Turkish Journal of Chemistry

Volume 30 | Number 5 Article 9

1-1-2006

Prediction of Acidity Constants of Thiazolidine-4-carboxylic Acid Derivatives Using Ab Initio and Genetic Algorithm-partial Least Squares

ALI NIAZI

SAEED JAMEH BOZORGHI

DAVOOD NORI SHARGH

Turk J Chem
30 (2006) , 619 – 628.

Prediction of Acidity Constants of Thiazolidine-4-carboxylic Acid Derivatives Using Ab Initio and Genetic Algorithm-Partial Least Squares

Ali NIAZI*, Saeed JAMEH BOZORGHI and Davood NORI SHARGH
Department of Chemistry, Faculty of Sciences, Azad University of Arak, Arak-IRAN
e-mail ali.niazi@gmail.com

Received 07.04.2006

A quantitative structure-property relationship study is suggested for the prediction of the acidity constants of some thiazolidine-4-carboxylic acid derivatives in aqueous solution. Ab initio theory was used to calculate some quantum chemical descriptors, including electrostatic potentials and local charges at each atom, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, etc. Modeling of the acidity constant of thiazolidine-4-carboxylic acid derivatives as a function of molecular structures was established by means of the partial least squares algorithm. The subset of descriptors, which resulted in a low prediction error, was selected by genetic algorithm. This model was applied for the prediction of the acidity constant of some thiazolidine-4-carboxylic acid derivatives, which were not in the modeling procedure. Relative errors of prediction lower than 1.5% were obtained by using the genetic algorithm-partial least squares (GA-PLS) method. The developed model has good prediction ability with a root mean square error of prediction of 0.0419 and 0.1013 for PLS and GA-PLS models, respectively.

Key Words: Ab initio, partial least squares, genetic algorithm, acidity constant, thiazolidine-4-carboxylic acid.

Introduction

Acidity constants can be a key parameter for understanding and quantifying chemical phenomena, such as reaction rates, biological activity, biological uptake, biological transport, and environmental fate.[1] It has been shown that acid-base properties affect the toxicity[2], chromatographic retention behavior,[3] and pharmaceutical properties[4] of organic acids and bases. Much of the theoretical foundation of modern organic chemistry is based on the observation of the effects on acid-base equilibrium of changing molecular structure.[5]

A successful strategy for the prediction of the acidity constant is the construction of quantitative structure-activity relationships (QSARs).[6] QSARs are mathematical equations relating chemical structure to a wide variety of physical, chemical, biological and technological properties. QSAR models can be used

*Corresponding author

to predict properties of compounds as yet unmeasured or even unknown. Thus, the QSAR approach saves resources and expedites the process of development of new molecules.[7]

A major step in constructing QSAR models is finding one or more molecular descriptors that represent variation in the structural property of the molecules by a number. A wide variety of descriptors have been reported to be used in QSAR analysis.[8−10] Recent progress in computational hardware and the development of efficient algorithms have assisted the routine development of molecular quantum chemical calculations. Quantum chemical calculations are thus an attractive source of new molecular descriptors, which can, in principle, express all of the electronic and geometric properties of molecules and their interactions.[11] Atomic charges, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, molecular polarizability, dipole moments, and energies of molecule are examples of quantum chemical descriptors used in QSAR studies.

Multiple linear regression (MLR) is commonly used in QSAR modeling.[12] The co-linearity problem of the MLR method has been overcome through the development of the partial least squares (PLS) method, which plays an important role in QSAR analysis.[13,14] PLS is a factor analysis-based method that was originally suggested and chemically applied by Wold et al.[14] We have recently reported the application of PLS modeling in spectrophotometric multivariate calibration.[15−22] PLS is used in conjunction with optimization techniques for feature selection.[23] It has already been shown that genetic algorithms (GAs)[24−30] can be successfully used as a feature selection technique.[31−35]

A GA is a stochastic method to solve optimization problems defined by a fitness criterion applying the evolution hypothesis of Darwin and different genetic functions, i.e. crossover and mutation.[30] Leardi et al.[30] demonstrated that GAs, after suitable modifications, produce more interpretable results, since the selected variables are less dispersed than in other methods.

Thiazolidine-4-carboxylic acid derivatives, as the largest group of 2-substituted thiazolidine-4-carboxylic acids, are important, both in biochemistry and pharmacology. The attractivity and biological activity of thiazolidines in biochemistry and pharmacology is evident.[36−38] In 1999, Butvin et al.[38] studied the acidity constant of thiazolidine-4-carboxylic acid derivatives in aqueous solution. In the present paper, the GA-PLS method was applied in QSAR for modeling the relationship between the acidity constant of 23 thiazolidine-4-carboxylic acid derivatives. Ab initio geometry optimization was performed at the B3LYP level, with a known basis set, 6-31^{++}G**. Local charges, dipole moment, polarizability, HOMO-LUMO energies, electrostatic potential on each atom, hardness, softness, electronegativity, and electrophilicity were calculated for each compound. A GA-PLS was used to model the relationship that existed between the selected descriptors and the acidity constant.

Materials and Methods

Hardware and software

The computations were made with an AMD 2000 XP (512 Mb RAM) microcomputer with the Windows XP operating system. All programs needed for GA variable selection and PLS modeling were written in MATLAB (version 6.5, MathWork, Inc.). The source code of the program is available from the authors upon request. Hyperchem (version 6.03, Hypercube, Inc.) and Gaussian 98 software[39] were used for geometric optimization of the molecules and calculation of the quantum chemical descriptors.

Acidity constant and descriptor generation

Butvin et al.[38] previously reported the acidity constant values of several 2-substituted thiazolidine-4-carboxylic acid derivatives in aqueous solution. These data are included in Table 1. Here, we used these data for the development of a QSAR on acidity constant. The molecular structures of all the thiazolidine-4-carboxylic acid derivatives were built with Hyperchem software for structural chemistry. Gaussian 98[39] was operated to optimize with the 6-31^{++}G** basis set for all atoms at the B3LYP level.[40,41] No molecular symmetry constraint was applied; instead, full optimization of all bond lengths and angles was carried out at the B3LYP/6-31^{++}G**level. The calculated descriptors for each molecule are summarized in Table 2. Local charges (LC) and electrostatic potential (EP)[42] at each atom, HOMO and LUMO energies, molecular polarizabilities (MP), and molecular dipole moment (MDP) were calculated by Gaussian 98. Quantum chemical indices of hardness (η), softness (S), electronegativity (χ), chemical potential (μ), and electrophilicity (ω) were calculated according to the method proposed by Thanikaivelan et al.[43]

Table 1. Acidity constant for different thiazolidine-2-carboxylic acid derivatives in aqueous solution (Experimental), the corresponding values calculated by PLS and GA-PLS methods (Predicted), and percent relative error (% RE).

			PLS (Run a)		GA-PLS (Run b)	
Compounds	Substituent	pK_a[38] (Exp.)	Predicted	% RE	Predicted	% RE
A1	H	6.19^t	6.26	1.13	6.20	0.16
A2	Methyl	6.17^p	6.25	1.30	6.20	0.49
A3	Dimethyl	5.86^t	5.75	-1.88	5.82	-0.68
A4	Ethyl-methyl	5.73^p	5.64	-1.57	5.68	-0.87
A5	Propyl	6.12^t	6.18	0.98	6.16	0.65
A6	Carboxyl	5.86^t	5.90	0.68	5.87	0.17
A7	Butyl	6.08^t	5.91	-2.80	6.05	-0.49
A8	Isobutyl	6.10^t	6.23	2.13	6.12	0.33
A9	Hexyl	5.94^p	5.89	-0.84	5.98	0.67
A10	Phenyl	5.31^t	5.24	-1.32	5.33	0.38
A11	Tolyl	5.50^t	5.61	2.00	5.48	-0.36
A12	2-Hydroxyphenyl	5.67^p	5.62	-0.88	5.70	0.53
A13	4-Hydroxyphenyl	5.51^t	5.68	3.09	5.56	0.91
A14	Styryl	5.35^t	5.25	-1.87	5.32	-0.56
A15	4-Metthoxyphenyl	5.80^p	5.64	-2.76	5.75	-0.86
A16	2-Chlorophenyl	4.95^p	5.10	3.03	4.91	-0.81
A17	4-Chlorophenyl	5.24^t	5.09	-2.86	5.19	-0.95
A18	4-Dimethylaminophenyl	5.83^t	5.76	-1.20	5.80	-0.51
A19	4-Carboxyphenyl	5.01^p	4.92	-1.80	4.96	-1.00
A20	3-Nitrophenyl	4.70^t	4.79	1.91	4.63	-1.49
A21	2-Hydroxy-3-methoxyphenyl	5.39^t	5.31	-1.48	5.35	-0.74
A22	5-Bromo-2-hydroxyphenyl	5.53^p	5.45	-1.45	5.49	-0.72
A23	1,4-Phenylenebis	5.17^t	5.11	-1.16	5.11	-1.16

t, the data used in the training set; p, the data used in the prediction set.

Data processing

The acidity constants of 23 specified thiazolidine-4-carboxylic acid derivatives were randomly classified into a training set (15 acidity constants data) and a prediction set (8 acidity constants data). The data were

centered to zero means and scaled to the unit variance. The GA was used to select the set of descriptors, which resulted in the best PLS model. The GA applied in this paper is an evolution of the algorithm described by Leardi[33]and uses a binary representation as the coding technique for the given problem; the presence or absence of a descriptor in a chromosome is coded by 1 or 0.[32,33]

Table 2. The calculated quantum chemical descriptors used in this study.

Descriptor name	Notation	Description
Local charges	LC_i	The local charges at each atom of the base unit of thiazolidine-2-carboxylic acids
Electrostatic potential	EP_i	The electrostatic potential at each atom of the base unit of thiazolidine-2-carboxylic acids
Molecular polarizability	MP	Total molecular polarizability
Dipole moment	DM	Total molecular dipole moment
HOMO	E_{HOMO}	Highest occupied molecular orbital energy
LUMO	E_{LUMO}	Lowest unoccupied molecular orbital energy
Electronegativity	χ	–0.5 (E_{HOMO}– E_{LUMO})
Hardness	η	0.5 (E_{HOMO} + E_{LUMO})
Softness	S	$1/\eta$
Electrophilicity	ω	$\chi^2/2\eta$

Regression methods

MLR modeling

The program used for MLR analysis was written in MATLAB. At the beginning, the correlations of each of the descriptors employed with pK_a values were examined. Meanwhile, the correlations of the remaining descriptors to each other were investigated, and those pairs with collinear relationships were determined. Finally, the remaining descriptors were used to construct the MLR model, in accordance with the forward selection method.[12]

PLS modeling

PLS is a method for building regression models on the latent variable decomposition, relating 2 blocks, matrices **X** and **Y**, which contain the independent, x, and dependent, y, variables, respectively. These matrices can be simultaneously decomposed into a sum of f latent variables, as follows:

$$X = TP^T + E = \sum t_f p_f^{'} + E \tag{1}$$

$$Y = UQ^T + F = \sum u_f q_f^{'} + F \tag{2}$$

in which T and U are the score matrices for X and Y, respectively, $P$and Q are the loadings matrices for X and Y, respectively, and E and F are the residual matrices. The 2 matrices are correlated by the scores T and U, for each latent variable, as follows:

$$u_f = b_f t_f \tag{3}$$

in which b_f is the regression coefficient for the $f$latent variable. The matrix Y can be calculated fromu_f, as Eq. (4), and the acidity constants of the new samples can be estimated from the new scores T^*, which are substituted in Eq. (4), leading to Eq. (5):

$$Y = TBQ^T + F \tag{4}$$

$$Y_{new} = T^*BQT \tag{5}$$

In this procedure, it is necessary to find the best number of latent variables, which normally is performed by using cross-validation based on determination of the minimum prediction error. Applications of PLS have been discussed by several researchers.[14−22]

Results and Discussion

The molecular structures of the 2-substituted thiazolidine-4-carboxylic acid derivatives are shown in Figure 1 and their acidity constants are represented in Table 1. The acidity constant values of these compounds vary between 4.70 and 6.19, as –R and –R' groups at the C_2 position of the thiazolidine-2-carboxylic acids changes. The PLS model was run twice. In the first run (run a), all calculated descriptors were considered in modeling, while in the second run (run b), after selection of descriptors by the GA, only the selected descriptors were considered in the modeling procedure.

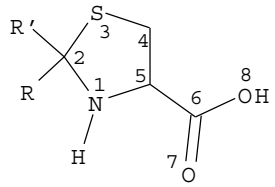

Figure 1. Structure of thiazolidine-4-carboxylic acids, in which R=R'=H is A1, R=CH_3 and R' = methyl radical is (A3), R=CH_3 and R'= ethyl radical is (A4), and in all other cases R=H and R' is alkyl or aryl substituent (Table 1).

Selection of descriptors using genetic algorithms

In order to select the most effective descriptors, the evolution of the population was simulated. Each individual of the population defined by a chromosome of binary values represented a subset of descriptors. The number of genes at each chromosome was equal to the number of descriptors (i.e. 13 local charges and 13 electrostatic potentials at each atom of the base unit of thiazolidine-2-carboxylic acids (Figure 1) and 8 descriptors, including molecular polarizability, HOMO and LUMO energies, electrophilicity, electronegativity, chemical potential, softness, and hardness). A gene took a value of one if its corresponding descriptor was included in the subset; otherwise, it took a value of zero. The population of the first generation was selected randomly. The parameters of the GAs used in this study were as follows: probability of mutation 1% and 90% for crossover; 100 runs; window size for smoothing was 3.

MLR analysis

Among the descriptors mentioned in Table 2, the most significant molecular descriptors were identified using MLR analysis with a stepwise forward selection method. The best equation obtained for the acidity constant of thiazolidine-2-carboxylic acids was:

$$\mathrm{p}K_a = 48.62 + 14.23\mathrm{LC5} + 8.23\mathrm{EP6} + 3.21\mathrm{EP8} + 1.02\mathrm{MP} + 0.86\mathrm{DM} + 0.21\chi + 0.16S$$

where LC5, EP6, EP8, MP, DM, χ, and S are the local charge on carbon atom C_5, electrostatic potentials on carbon atom C_6 and oxygen atom O_8, molecular polarizability, dipole moment, softness, and electronegativity, respectively. In this model, the highly correlated descriptors were not considered. As seen, the resulting model has 7 significant descriptors. Table 3 shows the descriptors' coefficients, the standard error of coefficients, the t values for the null hypothesis, and their related P values.

Table 3. Results of multiple linear regression analysis.

Descriptor	Coefficient	Standard error of coefficient	t value	P value
Intercept	48.62	2.89	10.23	0.0001
LC5	14.23	2.06	4.56	0.0001
EP6	8.23	2.23	3.28	0.001
EP8	3.21	1.44	2.14	0.001
MP	1.02	0.75	5.65	0.021
DM	0.86	0.46	8.74	0.001
χ	0.21	0.09	2.36	0.0001
S	0.16	0.03	2.55	0.0001

PLS modeling

Only the selected descriptors were considered in the modeling procedure. Local charges (LC5), electrostatic potential (EP2, EP6, and EP8), MP, DM,χ, and S were selected by GAs and used in PLS modeling. These descriptors were the effective parameters in determining the acidity constant of the studied thiazolidine-2-carboxylic acid derivatives.

The optimum number of factors (latent variables) to be included in the calibration model was determined by computing the prediction error sum of squares (PRESS) for cross-validated models using a high number of factors (half the number of the total standard +1), which is defined as follows:

$$PRESS = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \tag{6}$$

where y_i is the reference acidity constant for the ith compound and $\hat{y}_i$ represents the estimated acidity constant. The cross-validation method employed was to eliminate only one compound at a time and then PLS calibrated the remaining standard spectra. The acidity constants of the left-out sample were predicted by using this calibration. This process was repeated until each compound in the training set had been left out once.

One reasonable choice for the optimum number of factors would be the number that yielded the minimum PRESS. Since there are a finite number of compounds in the training set, in many cases, the minimum PRESS value causes overfitting for unknown acidity constants of compounds that were not included

in the model. A solution to this problem has been suggested by Haaland et al.[44] in which the PRESS values for all previous factors are compared to the PRESS value at the minimum. The F-statistical test can be used to determine the significance of PRESS values greater than the minimum. The maximum number of factors used to calculate the optimum PRESS was 8. In all instances, the number of factors for the first PRESS values whose F-ratio probability dropped below 0.75 was selected as the optimum. In Figure 2, the PRESS obtained by optimizing the training set of the descriptor data with PLS and GA-PLS models is shown; however, modeling of all descriptors by PLS requires an increased number of factors. The optimal number of factors for this data by PLS and GA-PLS models was 3 and 2, respectively. PRESS values were 0.1231 and 0.0345, using PLS and GA-PLS models, respectively.

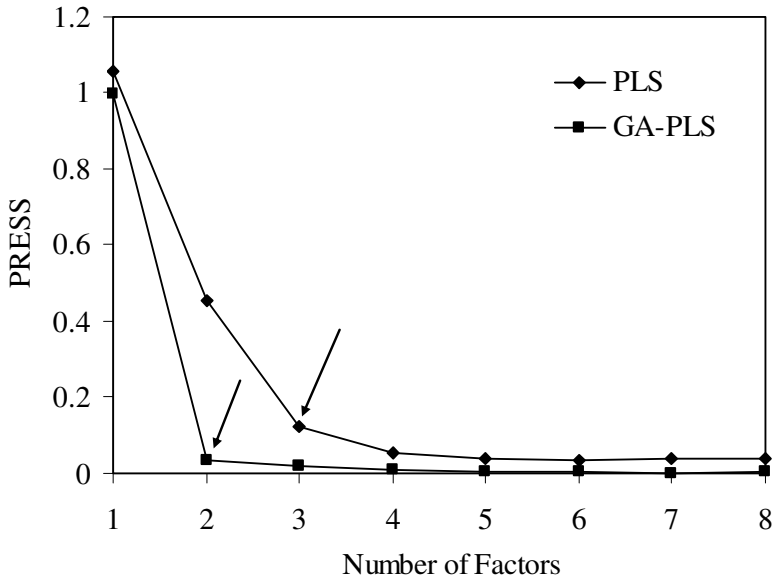

Figure 2. Variation of PRESS against number of factors obtained by the PLS and GA-PLS models.

In Table 1, the predicted values of pK_a obtained by the PLS and GA-PLS methods and the percent relative errors of prediction are presented. The plots of predicted pK_a versus experimental pK_a obtained by PLS and GA-PLS models are shown in Figure 3 (line equations and R^2 values are also shown). An agreement is observed between the predicted acidity constant and experimental values. The relative errors of prediction lower than 1.5% were obtained by using the GA-PLS method. The present study shows that the GA can be a good method for descriptor selection in QSAR studies. The results obtained on the data set of acidity constants demonstrate that the predictive ability of the models obtained with the descriptors selected by the GA is very often much better.

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) can be used:[24]

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n} (y_{pred} - y_{obs})^2}{n}} \tag{7}$$

where y_{pred} is the predicted acidity constant, y_{obs} is the experimental value of the acidity constant, and n is the number of data in the prediction set. The RMSEP for this data set by PLS and GA-PLS was 0.1013 and 0.0419, respectively.

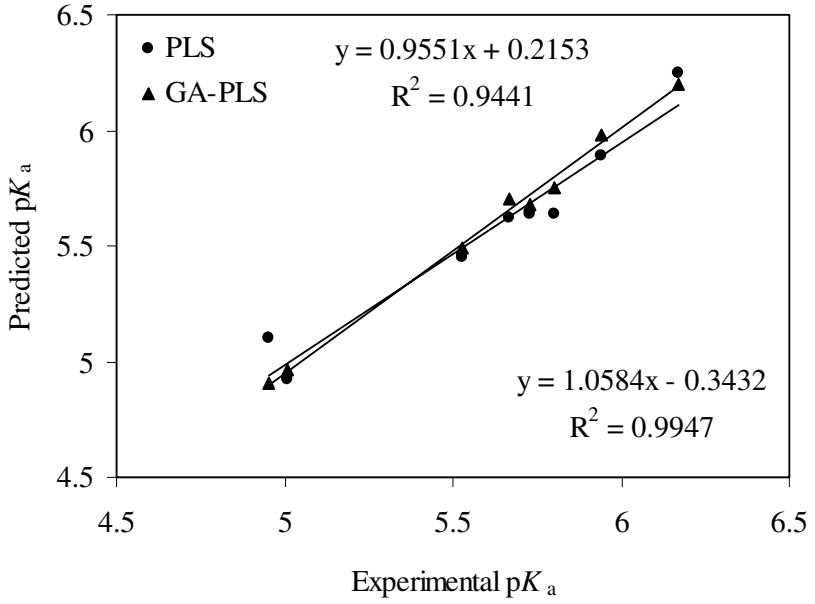

Figure 3. Plot of predicted pK_a estimated by PLS and GA-PLS modeling versus experimental pK_a, for thiazolidine-2-carboxylic acid derivatives.

Effective descriptors

Different quantum chemical descriptors were used in this study. Some of them were related to the properties of individual atoms in the basic structure of the thiazolidine-2-carboxylic acid derivatives (i.e. local charges and electrostatic potentials). It should be noted that the atomic properties of –R and –R' groups were not considered. Other calculated quantum chemical descriptors were related to the entire molecular structure of the thiazolidine-2-carboxylic acid derivatives (i.e. HOMO and LUMO energies, electronegativity, electrophilicity, hardness, softness, dipole moment, and polarizability).

The GA was used to select the most informative descriptors among the pool of the quantum chemical descriptors. In order to have a small subset of descriptors in the final models, the number of genes with a value of one was kept lower than genes with a value of zero. Among the descriptors relating to the atomic properties, the population of electrostatic potential was more than that of local charges. According to the selected descriptors, the electrostatic potentials of the C_2, C_5, C_6, and O_8 atoms were used in run b. As shown in Figure 1, these atoms are near the deprotonation site and the site substitution. According to the results, the electrostatic potential is more effective than local charges. This indicates the superiority of electrostatic potential for use in QSAR studies. Although GA did not select HOMO and LUMO energies for the modeling by PLS, it selected some combinations of these quantum chemical descriptors, such as electrophilicity, electronegativity, hardness, and softness. This fact is in direct agreement with the previous report.[9]

Conclusion

A GA-PLS model was established to predict the acidity constants of some thiazolidine-2-carboxylic acid derivatives in aqueous solution. A suitable model with high statistical quality and low prediction errors was

obtained. The model can accurately predict acidity constants of thiazolidine-2-carboxylic acid derivatives that do not exist in the modeling procedure. The quantum chemical descriptors concerning all the molecular properties and those of individual atoms in the molecule were found to be important factors controlling acidity behavior. It was found that the atoms near the deprotonation center and the site of substitution affected the acidity of the studied thiazolidine-2-carboxylic acids. Moreover, in this study, the electrostatic potential was more informative than the local charge.

References

1. D. Kara and M. Alkan, **Spectrochim. Acta Part A**, **56**, 2753 (2000).
2. Y.H. Zhao, L.H. Yuan and L.S. Wang, **Bull. Environ. Contam. Toxicol. 57**, 242 (1996).
3. P. Alines, **J. Planar Chromatogr. Mod. TLC, 9**, 52 (1996).
4. G.H. Rochester, **Acidity Functions,** Academic Press, New York, 1971.
5. L.P. Hammet, **Physical Organic Chemistry,** McGraw-Hill, New York, 1940.
6. V. Tantishaiyakul, **J. Pharm. Biomed. Anal. 37**, 411 (2005).
7. A.R. Katrizky, R. Petrukhin and D. Tatham, **J. Chem. Inf. Comput. Sci. 41**, 679 (2001).
8. R. Todeschini and V. Consonni, **Handbook of Molecular Descriptors,** Wiley-VCH, Weinheim, (Germany), 2000.
9. V. Consonni, R. Todeschinni, M. Pavan and P. Gramatica, **J. Chem. Inf. Comput. Sci. 42**, 693 (2002).
10. G. Krenke, E.A. Castro and A.A. Toropov, **J. Mol. Struct. (Theochem) 542**, 107 (2001).
11. R. Carbo-Dorca, L. Amat, E. Besalu, X. Girone's and D. Robert, **J. Mol. Struct. (Theochem) 504**, 181 (2001).
12. D.C. Montgomery and E.A. Peck, **Introduction to Linear Regression Analysis,** John Wiley, New York, 1982.
13. H.J.M. Verhaar, E.V. Ramos and J.L.M. Hermens, **J. Chemometr. 10**, 149 (1996).
14. K.G. Joreskog and H. Wold, **System Under Indirect Observations,** North Holland, Amsterdam, 1982.
15. J. Ghasemi and A. Niazi, **Microchem. J. 68**, 1 (2001).
16. J. Ghasemi, A. Niazi and A. Safavi, **Anal. Lett. 34**, 1389 (2001).
17. J. Ghasemi, R. Amini and A. Niazi, **Anal. Lett. 35**, 533 (2002).
18. J. Ghasemi and A. Niazi, **Talanta 65**, 1168 (2005).
19. J. Ghasemi and A. Niazi, **Anal. Chim. Acta 533**, 169 (2005).
20. A. Niazi, J. Ghasemi and A. Yazdanipour, **Anal. Lett. 38**, 2377 (2005).
21. J. Ghasemi, A. Nikrahi and A. Niazi, **Turk. J. Chem. 29**, 669 (2005).
22. A. Niazi and M. Sadeghi, **Chem. Pharm. Bull. 54**, (2006).
23. F. Ros, M. Pintore and J.R. Chretien, **Chemometr. Intell. Lab. Syst. 63**, 15 (2002).
24. M.J. Arcos, M.C. Ortiz, B. Villahoz and L.A. Sarbia, **Anal. Chim. Acta 339**, 63 (1997).
25. U. Depczynski, V.J. Frost and K. Molt, **Anal. Chim. Acta 420**, 217 (2000).

26. C.B. Lucasius and G. Kateman, **Chemometr. Intell. Lab. Syst. 19**, 1 (1993).
27. D.B. Hibbert, **Chemometr. Intell. Lab. Syst.** 19, 227 (1993).
28. R. Leardi, R. Boggia and M. Terrile, **J. Chemometr. 6**, 267 (1992).
29. R. Leardi, **J. Chemometr. 8**, 65 (1994).
30. R. Leardi, **Genetic Algorithms in Feature Selection. In Genetic Algorithms in Molecular Modelling,** J. Devillers (ed.), Academic Press, London, 1996.
31. R. Leardi and A.L. Gonzalez, **Chemomet. Intell. Lab. Syst. 41**, 195 (1998).
32. R. Leardi, **J. Chemometr. 14**, 643 (2000).
33. R. Leardi, **J. Chemometr. 15**, 559 (2001).
34. J. Ghasemi, A. Niazi and R. Leardi, **Talanta 59**, 311 (2003).
35. J. Ghasemi, D.M. Ebrahimi, L. Hejazi, R. Leardi and A. Niazi, **J. Anal. Chem. 61**, 92 (2006).
36. W.B. Rathbum, C.E. Killen, A.M. Hollesachau and H.T. Nagasawa, **Biochem, Pharmacol. 51**, 1111 (1996).
37. D.J. Johnson, D.G. Graham, V. Amarnath, K. Amarnath and W.H. Walentie, **Chem. Res. Toxicol. 9**, 910 (1996).
38. P. Butvin, J.A. Jaafreh, J. Svetlik and E. Havranek, **Chem. Papers 53**, 315 (1999).
39. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Franks, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johanson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J.A. Pople, GAUSSIAN 98, Gaussian, Inc., Pittsburg PA, 1998.
40. D. Nori-Shargh, B. Soltani and F. Deyhimi, **J. Mol. Struc. (Theochem) 585**, 257 (2002).
41. D. Nori-Shargh, M.M. Amini, F. Deyhimi, S. Jameh-Bozorghi and S. Aminzadeh, **J. Mol. Struc. (Theochem) 716**, 211 (2005).
42. I.N. Levine, **Quantum Chemistry,** 5^{th} ed., Prentice Hall, Upper Saddle River, NJ, USA, 2000.
43. P. Thanikaivelan, V. Subramanian, J.R. Rao and B.U. Nair, **Chem. Phys. Lett. 323**, 59 (2000).
44. D.M. Haaland and E.V. Thomas, **Anal. Chem. 60**, 1193 (1988).