

Simultaneous Spectrophotometric Determination of Rare-Earth and Transition Elements Using Partial Least-Squares (PLS) Multivariate Calibration¹

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Abstract—A spectrophotometric method for the simultaneous determination of rare-earth and transition elements in synthetic superconductors, $[(La_{1-x}Eu_x)_{1.82}Sr_{0.18}CuO_4]$, by the use of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as chelating agent was developed. The influence of chemical variables affecting the reaction was studied. A partial least-squares (PLS) multivariate calibration procedure was used to assess the data obtained from several calibration solutions measured over the wavelengths range 400–700 nm. The concentration range for Cu was $(1–12) \times 10^{-6}$ mol/L, while the range for the rare-earth elements La and Eu was $(2–8) \times 10^{-6}$ mol/L. The relative errors in the determinations were less than 5% in most cases.

INTRODUCTION

A large number of analytical methods have been used for the determination of rare-earth and transition elements in a wide variety of samples such as environmental, industrial, geological, and clinical ones. The increasing availability of powerful analytical techniques, such as X-ray fluorescence spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), mass spectrometry (MS) and neutron activation analysis [1, 2], has enabled the analysis of complex mixtures with a high accuracy and precision in the results. However, the most serious shortcoming of these techniques results from the fact that the analytical instrumentation utilized involves large money expenditure for most analytical laboratories.

On the other hand, the use of techniques of relatively low cost (such as spectrophotometry) for the multicomponent analysis of rare-earth and transition elements, often cannot be carried out successfully without previous chemical separations [3]. The difficulties arise when the elements (often complexed) give partly or fully overlapped spectra.

Nevertheless, the association of spectrophotometric techniques employing chelating agents and chemometric methods, such as partial least squares (PLS) multivariate calibration procedures, offers outstanding advantages for the analysis of complex mixtures [4, 5].

The analytical application of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br PADAP) as chelat-

ing agent has been extensively studied in previous works. Although it can be used for the spectrophotometric determination of many rare-earth elements [6–8], it has not been employed for the multicomponent analysis of rare-earth and transition elements in superconductors.

In this work, a spectrophotometric method in conjunction with a multicalibration partial least squares (PLS) method was applied to the analysis of ternary synthetic mixtures of two rare-earth elements (La and Eu) and a transition metal (Cu), which are the basic elements of the superconductor $(La_{1-x}Eu_x)_{1.82}Sr_{0.18}CuO_4$. The 5-Br-PADAP reagent was used for the spectrophotometric determination of these elements in concentrations ranging from $(0.1–14) \times 10^{-5}$ mol/L for Cu and $(0.2–14) \times 10^{-5}$ mol/L for La and Eu, and the influence of chemical variables affecting the reaction was studied.

THEORETICAL BACKGROUND

PLS method. This principal component-like method [9–12] is based on the projection of the original multivariate data matrices down onto smaller matrices (T , U) with orthogonal columns, which relates the information in the response matrix Y to the systematic variance in the descriptor matrix X , as shown below:

$$X = \bar{X} + TP' + E$$

$$Y = \bar{Y} + UC' + F$$

$$U = T + H \text{ (the inner relation),}$$

¹This article was submitted by the authors in English.

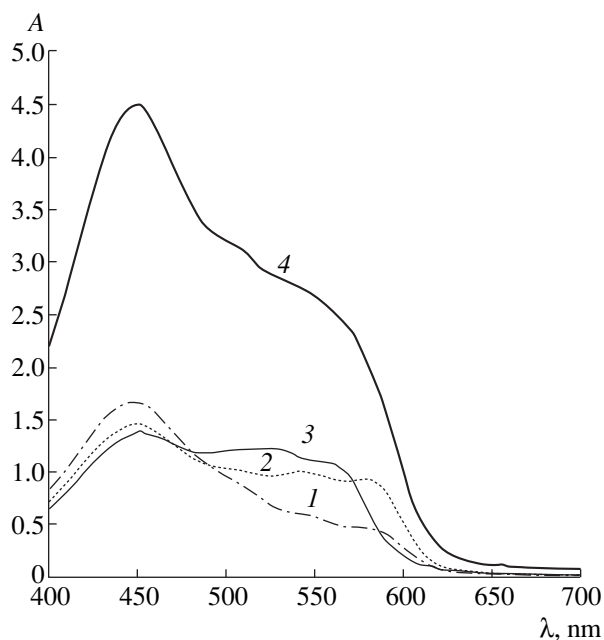


Fig. 1. Spectral curves of 5-Br-PADAP complexes of (1) lanthanum, (2) europium, (3) copper and (4) their mixture. pH 9.5. $C_{5\text{-Br-PADAP}} = 3.3 \times 10^{-5}$; $C_{\text{La}} = 1 \times 10^{-5}$; $C_{\text{Eu}} = 1 \times 10^{-5}$; $C_{\text{Cu}} = 1 \times 10^{-5}$ mol/L. For mixture, $C_{5\text{-Br-PADAP}} = 1 \times 10^{-4}$ mol/L.

where \bar{X} and \bar{Y} are the corresponding mean value matrices, T and U are the matrices of scores that summarize the x and y variables respectively, P is the matrix of loadings showing the influence of the x in each component, C is the matrix of weights expressing the correlation between Y and $T(X)$, and E , F , and H are the corresponding residuals matrices. The PLS calculations also give an auxiliary matrix W (PLS weights), which expresses the correlation between U and X and is used to calculate T .

In the present work, the response matrix Y consisted of three dependent variables (the concentration of each analyte) while matrix X consisted of the absorbance data. Determinations of the significant number of model dimensions was made by cross-validation.

PLS analysis was carried out using both the UNSCRAMBLER 6.11 software package obtained from CAMO AS, Norway, and the SIMCA 7.0 software package obtained from Umetri AB, Box 7960, 907 19 Umea, Sweden.

Spectrophotometric data. The method assumes that the absorbance of a mixture at any wavelength is the sum of absorbances of each formed chelate. In the j th wavelength, the absorbance addition A_j will be:

$$A_j = A_1bc_1 + \dots + A_nbc_n,$$

where the subscript indicates the number of samples from 1 to n .

In Fig. 1, the spectra of La(III), Eu(III), and Cu(II) 5-Br-PADAP complexes in the 400–700 nm wavelength range are shown. It can be seen that all peaks of elements are strongly overlapped with each other, which means that univariate analysis methods cannot be applied for resolving this mixture.

EXPERIMENTAL

Apparatus. The measurements were performed with a Hewlett Packard (HP-8452A model) spectrophotometer equipped with a diode array wavelength detector and a Hewlett Packard printer (ThinkJet model).

All measurements were made with 1.00-cm optical-path quartz cells, and the pH adjustment was performed with an Orion EA940 pH meter digitally equipped with a combined glass electrode and an internal reference Ag–AgCl electrode. The potentiometer was calibrated with three buffer solutions of pH values 4.05, 7.01 and 9.8, respectively.

Reagents. A 2×10^{-3} M 5-Br-PADAP (Merck) solution was prepared by dissolving an accurately weighed amount of reagent in ethanol (Merck). Lower concentrations were prepared by successive dilutions.

Standard solutions of La, Eu and Cu were prepared at 2.5×10^{-4} mol/L by dissolving suitable amounts of their nitrates (Merck) in twice distilled water. To demonstrate the noninterference in a solution of Sr(II) with 5 Br-PADAP, all solutions (samples and standards) were prepared by adding SrCl_2 (Mallinckrodt) at 1.6×10^{-5} mol/L of final concentration.

A buffer solution (pH 9.5) was prepared with borax and NaOH [13] reagents (Merck).

The ionic strength generated by the dissolution of superconductor ceramics in acid media, was simulated by adding $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Merck) at 0.1 mol/L of final concentration. To avoid the metal hydrolysis, a mixture of ethanol and Triton X-100 [14] was used. All solutions (samples and standards) were prepared by adding this mixture at a final concentration of 5% EtOH and

Table 1. Composition of the calibration matrix for La, Eu and Cu (10^{-6} mol $^{-1}$)

Element	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
La	2	4	5	6	7	8	6	7	5	4	5	6	6	8	7	2	3
Eu	2	4	5	6	7	6	4	5	7	6	6	5	7	7	8	3	2
Cu	12	8	6	4	2	2	6	4	4	6	5	5	3	1	1	11	11

0.5% Triton X-100 [15]. All chemical and solvents used were of analytical quality and twice distilled water was employed in all cases.

General procedure. The following components were placed in 25-mL volumetric flasks: a 5-mL portion of sodium tetraborate/NaOH buffer at pH 9.5, appropriate volumes of the La(III), Eu(III) and Cu(II) standard solutions in such a way that their final concentrations lay within the desired range, and the required amounts of 5-Br-PADAP, ethanol, NaClO₄ and triton X-100. The spectra for the mixtures studied were recorded between 400 and 700 nm taking absorbance data at 2 nm intervals, and the readings were made at constant time to allow for the stabilization of formed complexes. The calibration and prediction procedures were carried out by using 17 calibration standards and 6 synthetic samples (ternary mixtures) prepared with different concentrations of each metal, giving final concentrations of 1.6×10^{-5} mol/L in each case (standards and samples).

RESULTS AND DISCUSSION

Optimization of the measurement conditions.

Prior to attempting mixture resolution, we studied the stability of the different formed complex species between 5-Br-PADAP and La(III), Eu(III), Cu(II) as a function of pH, time, ionic strength, presence of surfactants and suitable amounts of Sr.

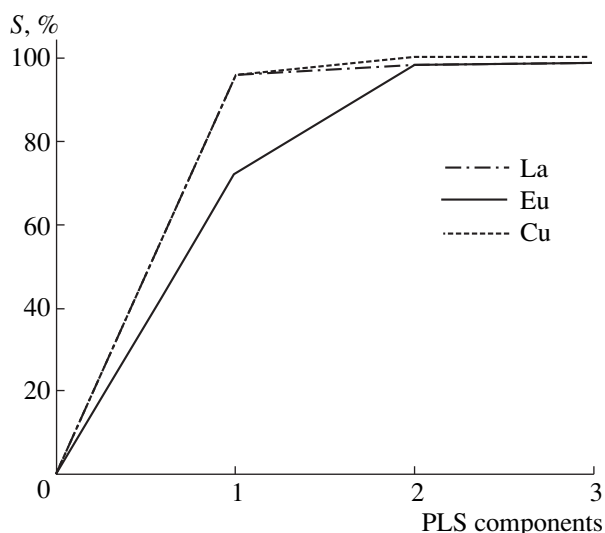


Fig. 2. Variance explained as a function of the number of PLS components used in the calibration process.

The variation in the absorbance of the La(III), Eu(III) and another rare-earth-5-Br-PADAP complexes with pH fits an inverted bell-shaped curve with a flat zone in the pH range from 9.0 and 10.9 [15].

On the other hand, because the Cu(II)-5-Br-PADAP complex showed good absorbances in this pH range, a pH value of 9.5 was selected. As regards temporal stability, an optimal reaction time of 15 minutes was

Table 2. Experimental and calculated concentration values and relative error (%) for La, Eu and Cu (10^{-6} mol/L) in the calibration matrix

N	La		k, %	Eu		k, %	Cu		k, %
	1	2		1	2		1	2	
1	2	2	0	2	2.1	5	12	11.9	-0.8
2	4	4	0	4	4	0	8	8	0
3	5	5.1	2	5	4.9	-2	6	9	0
4	6	5.9	-1.6	6	6	0	4	4.1	2.5
5	7	7.2	2.8	7	6.9	-1.4	2	1.9	-5
6	8	8.3	3.7	6	5.7	-5	2	2	0
7	7	6.6	-5.7	5	5.5	-10	4	3.9	-2.5
8	5	5.3	6	7	6.7	-4.2	4	3.9	-2.5
9	4	3.8	-5	6	6.2	3.3	6	6	0
10	6	5.8	-3.3	4	4.2	5	6	6	0
11	5	5	0	6	6	0	5	5	0
12	6	6.1	1.6	5	4.8	-4	5	5.1	2
13	6	6.3	5	7	6.7	-4.2	3	3	0
14	8	7.6	5	7	7.3	4.2	1	1.1	10
15	7	7	0	8	8	0	1	1	0
16	2	2.2	1	3	2.8	-3.3	11	11	0
17	3	3	0	2	1.9	-5	11	11	0

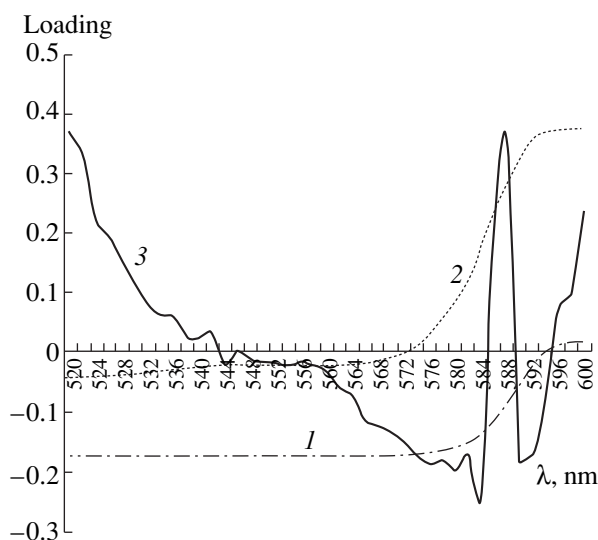


Fig. 3. Loadings plotted as a function of the wavelength (matrix *X*).

observed and, therefore, this time was selected for subsequent experiments.

To avoid the hydrolysis of the formed complexes at pH 9.5, a mixture of ethanol 5% and triton X-100 0.5% of final concentration was used.

This mixture allowed us not only to avoid the hydrolysis, but also to improve the absorption properties of complexes [16, 17].

As regards 5-Br PADAP, the optimum ligand-to-metal ratio was found to be 1 : 2. In order to ensure a small excess of chelating agent, we adopt a ratio of 3 : 1 in all experiments. The influence of the ionic strength was studied with the purpose of simulating the real conditions of acid attack in the sample. We found no variation in the absorbance values for synthetic samples after adding increasing amounts of NaClO₄. For this reason, all calibration solutions and samples were treated with a final concentration of 0.1 M NaClO₄. We also evaluated the influence of Sr(II) in standards and samples. However, this element does not form complexes with 5-Br-PADAP. To demonstrate that it does

not react with the chelating agent, all standards and samples were added with a solution of SrCl₂ 1.6 × 10⁻⁶ mol/L, corresponding to the same final concentration of the metals under study.

PLS analysis of ternary mixtures: calibration set.

All variables (absorbance and concentration matrices) used in the PLS calculations were initially autoscaled to zero mean and unit variance. The statistical significance of the screened models was judged by the correlation coefficient (*r*), the root mean square error (RMSE) and the F-statistic.

The predictive ability was evaluated by the cross-validation coefficient (*Q*), which is based on the prediction error sum of squares (PRESS). The VIP (variable importance for the projection) parameter [18] was used to unravel which absorbance variables were the most relevant to explain the concentration matrix *Y*.

The calibration matrix was constructed with 17 calibration standards. The selected concentration ranges were from 2 × 10⁻⁶ mol/L to 8 × 10⁻⁶ mol/L for La and Eu; and 1 × 10⁻⁶ mol/L to 1.2 × 10⁻⁵ mol/L for Cu. A preliminary analysis of the obtained PLS models showed that the useful wavelength range was between 520 to 600 nm. The composition of the calibration matrix of the ternary mixture is given in Table 1.

The PLS analysis for the calibration matrix resulted in a significant three-component model with the following statistics: *r* = 0.995, *Q* = 0.992, RMSE (La) = 0.00258, RMSE (Eu) = 0.00255, RMSE (Cu) = 0.00065. The model accounted for 98.9% (87.9%, 10.6%, and 0.4%, respectively) of variance in the concentration matrix *Y*. The number of significant PLS components was determined using a leave-one-out cross-validation procedure.

Figure 2 shows the percentage variances obtained for the ternary mixture in the calibration process, and Fig. 3, shows the model loadings each of which is related to one or more of the elements in the mixtures. The residual values showed a reasonable central tendency and the agreement between the measured and calculated values is very good as shown in Table 2.

Model validation: sample set. It is well known that the real predictive ability of any calibration PLS model

Table 3. Experimental and calculated concentration values and relative errors (%) for La, Eu and Cu (10⁻⁶ mol/L) in the synthetic samples

N	La		<i>k</i> , %	Eu		<i>k</i> , %	Cu		<i>k</i> , %
	1	2		1	2		1	2	
1	3	2.9	-3.3	3	3.1	3.3	10	10	0
2	6	6.4	6.6	8	7.7	-3.7	2	1.9	-5
3	7	6.9	-1.4	6	6	0	3	3.2	6.6
4	2	2	0	4	3.9	-2.5	10	10.1	1
5	5	5.2	4	4	3.8	-5	7	7.1	1.4
6	9	8.9	-1.1	5	4.7	-6	2	2.1	5

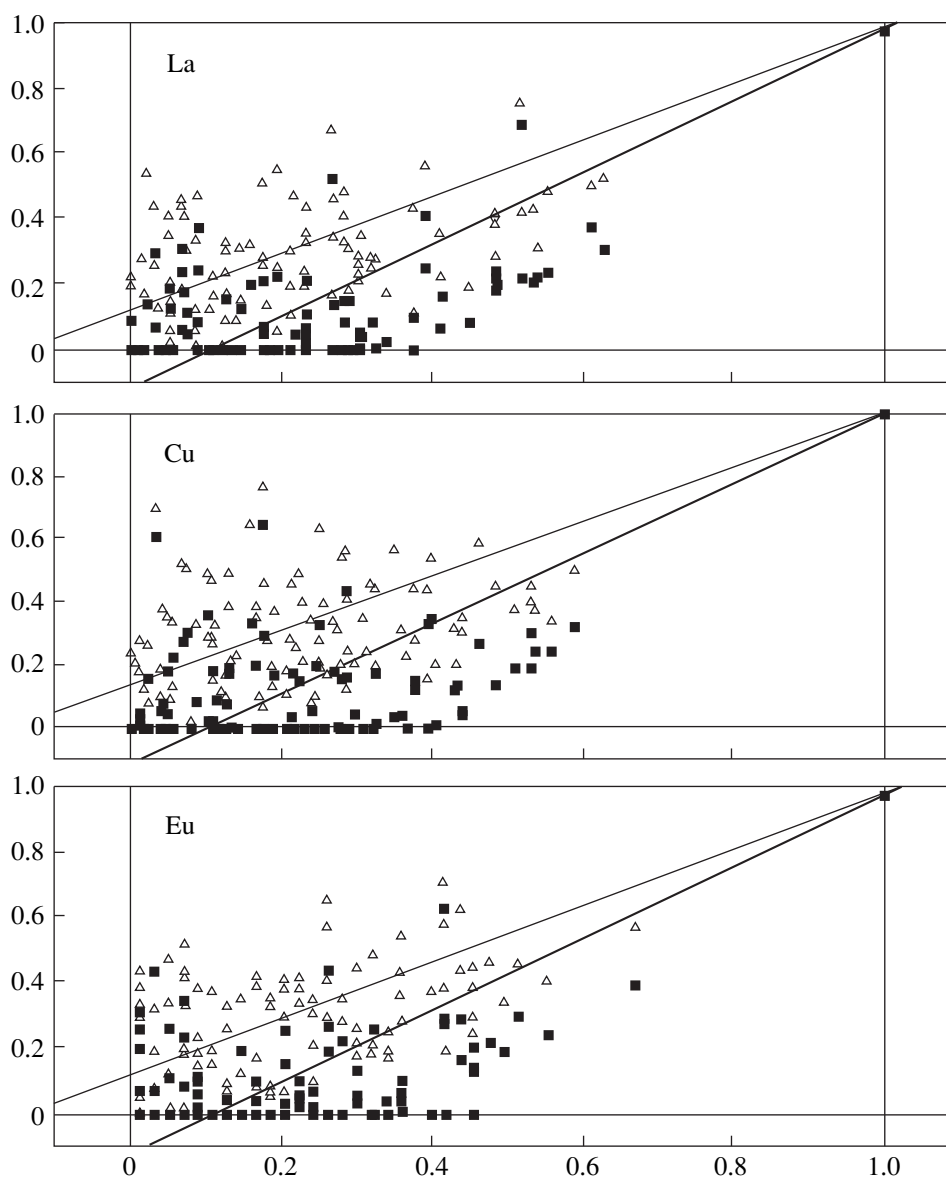


Fig. 4. Results of the permutation test. The R^2 and Q^2 values were obtained from 100 permutations and 3 PLS components.

cannot be judged solely by using internal validation (i.e., cross-validation); it has to be validated on the basis of predictions for compounds not included in the calibration set [17]. Thus, in order to demonstrate the applicability of the proposed method, a set of synthetic samples containing the three analytes in variable proportions was prepared and analyzed.

Table 3 shows the results obtained by applying the developed PLS model. As can be seen, the relative errors were quite acceptable, as they were less than 5% in the most cases.

The predictability of a PLS model may also be examined in another way, that is, with a technique based on response permutation [19]. Thus, several PLS models are recalculated by using the concentration data

(matrix Y) randomly reordered. These permuted data are later related to the unperturbed absorbance data (matrix X) by refitting the model and including cross-validation.

In each round of calculation, pairs of R^2 and Q^2 are recorded and plotted against the absolute value of the correlation coefficient between the original response variable and its permutations. In Fig. 4 are shown the obtained results from 100 permutations of the calibration matrix for each one of the analytes under study. The intercepts of the two regression lines (for R^2 and Q^2) indicate the degree of overfit and overprediction. In general, intercept limits for $R^2 < 0.3$ and $Q^2 < 0.05$ indicate valid models, such as is the case of our PLS model developed.

CONCLUSIONS

Based on the results obtained in this work, the proposed spectrophotometric method permits the simultaneous determination of lanthanum, europium, and copper in a synthetic superconductor $(\text{La}_{1-x}\text{Eu}_x)_{1.82}\text{Sr}_{0.18}\text{CuO}_4$. The proposed method can be used without previous chemical separations which provides evidence for the great potential of the PLS method for the simultaneous determination of analytes that present a substantial overlap in the sample spectra. Because the developed method provide expeditious and precise results, this is suitable for the routine analysis of superconductor samples.

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REFERENCES

1. Skoog, D. and Leary, J., *Analisis Instrumental*, Espana: Mc Graw-Hill, 1994.
2. Willard, H., Merritt, L., Dean, J., and Settle, F., *Métodos Instrumentales de Analisis*, México: Grupo Editorial Iberoamérica, 1990.
3. Kuban, V. and Gladilovich, D., *Coll. Czech. Chem. Commun.*, 1988, vol. 53, p. 1664.
4. Martents, H. and Naes, T., *Multivariate Calibration*, New York: John Wiley and Sons, 1989.
5. Bautista, R., Jimenez, A., Jimenez, F., and Arias, J., *Talanta*, 1996, vol. 43, p. 421.
6. Preisler, J., Jankar, L., and Sommer, L., *Collect. Czech. Chem. Commun.*, 1993, vol. 58, p. 1495.
7. Arai, J., Iwata, Y., and Umezawa, K., *Ph. Review B*, 1996, vol. 54, no. 17, p. 12557.
8. Suzuki, T. and Sera, M., *Ph. Review B*, 1994, vol. 49, no. 17, p. 12392.
9. Beebe, K., Pell, R., and Seasholtz, M., *Chemometrics, a Practical Guide*, New York: John Wiley and Sons, 1998.
10. Kramer, R., *Chemometric Techniques for Cuantitative Analysis*, New York: Marcel Dekker, 1998.
11. Cela, R., *Quimiometria Practica*, Espana: Publicaciones Universidad de Santiago de Compostela, 1994.
12. Beebe, K., Kowalsky, B., *Analytical Chemistry*, 1987, vol. 59, no 17, p. 1007A.
13. Meites, L., *Handbook of Analytical Chemistry*, New York: Mc Graw-Hill, 1982.
14. Savvin, S., Chernova, K., and Kudryatseva, L., *Plenum Publishing Corporation*, 1979, vol. 51, p. 60.
15. D'Angelo, J., Fernandez, J., Martinez, L., and Marchevsky, E., *Journal of Analytical Chemistry*, 1999, vol. 54, no. 6, p. 665.
16. Martinez, L., Perino, E., Marchevsky, E., and Olsina, R., *Talanta*, 1993, vol. 40, no. 3, p. 385.
17. Martinez, L., Gasquez, J., Olsina, R., and Marchevsky, E., *Chemia Analityczna*, 1996, vol. 41, p. 275.
18. Wold, S., *In Chemometric Methods in Molecular Design*. Weinheim: van de Waterbeemd, H., Ed., VCH, 1995, vol. 2, p. 195.
19. Wold, S. and Eriksson, L., *In Chemometric Methods in Molecular Design*. Weinheim: van de Waterbeemd, H., Ed., VCH, 1995, vol. 2, p. 309.