



Eclética Química

ISSN: 0100-4670

atadorno@iq.unesp.br

Universidade Estadual Paulista Júlio de
Mesquita Filho
Brasil

Matos, G. D.; Tarley, C. R. T.; Ferreira, S. L. C.; Arruda, M. A. Z.
Use of experimental design in the optimisation of a solid phase preconcentration system for Cobalt
determination by GFAAS
Eclética Química, vol. 30, núm. 1, janeiro-março, 2005, pp. 65-74
Universidade Estadual Paulista Júlio de Mesquita Filho
Araraquara, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=42930109>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System
Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal
Non-profit academic project, developed under the open access initiative

Use of experimental design in the optimisation of a solid phase preconcentration system for Cobalt determination by GFAAS

G. D. Matos¹, C. R. T. Tarley¹, S. L. C. Ferreira² e M. A. Z. Arruda^{1*}

¹Departamento de Química Analítica, Universidade Estadual de Campinas (Unicamp), Campus Universitário Zeferino Vaz, P.O. Box, 6154, 13084-971, Campinas, São Paulo, Brasil

²Departamento de Química Analítica, Universidade Federal da Bahia (UFBA), Campus Universitário da Ondina, 40170-290, Salvador, Bahia, Brasil

*To whom correspondence should be addressed.

E-mail: zezzi@iqm.unicamp.br

Abstract: In this work is proposed a solid phase preconcentration system of Co^{2+} ions and its posterior determination by GFAAS in which fractional factorial design and response surface methodology (RSM) were used for optimization of the variables associated with preconcentration system performance. The method is based on cobalt extraction as a complex Co^{2+} -PAN (1:2) in a mini-column of polyurethane foam (PUF) impregnated with 1-(2-pyridylazo)-naphthol (PAN) followed by elution with HCl solution and its determination by GFAAS. The chemical and flow variables studied were pH, buffer concentration, eluent concentration and preconcentration and elution flow rates. Results obtained from fractional factorial design 2^{5-1} showed that only the variables pH, buffer concentration and interaction (pH X buffer concentration) based on analysis of variance (ANOVA) were statistically significant at 95% confidence level. Under optimised conditions, the method provided an enrichment factor of 11.6 fold with limit of detection and quantification of 38 and 130 ng L⁻¹, respectively, and linear range varying from 0.13 to 10 µg L⁻¹. The precision (n = 9) assessed by relative standard deviation (RSD) was respectively 5.18 and 2.87% for 0.3 and 3.0 µg L⁻¹ cobalt concentrations.

Keywords: Experimental Designs; preconcentration system; polyurethane foam; cobalt.

Introduction

Cobalt is considered an essential element for living organisms in which present important role in metabolic process mainly those involving the vitamin B₁₂ [1]. Due to its low concentration mainly in natural water samples (0.1-0.5 µg L⁻¹) [2] analytical methods with high sensitivity for its determination are required. In this way, in atomic spectrometry including flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS), the methods for cobalt determinations commonly are accomplished by inserting preconcentration step previous to measurements. In GFAAS, the methods are more

promising due to higher power of detection than FAAS, thus indicating that preconcentration systems associate with GFAAS is an attractive approach to enhance its performance based on sensitivity.

Cobalt determination by GFAAS after preconcentration has usually been carried out by solid phase extraction [3], coprecipitation [4] and sorption on knotted reactor [5]. The process of solid phase extraction has been the most used because they usually do not employ hazardous solvent such as those liquid-liquid extraction system, present easy recovery of solid phase, high enrichment factors and may also be combine with flow systems [6]. Although the solid phase preconcentration flow systems have to become an important analytical

approach for metal determination, many procedures are still optimised using univariate methodology. Particularly, in flow system in which several chemical and flow variables are optimised, the univariate methodology process may lead to erroneous conclusions when the effect of one particular variable is dependent to others [7]. Furthermore, such optimisation presents time consuming and is less economical. In this way, in order to circumvent this drawbacks, experimental designs based on multivariate optimisation seems the most useful tool for searching those optimum conditions in an analytical method.

The first step of multivariate optimisation is accomplished screening the factors studied (full factorial or fractional factorial) in order to obtain their significant effects in the analytical system. In a full factorial the combination of K variables is investigated by two levels, thereby this design will consist of 2^K experiments. Thus, to evaluate 7 variables 128 experiments will be need; for 8 variables 256 experiments have to be carried out; therefore it is obvious that the number of experiments depends on the number of variables. The fractional factorial design has successfully been used when several variables need to be optimised. It is based on a fraction ($1/2, 1/4, 1/8, \dots, 1/2^p$) of the full factorial and establish that the effect of third order or higher are negligible; so the number of experiments assume 2^{K-p} experiments whereas p is the size of the fraction [8]. Hence, if $p = 1$, the screening of 7 variables by using a fractional factorial design is accomplished with only 64 experiments. After established the significant factors from full or fractional design the optimum operation conditions is attained by using simultaneous designs more complete such as Doehlert designs, central composite and star design plus central point [9-12]. With these designs, quadratic function as below demonstrated are obtained, in which describe the presence of surfaces being possible to attain the optimum condition.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_1X_1^2 + b_2X_2^2 + b_{12}X_1X_2$$

where X_1 and X_2 are the factors studied; b_0 is an independent term; b_1 and b_2 are the coefficients of the linear terms and b_{12} is the coefficient involved with the interactions between the factors.

Several studies involving experimental

designs have been employed for achieve optimum condition in solid phase preconcentration procedures for organic and inorganic species determination [13,14].

Thus, the aim of this work was to establish a multivariate methodology based on fractional factorial designs 2^{5-1} and star design plus central point for optimisation of variables associated to solid phase preconcentration of cobalt onto a polyurethane foam mini-column impregnated with 1-(2-pyridylazo)-naphthol (PAN) with posterior determination by GFAAS. PAN was chosen due to remarkable capacity to complex transitions metals. In addition, this reagent has been immobilized on Dowex 50W X4-400 cation-exchange resin on solid phase spectrophotometry procedures for copper determination [15] Also, it has been impregnated on Amberlite XAD-2 [16] and Ambersorb 563 resin [17] in procedures for trace metals determination by FAAS.

Experimental

Instrumentation

The absorbance measurements based on peak area were performed in a Perkin-Elmer AAnalyst 600 atomic absorption spectrometer equipped with a longitudinal Zeeman-effect background correction system, as well as graphite atomiser tube with integrated L'vov platforms. Cobalt hollow cathode lamp used as radiation source was operated at standard conditions as recommended by manufacturer. For preconcentration system, a home-made injector commutator was used to select preconcentration/elution steps while all solutions were propelled by an Ismatec Model IPC peristaltic pump with Tygon tubes and connections made of Teflon. The mini-column used for packing the polyurethane foam impregnated with 1-(2-pyridylazo)-naphthol (PAN) was made in polyethylene tube (6 cm length and 4 mm i.d.). The pH of solutions was measured with a Digimed DM 20 pH meter.

Reagents and solutions

Deionised water, obtained from Milli-Q system, was used to prepare the solutions and all reagents were analytical grade. Cobalt reference

standard solutions were prepared immediately before use, by dilution of a 1000 mg L⁻¹ stock standard solutions (Merck). Stock solutions of phosphate and borate buffer (Merck) were, respectively, prepared from KH₂PO₄ and Na₂B₄O₇·10H₂O salts dissolved in 1000 mL of deionised water and pH adjusted with 1.0 mol L⁻¹ HCl solution or 1.0 mol L⁻¹ NaOH solution.

For preparing the 1-(2-pyridylazo)-naphthol solution at 0.05 % (w/v) concentration, 0.025 g of the reagent was dissolved in 50 mL of ethanol (99.5% v/v) (J. T. Baker).

Commercial polyurethane foam open-cell polyether-type (PUF) was used as a support material to PAN provided 10-12 cells per linear cm resilience and had a density of 23 mg cm⁻³. Before packing into mini-column, PUF was submitted to the treatment as previously described [18].

Preparation of mini-column of PUF impregnated with PAN

The loading of PAN onto PUF was performed by percolating the 0.05 % (w/v) PAN solution through a mini-column packed with 100 mg of polyurethane foam at a flow rate of 2.5 mL min⁻¹ for 5 min. Then, a 10% (v/v) sodium hydroxide solution was percolated through mini-column in order to remove the excess of PAN until effluent became colourless. Afterwards, at the same flow rate, the mini-column was washed with 5% (v/v) nitric acid solution and deionised water to prevent any metal contamination.

Preconcentration system

The preconcentration step was accomplished by propelling a cobalt solution buffered at pH 8.2 with borate buffer through 100 mg of PUF-PAN packed into mini-column at flow rate of 5.0 mL min⁻¹, where Co²⁺ ions were retained by complex formation as Co²⁺-PAN (1:2). After preconcentration, the elution step was made by switching the position of injector whose Co²⁺ ions were displaced from mini-column by 1.0 mL of 0.1 mol L⁻¹ HCl at the same preconcentration flow rate. The eluate collected in flasks was then analysed by GFAAS. The graphite furnace program applied for cobalt determination was carried out by recommendation of manufactures.

Optimisation strategy

The first step of the multivariate studies was carried out aiming to screen the effect of five factors in the preconcentration system. For this task, a fractional factorial design 2⁵⁻¹ without replicates was conducted with only 16 experiments. In order to analyse which effects from factors and their interactions that possibly to be confounded, the generator *I* = abcde of fractional factorial design was adopted. The flow and chemical variables including sample pH, preconcentration and elution flow rates, buffer and eluent concentration in which commonly affect the solid phase preconcentration were evaluated. Minimum and maximum levels of these variables are summarised in Table 1.

Table 1. Factors and experimental domain used in the fractional factorial design 2⁵⁻¹ for multivariate analyses of the cobalt preconcentration system

Factors	Levels	
	Minimum (-)	Maximum (+)
pH	6.0	8.0
Preconcentration flow rate (PFR) (mL min ⁻¹)	2.0	5.0
Buffer concentration ^a (BC) (mol L ⁻¹)	0.01	0.05
Eluent concentration (EC) (HNO ₃) (mol L ⁻¹)	0.1	1.0
Elution flow rate (EFR) (mL min ⁻¹)	2.0	5.0

a. KH₂PO₄/NaOH

These experiments were performed under a random order by preconcentration 25 mL of cobalt solution $2.0 \mu\text{g L}^{-1}$ followed by elution with 1.0 mL of HCl solution.

After establishing the significant factors in the preconcentration system, assays based on design 2^2 plus central point were carried out in order to achieve the best results in central point. Additional design based on EVOP (*Evolution Operation*) was made by shifting the direction of factors so that higher analytical response could be obtained in central point. Once obtained such conditions, the star design plus central point, in which makes possible to achieve the quadratic function was

performed. Finally, from quadratic function as well as the respectively response surface, the optimum values of the factors studied were obtained.

Results and Discussion

Fractional Factorial design for assessing the effect of experimental variables

The fractional factorial design 2^{5-1} performed without replicates was employed as the first screening to evaluate the result and estimate of the main effects (in this case called as estimate of the contrast) to the preconcentration system of cobalt. The experimental results are shown in Table 2.

Table 2. Fractional factorial design 2^{5-1} and the results obtained for cobalt determination after preconcentration onto PUF-PAN. The generator of fractional factorial design is $I = abcde$

Runs	a pH	b PFR	c BC	d EC	e EFR	Response (peak area)
1	-	-	-	-	+	0.0188
2	+	-	-	-	-	0.0704
3	-	+	-	-	-	0.0182
4	+	+	-	-	+	0.0625
5	-	-	+	-	-	0.0070
6	+	-	+	-	+	0.0287
7	-	+	+	-	+	0.0074
8	+	+	+	-	-	0.0253
9	-	-	-	+	-	0.0205
10	+	-	-	+	+	0.0711
11	-	+	-	+	+	0.0155
12	+	+	-	+	-	0.0646
13	-	-	+	+	+	0.0107
14	+	-	+	+	-	0.0347
15	-	+	+	+	-	0.0109
16	+	+	+	+	+	0.0289

PFR = preconcentration flow rate, BC = buffer concentration, EC = eluent concentration, EFR = elution flow rate.

A briefly evaluation from data shown in Table 2, demonstrate that higher analytical response are obtained in the runs 2, 4, 10 and 12, thus previously indicating that only pH and buffer concentration factors are significant. The significance of factors can be confirmed by probability cumulative plot displayed in Fig. 1. As can be illustrates, all points nearly on a linear curve on probability cumulative plot are not significant, thus attesting that only pH, buffer concentration and interaction (pH \times buffer concentration) are statistically significant at 95% confidence level.

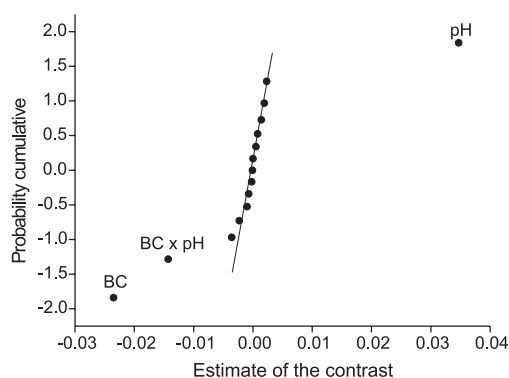


Figure 1. Probability cumulative plot , BC = phosphate buffer concentration.

As a chemical evaluation, the positive contrast obtained for pH indicates that cobalt complexation with PAN reagent takes place in pH range above the experimental domain *i.e.*, its complexation is favored at pH higher than 8. On the other hand, negative contrast obtained for buffer concentration shows that higher concentration provides a decrease in the analytical signal probably due to competition between phosphate anions with PAN for cobalt ions. The effects for preconcentration and elution flow rate factors, as well as its interactions were not significant, thus indicating that a fast kinetic process is involved in the formation of the Co^{2+} -PAN (1:2) complex. The insignificance of eluent concentration factor indicates that 0.1 mol L^{-1} HCl solution is enough to release the cobalt retained by PAN in the mini-column.

After establishing pH and buffer concentration as statistically significant factors, a new factorial design based on 2^2 plus central point was evaluate. These experiments were performed setting all the other factors fixed: 5.0 mL min^{-1} preconcentration flow rate, 0.1 mol L^{-1} HCl as eluent and 5.0 mL min^{-1} elution flow rate. Maximum and minimum levels, central point and results are showed in Table 3.

Table 3. Design 2^2 plus central point using $\text{KH}_2\text{PO}_4/\text{NaOH}$ as buffer solution

Run	pH	BC	Response (peak area)
1	-	-	0.0175
2	+	-	0.0603
3	-	+	0.0080
4	+	+	0.0252
5	0	0	0.0155
6	0	0	0.0143
7	0	0	0.0159

Levels (-), (0) and (+) are attributed, respectively to pH values of 6, 7 and 8 and buffer concentration (BC) 0.01, 0.03 and 0.05 mol L^{-1} .

As one can see, it is possible to note that in the central point does not present the best analytical response. Therefore, a new experiment using EVOP based on design 2^2 plus central point was performed so that an optimum region was attained. However,

for these experiments the phosphate buffer was changed to a borate buffer because it provides a much better buffering capacity in this new pH range (7.0-9.0). The results obtained are shown in Table 4, together with the corresponding matrix design.

Table 4. Design 2^2 plus central point using $\text{Na}_2\text{B}_4\text{O}_7/\text{HCl}$ as buffer solution

Run	pH	BC	pH	BC (mol L ⁻¹)	Response (peak area)
1	-	-	7.0	0.006	0.0827
2	+	-	9.0	0.006	0.1402
3	-	+	7.0	0.014	0.0990
4	+	+	9.0	0.014	0.1151
5	0	0	8.0	0.010	0.1908
6	0	0	8.0	0.010	0.1837
7	0	0	8.0	0.010	0.1849

Levels (-), (0) and (+) are attributed, respectively to pH 7, 8 and 9 and buffer concentration 0.006, 0.01 and 0.014 mol L⁻¹.

As one shown, in the range tested for these factors the best results were observed in central point. According to these data, it was necessary to evaluate the significance of linear regression model for further application of star design plus central point. Thus, test for significance of the regression model and test for lack of fit were performed by analysis of variance (ANOVA). In this sense, according to *F*-test, the ratio between medium quadratic of lack of fit (lof) and pure experimental error (pe) was compared to tabled values of *F*-distribution. Hence, as $F_{\text{lof/pe}}$ (368.7) exceeded the critical $F_{2,2,95\%}$ (19.0), the linear model presents lack of fit and obviously it is considered unsatisfactory. Once known that the best results were obtained around central point as well as the linear model was not satisfactory, the star design plus central point (three measurements) was carried out in order to

obtain a quadratic function. The levels used and respectively responses are summarized in Table 5. The ANOVA results obtained from this design showed that the quadratic model did not show lack of fit since $F_{\text{lof/pe}}$ (10.86) was less than the critical $F_{3,2,95\%}$ (19.16), thus emphasizing that the model is significant. Moreover, the regression component explained by 97.83% also corroborates the significance of quadratic model. The ratio between medium quadratic of regression component and residual component (45.05) was also compared to tabled values of *F*-distribution, whose value was higher than the critical ($F_{5,5,95\%} = 5.05$ - significant regression). Overall the results indicated that the quadratic model was satisfactory as can be observed by equivalent results between experimental response and expected response by quadratic model (Table 6).

Table 5. Factorial design 2² plus central point plus star using Na₂B₄O₇/HCl as buffer solution

Run	pH	BC	Experimental response (peak area)	Expected response by quadratic model
1	-	-	0.0827	0.0790
2	+	-	0.1402	0.1483
3	-	+	0.0990	0.0865
4	+	+	0.1151	0.1140
5	0	0	0.1908	0.1865
6	0	0	0.1837	0.1865
7	0	0	0.1849	0.1865
8	-1.4142	0	0.0340	0.0443
9	0	1.4142	0.1173	0.1263
10	1.4142	0	0.1183	0.1124
11	0	-1.4142	0.1497	0.1454

Levels -1.4142, (-), (0), (+) and 1.4142 are attributed, respectively for pH values of 5.6, 6.0, 7.0, 8.0 and 8.4 and for buffer concentration 0.0018, 0.0100, 0.0300, 0.050 and 0.0582 mol L⁻¹.

Table 6. Validation of the method for cobalt determination in spiked mineral water samples

Samples	Concentration of cobalt added (µg L ⁻¹)	Concentration of cobalt found ^a (µg L ⁻¹)	Recovery (%)
Mineral Water (brand 1)	0	< LOQ	-
	5.0	5.3 ± 0.2	106
Mineral Water (brand 2)	0	< LOQ	-
	5.0	5.1 ± 0.3	102
Mineral Water (brand 3)	0	< LOQ	-
	5.0	4.9 ± 0.1	98
Mineral Water (brand 4)	0	< LOQ	-
	5.0	4.7 ± 0.3	94

a. The results are expressed as mean value ± S.D based on three replicates (n = 3) determinations. Confidence interval, 95%.

The Eq.(2) of the quadratic model was following:

$$v = 0,1865 + 0,0241\text{pH} - 0,0068\text{BC} - 0,0541\text{pH}^2 - 0,0254\text{BC}^2 - 0,0104\text{pHBC} \quad \text{Eq.(2)}$$

The response surface as well as contour plot constructed from this equation is shown in Fig. 2.

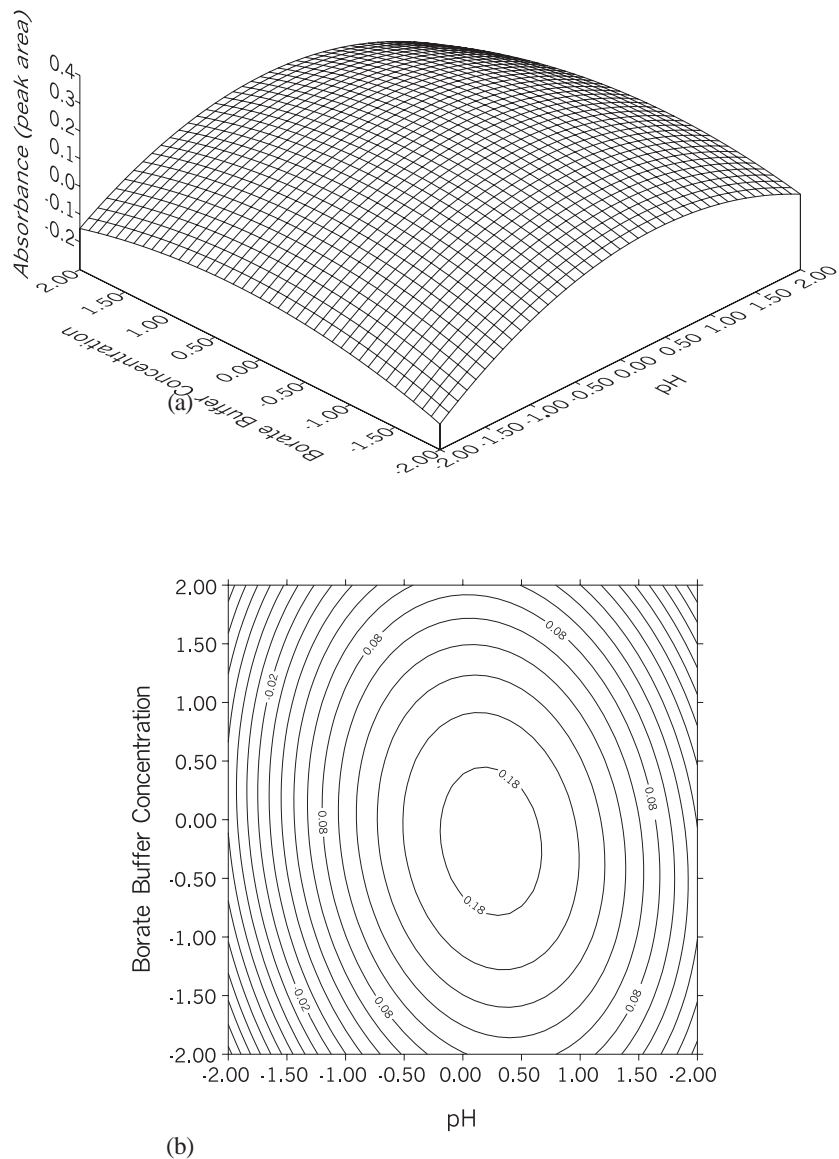


Figure 2. Response surface (a) and contour plot (b) obtained under optimised conditions.

This response surface has a maximum, whose coordinate is calculated by solving the system of equation:

$$\delta v / dpH = 0 \quad \text{and} \quad \delta v / dBC = 0$$

The critical point is located at the position given by 8.2 in pH and $9.3 \times 10^{-3} \text{ mol L}^{-1}$ in borate buffer concentration.

Analytical features and validation of the cobalt preconcentration method

According to results obtained from linear range, cobalt can be determined in the 0.13 to 10 mg L^{-1} range whose linear regression was 0.997. As 5.0 mL min^{-1} sampling flow rate was used in this procedure, 25 mL of sampling volume require a sampling time of 5 min.

The preconcentration factor (PF) was calculated by slope ratio of the calibration curves obtained with and without the preconcentration step. This procedure is the most used to evaluate the sensitivity obtained by insert a preconcentration step previous measures. So, the preconcentration factor obtained in this work was 11.6. Although preconcentration factor is considered the most usual procedure to evaluate the performance of preconcentration system, this concept cannot be used alone because, in general, higher preconcentration factors are obtained when high sample volume preconcentration are employed. In this situation, the sample throughput, which is an important factor on preconcentration system, is not considered. Therefore, as the present preconcentration procedure is accomplished by off-line mode, the sample consumption based on consumptive index (CI) becomes an efficient way to evaluate the performance of preconcentration system [19]. Consumptive index is expressed by volume of analyte solution V_s and the PF ratio ($CI = V_s / PF$), thus indicating the necessary volume to attain one unit of preconcentration factor. In this way, consumptive index obtained in the present work was 2.15 mL in which is much less than previous works [20-26].

The limits of detection (LOD) as quantification (LOQ) were obtained by means of literature [27], in which was defined, respectively, as the ratio of three and ten times the standard deviation of the blank solution ($n=20$) by slope of the analytical curve. The respectively LOD and LOQ for cobalt were 38 and 130 ng L^{-1} , respectively.

The precision, calculated as relative standard deviation (RSD) for 9 replicates, was 5.2 and 2.9 % for 0.3 and 3.0 mg L^{-1} , respectively. As an application, the method was employed for cobalt determination in mineral waters. As one can see in Table 6, the cobalt concentration in analysed samples was below to the limit of quantification (130 ng L^{-1}). Thus, the accuracy of the method was carried out from test of addition and recovery, whose results ranging from 94 to 106% makes possible to confirm the accuracy of the method. It is important to emphasize that although cobalt was not directly determined in these samples the limit of quantification of the present method shows that cobalt can be determined in natural water according to common levels (0.1 to 0.5 mg L^{-1}) [2].

Conclusions

The proposed cobalt preconcentration method, which involves solid phase extraction in a mini-column containing polyurethane foam impregnated with 1-(2-pyridylazo)-naphthol can be considered a suitable analytical strategy for cobalt determination in water samples. The present method is considered simple and provides economy of chelating agent unlike many preconcentration procedures, in which commonly employ unloaded solid support, thus requiring additional lines in the flow system to the chelating agents. Moreover, based on consumptive index, the proposed method requires only 2.15 mL of sample to provides one unit of preconcentration factor that is lower than others solid phase preconcentration procedure for cobalt determination.

Regarding the multivariate optimisation, it was possible note the usefulness of experimental designs in the optimisation of cobalt preconcentration method based on solid phase extraction. In addition, fractional factorial was efficiently used to estimate the main effects as well as the interactions of variables using few experiments as that employed in a usual full factorial. It is an important characteristic on experimental designs mainly if one considers preconcentration systems, in which several chemical and flow variables has to be optimised. Furthermore, using factorial design it was possible to obtain optimum conditions for pH and borate buffer concentration in which could never be attained if univariate procedure for optimisation was used.

Acknowledgements

The authors acknowledge the FAPESP (grant number 01/05614-0) and CAPES for financial support. G. D. M., S. L. C. F. and M. A. Z. A. are grateful

to CNPq for scholarships. Authors also thank to Prof. Carol H. Collins for language assistance.

Recebido em: 09/11/2004

Aceito em: 21/12/2004

G. D. Matos, C. R.T. Tarley, S. L. C. Ferreira e M. A. Z. Arruda. Uso de planejamento experimental na otimização de um sistema de pré-concentração em fase sólida para a determinação de cobalto por GFAAS

Resumo: No presente trabalho é proposto um sistema de pré-concentração em fase sólida de íons Co^{2+} com posterior determinação por GFAAS, cuja otimização das variáveis associadas ao desempenho do sistema de pré-concentração foi realizada por planejamento fatorial fracionário e metodologia de superfície de resposta (MSR). O método é baseado na extração de cobalto como um complexo Co^{2+} -PAN (1:2) em uma mini-coluna de espuma de poliuretano (EPU) impregnada com 1-(2-piridilazo)-naftol (PAN) seguido pela eluição com solução de HCl e determinação por GFAAS. As variáveis químicas e de fluxo estudadas foram pH, concentração do tampão, concentração do eluente e vazões de pré-concentração e eluição. Os resultados obtidos a partir do planejamento fatorial fracionário 2^{5-1} mostraram, com base na análise de variância (ANOVA), que apenas as variáveis pH, concentração do tampão e a interação (pH X concentração do tampão) foram estatisticamente significativas com nível de 95% de confiança. Nas condições otimizadas, o método forneceu um fator de enriquecimento de 11,6 vezes com respectivos limites de detecção e quantificação de 38 e 130 ng L^{-1} e faixa linear variando de 0,13 a 10 mg L^{-1} . A precisão ($n=9$) avaliada em termos de desvio padrão relativo (DPR) foi respectivamente de 5,18 e 2,87% para concentrações de cobalto de 0,3 e 3,0 mg L^{-1} .

Palavras-chave: Planejamento Experimental; sistema de pré-concentração; espuma de poliuretano; cobalto.

References

- [1] C. C. Nascentes, M. A. Z. Arruda, *Talanta* 61 (2003) 759.
- [2] T. Braun, M. N. Abbas, *Anal. Chim. Acta* 119 (1980) 113.
- [3] S. L. C. Ferreira, H. C. dos Santos, R. C. Campos, *Talanta* 61 (2003) 789.
- [4] M. Hiraide, Z. S. Chen, H. Kawaguchi, *Talanta* 43 (1996) 1131.
- [5] X. P. Yan, W. VanMol, F. Adams, *Lab. Robotics Automat.* 9 (1997) 191.
- [6] V. A. Lemos, R. E. Santelli, M. S. Carvalho, S. L. C. Ferreira, *Spectrochim. Acta Part B* 55 (2000) 1497.
- [7] J. M. Bosque Sendra, M. Nechar, M. F. Molina, *Microchim. Acta* 134 (2000) 43.
- [8] T. Lundstedt, E. Seifert, L. Abramo, B. Thelin, A. Nystrom, J. Pettersen, R. Bergman, *Chemo. Intell. Lab. Syst.* 42 (1998) 3.
- [9] P. W. Araujo, R. G. Brereton, *Trends Anal. Chem.* 15 (1996) 26.
- [10] P. W. Araujo, R. G. Brereton, *Trends Anal. Chem.* 15 (1996) 63.
- [11] E. R. Pereira-Filho, R. J. Poppi, M. A. Z. Arruda, *Quim. Nova* 25 (2002) 246.
- [12] M. Nechar, M. F. Molina, J. M. Bosque-Sendra, *Anal. Chim. Acta* 382 (1999) 117.
- [13] S. L. C. Ferreira, A. S. Queiroz, M. S. Fernandes, H. C. Santos, *Spectrochim. Acta Part B* 57 (2002) 1939.
- [14] C. Huang, Y. Su, Y. Hsieh, *J. Chromatography A* 977 (2002) 9.
- [15] F. Lazaro, M. D. Luque de Castro, M. Valcarcel, *Anal. Chim. Acta* 214 (1998) 217.
- [16] S. L. C. Ferreira, A. F. Dantas, N. M. L. Araújo, A. C. S. Costa, *Talanta* 48 (1999) 1173.
- [17] I. Narin, M. Soylak, *Talanta* 60 (2003) 215.
- [18] S. L. C. Ferreira, D. S. De Jesus, R. J. Cassella, A. C. S. Costa, M. S. Carvalho, R. E. Santelli, *Anal. Chim. Acta* 378 (1999) 287.
- [19] E. N. V. M. Carrilho, J. A. Nóbrega, T. Gilbert, *Talanta* 60 (2003) 1131.
- [20] A. Alexandrova, S. Arpadjan, *Analyst* 118 (1993) 1309.
- [21] M. Kumar, D. P. S. Rathore, A. K. Singh, *Analyst* 125 (2000) 1221.
- [22] M. Kumar, D. P. S. Rathore, A. K. Kingh, *Fresenius J. Anal. Chem.* 370 (2001) 377.
- [23] G. Chakrapani, D. S. R. Murty, P. L. Mohanta, R. Rangaswamy, *J. Geochem. Explor.* 63 (1998) 145.
- [24] M. Kumar, D. P. S. Rathore, A. K. Singh, *Microchem. Acta* 137 (2001) 127.
- [25] A. Ramesh, K. R. Mohan, K. Sessaiah, N. D. Jeyakumar, *Anal. Lett.* 34 (2001) 219.
- [26] D. Atanasova, V. Stefanova, E. Russeva, *Talanta* 45 (1998) 857.
- [27] L. G. Long, J. D. Winefordner, *Anal. Chem.* 55 (1983) 713.