Use of 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of zinc(II) by F AAS

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Abstract

This study presents the development of an on-line preconcentration system for zinc(II) determination in aqueous samples. The analyte was trapped in a mini-column filled with a chelating resin based on a chitosan biopolymer modified with 8-hydroxyquinoline obtained by the diazotization reaction. Flow and chemical variables of the system, as well as the potential interference ions, were optimized through a multivariate procedure. The factors selected were sample pH, eluent concentration (HNO_3), and sample and eluent flow rates. It was verified through a full factorial design that the sample pH and eluent flow rate factors were statistically significant at the 95% confidence level. A final optimization of the significant factors was carried out using a Doehlert matrix. The preconcentration system was linear between 2.5 and 75 $\mu g\,L^{-1}$, with a regression coefficient of 0.9995. The enrichment factor was 17.6. The limits of detection and quantification were 0.8 and 2.5 $\mu g\,L^{-1}$, respectively. The repeatability and the analytical frequency were, respectively, 2.7 (25.0 $\mu g\,L^{-1}$, $n = 8$) and 18 samples per hour. Results for recovery tests using mineral water samples were between 85 and 93%. Certified reference materials were analyzed in order to check the accuracy of the proposed method.
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1. Introduction

The analytical control of heavy metals in several matrixes, including drinking water, is an important issue for the environmental and health research areas, given that the development of sensitive and selective techniques to obtain adequate detection limits are in great demand. Zinc(II) is considered an essential trace element for human beings because of its relationship with insulin production and because it acts as a catalyst for more than 200 enzymes [1,2]. An excessive consumption of zinc(II) (50 mg/day) can inhibit the absorption of copper(II) acquired from the human diet [3]. Also, a 160 mg/day zinc(II) supplementation for 16 weeks has been associated with a reduction in high-density plasmatic lipoprotein for men [4].

Although flame atomic absorption spectrometry (F AAS) is one of the most commonly applied techniques for the determi-

nation of several metal elements in a variety of sample matrixes, this technique has some limitations, especially those related to the low sensitivity [5]. To overcome these limitations, a preconcentration step prior the instrumental analysis is mandatory. Of the several enrichment procedures, the combination of solid-phase extraction (SPE) and flow injection (FI) in an on-line system is one of the most effective methods due to the low consumption of samples and reagents, high analytical throughput and minimal waste production [6–9].

In general, a sorbent is expected to have fast metal ion-exchange kinetics, resistance in different solvents, and thermal and chemical stability [10,11]. A great variety of functionalized materials have been used as sorbents for SPE in on-line preconcentration systems for the determination of several metals. Polymeric chelating resins [12–14], silica gel grafted with adsorbents [15–17] and, more recently, biopolymers, such as *Bacillus sphaericus*-loaded Diaion SP-850 [18], *Agrobacterium tumefaciens* immobilized on Amberlite XAD 4 [19] and *Saccharomyces cerevisiae* immobilized on sepiolite [20], are examples of these materials. Of the biopolymers, chitosan has been receiving special attention because it is derived

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from chitin, which is the second most abundant biopolymer in nature and a waste product of seafood processing industries [21]. The ability of chitosan to adsorb metal ions has been applied in the preconcentration and determination of copper(II), cadmium(II) and lead(II) in water samples [21,22]. The influence of sample pH, particle size and adsorbent weight on chromium determination has been studied using a crosslinked chitosan [23]. The use of chitosan functionalized with complexing agents is a very recent approach and it has been proposed for the determination of trace metals. The chelating resin obtained through the functionalization of chitosan with 8-hydroyquinoline by the diazotization reaction has been used for copper(II), cadmium(II) and lead(II) determination in aqueous samples [6,24]. A chelating resin-based chitosan biopolymer modified with 8-hydroxyquinoline-5-sulfonic acid using a spray drying technique for immobilization has been applied to copper(II) and cadmium(II) determination in aqueous samples [25]. The on-line collection/concentration of trace elements and their determination using inductively coupled plasma-atomic emission spectrometry has been carried out using a novel chitosan resin derivatized with a serine diacetic acid moiety [26]. Selective concentration and ultratrace determination of silver in environmental water samples have been carried out using a chitosan-based chelating resin [27]. Also, adsorption of platinum(IV), palladium(II) and gold(III) from aqueous solutions onto L-lysine-modified crosslinked chitosan resin has been studied [28].

Recently, our research group has developed solid-phase F AAS procedures for the determination of heavy metals in aqueous samples [6,24,25,29–31]. In continuation of these studies, the possibility of developing a sensitive and selective on-line FI-F AAS procedure for the determination of zinc(II) was investigated. The procedure is based on the retention of zinc(II) on a chelating resin based on chitosan modified with 8-hydroxyquinoline obtained by the diazotization reaction developed previously in our laboratory [6,24]. Its applicability to zinc(II) determination in freshwater samples using on-line FI-F AAS is discussed. Also, in this study a two-level full factorial experimental design and Doehlert matrix were the multivariate tools used not only for optimization of the factors affecting the preconcentration system but also to investigate possible interferences in the proposed procedure.

2. Experimental

2.1. Instrumentation

A Varian Model SpectrAA 50 (Australia) flame atomic absorption spectrometer equipped with a deuterium lamp as a background corrector, and a zinc cathode lamp (Hitachi HLA-4S) was used for the analysis. The instrument was used under conditions suggested by the manufacturer. The analytical signals were measured as peak area. An Ismatec-IPC peristaltic pump with eight channels provided with Tygon® and polyethylene tubes with 0.8 mm internal diameter (i.d.) were used to pump the solutions through the mini-column. A manifold with four three-way solenoid valves was used to select the precon-

centration and elution steps. Solenoid valves were controlled by a microcomputer running software written in Quick Basic 4.5. A 320 Mettler Toledo pH meter was used to adjust the pH of the solutions.

As the certified material, bovine muscle powder (0.5059 g) of the standard reference material NIST 8414 (National Institute of Standards and Technology, USA) was decomposed through acid digestion using an MLS-1200 MEGA microwave oven (Milestone, Sorisole, Itália). The certified material was submitted to the following microwave program: 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W and 5 min at 650 W, followed by 5 min of ventilation. Deionized water was added to give a final volume of 50 mL.

2.2. Reagents and solutions

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 laboratory glassware was kept overnight in a 2% (v/v) Extran® (Merck, Darmstadt, Germany) solution and then again overnight in a 10% (v/v) hydrochloric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

Working standard solutions of Zn(II) were prepared daily by dilution of a 2000 mg L^{-1} zinc(II) stock solution (atomic absorption grade, Fluka, Switzerland). Nitric acid solutions (Merck, Darmstadt, Germany) used as the eluent in the flow system were prepared by appropriate dilution with deionized water from the concentrated acid.

Acetic acid–acetate buffer (pH 3–5) was prepared by mixing appropriate ratios of a 2 mol L^{-1} acetic acid solution (Carlo Erba, Milan, Italy) and a 2 mol L^{-1} sodium acetate solution (Vetec, Brazil).

Sorensen buffer solution (pH 6–8) was prepared by mixing 0.084 mol L^{-1} Na$_2$HPO$_4$ and 0.067 mol L^{-1} KH$_2$PO$_4$ (Vetec, Brazil) in appropriate ratios.

The working solutions were prepared adding 10 mL of buffer solution and their pH was adjusted with 0.01 mol L^{-1} HCl or 0.01 mol L^{-1} NaOH, the final volume of the solution being 100 mL. Only a 10 mL volume of a working standard solution containing 100 μg L^{-1} of zinc(II) was introduced into the flow system.

Commercial mineral water samples from Bugres River (Rancho Queimado, Santa Catarina, Brazil), bovine muscle powder of the standard reference material NIST 8414 (National Institute of Standards and Technology, USA) and trace elements in freshwater of the standard reference material NIST (SRM 1643e) were used to check the accuracy of the proposed method.

2.3. Preparation of chitosan modified with 8-hydroxyquinoline

The procedure for the modification of chitosan with 8-hydroyquinoline was carried out as described in the literature [6]. The gel microspheres of chitosan were obtained mixing gelified chitosan with an acetic acid solution followed by precipitation

with a solution of NH_3 using a peristaltic pump to drip the colloidal suspension. These gel microspheres were placed into a sealed flask at $50\,^{\circ}C$ with $300\,mL$ of a solution in chloroform containing *p*-nitrobenzoyl chloride and $10\,mL$ of triethylamine to promote the reaction. The gel microspheres were filtered and washed with chloroform to remove the excess of reagents. The benzoylated gel microspheres were crosslinked with glutaraldehyde 10% (w/v) and then the $–NO_2$ group was reduced to $–NH_2$ with $300\,mL$ of sodium dithionite 5% (w/v) and the microspheres were slowly poured into the reaction in a sealed flask at $45\,^{\circ}C$. This aminophenyl derivative was diazotized for $40\,min$ at $0\,^{\circ}C$ with $200\,mL$ of sodium nitrite 3% (w/v) at acetic acid 10% (v/v). After filtering and washing, the modified benzoylated chitosan gel was mixed with $100\,mL$ of 8-hydroxyquinoline 3% (w/v), previously dissolved in a solution of NaOH 5% (w/v) in ethyl alcohol. The chitosan derivative was ready for use after washing with $100\,mL$ of $1\,mol\,l^{-1}$ HNO_3 and then with distilled water to remove the acid solution.

2.4. On-line preconcentration system

The diagram of the flow system is shown schematically in Fig. 1. The flow system comprised a peristaltic pump fitted with Tygon tubing, four three-way solenoid valves and a mini-column filled with the proposed sorbent. The mini-column with a $110\,mm$ length and $3\,mm$ i.d. was sealed at both ends with small glass wool beds to prevent material losses, the working length being $75\,mm$. This system was coupled to a flame atomic absorption spectrometer. The loading and desorption steps were time-controlled. In the sample-loading step (Fig. 1A), valve V1 was initially open and the others were closed (selected according to the experimental optimization design procedure), so that
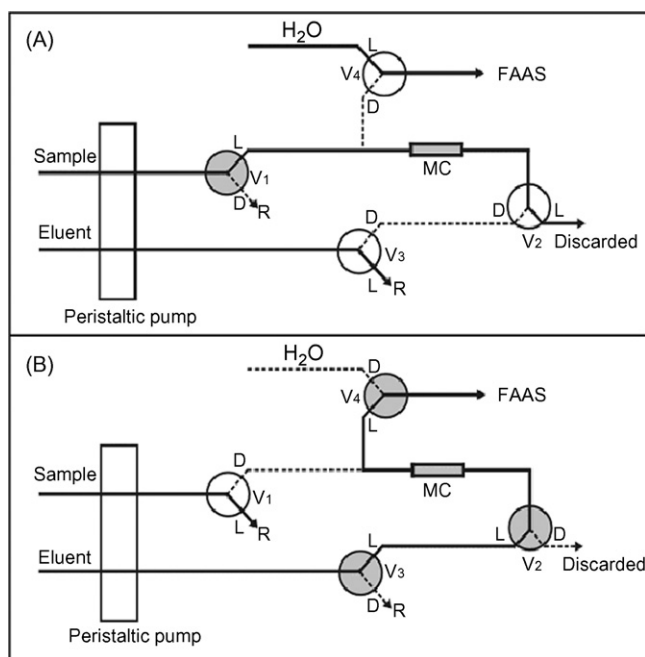
Table 1
Variables and levels used in the full factorial design

Variable	Minimum (−)	Maximum (+)	Central point
Sample pH	4.0	8.0	6.0
Sample flow rate (mL min^{-1})	4.2	6.2	5.2
Eluent flow rate (mL min^{-1})	4.2	6.2	5.2
Eluent concentration (mol L^{-1})	0.5	1.5	1.0

the sample or standard solution was pumped through the mini-column where ion exchange takes place and the effluent flowed towards the waste. Valve V1 was then closed and V2, V3 and V4 were opened (selected according to the experimental optimization design procedure) and the eluent percolated through the mini-column displacing the Zn(II) ions from the adsorbent (Fig. 1B). The eluate was taken directly to the nebulizer-burner system of the flame atomic absorption spectrometer.

3. Results and discussion

3.1. Factorial and surface response optimization

A 2^4 two-level full factorial design with a central point (C), resulting in 17 runs in total, was carried out in duplicate to determine the influence of the selected factors and their interactions in the preconcentration system. Preliminary tests were performed to investigate the factors that could influence the Zn(II) retention on the chitosan adsorbent modified with 8-hydroxyquinoline. The factors which were shown to be of importance in the preconcentration procedure were: sample pH, eluent concentration (HNO_3), sample flow rate and eluent flow rate. Table 1 shows the minimum and maximum levels used for the selected factors and Table 2 shows the experimental design and the respective analytical signals.

Analysis of variance (ANOVA) and *P*-values were used to check the significance of the effects on the preconcentration system. The main effects and their interactions can be seen in the Pareto chart shown in Fig. 2. The sample pH, eluent flow rate and

Fig. 1. On-line preconcentration system: (A) loading step and (B) desorption step. V_1, V_2, V_3 and V_4: solenoid valves; L: open way; D: closed way; R: sample or eluent flow return.
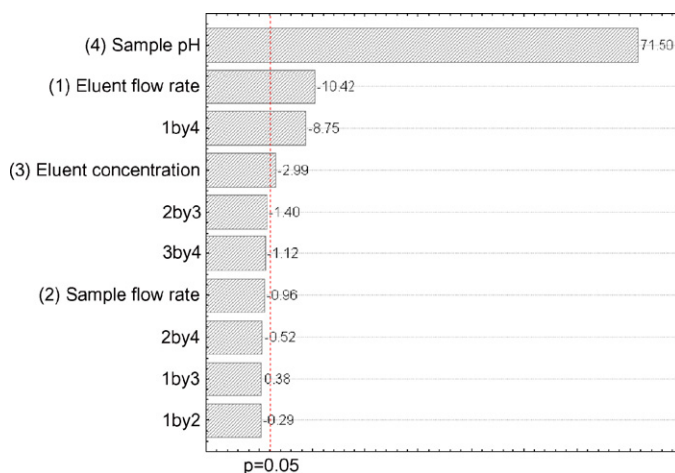

Fig. 2. Pareto chart obtained from the full factorial design used for optimization of preconcentration of zinc(II) in water samples.

Table 2
Experimental values used during the multivariate optimization (sample volume 10.0 mL; sample concentration 100.0 μg L^{-1}; sorbent mass 100.0 mg)

Run	Sample pH	Eluent concentration (mol L^{-1})	Sample flow rate (mL min^{-1})	Eluent flow rate (mL min^{-1})	Integrated absorbance	Integrated absorbance
1	4	0.5	4.2	4.2	0.1602	0.1696
2	4	0.5	4.2	6.2	0.1079	0.1214
3	4	0.5	6.2	4.2	0.1527	0.1474
4	4	0.5	6.2	6.2	0.1064	0.1039
5	4	1.5	4.2	4.2	0.1026	0.1201
6	4	1.5	4.2	6.2	0.0818	0.0800
7	4	1.5	6.2	4.2	0.1037	0.0923
8	4	1.5	6.2	6.2	0.0632	0.0475
9	8.0	0.5	4.2	4.2	2.3854	2.3342
10	8.0	0.5	4.2	6.2	1.8404	1.8400
11	8.0	0.5	6.2	4.2	2.4415	2.3979
12	8.0	0.5	6.2	6.2	1.8580	1.8475
13	8.0	1.5	4.2	4.2	2.3316	2.2899
14	8.0	1.5	4.2	6.2	1.8338	1.8027
15	8.0	1.5	6.2	4.2	2.1997	2.2115
16	8.0	1.5	6.2	6.2	1.6789	1.6974
17 (CP)[a]	6.0	1.0	5.2	5.2	0.8283	0.8379

[a] Central point.

eluent concentration, as well as the interaction between sample pH and eluent flow rate, were the factors statistically significant at the 95% confidence level. The eluent concentration showed lower significance in relation to the other two significant factors and was fixed at 0.5 mol L^{-1} in order to prolong the lifetime of the adsorption material and reduce reagent consumption. The sample flow rate was not statistically significant and, therefore, its value was fixed at 4.2 mL min^{-1} to guarantee a better stability in the preconcentration system in spite of the reduction in the analytical frequency.

The significant variables indicated by the full factorial design (sample pH and eluent flow rate) were optimized using a Doehlert matrix. In this case, seven experiments were carried out as shown in Table 3. All experiments were carried out in duplicate. The data obtained from the Doehlert matrix were used to build the surface response shown in Fig. 3 which is described by a quadratic equation (Eq. (1)), where x and y represent, respectively, the sample pH and sample flow rate

$$Z = -25.859 + 5.497X + 2.87Y - 0.343X^2 - 0.035XY - 0.277Y^2 \tag{1}$$

Table 3
Doehlert matrix used for sample pH and eluent flow rate optimization to obtain the response surface for determination of zinc in aqueous samples by FI-F AAS

Run	pH	Eluent flow rate (mL min^{-1})	Integrated absorbance
1	6.5	4.7	1.7538
2	7.0	5.2	1.9567
3	7.0	4.2	2.0600
4	7.5	4.7	2.2711
5	8.0	5.2	2.2143
6	8.0	4.2	2.2410
7	8.5	4.7	2.0512

The Doehlert study shows the optimal conditions for a maximum integrated absorbance value using a sample pH of 7.8 and eluent flow rate of 4.7 mL min^{-1}.

3.2. Effect of foreign ions

In general, the effect of the interference of foreign ions on the extraction efficiency of a method is investigated through a univariate procedure, in which one possible concomitant ion is added each time to the working solution. Thus, the effect of each ion on the preconcentration procedure is evaluated individually. This study is tedious and time-consuming and is not representative of a real situation, in which a sample may contain several
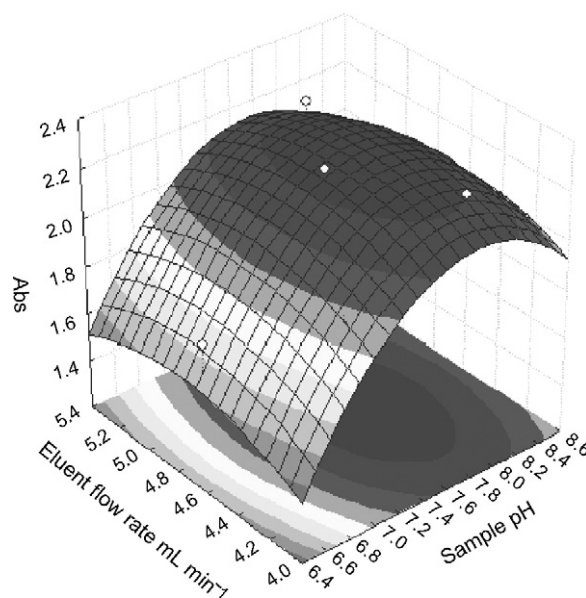

Fig. 3. Response surface obtained using Doehlert matrix to optimize sample pH and sample flow rate.
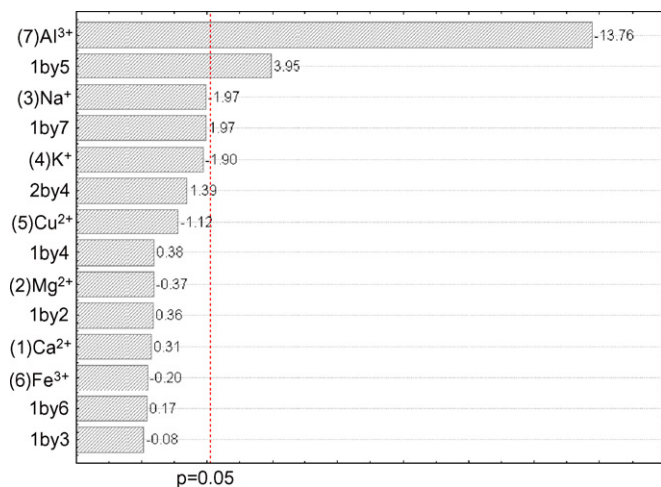
Fig. 4. Pareto chart of effects of foreign ions on zinc sorption in the proposed preconcentration system.

ions at the same time. For this reason, in this study, interference was investigated using a 2^{7-3} fractional factorial experimental design including a central point, resulting in 17 experiments.

Fig. 4 shows the Pareto chart, where the main and interactive effects of the concomitant ions studied with regard to the analytical response can be seen. The concentration of each concomitant ion studied was 10^{-4} mol L^{-1}. This study suggests that Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$, Cu^{2+} and Fe^{3+} ions do not interfere in the zinc(II) preconcentration at a 95% confidence level. For Al^{3+} ions a great reduction in the analytical signal was observed using the proposed preconcentration procedure. However, the levels of Al^{3+} concentration in the real samples are much lower than the level studied in this research [32,33] and, therefore, this ion will not interfere in the proposed method to quantify zinc(II) in aqueous samples.

3.3. Analytical features

The calibration graph obtained using optimized conditions is given as $A = 0.01523 + 0.01986 \times C$ in the linear range of 2.5–75 µg L^{-1}, where C is zinc(II) concentration in solution (µg L^{-1}). The correlation coefficient obtained from this graph was 0.9995. The limits of detection (LOD) and quantification (LOQ) were calculated as $3\sigma/S$ and $10\sigma/S$, respectively, where S is the slope of the calibration curve and σ is the standard deviation of 11 consecutive measurements of the blank solution. The LOD and LOQ values were, respectively, 0.8 µg L^{-1} and 2.5 µg L^{-1}. The precision of the procedure was 2.7%, calculated as the relative standard deviation of eight consecutive measurements of a 25 µg L^{-1} zinc(II) solution. The enrichment factor, calculated as the ratio of the slope of the calibration graphs with and without preconcentration, was 17.6.

The proposed method was applied to the analysis of mineral water samples collected from the Bugres River, in the town of Rancho Queimado, Brazil. The concentrations of the analyte in the water samples were below the LOD of the method. In order to evaluate the accuracy of the preconcentration procedure, recovery experiments were carried out with spiked water samples (10 µg L^{-1}). The efficiency of the on-line preconcen-

tration system was good for all samples analyzed, resulting in recoveries of between 85 and 93%. The accuracy of the proposed method was also investigated by analyzing two certified reference materials ($N = 3$) and a good agreement with the certified data was obtained. The first reference material was Bovine Muscle Powder NIST 8414 with a zinc(II) concentration of 142 ± 14 µg g^{-1}, and the result obtained using the proposed method was 131 ± 14 µg g^{-1}, corresponding to a 92% recovery. The second reference material was freshwater SRM 1643e, with a zinc(II) concentration of 79 ± 2 µg L^{-1}, and the result using the proposed method was 71 ± 1 µg L^{-1}.

4. Conclusions

The use of chitosan modified with 8-hydroxyquinoline as an adsorbent for the determination of zinc(II) in aqueous samples in an on-line FI-F AAS system was very efficient, presenting an excellent sensitivity and analytical frequency. Chemometric tools allow the optimization of the proposed system and checking of possible effects of concomitant ions in a more efficient way than the univariate method requiring a low number of experiments. The proposed chelating resin and FI–F AAS system gave good results for the recovery test carried out on real samples and certified materials, low limit of detection, good precision and relatively high adsorption kinetics, which resulted in greater analytical throughputs.

Acknowledgement

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