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Development of an on-line preconcentration system for zinc determination in biological samples

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Abstract

An on-line preconcentration system for zinc determination in 24-h urine, blood plasma and erythrocyte matrices by flame atomic absorption spectrometry (FAAS) was used. This procedure was based on adsorption of Zn(II) ions onto a minicolumn filled with silica gel, chemically modified with niobium(V) oxide (Nb_2O_5–SiO_2). The determination of the optimum conditions for Zn(II) preconcentration was done using two-level full factorial and Doehlert designs. In the optimization procedure, four variables (sample pH, eluent concentration, sample flow rate and eluent flow rate) were investigated. The results obtained from the full factorial design demonstrated that the sample pH and sample flow rate variables, and their interactions, were statistically significant. A Doehlert matrix was used in order to determine the optimum conditions for the sample pH and sample flow rate. The optimized conditions for sample pH and flow rate sampling were 6.6 and 7.1 ml min^{-1}, respectively, to obtain the maximum Zn(II) preconcentration and determination in the biological samples studied. Parameters of analytical curve, precision, effect of other ions in the proposed system and accuracy were achieved to assess the proposed method. The accuracy was confirmed by analysis of certified reference materials (urine Seronorm™ Trace Elements) and recovery tests in blood plasma and erythrocyte samples. Detection limit ($3\sigma/S$) of 0.77 μg l^{-1}, precision (calculated as relative standard deviation) of 1.5% for Zn(II) concentration of 10 μg l^{-1} ($n = 7$) and a sampling frequency of 27 samples/h were obtained from the proposed system.
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Keywords: Zinc; Multivariate optimization; Preconcentration; Nb_2O_5–SiO_2; Blood; Urine

1. Introduction

Zinc is considered an essential trace element in human because zinc is a co-factor in more than 200 enzymes and is necessary for the production of insulin [1,2].

Some analytical methods were proposed to determine zinc in biological matrices. Wang et al. [3] developed a flow injection on-line dilution procedure with detection by ICP-MS to determine copper, zinc, arsenium, load, selenium, nickel and molibidenium in human urine. The effect of matrix was minimized by employing a dilution factor of 16.5 with on-line standard addition and ^{103}Rh as internal standard to compensate for signal flutuation. Szpunar et al. [5] also used standard addition technique to compensate signal suppression for determination of zinc and copper in human plasma and urine by ICP-MS. For determination of copper, zinc and iron in serum by simultaneous atomic absorption spectrometry (AAS), Correia et al. [4] diluted the sample 80-fold with 0.01% (w/v) Triton X-100 and 1% (v/v) nitric acid to reduce matrix effect.

Zinc detection by flame atomic absorption spectrometry (FAAS) has a number of advantages including high selectivity, speed and fairly low operational cost [6]. However, preconcentration is usually required for the determination of zinc in blood and urine samples by FAAS and preconcentration by on-line continuous flow solid phase extraction offers easy solid phase recovery, high preconcentration factors, simplicity, flexibility and high sample frequency [7]. This configuration normally involves the optimization of chemical and physical variables during the adsorption of the metal in the sorbent and its desorption with an appropriate eluent [8].

Among the many available materials for solid phase extraction, silica gel has been used with success as support for various chelating agents such as dithione [9], 1-nitro-2-naphthol [10], calmagite [11], 2-(2-thiazolylazol)-*p*-cresol [12], 1-(2-pyridylazol)-2-naphthol [13], dithiocarbamates [14] and dithiophosphates [15]. The metal adsorption properties of inorganic

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functionalized silica have been rarely explored. In this sense, silica gel chemically modified with zirconium(IV) oxide [16], zirconium(IV) phosphate [17] and niobium(V) oxide [18] was recently used and showed its analytical potentiality for metal preconcentration.

Recently, the optimization of variables from preconcentration systems has been achieved through the use of multivariable methods. The optimization of analytical procedures by multivariate techniques is faster, more economical and effective than traditional univariate optimization, and takes possible interactions between the factors that influence the analytical response into consideration [19]. In this sense, the number of works that use multivariable methods for optimization in on-line preconcentration systems is increasing [20–22].

Our research group has been exploring the use of niobium(V) oxide covalently bounded on silica gel surface (Nb_2O_5–SiO_2) adsorbent and on-line systems for metal preconcentration. Continuing our previous communication [23–25], the purpose of this work is to assess the feasibility of the use of Nb_2O_5–SiO_2 for the first time as an adsorbent in an on-line system for determination of Zn(II) from 24-h urine, blood plasma and erythrocyte matrices. The proposed method presents advantages such as use small amount of biological samples (500 μl), no requer sample digestion, high analytical frequency (27 samples/h) and it uses no expensive analytical instrument. In addition, the optimization of this system was done using a two-level full factorial design and Doehlert matrix.

2. Experimental

2.1. Instrumentation

A Varian Model SpectrAA 50 (Mulgrave, Vic., Australia) flame atomic absorption spectrometer equipped with deuterium lamp background corrector was used for the analysis. The zinc cathode lamp (Hitachi HLA-4S) was run under conditions suggested by the manufacturer (current: 5 mA). The wavelength (213.9 nm), the bandwidth of the slit (1 nm) and the burner height (7.5 mm) had suggested values. The flame composition was: acetylene (flow rate, 2 l min^{-1}) and air (10 l min^{-1}). Aspiration flow rate was 4.5 ml min^{-1}. The analytical signals were measured as peak height. A 320 Mettler Toledo pH meter was used to adjust the pH of the solutions. An Ismatec-IPC peristaltic pump with eight channels provided with Tygon® tubes and polyethylene tubes with 0.8 mm i.d. were used to pump the solutions through the minicolumn. A manifold with four three-way solenoid valves was used to select preconcentration and elution steps. The connections of the preconcentration flow system were made of Y-shaped Teflon. Solenoid valves were controlled by a microcomputer running software written in Quick Basic 4.5.

2.2. Reagents

Ultrapure water from a Milli-Q® (Bedford, MA, USA) water purification system (Millipore®) was used to prepare all solutions. All chemicals were of analytical grade and were used without previous purification. The hydrochloric and nitric acid were suprapure quality from Merck (Darmstadt, Germany). The laboratory glassware was kept overnight in a 2% (v/v) Extran® (Merck) solution and 10% (v/v) nitric acid solution, respectively. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

Working standard solutions of zinc(II) (100 μg l^{-1}) were prepared by dilution of 2000 mg l^{-1} zinc(II) stock solution (Fluka, Switzerland) using 1% (v/v) nitric acid solution.

Sorensen buffer solution (pH 7) was prepared by mixing 0.084 mol l^{-1} Na_2HPO_4 and 0.067 mol l^{-1} KH_2PO_4 (Vetec, Rio de Janeiro, Brazil) at a ratio of 1:0.02.

Hydrochloric acid solutions (Merck) used as eluent in flow system were prepared by appropriate dilution with water from the concentrated acid.

The Nb_2O_5–SiO_2 was prepared in accordance with the work described by Budziak et al. [23].

2.3. Preparation of the minicolumn

A minicolumn with length and i.d. of 43 mm and 3 mm, respectively, was filled with 100 mg of Nb_2O_5–SiO_2 adsorbent material. The ends of this minicolumn were sealed with small glass wool beds to prevent material losses. The minicolumn was coupled with a flame atomic absorption spectrometer. The sorbent packed minicolumn used in proposed procedure did not show any over pressure or swelling in the conditions used in this work. Besides, the same Nb_2O_5–SiO_2 minicolumn was used during all experiments without lost of signal, indicating long life of this adsorbent material, stability and suitability for zinc determination.

2.4. Preparation of samples

The certified reference material of urine Seronorm™ Trace Elements no. 403125 (Nycomed, Pharma) was diluted with 5 ml of ultrapure water just before the analysis.

A total of five 24-h urine samples and five blood samples, which generated five blood plasma and five erythrocyte samples, were provided by a hospital in the city of Florianópolis, SC, Brazil. The 24-h urine is defined as the total urine collected for a patient in a period of 24-h.

The urine samples were centrifuged at 3000 rpm for 10 min and then 5 ml of the supernatant was diluted to a final volume of 50 ml after pH correction. The blood samples were centrifuged at 3000 rpm for 15 min at a temperature of 4 °C. Blood plasma was collected by aspiration of the supernatant, which was stored in adequate plastic tubes at a temperature of −20 °C prior to analyses. The erythrocytes remaining in the tubes containing anticoagulant were washed with 5 ml of 0.9% (v/v) saline solution and centrifuged at 10,000 rpm for 10 min at a temperature of 4 °C. This procedure was done twice more. Afterwards, the saline solution and erythrocytes were withdrawn one by one. The erythrocytes were stored frozen (−70 °C) until the analysis [26]. Both plasma and erythrocyte samples were diluted by a factor of 1:100 before the preconcentration procedure. These matrices did not need a pH correction because their pH is very close to 7.0.

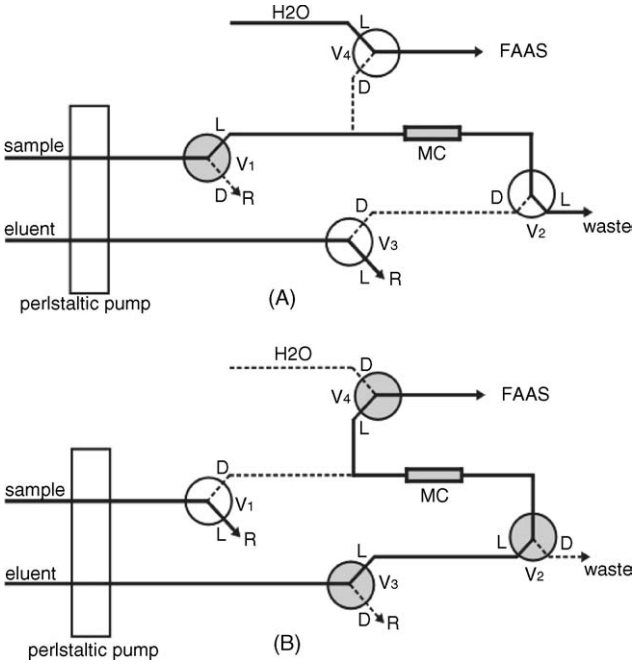

Fig. 1. Diagram of the on-line preconcentration system used in this study. (A) adsorption process and (B) dessorption process. V: valve, L: open way, D: closed way, MC: minicolumn containing adsorbent, R: sample or eluent back stream, hatched circle: valve on and white circle: valve off.

2.5. On-line preconcentration system

The diagram of the flow system is shown schematically in Fig. 1. The flow system was made up of a peristaltic pump fitted with Tygon tubing, four three-way solenoid valves and a minicolumn filled with 100 mg of Nb_2O_5–SiO_2 sorbent material. It was coupled with a flame atomic absorption spectrometer. In the sample loading step (Fig. 1A), valve V_1 is initially activated and the others are turned off, so that the sample or standard solution, with pH adjusted to 7.0 using Sorensen buffer solution, was pumped at 6.3 ml min^{-1} through the minicolumn where ion exchange takes place and the effluent flows towards waste (W). After that, water was pumped through the minicolumn for 5 s to eliminate residues from the sample matrix. In the elution step (Fig. 1B), valve V_1 is turned off and V_2, V_3 and V_4 are activated and a 1.3 mol l^{-1} hydrochloric acid solution percolated through the minicolumn at a flow rate of 4.0 ml min^{-1} displacing the Zn(II) ions from the adsorbent. The eluate was taken directly to the nebulizer-burner system of the flame atomic absorption spectrometer. An additional step to regenerate the minicolumn was not necessary because the very same eluent regenerated the adsorbent active sites [23,24].

2.6. Optimization strategy

The optimization procedure was carried out using two-level full factorial and Doehlert designs. All experiment was done in duplicate and 10.0 ml of a 100 μg l^{-1} zinc(II) working solution was used. The four variables regarded as factors in this study were: sample pH, eluent concentration, eluent flow rate and sample flow rate. Both optimization designs, the two-level full factorial and the Doehlert matrix, were available using absorbance and/or sensibility efficiency (SE) like the response for optimization of computer programs. The SE is defined as the analytical signal of an on-line enrichment system for a preconcentration time of 1 min [20]. The SE was used because it includes the sampling time as an implicit factor in the analytical response. In other words, the SE takes the best sensibility with the highest sampling frequency into consideration. The experiment data were processed using Statistica computer program [27].

Table 1
Levels and factors used in factorial design

Factor	Low (−)	High (+)
Sample flow rate (ml min^{-1})	3.0	7.0
Eluent flow rate (ml min^{-1})	3.0	5.0
Eluent concentration (HCl, mol l^{-1})	0.6	2.0
Sample pH	3.0	7.0

3. Results and discussion

3.1. Factorial design

The factors (chemical and flow variables) chosen considering the on-line preconcentration system were: eluent flow rate, sample flow rate, eluent concentration and sample pH. A two-level full factorial design 2^4 with a central point (C), 17 runs total was carried out in duplicate to determine the influence of the selected factors and their interactions in the preconcentration system. In accordance with the data obtained in the previous experiments, maximum (+1) and minimum (−1) values of each factor were chosen (Table 1). Analysis of variance (ANOVA) and *P*-value significant levels were used to check the significance of the effects on the preconcentration system. The main effects and their interactions can be observed in the Pareto chart shown in Fig. 2. In accordance with this chart, the factors of the sample pH and sample flow rate, and their interactions, are highly significant. The positive values obtained in this study

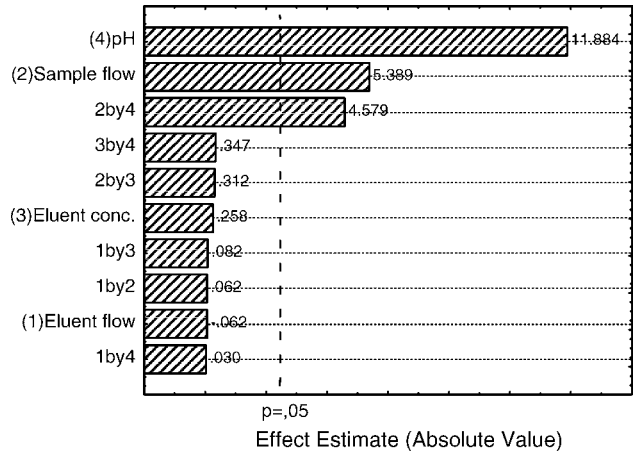

Fig. 2. Pareto chart of standardized effects for variables (1, Eluent flow rate; 2, sample flow rate; 3, eluent concentration and 4, sample pH) and their interactions (2 × 4, 2 × 3, 1 × 3, 1 × 2 and 1 × 4) in the Zn(II) preconcentration using sensibility efficiency as response.

Table 2
Doehlert matrix used to obtain the response surface

Experiment	Sample pH	Sample flow (ml min^{-1})	Absorbance	Efficiency signal	Time (s)
1	6	5	0.4250	0.1212	120
2	8	5	0.1994	0.0997	120
3	5	7	0.2463	0.1699	87
4	7	7	0.3328	0.2295	87
5	9	7	0.1302	0.0898	87
6	6	9	0.2595	0.2218	70
7	8	9	0.2100	0.1795	70

(+11.38; +5.38e+4.57) indicate that by increasing these factors, the analytical signal will increase too.

3.2. Doehlert design

The results obtained by factorial design demonstrated the necessity of a final optimization of the sample pH and sample flow rate variables. The factors of eluent concentration and eluent flow rate were not significant and were fixed at 1.3 mol l^{-1} and 4.0 ml min^{-1}, respectively. These values were chosen because they are average values from the maximum and minimum values used for factorial design. The significant variables (sample pH and sample flow rate) were optimized using a Doehlert matrix. In this study, seven experiments were carried out in accordance with that shown in Table 2. All experiments were done in duplicate.

The absorbance and the sensibility efficiency obtained in this experiment were used to feed the Doehlert matrix and the obtained surface response is shown in Fig. 3. The Eqs. (1) and (2) represent the response surface when used absorbance and sensibility efficiency as analytical response, respectively.

$$\begin{aligned}\mathrm{SE} = {} & -2.155 + 0.484\,\mathrm{pH_{sample}} + 0.25\,\mathrm{flow_{sample}} \\ & -0.036\,\mathrm{pH^2_{sample}} - 0.0008\,\mathrm{pH_{sample}\,flow_{sample}} \\ & -0.017\,\mathrm{flow^2_{sample}} \end{aligned} \quad (1)$$

$$\begin{aligned}\mathrm{SE} = {} & -1.746 + 0.348\,\mathrm{pH_{sample}} + 0.212\,\mathrm{flow_{sample}} \\ & -0.025\,\mathrm{pH^2_{sample}} - 0.003\,\mathrm{pH_{sample}\,flow_{sample}} \\ & -0.012\,\mathrm{flow^2_{sample}} \end{aligned} \quad (2)$$

These results indicated that there is a maximum value for the pH sample and flow rate sample on the surface response using both, absorbance or sensibility efficiency, as analytical signal. Absorbance was used with Eqs. (3) and (4) to calculate the values of pH sample and sample flow rate variables, and sensibility efficiency with Eqs. (5) and (6).

$$\frac{\partial \mathrm{SE}}{\partial \mathrm{pH_{sample}}} = 0.453 - 0.072\,\mathrm{pH_{sample}} - 0.0008\,\mathrm{flow_{sample}} \quad (3)$$

$$\frac{\partial \mathrm{SE}}{\partial \mathrm{flow_{sample}}} = 0.25 - 0.0008\,\mathrm{pH_{sample}} - 0.034\,\mathrm{flow_{sample}} \quad (4)$$

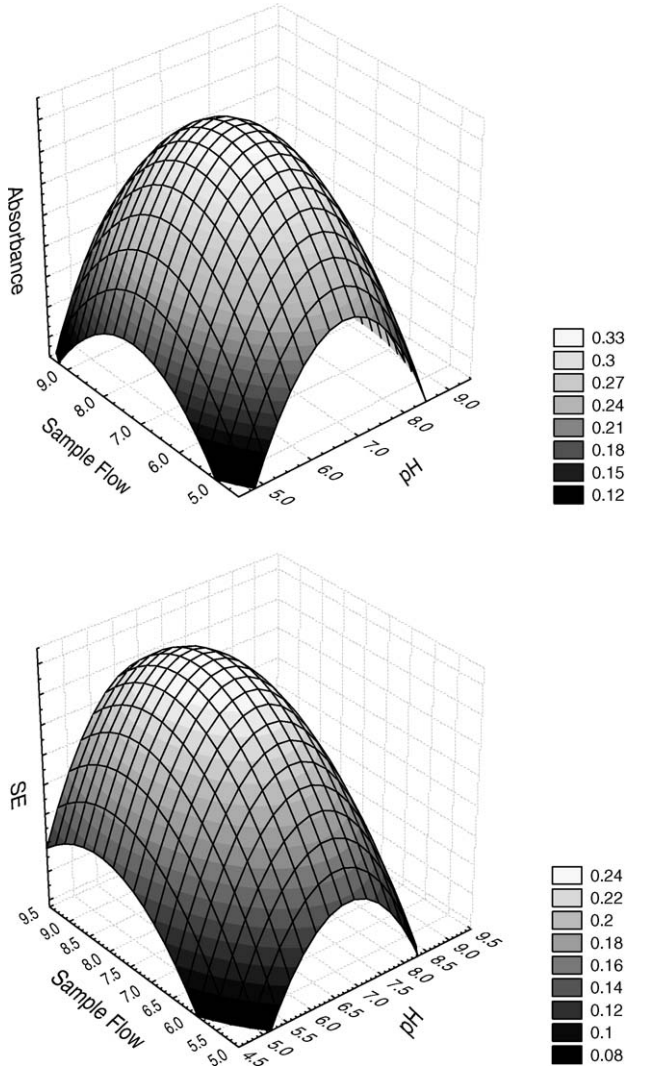

Fig. 3. Response surface graph obtained from Zn(II) extraction in biological samples using Nb_2O_5–SiO_2 adsorbent and analytical response as (A) absorbance and (B) sensibility efficiency.

$$\frac{\partial \mathrm{SE}}{\partial \mathrm{pH_{sample}}} = 0.348 - 0.050\,\mathrm{pH_{sample}} - 0.003\,\mathrm{flow_{sample}} \quad (5)$$

$$\frac{\partial \mathrm{SE}}{\partial \mathrm{flow_{sample}}} = 0.212 - 0.003\,\mathrm{pH_{sample}} - 0.024\,\mathrm{flow_{sample}} \quad (6)$$

The corresponding values of the maximum are $\mathrm{pH_{sample}}$ = 6.62 and $\mathrm{flow_{sample}}$ = 7.10 ml min^{-1}, when used absorbance as response and $\mathrm{pH_{sample}}$ = 6.58 and $\mathrm{flow_{sample}}$ = 7.96 ml min^{-1}, when used sensibility efficiency as response. These results show that both analytical responses are adequate to optimized the proposed system. However, in this work, a sample pH = 7.0 was used to match the pH bilologycal matrices and a sample flow rate = 6.3 ml min^{-1} was used to avoid leaks in the flow system observed at higher flow rates.

3.3. Effect of foreign ions

The effect of potential interfering species in the determination of 100 μg l^{-1} of Zn(II) was studied. In this study, an interfering

Table 3
Effect of foreign ions

Foreign ions	Concentration ($mg\,l^{-1}$)	Foreign ions	Concentration ($mg\,l^{-1}$)
Sodium	10	Barium	50
Calcium	20	Potassium	50
Iron	5	Cadmium	20
Copper	3	Chromium	5
Lead	10		

specie was one whose amount introduced in the working solution changed more than 10% the signal of the Zn(II) alone. Table 3 contains the information about some species studied and the amount of these species that changed the signal of Zn(II).

3.4. Analytical features

The calibration graph obtained using optimized conditions is given as $A = 0.07281 + 0.00511 \times C$ in the linear range of 10–100 $\mu g\,l^{-1}$, where C is Zn(II) concentration in solution ($\mu g\,l^{-1}$). The correlation coefficient obtained from this graph was 0.9955. The limit of detection (LOD) was calculated as $3\sigma/S$, where S is the slope of the calibration curve and σ is the standard deviation of 11 consecutive measurements of the blank solution. The value of the LOD was 0.77 $\mu g\,l^{-1}$ in 10 ml of the blank solution. The precision of the procedure, calculated as relative standard deviation of seven consecutive measurements of a 10 $\mu g\,l^{-1}$ Zn(II) solution, was 1.5%. The enrichment factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, was 77 for a 95 s preconcentration time. The sampling frequency of 27 samples/h was obtained from the proposed system.

3.5. Analytical application

In order to evaluate the accuracy of the developed procedure, Zn(II) was determined in standard reference material (urine Seronorm^{TM} Trace Elements) and 24-h urine and blood samples (obtained from a hospital in the city of Florianópolis, SC, Brazil). The results are presented in Table 4. The values of Zn(II) found in blood plasma and erythrocytes are in accordance with the data related in the literature [22]. Recovery tests, adding 20 $\mu g\,l^{-1}$ of Zn(II) in all studied samples, were carried out. The recovery of Zn(II) obtained from this study was between 78% and 118%. The result found by applying the proposed procedure to the urine Seronorm^{TM} Trace Elements was 425 $\mu g\,l^{-1}$, while the certified value was between 423 and 470 $\mu g\,l^{-1}$.

Table 4
Results of the Zn(II) determination in 24-h urine, blood plasma and erythrocytes using the proposed methodology

Samples	24-h urine (mg Zn/24-h)	Plasma blood ($\mu g\,Zn\,ml^{-1}$)	Erythrocytes ($\mu g\,Zn\,ml^{-1}$)
1	180	1.4	14.2
2	191	0.5	12.9
3	127	0.5	17.1
4	40	1.9	26.6
5	77	0.4	14.8

The data obtained in this study indicate that the proposed procedure is not affected by the sample matrix. Therefore, it can be satisfactorily applied to determine Zn(II) in the studied biological matrices.

4. Conclusion

The proposed on-line preconcentration system using a mini-column filled with Nb_2O_5–SiO_2 sorbent is an attractive alternative to determine Zn(II) in urine, blood plasma and erythrocyte samples. The amount of biological samples necessary to carry out the analysis is very low and there are no problems with the interference matrix. The on-line preconcentration procedure is simple, presented good sensibility and precision to determine traces of Zn(II) in the studied samples using FAAS.

The use of full factorial and Doehlert designs allows the optimization of the proposed system, while taking the interactions among the variables into consideration. This procedure showed to be more efficient than the univariate method and was achieved with few experiments.

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References

[1] A.F. Santos Jr., P.N.P. Santos, M.G.A. Korn, Rev. Bras. Anal. Clín. 35 (4) (2003) 169.
[2] A.S. Prasad, D. Oberleas, Trace Elem. Hum. Health Dis. 1 (1976).
[3] J. Wang, E.H. Hansen, B. Gammelgaard, Talanta 55 (2001) 117.
[4] P.R.M. Correia, E. Oliveira, P.V. Oliveira, Anal. Chim. Acta 458 (2002) 321.
[5] J. Szpunar, J. Bettmer, M. Robert, H. Chassaigne, K. Cammon, R. Lobinski, O.F.X. Donard, Talanta 44 (1997) 1389.
[6] V.A. Lemos, R.E. Santelli, M.S. de Carvalho, S.L.C. Ferreira, Spectrochim. Acta B 55 (1998) 1497.
[7] M.G. Pereira, M.A.Z. Arruda, Microchim. Acta 141 (2003) 115.
[8] V.A. Lemos, P.X. Baliza, J.S. Santos, L.S. Nunes, A.A. Jesus, M.E. Rocha, Talanta 66 (2005) 174.
[9] C. Shuyu, Z. Zhifeng, Y. Huaming, Anal. Chim. Acta 451 (2) (2002) 305.
[10] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta 54 (5) (2001) 935.
[11] S.L.C. Ferreira, V.A. Lemos, B.C. Moreira, A.C.S. Costa, R.E. Santelli, Anal. Chim. Acta 403 (1–2) (2000) 259.
[12] R.J. Cassela, V.A. Salim, L.S. Jesuíno, R.E. Santelli, S.L.C. Ferreira, M.S. Carvalho, Talanta 54 (1) (2001) 61.
[13] S.L.C. Ferreira, C.F. Brito, Anal. Sci. 15 (1999) 189.
[14] I.I. Chen, S. Xu, Z. Fang, Anal. Chim. Acta 298 (2) (1994) 167.
[15] S.M. Sella, A.K. Avila, R.C. Campos, Anal. Lett. 32 (1999) 2091.
[16] E. Vassileva, N. Furuta, Fresenius J. Anal. Chem. 370 (2001) 52.
[17] N. Nagata, L.T. Kubota, M.I.M.S. Bueno, P.G.P. Zamora, J. Colloid Interface Sci. 200 (1998) 121.
[18] S. Denofre, Y. Gushikem, S.C. DeCastro, Y.J. Kawano, Chem. Soc. Faraday Trans. 89 (1993) 1057.

[19] S.L.C. Ferreira, W.N.L. dos Santos, C.M. Quintella, B.B. Neto, J.M. Bosque-Sendra, Talanta 63 (2004) 1061.
[20] S.L.C. Ferreira, W.N.L. dos Santos, M.A. Bezerra, V.A. Lemos, J.M. Bosque-Sendra, Anal. Bioanal. Chem. 375 (3) (2003) 443.
[21] W.N.L. dos Santos, C.M.C. Santos, S.L.C. Ferreira, Microchem. J. 75 (2003) 211.
[22] M.A. Bezerra, A.L.B. Conceição, S.L.C. Ferreira, Anal. Bioanal. Chem. 378 (2004) 798.
[23] D. Budziak, E.L. da Silva, S.D. de Campos, E. Carasek, Microchim. Acta 141 (2003) 169.
[24] E.L. da Silva, E.M. Ganzarolli, E. Carasek, Talanta 62 (2004) 727.
[25] E.L. da Silva, D. Budziak, E. Carasek, Anal. Lett. 37 (2004) 1909.
[26] D. Mafra, S.M.F. Cozzolino, Clin. Biochem. 37 (2004) 67.
[27] Statistica for Windows, StatSft, Inc. (1999). 2300 East 14th Street, Tulsa, OK 741014, USA.