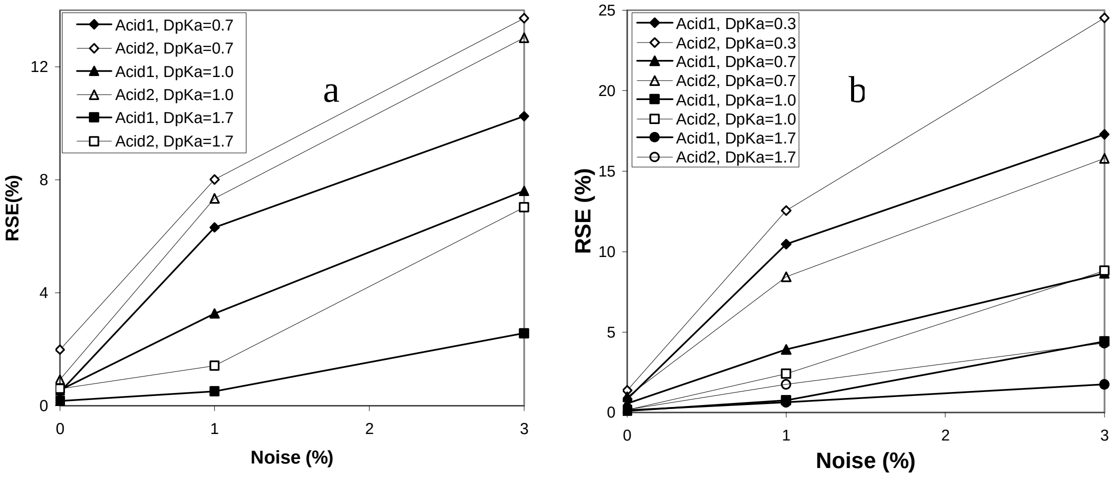


Figure 4. Plots of RSE vs. added noise for acids 1 and 2 of three component systems for cases where total acidity is high (i.e., pK_a of the strongest acid is 2) (a) and total acidity is low (i.e., pK_a of the strongest acid is 5) (b).

Figure 4b show the results when the systems studied contain weak acids (i.e., pK_a of strongest acid is 5.0). The errors obtained in this case are lower than that found for the systems discussed in the previous paragraph. As seen, the RSE is too high in the presence of noise when ΔpK_a is 0.3 while except the RES for acid number one is acceptable when noise is 1%. However, increasing ΔpK_a to 0.7, causes a good result for acid number one and an acceptable result for acid number two in the presence of 1% noise, while an acceptable result is obtained for acid number one if 3% noise is added to the data. If the difference between acidity constants increases to 1.0, very good results are obtained for both acids in the presence of 1% noise. Meanwhile, the results obtained in the presence of 3% noise is good for acid number one and acceptable for acid number two. Finally, The ΔpK_a of 1.7 is sufficient enough to give excellent results in the presence of 1% noise and very good results when noise is 3%. Thus, it can be concluded that the three acids can be determined simultaneously by application of PLS using the pH-metric titration data, if the difference between the acidity of components are at least 1.7, even if 3% noise is present in the experimental data.

Four-component systems

Effect of relative acidity.

Table 3 represents the acidity constant (pK_a) of the acids used in four-component systems and the corresponding results of PLS regression are given in Table 7. Since the systems become complicated when the number of components is four, higher prediction errors are expected for these systems. As shown in Table 7, even for noise-free data the resulting RSE are greater than those obtained for two or three components systems and, in some cases the RSE is greater than 10%, especially when ΔpK_a is small.

Figure 5a shows the variation of the RSE vs. ΔpK_a for the cases in which pK_a of the strongest acid is 2.0. In most cases, a gradual decrease in RSE is observed with increasing ΔpK_a of the system. The errors associated with acids number one and two are higher than those of acids number three and four, when ΔpK_a is 0.7 or lower. However, when ΔpK_a increases to 1.0 or greater, the errors due to acids two and three become greater than those for acids 1 and 4. These variations are shown in Figure 6. Acids number one and two are stronger than two other acids and, thus, their titration curves are more similar to each other specially when the difference between their acidity is low. Hence, higher prediction errors are expected for these acids at small ΔpK_a values. At high ΔpK_a values, similarity between the titration curves decreased and, hence, the degree of overlapping between titration curves becomes important. Thus, the errors due acids number two and three which their titration curves overlap with each other and with those of acid number one and four receptively, predicted less accurately.

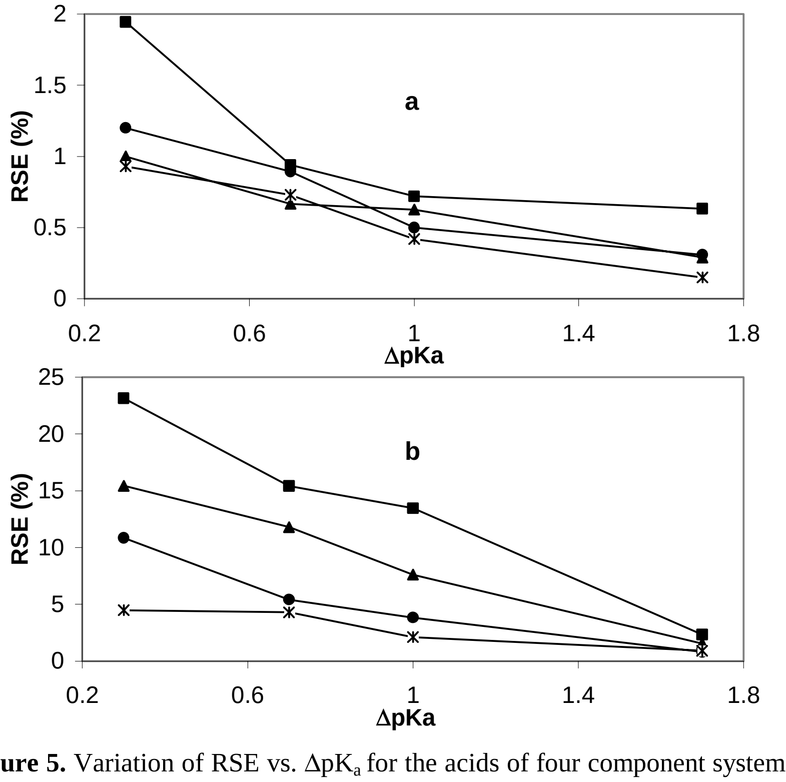


Figure 5. Variation of RSE vs. ΔpK_a for the acids of four component systems for noise free data (a) and in the presence of 1% added noise (b).

Effect of noise.

Because of the complexity of the data in the case of four components systems, the noise has considerable effects on the results of PLS regression for such systems. For some of the systems indicated in Table 3, the concentration of acids could not be predicted in the presence of 3% noise (Table 7). Only for sys$_{44}$ and sys$_{45}$, with ΔpK_a values of 1.7, good results are obtained in the presence of 3% noise.

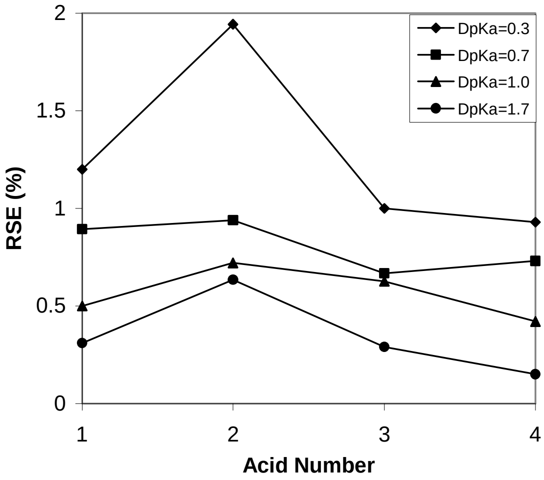


Figure 6. Plots of RSE against acid number for quaternary mixtures when ΔpK_a is 1 and pK_a of the strongest acid is 2.

While in cases the sys$_{43}$, sys$_{47}$ and sys$_{48}$, which ΔpK_a values of 1.0, only for acids number one and four good results are obtained in the presence of 3% noise. The variations of RSE against ΔpK_a in the presence of 1% noise are shown in Figure 5b. As expected, the RSE decreases by increasing ΔpK_a. The errors due to acids number two and three are greater than those of acids number one and four, in all cases. Meanwhile, by increasing the ΔpK_a, the errors of acids are going to be close to each other. Thus, it can be concluded that when ΔpK_a is 1.7 or greater, the concentration of acids in quaternary mixtures can be predicted with good accuracy in the presence of 3% noise and, of course, better results are obtained when the noise become 1%.

Conclusions

A systematic study has been conducted on the influences of factors that affect the prediction ability of the PLS method applied to the pH-metric titration of mixtures of weak acids by a strong base. The results indicated that, by using the noise-free data, the prediction of the concentration of acids can be done accurately even if the difference between the acidity constants of the acids being titrated is 0.3. While, by increasing the number of unknown components in the titration mixtures, the error becomes higher. It was found that the total acidity of the acid mixtures (i.e., sum of acidity constants of acids) rather than their relative acidity is another factor that controls the prediction ability of the model. If the acids being titrated become weaker, the resulted errors will decrease. Incorporation of noise into the simulated data caused a decreased performance of the model. In the presence of noise, a high value of ΔpK_a is required. For two-component mixtures, the 1% noise did not show a significant effect on the results, and 3% noise destroyed the model performance when ΔpK_a was 0.7 or lower. Simultaneous determination of acids in ternary and quaternary mixtures in the presence of 3% noise is achievable only if ΔpK_a is 1.7 or larger.

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Povzetek

Opravili smo sistematično raziskavo vplivov različnih dejavnikov, kot so relativna kislost, število sestavin ter dodani šum, na hkratno določitev vsebnoti šibkih kislin z multivariantno pH-metrično titracijo. V ta namen smo za interpretacijo simuliranih titrimetričnih podatkov uporabili regresijsko metodo delnih najmanjših kvadratov (PLS). Raziskali smo veliko število različnih mešanic kislin. Opredelili smo vpliv dodanega šuma na napovedne zmožnosti PLS regresije.