

# Combining XRF analysis and chemometric tools for a preliminary classification of argentine soils<sup>†</sup>

G. Custo,<sup>1</sup> S. Boeykens,<sup>2</sup> D. Cicerone,<sup>1,3</sup> and C. Vázquez<sup>1,2\*</sup>

<sup>1</sup> Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Av. del Libertador 8250, 1429 Buenos Aires, Argentina

<sup>2</sup> Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Química de Sistemas Heterogéneos, Paseo Colón 850, 1063 Buenos Aires, Argentina

<sup>3</sup> Universidad Nacional de General San Martín, Escuela de Posgrado, Av. 52 No. 3563, 1650, San Martín. Argentina

Received 10 March 2001; Accepted 1 October 2001

**A procedure for the non-destructive elemental analysis of soils using wavelength-dispersive x-ray fluorescence spectrometry (WDXRF) is proposed. The determination of minor and trace elements is considered. It does not require any sophisticated treatment of the sample. The method was validated using certified soil standard reference materials, obtaining satisfactory agreement between the WDXRF results and the certified values. The multielemental information provided by the proposed method was used to model a classification of Argentine soils by chemometric analysis. Copyright © 2002 John Wiley & Sons, Ltd.**

## INTRODUCTION

The analysis of soil samples by x-ray fluorescence has been used but continues to develop, as new sample preparation and matrix correction procedures have become available.<sup>1,2</sup> Problems in developing the analysis arise from the heterogeneity of the system and matrix effects.<sup>3–5</sup>

Soils are natural bodies comprised of solids (mineral and organic matter), liquids and gases that occur on the land surface. They occupy space and are characterized by horizons or layers that are distinguishable from the initial material as a result of additions, losses, transfers and transformations of energy and matter or have the ability to support rooted plants in a natural environment.<sup>6</sup>

Taking into account the heterogeneity of the system under study, the fusion procedure is usually recommended. Since soils are natural materials, the presence of organic matter, coming from littering decomposition, could form metal carbides with melting-points higher than the temperature of fusion. This procedure does not provide homogenization and in these cases the fused method is time consuming. On the other hand, a similar matrix composition between samples and standards is needed in order to diminish the absorption-enhancement effects.

Although multielemental analysis has been performed using techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), these techniques require a rigorous sample preparation before analysis.

In this paper, a procedure using wavelength-dispersive x-ray fluorescence spectrometry (WDXRF) is proposed to determine the chemical composition of soils from different sites in Argentina. This multielemental information was used to develop a model of classification of soils by chemometric analysis.

## EXPERIMENTAL

### Sample collection

Horizontal and vertical variations of soil properties were taken into account in the selected stratified random sampling strategy.<sup>7</sup> Undisturbed and mechanically disturbed soil samples were taken from three sites: Puerto Mineral (province of Misiones), Olavarría (province of Buenos Aires) and San Martín de los Andes (province of Neuquén).

Large and undisturbed soil column samples were isolated from excavated pits 1.5–2 m in diameter and almost 3 m deep and used to determine physical properties such as porosity and bulk density. Columns were slowly shaped into a cylindrical form. As the size of the columns reached the desired dimensions (30 cm in diameter and 60 cm in depth) they were wrapped with Parafilm in order to prevent further contamination, and to preserve the integrity of the soil structure. Finally, the columns were removed from the pits and placed in sampling holders filled with chips in order to prevent damage during transport to the laboratory.

Subsamples from Horizon O (top soil), Horizon A (~0.15 m), Horizon B (~0.15–1.0 m) and Horizon C (<1.5 m) were taken, dried in an oven for 24 h at 60 °C, ground manually in a porcelain mortar and sieved in order to work with particles smaller than 50 µm.

### Preparation of synthetic standards and samples

X-ray spectrometry is a comparative method that requires standard samples for the quantitative evaluation of specimens. Standard reference materials are available for the

\*Correspondence to: C. Vázquez, Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Av. del Libertador 8250, 1429 Buenos Aires, Argentina. E-mail: vazquez@cnea.gov.ar

<sup>†</sup>Presented at SARX-2000, 7th Latin-American Conference on Analysis by X-ray Techniques, São Pedro, Brazil, 19–24 November 2000.

**Table 1.** Final analyte concentration values in synthetic standards generated from SRM

Synthetic std.	Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	TiO <sub>2</sub> <sup>a</sup>	CaO <sup>b</sup>	Zn <sup>b</sup>	Cu <sup>b</sup>	Ba <sup>b</sup>	Sr <sup>b</sup>	Ni <sup>b</sup>	Cr <sup>b</sup>	Mn <sup>b</sup>	Zr <sup>b</sup>
1	10.15	3.00	0.4	2200	133	266	40	40	267	1800	100
2	10.05	3.00	0.38	2100	133	266	40	40	266	1470	100
3	11.84	2.00	0.22	1000	67	140	80	20	67	698	300
4	11.67	2.00	0.19	1000	67	140	82	20	67	681	300
5	13.27	1.01	0.10	500	267	532	120	100	133	2780	550
6	13.27	1.01	0.11	500	267	532	120	100	133	2710	550

<sup>a</sup> Data in g per 100 g.<sup>b</sup> Data in µg g<sup>-1</sup>.

evaluation of various types of soils, but their composition is not always in accordance with the collected sample. Therefore, synthetic standards generated from one standard reference material were prepared.

A set of synthetic standards was prepared from three standard reference materials (SRMs), IAEA Soil 5, IAEA Soil 7 and GBW07405 (GSS-5), by adding convenient quantities of the analytes, namely Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Zr and Ba. Standard reference solutions were prepared from Titrisol (Merck) (1000 µg ml<sup>-1</sup>). This procedure is intended to maintain the original SRM chemical composition of major elements and, at the same time, allows a larger range than the certified values for trace elements. In this way, a complete set of synthetic standards that may be employed for different soil characterizations was obtained. New analyte concentrations were calculated (Table 1).

Standard and soil samples were prepared as pressed pellets. A 6 g amount of soil powder and 0.5 ml of a saturated solution of Poliviol were placed in a 100 ml plastic jar. The slurry obtained was thoroughly mixed with a glass rod. The jar was placed in a microwave oven at very low power for 10 min, until complete evaporation of the water. The mixed powder was compacted into discs (31 mm diameter mould) by pressing, for 15 s at 20 cm<sup>2</sup>.

Duplicate synthetic standards were prepared, so that four replicate discs were obtained for each of them. This procedure resulted in very resistant and homogeneous pellets.

The validation of the method was checked by determining the same elements in the standard reference materials GBW07405 (GSS 5) and IAEA Soil 7. These materials were prepared under the same conditions as the samples. Four replicates were made for each standard.

### Instrumental conditions

A Philips PW 1400 WDXRF spectrometer, equipped with a W anticathode x-ray tube operated at 50 kV and 40 mA, was used for the measurements. Analytical lines and background intensities (counts s<sup>-1</sup>) were measured on both sides of the pellets and the results were averaged. LiF (2,0,0) was employed for crystal diffraction and was replaced with LiF (2,2,0) for Cu measurements. The K $\alpha$  lines were selected as the fluorescent line for all elements and measuring time 60 s, except for Fe, Ti and Ca for which 20 s was employed. Samples were measured under vacuum.

For calibration, the pellets of standards and samples were exposed to primary radiation from the x-ray tube and

the resulting fluorescent radiation, which is characteristic of the constituents present in the soils, was measured. The spectrometer was calibrated for the elements present in the standards using the prepared synthetic standards.

### Data processing

Measured intensities for the soil samples and the synthetic standards were processed using least-squares regression analysis and statistical evaluation (TBLCURVE, Ver. 1991). The equation  $Y = a + bx$  was used to compute the analyte concentration of the samples,  $Y$  = intensity (counts/s);  $x$  = concentration (µg/g/100g).

In order to develop a soil classification scheme based on the chemical composition, the results from the foregoing data processing were evaluated by a combination of principal component analysis (PCA) and a clustering technique.<sup>8-10</sup> MATLAB (Ver. 5.3, 1999) software was selected as a chemometric tool.

## RESULTS AND DISCUSSION

The detection limits [ $DL(\mu\text{g g}^{-1})$ ] are given in Table 2 and were calculated by the following equation:

$$DL = \frac{3SBD}{m}$$

where  $SBD$  is the standard deviation of the background and  $m$  is the slope of the calibration curve.

The concentrations of the elements in the certified standards were measured and calculated using the calibration curves from the synthetic standards. Very good agreement with the certified values was obtained. The results of the validation are shown in Table 2. The uncertainty of measurement was about 10% or less for the majority of the studied elements. The relative standard deviation was about 10%, for  $n = 10$ .

Quantitative results obtained for eight trace elements (Cr, Mn, Ni, Cu, Zn, Sr, Zr and Ba) and three minor elements (Ti, Ca and Fe) in 18 Argentine soils samples are presented in Table 3.

The PCA analysis, a recommended visualization technique, was applied to the results in Table 3, constituting a matrix of 11 (variables, elementary composition)  $\times$  18 (samples). This reduced the redundant original variable space to an optimal lower dimensional abstract space, whose variables contained uncorrelated information. This dimension

**Table 2.** Results obtained from the certified standards

	Standard GBW07405 (GSS 5)		Standard IAEA Soil 7		Detection limit ( $\mu\text{g g}^{-1}$ )
	XRF ( $\mu\text{g g}^{-1}$ )	Certified ( $\mu\text{g g}^{-1}$ )	XRF ( $\mu\text{g g}^{-1}$ )	Certified ( $\mu\text{g g}^{-1}$ )	
Zn	550 $\pm$ 60	494 $\pm$ 39	120 $\pm$ 12	104 (101–113)	5
Sr	38 $\pm$ 4	42 $\pm$ 6	110 $\pm$ 10	108 (103–114)	8
Ba	281 $\pm$ 30	296 $\pm$ 40	173 $\pm$ 20	159 (131–196) <sup>a</sup>	10
Zr	290 $\pm$ 30	272 $\pm$ 25	170 $\pm$ 20	185 (180–201)	8
Ni	50 $\pm$ 5	40 $\pm$ 5	35 $\pm$ 5	26 (21–37) <sup>a</sup>	5
Mn	1570 $\pm$ 150	1360 $\pm$ 111	590 $\pm$ 60	631 (604–650)	5
Cu	160 $\pm$ 20	144 $\pm$ 9	< DL	11 (9–13)	5
	XRF (g/100 g)	Certified (g/100 g)	XRF (g/100 g)	Certified (g/100 g)	
Ca	0.08 $\pm$ 0.009	(0.095) <sup>a</sup>	—	185 (180–201)	10
Ti	0.59 $\pm$ 0.05	0.629 $\pm$ 0.032	0.2 $\pm$ 0.04	0.30 (0.26–0.37) <sup>a</sup>	10
Fe	12.10 $\pm$ 1	12.62 $\pm$ 0.27	3.0 $\pm$ 0.5	2.5 (2.52–2.62) <sup>a</sup>	10

<sup>a</sup> Not certified.**Table 3.** Determination of metals in soil samples by WDXRF

Sample	Cr <sup>a</sup>	Mn <sup>a</sup>	Ni <sup>a</sup>	Cu <sup>a</sup>	Zn <sup>a</sup>	Sr <sup>a</sup>	Zr <sup>a</sup>	Ba <sup>b</sup>	Ca <sup>b</sup>	Ti <sup>b</sup>	Fe <sup>b</sup>
MIS 1	80 $\pm$ 8	1759 $\pm$ 80	19 $\pm$ 2	111 $\pm$ 10	45 $\pm$ 4	49 $\pm$ 5	739 $\pm$ 75	659 $\pm$ 66	0.18 $\pm$ 0.01	0.96 $\pm$ 0.01	4.0 $\pm$ 0.4
MIS 2	120 $\pm$ 12	931 $\pm$ 40	43 $\pm$ 4	104 $\pm$ 10	17 $\pm$ 2	45 $\pm$ 5	818 $\pm$ 82	499 $\pm$ 50	0.16 $\pm$ 0.01	1.6 $\pm$ 0.2	4.5 $\pm$ 0.4
MIS 3	59 $\pm$ 6	1276 $\pm$ 60	11 $\pm$ 2	106 $\pm$ 10	29 $\pm$ 3	44 $\pm$ 4	835 $\pm$ 83	395 $\pm$ 40	0.11 $\pm$ 0.01	0.94 $\pm$ 0.01	3.8 $\pm$ 0.4
MIS 4	148 $\pm$ 15	1574 $\pm$ 80	22 $\pm$ 2	100 $\pm$ 10	42 $\pm$ 4	25 $\pm$ 2	664 $\pm$ 66	356 $\pm$ 35	0.19 $\pm$ 0.01	2.9 $\pm$ 0.3	6.1 $\pm$ 0.6
MIS 5	84 $\pm$ 4	923 $\pm$ 45	24 $\pm$ 2	115 $\pm$ 10	22 $\pm$ 2	41 $\pm$ 4	864 $\pm$ 86	453 $\pm$ 45	0.060 $\pm$ 0.003	0.91 $\pm$ 0.09	3.8 $\pm$ 0.4
MIS 6	325 $\pm$ 16	762 $\pm$ 40	45 $\pm$ 4	113 $\pm$ 10	25 $\pm$ 2	37 $\pm$ 4	342 $\pm$ 34	290 $\pm$ 29	0.16 $\pm$ 0.01	0.75 $\pm$ 0.07	7.5 $\pm$ 0.7
OLA 1	429 $\pm$ 43	1536 $\pm$ 80	17 $\pm$ 2	86 $\pm$ 8	41 $\pm$ 5	192 $\pm$ 20	265 $\pm$ 26	665 $\pm$ 66	5.5 $\pm$ 0.5	0.23 $\pm$ 0.02	4.2 $\pm$ 0.4
OLA 2	42 $\pm$ 4	740 $\pm$ 35	22 $\pm$ 2	78 $\pm$ 8	34 $\pm$ 3	318 $\pm$ 30	269 $\pm$ 26	434 $\pm$ 43	3.0 $\pm$ 0.3	0.39 $\pm$ 0.04	3.3 $\pm$ 0.3
OLA 3	18 $\pm$ 2	865 $\pm$ 42	5.0 $\pm$ 0.5	92 $\pm$ 9	40 $\pm$ 4	191 $\pm$ 19	241 $\pm$ 24	903 $\pm$ 90	2.1 $\pm$ 0.2	0.19 $\pm$ 0.02	3.1 $\pm$ 0.3
OLA 4	18 $\pm$ 2	806 $\pm$ 40	14 $\pm$ 2	84 $\pm$ 8	41 $\pm$ 4	196 $\pm$ 20	269 $\pm$ 26	656 $\pm$ 65	6.2 $\pm$ 0.6	0.29 $\pm$ 0.03	3.1 $\pm$ 0.3
OLA 5	42 $\pm$ 4	878 $\pm$ 42	22 $\pm$ 2	70 $\pm$ 7	17 $\pm$ 2	317 $\pm$ 30	277 $\pm$ 27	417 $\pm$ 41	4.7 $\pm$ 0.5	0.36 $\pm$ 0.04	3.1 $\pm$ 0.3
SAN 1	132 $\pm$ 10	1497 $\pm$ 75	9.0 $\pm$ 0.9	105 $\pm$ 10	85 $\pm$ 8	37 $\pm$ 4	18 $\pm$ 2	263 $\pm$ 26	2.5 $\pm$ 0.2	0.49 $\pm$ 0.05	6.4 $\pm$ 0.6
SAN 2	108 $\pm$ 10	1347 $\pm$ 70	25 $\pm$ 2	97 $\pm$ 10	90 $\pm$ 9	279 $\pm$ 30	183 $\pm$ 18	354 $\pm$ 35	2.6 $\pm$ 0.2	0.76 $\pm$ 0.07	7.2 $\pm$ 0.7
SAN 3	198 $\pm$ 20	956 $\pm$ 50	6.0 $\pm$ 0.6	100 $\pm$ 10	60 $\pm$ 6	28 $\pm$ 3	26 $\pm$ 2	671 $\pm$ 67	1.7 $\pm$ 0.1	0.60 $\pm$ 0.06	5.6 $\pm$ 0.6
SAN 4	216 $\pm$ 20	1350 $\pm$ 70	34 $\pm$ 3	118 $\pm$ 11	65 $\pm$ 6	250 $\pm$ 25	189 $\pm$ 20	470 $\pm$ 47	2.4 $\pm$ 0.2	0.93 $\pm$ 0.09	8.2 $\pm$ 0.8
SAN 5	39 $\pm$ 4	1256 $\pm$ 60	26 $\pm$ 3	90 $\pm$ 9	60 $\pm$ 6	261 $\pm$ 25	274 $\pm$ 27	445 $\pm$ 44	1.7 $\pm$ 0.2	0.72 $\pm$ 0.07	5.2 $\pm$ 0.5
SAN 6	23 $\pm$ 3	918 $\pm$ 45	17 $\pm$ 2	117 $\pm$ 10	59 $\pm$ 6	200 $\pm$ 20	213 $\pm$ 21	527 $\pm$ 52	1.9 $\pm$ 0.2	0.70 $\pm$ 0.07	5.7 $\pm$ 0.6
SAN 7	81 $\pm$ 8	905 $\pm$ 45	26 $\pm$ 3	117 $\pm$ 10	50 $\pm$ 5	270 $\pm$ 30	250 $\pm$ 42	526 $\pm$ 52	1.5 $\pm$ 0.1	0.80 $\pm$ 0.08	7.3 $\pm$ 0.7

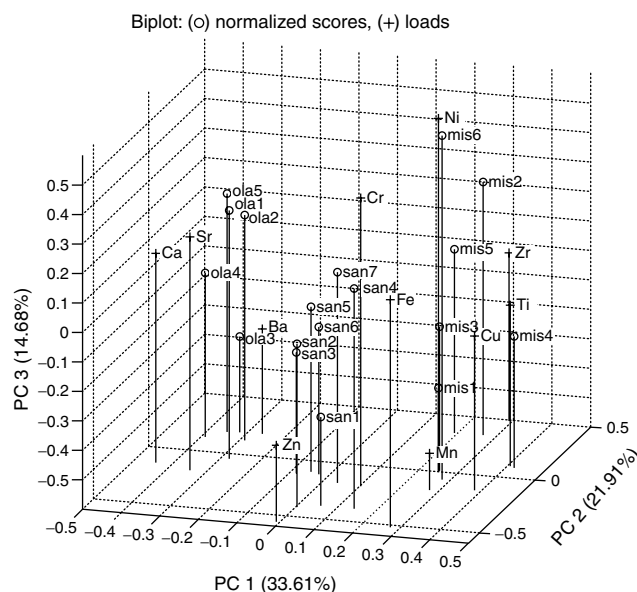
<sup>a</sup> Data in  $\mu\text{g g}^{-1}$ .<sup>b</sup> Data in g per 100 g.

decrease allowed the objects to be mapped in a two- or three-dimensional space (biplot). The coordinates of objects in this new abstract space, the so-called scores, were then used as input data in the clustering analysis.

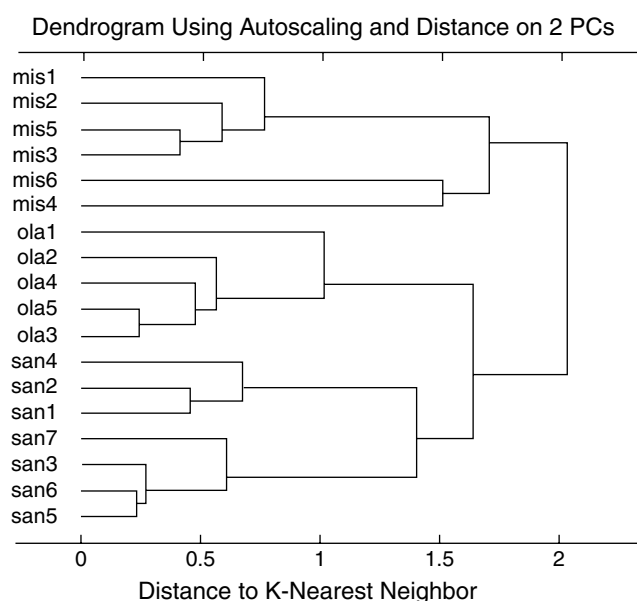
The cumulative contributions to the total variance of the first four resulting principal components (PC1, PC2, PC3 and PC4) were 33.6, 54.5, 70.2 and 80.6%, respectively. In the biplot (Fig. 1), one can also see the so-called load values of the chemical elements (old variables) for three PCs. As the Olavarría (ola) soil samples grouped together close to Ca, Ba and Sr load values, these elements are sensitive for discriminating these samples. The same reasoning applies to the rest of the samples. Thus Cr, Fe and Zn are sensitive elements for discriminating samples of San Martín de Los

Andes (san) and Fe, Ti, Ni, Mn, Cu and Zr for Puerto Mineral (mis) samples.

Dissimilarity of chemical composition of soil samples was studied through clustering analysis. The cluster technique is based on the similarity of the samples expressed according to a coefficient of dissimilarity. Figure 2 shows a dendrogram obtained using Euclidean distances and the *k*-nearest neighbor algorithm. This type of diagram constitutes a useful representation that facilitates the comparison of samples with large concentration ranges for the various components. Samples from Misiones are clearly grouped together. Two distinct clusters associated with San Martín and Olavarría sites are also present. This suggests that the compositions of ola and san samples are closer than to mis samples.



**Figure 1.** Results from principal components analysis of soil samples. (+) loads of the original variables; (o) scores of the samples; mis samples from Puerto Mineral, Misiones; ola, samples from Olavarría, Buenos Aires; san, samples from San Martín de los Andes, Neuquén.



**Figure 2.** Dendrogram obtained from the PC model data using *k*-nearest neighbors and Euclidean distance. mis, Samples from Puerto Mineral, Misiones; ola, samples from Olavarría, Buenos Aires; san, samples from San Martín de los Andes, Neuquén.

## CONCLUSIONS

The potential of WDXRF to supply multielemental chemical compositions of soils has been extensively recognized.

The presented WDXRF method is fast and simple and the sample preparation does not require any pre-concentration procedure. This saves on analysis time and eliminates contamination risks. Direct determination reduces significantly the costs of the analysis, avoiding the use of chemical reagents. At the same time, this procedure allows highly resistant discs to be obtained because of the good agglomerating properties of the product.

Synthetic standards prepared in the laboratory were satisfactory. The procedure provided a simple and economic way of preparing reliable calibration curves. In the case of soil samples, the preparation of synthetic standards using suitable quantities of the required elements reduces the effects among the elements.

A compromise option was taken between the sample size of the particle and the concentration range of the analytes for samples coming from the same site. A particle size of 50  $\mu\text{m}$  gave satisfactory results for this set of samples, avoiding a longer grinding time.

The detection limits, precision and accuracy were acceptable for this kind of analysis.

The results obtained with this method, treated with taxonomy statistics, allowed us to build a preliminary model for the classification of three different types of Argentine soils. It is evident that more samples from different sites of the country must be studied in order to test the model.

This work is valuable not only for the study of soil composition but also for contributing to a future database that will be needed for further characterization of Argentine soils.

## Acknowledgements

The authors thank Martha Ortiz, Marta Hernández and Horacio Bellavigna for helping with the sample preparation and measurements.

## REFERENCES

- Costa MM, Barreiros MA, Carvalho ML, Queralt I. *X-Ray Spectrom.* 1999; **28**: 410.
- Szalóki I, Somogyi A, Braun M, Tóth A. *X-Ray Spectrom.* 1999; **28**: 399.
- LeHouillier R, Samson C, Claisse F. *Can. Spectrosc.* 1972; **17**: 141.
- LeHouillier R, Turmel S, Claisse F. *Can. Spectrosc.* 1976; **21**: 50.
- Tertain R, Vié le Sage R. *X-Ray Spectrom.* 1977; **6**: 123.
- Potts PJ. *A Handbook of Silicate Rock Analysis*. Blackie: Glasgow, 1987; 226–325.
- Crepin J, Johnson RL. In *Soil Sampling and Methods of Analysis*, Carter MR (ed.). Lewis: Boca Raton, FL, 1993; Chapt. 2.
- Massart DL, Vandeginste BGM, Deming SN, Michotte Y, Kaufman L. *Chemometrics: a Textbook*. Elsevier: Amsterdam, 1988; 339–383.
- Peralta-Zamora P, Cornejo-Ponce L, Nagata N, Poppi RJ. *Quími. Nova* 1997; **20**: 469.
- Swerts J, Aerts A, De Biscop N, Adams F, Van Espen P. *Chemom. Intell. Lab. Syst.* 1994; **22**: 97.