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A new functionalized resin and its application in preconcentration system with multivariate optimization for nickel determination in food samples

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Abstract

In this work, Amberlite XAD-2 resin functionalized with 4,5-dihydroxy-1,3-benzenedisulfonic acid was synthesized, characterized and applied as a new packing material for an on-line system to nickel preconcentration. The method is based on the sorption of Ni(II) ions in a minicolumn containing the synthesized resin, posterior desorption using an acid solution and measurement of the nickel by spectrophotometry (PAR method). The optimization of the system was performed using factorial design and Doehlert matrix considering five variables: eluent concentration, PAR solution pH, sample flow rate, PAR solution concentration and sample pH. Signals were measured as peak height by using an instrument software. Using the experimental conditions defined in the optimization, the method allowed nickel determination with achieved sampling rate of 25 samples per hour, detection limit (3 s) of 2 $\mu g\, l^{-1}$ and precision (assessed as the relative standard deviation) of 8.2–2.6%, for nickel solutions of 10.0–200.0 $\mu g\, l^{-1}$ concentration, respectively. The experimental enrichment factor of the proposed system was 46, for 120 s preconcentration time. The proposed procedure was applied for nickel determination in food samples. Recoveries of spike additions (5 or 10 $\mu g\, g^{-1}$) to food samples were quantitative (94–110%).

Keywords: Nickel; Synthesis; Multivariate optimization; Preconcentration; Amberlite XAD-2

1. Introduction

Nickel determination at trace levels is required in several areas of the science, such as environmental chemistry, toxicology, geology, biochemistry, etc. Preconcentration methods generally are associated with determination of this metal, because some conventional techniques, e.g. spectrophotometry and flame atomic absorption spectrometry (FAAS), have not adequate sensitivity for these analysis. The use of solid sorbents in preconcentration methods presents several advantages over liquid–liquid extraction in terms of simplicity, reliability, and the ability to obtain a high enrichment factor [1]. Furthermore, it reduces the use of organic solvents that could be toxic and expensive. Many procedures involving nickel preconcentration can be found in literature employing a variety of materials, such as silica [2–4], activated carbon [5], fullerene [6], naphthalene [7] and Amberlite XAD-2 [8,9].

An important strategy for metal enrichment is the incorporation of complexing reagents in solid supports to adsorb and preconcentrate metal ions from solutions. The incorporation reduces problems of leaching of the ligand from the support. These supports include silica [10], polyurethane foam [11–13] and polymeric resins [14–17]. Modified polymeric resins have been employed in preconcentration and separation methods. Ligands can be coupled on polymeric sorbent through several groups, such as an azo

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[18–21] or methylene group [22]. Immobilization via an azo linkage is the most commonly employed method. However, this synthetic procedure leaves residual amine groups on the polymer surface as a consequence of incomplete reaction [23,24]. Furthermore, several preconcentration methods employing other groups and ligands to produce powerful sorbents has been described [25,26].

Solid-phase extraction (SPE) combined with on-line systems results in methods very opportune for determinations of trace metals due to its flexibility, simplicity, versatility and high sampling frequencies. Many procedures of on-line preconcentration generally involve a first step of sorption of the metal ions in the sorbent at convenient pH, and a second step of dessorption of the metallic species with an appropriate eluent [27]. This eluent is taken directly to on-line mesurement, significantly reducing time consuming for analysis. Therefore, these methods can be used in conjunction with different spectrometric detectors [28].

An important tool to study variables simultaneously is the optimization of analytical systems by multivariate designs, resulting in approaches faster and more cost-effective than traditional univariate optimization [29–31]. Generally, two steps are involved in multivariate optimization of analytical procedures: a preliminary evaluation that selects the significant variables in the procedure using factorial design, and an appropriate estimation of the real functional relationship among the analytical response and significant factors. This way, the optimum values for these factors can be calculated. A Doehlert matrix is a chemometric tool, used for estimation of critical points, which has been widely used in optimization of analytical methods [32–35]. In a process involving two variables (*X* and *Y*) and an analytical response (*Z*), the quadratic model is described as:

$$Z = a + b\,X + cY + dX_2 + eY_2 + fXY \qquad (1)$$

where *a* is the constant term, *b* and *c* the coefficients of linear terms, *d* and *e* the coefficients of quadratic terms and *f* the coefficient of interaction among the factors. Identification of critical points is carried out with application of Lagrange criterion in the equation obtained during the optimization.

This paper describes the preconcentration of nickel using a new 4,5-dihydroxy-1,3-benzenedisulfonic acid–Amberlite XAD-2 (DHBS–XAD) resin in on-line system. The optimization step of the chemical and flow variables of the on-line system was performed using factorial design and Doehlert matrix.

2. Experimental

2.1. Instrumentation

Flow system was made up of a peristaltic pump (Milan, model 204, Colombo, Brazil) furnished with silicone tubes to deliver all solutions, a flow-through cell, a six-port rotary valve (Rheodyne model 5041, Cotati, USA) and a DHBS-XAD packed minicolumn for the on-line nickel preconcentration. The laboratory-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm contains about 100 mg of DHBS–XAD. A syringe was used to place the sorbent in column. Plastic foams were put at both sides of minicolumn to keep the packing material in the place. Afterwards, the column was washed with ethanol, 5% (v/v) nitric acid solution and deionized water, respectively, at 2.50 ml min^{-1} flow rate. Washing with nitric acid and ethanol was necessary in order to prevent any metal or organic contamination, respectively. The manifold was built up with PTFE (polytetrafluorethylene) tube with 0.5 mm of internal diameter.

A Varian Model Cary 50 (Mulgrave, Victoria, Australia) UV–vis spectrophotometer equipped with xenon lamp was used to perform absorbance measurements. Preconcentration system was adapted to flow-through cell system of the UV–vis spectrophotometer.

A Digimed DM 20 (Santo Amaro, Brazil) pH meter was used for pH measurements. Infrared spectra were recorded on an ABB Bomen MB series model MB100 Fourier transform IR spectrometer. A Thermo Finnigan Flash elemental analyzer 1112 series was used for elemental analysis.

2.2. Reagents

Laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with deionized water. Deionized water from a water purification system (Quimis, Brazil) was used to prepare all solutions. All reagents were of analytical reagent grade. Nickel(II) working solutions at $\mu\mathrm{g\,l}^{-1}$ level were prepared daily by diluting a 1000 $\mu\mathrm{g\,ml}^{-1}$ stock solution (Merck). Hydrochloric acid solutions were prepared by direct dilution with deionized water from the concentrated solution (Merck) and used as eluent. The disodium salt of 4,5-dihydroxy-1,3-benzenedisulfonic (DHBS) acid (Sigma), also known as Tiron, was used for synthesis of the sorbent. Amberlite XAD-2 (Sigma) 20–60 mesh, methylene chloride (Vetec, Brazil), octanol (Merck), nitrobenzene (Merck) and aluminum chloride (Vetec, Brazil) were also used for synthesis. For on-line detection of Ni(II) ions, a buffered 4-(2-pyridilazo)resorcinol (PAR) solution was used. Borate (7.0 and 7.5) and ammoniacal (8.0, 8.5 and 9.0) buffers were used to adjust the sample and PAR solution pH. Borate buffers were prepared by adding a convenient amount of hydrochloric acid to sodium borate solutions (0.5 mol l^{-1}) to result in solutions of appropriate pH. Ammoniacal buffers were prepared by adding ammonia to ammonium chloride solutions (0.5 mol l^{-1}).

2.3. Synthesis of the DHBS–XAD resin

The sorbent DHBS–XAD was prepared by a modified procedure described previously for similar resins [36,37]. Amberlite XAD-2 resin (3 g) was treated with 10 ml octanol and 20 ml methylene chloride. Anhydrous aluminum chloride (7 g) was added in small increments to the mixture. The system was refluxed for 24 h at 90 °C. The solid was filtered and washed with acetone and twice with 1:1 (v/v) aqueous hydrochloric acid, finally washed with water until neutral, then with acetone, and dried in a vacuum. The chloromethylated copolymer was suspended in a mixture of 30 ml nitrobenzene and 1.0 g of DHBS. Then, the system was refluxed for 72 h at 70 °C with continuous stirring. The mixture was filtered and the resin was washed with 1:1 (v/v) aqueous hydrochloric acid, chloroform, alcohol and ether, respectively.

2.4. Sample preparation

Food samples (dry shrimp) obtained from supermarkets of Jequié, Brazil, were triturated, homogenized and dried overnight at 100 °C, and were kept in ambient condition. Digestion of this material was carried out treating about 0.4 g of the sample with 4.0 ml of 1:1 (v/v) nitric acid solution and keeping it overnight in a Teflon vessel [14]. Afterwards, the Teflon vessel was closed and put into a pressurized digestion system. The thermal heating was made in a stove at 150 °C for 6 h. After cooling at room temperature, the solutions were adjusted to pH 7.0 with a 10% (w/v) sodium hydroxide solution and an appropriate buffer solution. A masking solution was added and the volume was diluted to 100 ml. At least one blank solution was run for each sample in order to evaluate nickel contamination by the reagents used.

2.5. On-line preconcentration system

The operation of the on-line nickel preconcentration system is presented in Fig. 1 and run-through two simple steps. In step A (preconcentration), a buffered solution (S) containing nickel(II) ions was percolated through the minicolumn (C) that retained the metal. Thus, nickel(II) ions were retained on the DHBS–XAD sorbent and the remaining solution was discharged (W). Flow rate of S was involved in optimization process and it determining the sample volume that pass in the minicolumn. After a fixed period, the six-port valve (V) was switched to step B (elution) and a stream of eluent (E) displaced nickel(II) ions. This eluent reacted with PAR buffered solution (R) at convenient pH and the mixture flows through a reaction coil (RC) and a flow-through cell. So, the absorbance of the system was read at 550 nm in a spectrophotometer (ST). PAR solution (R) and eluent solution (E) flow rates were fixed at 5.0 ml min^{-1}. Peak height measurements (maximum absorbance) were proportional to the nickel concentration, and were obtained by using an instrument software.

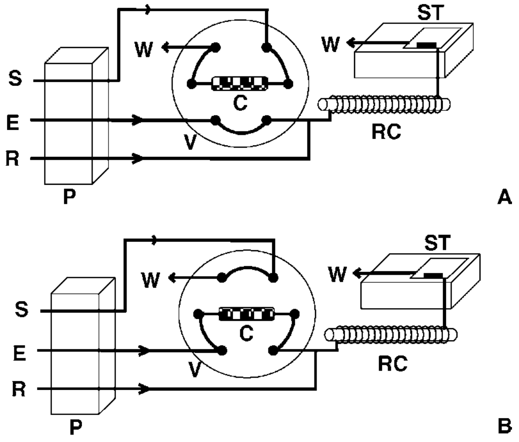

Fig. 1. Schematic diagram of the flow system used to preconcentration and determination of nickel. S, sample; E, eluent; R, PAR solution; P, peristaltic pump; C, DHBS–XAD minicolumn; W, waste; V, six-port valve; RC, reaction coil (200 cm); ST, spectrophotometer; A, six-port valve in preconcentration position; B, six-port valve in elution position.

2.6. Optimization strategy

The optimization step was carried out using a two-level full factorial and Doehlert designs [30,38]. A 100 $\mu\mathrm{g\,l}^{-1}$ nickel(II) working solution was used. Experiments were performed in duplicate, on a random order. The variables regarded as factors were: eluent concentration, PAR solution pH, sample flow rate, PAR solution concentration and sample pH. Experimental data were processed using the Statistica computer program [39].

3. Results and discussion

3.1. Resin characterization

Elemental analysis (found: C, 48.1%; H, 3.2%, calculated for $C_{15}H_{14}O_8S_2$: C, 46.6%; H, 3.6%) show that on an average one DHBS molecule is present in the resin per repeated unit of the polymer. A proposed structure is shown in Fig. 2. Infrared spectrum of DHBS–XAD is compared with that of free Amberlite XAD-2. There are additional bands at 3500–3410, 1345, 1335 and 635 cm^{-1}, which appear to originate due to modification of resin by the ligand and are characteristic of O–H, sulfonic group, C–OH and C–S, and vibrations, respectively.

3.2. Factorial design

The factors chosen considering the on-line preconcentration system were: eluent concentration (EC), PAR solution pH ($\mathrm{pH_{PAR}}$), sample flow rate (SF), PAR solution

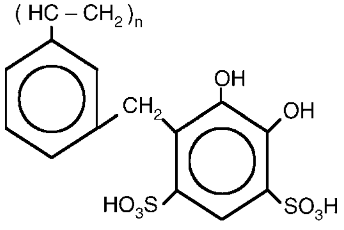

Fig. 2. Proposed structure for DHBS–XAD.

Table 1
Factors and levels used in factorial design

Factor	Level	
	Low (−)	High (+)
Eluent concentration, EC × 10^{-2} (mol l^{-1})	1.0	5.0
PAR solution pH, pH_{PAR}	7.0	9.0
Sample flow rate, SF (ml min^{-1})	9.3	14.0
PAR solution concentration, PC × 10^{-4} (mol l^{-1})	1.0	2.0
Sample pH, pH_S	7.0	9.0

concentration (PC) and sample pH (pH_S). A two-level full factorial design of 2^5 with 32 runs was carried out in duplicate to determine the influence of each factor and its interactions in the preconcentration system. Table 1 shows minimum and maximum to each factor, chosen according to previous experiments. SF and preconcentration time were varied accordingly to pass the same sample volume (14.0 ml) by minicolumn. Thus, preconcentration times used were 60 and 90 s, when employed high and low sample flow rate values, respectively. Response in the factorial design was the peak height (*h*), defined as the maximum absorbance reached in each run.

Analysis of variance (ANOVA) [40] and *P*-value significant levels were used to check the significance of the effects. Pareto chart in Fig. 3 also shows the significance of factors. In the interpretation of this graph, it should be considered that bar lengths are proportional to the absolute value of the estimated effects. According to this chart, the factors eluent concentration (EC) and PAR solution pH (pH_{PAR}) are highly significant. An increase in these factors increases the analytical signal. pH_{PAR} is an important factor because it demonstrates the pH value more favorable to the formation of the Ni(II)–PAR complex, after the elution. The higher value of EC provides an enhancement in analytical signal because there is a fast change in pH of the column, improving the desorption. Interaction between these factors (EC × pH_{PAR}) is also important because the eluent solution containing the cation merges with the reagent solution in a T-piece. In this process, eluent solution pH should increase quickly to favor the Ni(II)–PAR complex formation.

Pareto chart shows that sample pH (pH_S) and sample flow rate (SF) are also significant factors. In that graph, the effects of these factors have negative values. So, an increasing of pH_S or SF decreases the analytical signal. Increasing of pH_S decreases the analytical signal probably due the formation of hydroxy-complexes of nickel at high pH values. These complexes are not retained in the minicolumn, decreasing nickel amount sorbed by DHBS–XAD. Sample flow rate determinates the velocity that Ni(II) ions passes by minicolumn. These results indicate that nickel sorption is minor at high flow rates because Ni(II) ions pass too quickly that the contact time between the phases is not sufficient for a complete retention. PAR solution concentration (PC) is less significant than others, according to the absolute value of the effect of this factor in Pareto chart. The interactions (pH_S × pH_{PAR}), (pH_S × EC), (SF × PC) and (SF × pH_{PAR}) are also statistically significant.

3.3. Doehlert designs

Some factors studied in the previous experiment require a final optimization, according to factorial design in 3.2. So, the factors EC, pH_{PAR}, pH_S and SF were optimized using Doehlert designs. Considering also the results of factorial design, PC was fixed at 1.0 × 10^{-4} mol l^{-1} to avoid rapid and unnecessary consumption of reagent. The other four factors were optimized using two Doehlert designs. The interaction (EC × pH_{PAR}) has the most significant effect in the system as can be seen in Fig. 3. A Doehlert design involving these two factors was then performed. Two others factors, pH_S

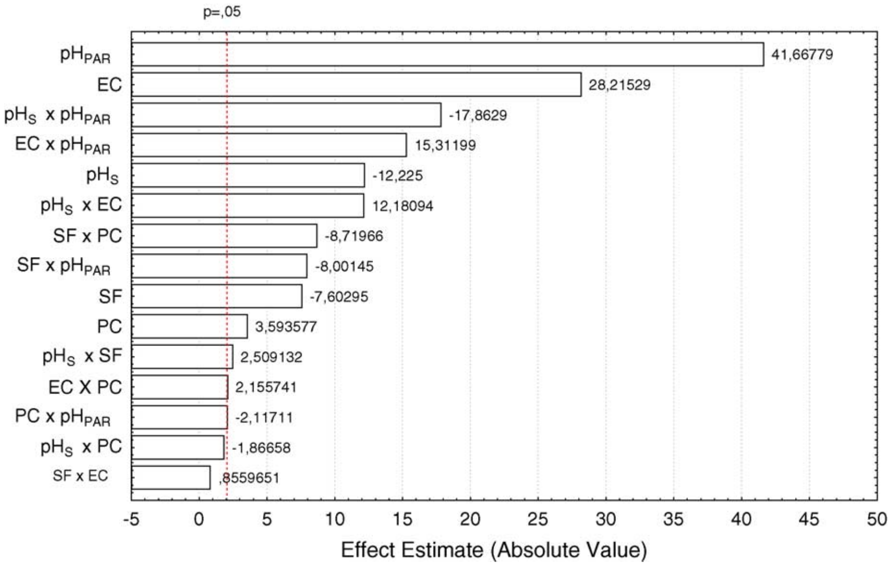

Fig. 3. Pareto chart of standardized effects for variables in the nickel preconcentration. EC, eluent concentration; pH_{PAR}, PAR solution pH; PC, PAR solution concentration; SF, sample flow rate; pH_S, sample pH.

Table 2
Doehlert matrix for design 1

Experiment	EC × 10^{-2} (mol l^{-1})	pH_{PAR}	Peak height (*h*)
1	3.0	9.0	0.144
2	1.0	8.5	0.066
3	5.0	8.5	0.186
4	3.0	8.0	0.174
5	3.0	8.0	0.155
6	3.0	8.0	0.169
7	1.0	7.5	0.069
8	5.0	7.5	0.193
9	3.0	7.0	0.170

EC eluent concentration and pH_{PAR} PAR solution pH.

and SF have also significant effect, individually. Then, for optimization of these variables, a second Doehlert design was performed.

3.4. *Design 1: EC and pH_{PAR}*

For this design, optimized factors were EC and pH_{PAR}. The factors pH_S and SF were fixed at 7.0 and 9.3 ml min^{-1}, respectively. These values were chosen according the factorial design, considering the effect of the factor observed in Fig. 3. For pH_S and SF, the effect is negative, so low values increases the analytical signal if considered individually. Experiments required for this design are described in Table 2. The factors eluent concentration and PAR solution pH were varied from 1.0×10^{-2} to 5.0×10^{-2} mol l^{-1} and 7.0–9.0, respectively. Experimental data were used in the Doehlert matrix. The equation that represents the relationship among EC, pH_{PAR} and the analytical signal or peak height (*h*) is the following:

$$h = -0.521 + 0.137\ pH_{PAR} - 0.009\, pH_{PAR}^2 + 9.08\, EC - 88.01\, EC^2 - 0.094\, EC\ pH_{PAR} \qquad (2)$$

There is a good agreement among the model predicted peak height and the experimental values as can be seen in Table 2. The corresponding response surface is shown in Fig. 4. These results indicated that there is a maximum on the surface response and this was calculated from the following equations:

$$\delta h/\delta pH_{PAR} = 0.137 - 0.018\, pH_{PAR} - 0.094\, EC \qquad (3)$$

$$\delta h/\delta EC = 0 = 9.08 - 0.094\, pH_{PAR} - 176.02\, EC \qquad (4)$$

The corresponding values of the maximum are $pH_{PAR} = 7.3$ and $EC = 4.8 \times 10^{-2}$ mol l^{-1}.

3.5. *Design 2: pH_S and SF*

Variables pH_{PAR} and EC were fixed at values 7.3 and 4.8×10^{-2} mol l^{-1}, respectively, according to the results obtained in design 1. Table 3 describes experiments required for Doehlert design 2. Factors pH_S and SF were varied from 7.0 to 9.0 and 9.3–14.0 ml min^{-1}, respectively. Obtained data were used in the Doehlert matrix and the function, which represents the relationship among pH_S, SF and analytical signal or peak height (*h*) for nickel preconcentration system is:

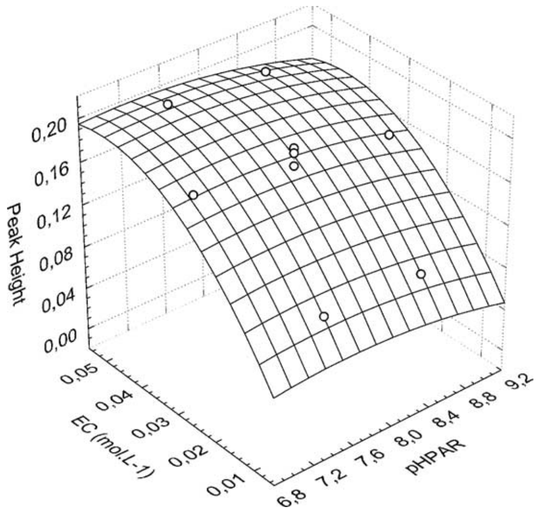

Fig. 4. Surface response fit to data in Table 2. EC, eluent concentration (mol l^{-1}) and pH_{PAR}, PAR solution pH.

$$h = -1.93 + 0.432\ pH_S - 0.033 pH_S^2 + 0.106\, SF - 0.006\, SF^2 + 0.004\, pH_S\ SF \qquad (5)$$

This model fits experimental data. Corresponding surface response is shown in Fig. 5. There is a maximum on the surface response and this was calculated from the equations:

$$\delta h/\delta pH_S = 0 = 0.432 - 0.066\ pH_S + 0.004\, SF \qquad (6)$$

$$\delta h/\delta SF = 0 = 0.106 + 0.004\ pH_S - 0.012\, SF \qquad (7)$$

Maximum values are $pH_S = 7.1$ and SF = 11.3 ml min^{-1}.

3.6. *Final optimization*

Fatorial and Doehlert designs were performed and it demonstrated that the optimum conditions for a maximum analytical signal are: 1.0×10^{-4} mol l^{-1} PAR solution, pH_S 7.1, pH_{PAR}7.3, 4.8×10^{-2} mol l^{-1} *E* and SF 11.3 ml min^{-1}. For a SF of 11.3 ml min^{-1}, it was used 120 s preconcentation time. Considering 20 s of elution time for each run, the sampling rate achieved was 25 h^{-1}.

Table 3
Doehlert matrix for design 2

Experiment	SF (ml min^{-1})	pH_S	Peak height (*h*)
1	12.0	9.0	0.0889
2	9.3	8.5	0.0733
3	14.0	8.5	0.0756
4	12.0	8.0	0.1650
5	12.0	8.0	0.1600
6	12.0	8.0	0.1650
7	9.3	7.5	0.1750
8	14.0	7.5	0.1721
9	12.0	7.0	0.1710

SF, sample flow rate, pH_S, sample pH.

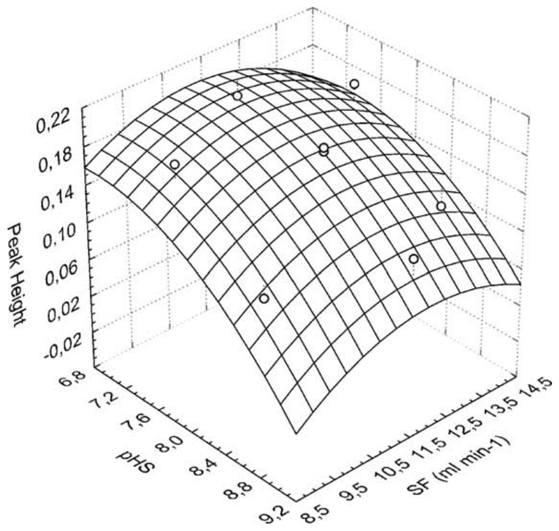

Fig. 5. Surface response fit to data in Table 3. SF sample flow rate (ml min^{-1}) and pH$_S$ sample pH.

3.7. Analytical features

The calibration graph under the conditions optimized by factorial and Doehlert designs is given as $A = 9.3 \times 10^{-3} + 1.6 \times 10^{-3}C$ in the range of 2–200 μg l^{-1} (C is nickel concentration in solution, μg l^{-1}). The precision of the procedure, determined as the relative standard deviation in sample solutions containing between 10 and 150 μg l^{-1} of nickel is in the range of 8.2–2.6%, respectively, calculated by seven measurements. The limit of detection (LOD), defined as the nickel concentration that gives a response equivalent to three times the standard deviation (s) of the blank ($n = 11$), was found to be 2 μg l^{-1} in 22.60 ml of sample solution.

When nickel was determined directly by measuring of the absorbance of Ni(II)–PAR complex, without preconcentration, the calibration graph equation was $A = 5.4 \times 10^{-3} + 3.5 \times 10^{-5}C$, for the concentration range of 50.0–2000.0 μg l^{-1}. The experimental enrichment factor of the proposed system, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration [28] was 46, for 120 s preconcentration time. Concentration efficiency (18 h^{-1}), consumption index (1.9 ml) and other important analytical parameters for online systems were also calculated [28]. In order to determinate the phase transfer factor, 11.3 ml of a 100.0 μg l^{-1} nickel solution was percolated by the column. The desorption was carried out with 1.00 ml of 4.8×10^{-2} mol l^{-1} eluent solution and measured by PAR method [41]. In these conditions, the phase transfer factor of the column, defined as the ratio between the analyte mass in original sample and that in the concentrate was 0.80.

3.8. Effect of foreign ions

Table 4
Maximum tolerable amounts of foreign ions in on-line system using DHBS–XAD minicolumn after addition of masking solution (nickel concentration = 100 μg l^{-1})

Substance	Maximum tolerable amount
Na^+, Cl^-, $SO_4{}^{2-}$, Br	5 g l^{-1}
K^+, $NO_3{}^-$	2 g l^{-1}
Mg^{2+}, Al^{3+}, Ca^{2+}, Fe^{3+}	15 mg l^{-1}
Pb^{2+}, $PO_4{}^{2-}$	5 mg l^{-1}
Zn^{2+}	4 mg l^{-1}
Cu^{2+}, Cd^{2+}	2 mg l^{-1}
Co^{2+}	100 μg l^{-1}

The effect of potential interfering species in the determination of 100 μg l^{-1} nickel(II) was studied. Amounts of each species were considered tolerable, when the signal in the presence of the species resulted in a deviation of the peak height less than 5%, compared with the signal for nickel alone. Cations Fe^{3+} (5000 μg l^{-1}), Zn^{2+} (1000 μg l^{-1}), Cd^{2+} and Cu^{2+} (500 μg l^{-1}) and Co^{2+} (100 μg l^{-1}) interfere on nickel preconcentration. This interference was minimized by addition of a masking in sample solution. Acetate, fluoride, tartarate and citrate were tested as maskings. Best results were obtained by addition of 10 ml of a 10% (w/v) sodium citrate and sodium fluoride solution to 100 ml of sample solution. The results of system selectivity with masking addition are given in Table 4.

3.9. Application

In order to evaluate the accuracy of the developed procedure, nickel was determined in standard reference material (spinach leaves-NIST 1570a). An amount of 0.5 g of this material was decomposed according to previously described procedure for food samples. Result found by proposed methodology was 2.09 ± 0.08 μg g^{-1}, for $n = 4$ and at a confidence level of 95% level. It was found that there is no significant difference between results obtained by the proposed method and the certified results (2.14 ± 0.10 μg g^{-1}).

Proposed method has been applied for nickel determination in food samples collected from supermarkets of Jequié, Brazil. The results are described in Table 5. Recoveries (R)

Table 5
Results obtained for nickel determination in dry shrimp samples ($n = 4$)

Sample	Added (μg g^{-1})	Nickel found by proposed methodology (μg g^{-1})	Recovery (%)
Brand 1	0	<LOD	–
	5	5.1 ± 0.2	102 ± 2
	10	10.5 ± 0.1	105 ± 2
Brand 2	0	<LOD	–
	5	4.7 ± 0.6	94 ± 2
	10	9.5 ± 0.7	95 ± 1
Brand 3	0	<LOD	–
	5	4.9 ± 0.1	98 ± 1
	10	9.8 ± 0.4	98 ± 3
Brand 4	0	<LOD	–
	5	5.5 ± 0.2	110 ± 2
	10	10.4 ± 0.3	104 ± 1

Confidence interval 95%; LOD, limit of detection.

of spike additions (5 or 10 $\mu g\,g^{-1}$) to four samples were quantitative (94–110%). R was calculated as follows: $R\,(\%) = \{(C_m - C_o)/m\} \times 100$. Where C_m is a value of nickel in a spiked sample, C_o a value of nickel in a sample and m the amount of nickel spiked. These results also proved that the procedure could be applied satisfactorily for nickel determination in food samples contaminated by this metal.

4. Conclusion

This work demonstrates the potentialities of functionalized DHBS–XAD resin combined with spectrophotometry and a flow injection system. This combination resulted in a simple, sensitive and inexpensive analytical procedure successfully used to nickel preconcentration and determination in biological matrices. The properties of the developed made it very suitable for its application in FI on-line microcolumn preconcentration and separation systems. Optimization of this system by multivariate designs was advantageous because it allowed to study the interactions between variables simultaneously. It made possible to understand circumstances that are not well explained by traditional approaches.

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