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Valfredo Azevedo Lemos[a]; Juracir Silva Santos[a]; Patrícia Xavier Baliza[a]
[a] Universidade Estadual do Sudoeste da Bahia, Laboratório de Química Analítica (LQA), Jequié-BA, Brazil

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Synthesis of α-Nitroso-β-Naphthol Modified Amberlite XAD-2 Resin and its Application in On-Line Solid Phase Extraction System for Cobalt Preconcentration

Valfredo Azevedo Lemos,* Juracir Silva Santos, and Patrícia Xavier Baliza

Universidade Estadual do Sudoeste da Bahia, Laboratório de Química
Analítica (LQA), Campus de Jequié, Jequié-BA, Brazil

ABSTRACT

In this work, an on-line system for preconcentration and determination of cobalt at $\mu g\,l^{-1}$ level is proposed. Amberlite XAD-2 functionalized with α-nitroso-β-naphthol (NN-XAD) packed in a minicolumn was used as sorbent. Cobalt (II) ions were sorbed in the minicolumn, from which it could be eluted by hydrochloric acid solution. This eluate reacted with Nitroso Salt R and the absorbance of the complex was read at 510 nm in a spectrophotometer. Signals were measured as peak height by using instrument software. Achieved sampling rate was 45 samples per hour.

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*Correspondence: Valfredo Azevedo Lemos, Universidade Estadual do Sudoeste da Bahia, Laboratório de Química Analítica (LQA), Campus de Jequié, Jequié-BA, Brazil 45200-000; Fax: +55-73-5256683; E-mail: vlemos@uesb.br.

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Analytical parameters were evaluated and the results demonstrated that cobalt can be determined, with sample pH in the range of 7.0–8.5, preconcentration time of 60 s with a sample flow rate of 5.0 mL min^{-1}. The detection limit (3 s) was 6.0 μg l^{-1} and the precision (assessed as the relative standard deviation) reached values of 6.1 to 1.9% in cobalt solutions of 10 to 300 μg l^{-1} concentration, respectively. The proposed procedure was applied in natural waters. Recoveries of spike additions (10, 25, or 50 μg l^{-1}) to natural water samples were quantitative (92–106%).

Key Words: Preconcentration; Functionalization; Cobalt; Amberlite XAD-2.

1. INTRODUCTION

There is current interest in developing chelating matrices and exploring them for metal enrichment. These materials are important metal ion collectors suitable for metal ion enrichment. In the production of such resins, chelating ligands are frequently sorbed onto a matrix[1,2] or a ligand can be covalently coupled with a polymer backbone through a spacer arm, generally $-N=N-$[3,4] or $-CH_2-$ group.[5,6] Synthesis results in systems free from ligand leaching problems, but their metal-ion capacities have moderate values only.[7] However, they may be increased by an extensive functionalization of an appropriately cross-linked polymer. It is easily possible if ligand molecules of small size are chosen.

Amberlite XAD (styrene-divinyl-benzene copolymer) is a support widely used to develop several chelating resins for preconcentration procedures due to its good physical and chemical properties such as porosity, high surface area, durability, and purity. This support has been used for collection of metal complexes[8–10] or sorbed with 1-(2-pyridylazo)-2-naphthol (PAN),[11] 2-(2′-thiazolylazo)-5-dimethyl-aminophenol (TAM)[12] and 2-(2′benzothiazolylazo)-p-cresol.[13] The polymers have been also functionalized with calmagite,[14] 5-palmitoyl-8-hydroxyquinoline,[15] PAN,[16] chromotropic acid,[17] di(2-ethylhexyl)phosphoric acid,[18] tiron,[19] Alizarin Red-S,[20] pyrocathecol violet,[21] nitroso R salt,[22] salicylic acid,[23] and thiosalicylic acid.[24] A previously published paper[22] describes the synthesis, characterization, and application of a resin functionalized with Nitroso R Salt to cobalt preconcentration with detection by FAAS. In that paper, authors determined cobalt in water and biologic samples.

On-line preconcentration systems using solid-phase extraction (SPE) are very opportune for determinations of trace metals due to its flexibility, simplicity, high sampling rate, and versatility, which allow the method to be used in conjunction with different spectrometric detectors. Many procedures of on-line preconcentration can be found on literature employing a variety of materials, such as chelating resins,[25] ion-exchangers,[26,27] silica,[28,29] activated alumina,[30,31] activated carbon,[32] fullerene,[33] or polyurethane foam (PUF).[34–36]

In the present paper, an on-line system for enrichment and determination of cobalt is proposed, using a minicolumn of Amberlite XAD-2 resin functionalized with α-nitroso-β-naphthol (NN-XAD). This resin was synthesized, characterized, and applied for preconcentration of cobalt. Chemical and flow variables were studied. Moreover, analytical features and interferents were determined and the proposed procedure was applied in natural waters.

2. EXPERIMENTAL

2.1. Instrumentation

A Varian Model Cary 50 (Mulgrave, Victoria, Australia) UV-Visible Spectrophotometer equipped with xenon lamp was used for absorbance measurements. Infrared spectra were recorded in an ABB Bomen MB series model MB100 Fourier transform IR spectrometer. A Thermo Finnigan Flash elemental analyzer 1112 series was used for elemental analysis.

The manifold of the preconcentration system was adapted to flow-through cell system of the UV-Visible Spectrophotometer. Flow system was made up of a peristaltic pump (Millan, model 204, Colombo, Brazil) furnished with Tygon tubes to deliver all solutions, a flow-through cell and a NN-XAD packed minicolumn for the on-line preconcentration of cobalt. The manifold was built up with PTFE (polytetrafluorethylene) tube with 0.5 mm of internal diameter. A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used.

The laboratory-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm contains about 100 mg of NN-XAD. A syringe was used to put the sorbent in column. Plastic foams were placed at both sides of minicolumn to keep the packing material in the place. Afterward, 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.

2.2. Reagents

Deionized water from an water purification system (Quimis, São Paulo, Brazil) was used to prepare all solutions. All reagents were of analytical reagent grade. Cobalt (II) working solutions at $\mu g\,l^{-1}$ level were prepared daily by diluting a $1000\,\mu g\,mL^{-1}$ cobalt (II) stock solution (Merck). Hydrochloric acid solutions were prepared by direct dilution with deionized water from the concentrated suprapur solution (Merck). The laboratory glassware was kept overnight in a 5% v/v nitric acid solution. Afterward, it was rinsed thoroughly with ultrapure water. Acetate (3.0–5.0), TRIS (*tris*-(hydroxymethyl) aminomethane)[37] (6.5–7.5), borate (7.0–8.5), and ammoniacal (9.25) buffers were used to adjust the sample pH. Amberlite XAD-2 (Sigma) 20–60 mesh and α-nitroso-β-naphthol (Merck) were used for synthesis of the sorbent.

2.3. Synthesis of the Resin

NN-XAD was prepared by the procedure described previously for similar resins.[38,39] Amberlite XAD-2 resin (5g) was treated with a nitrating mixture, containing 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and the mixture stirred at 60°C for 1h in a water-bath. Thereafter, the reaction mixture was poured into an ice-water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid, and thereafter treated with a reducing mixture of $SnCl_2$, concentrated hydrochloric acid, and ethanol. The system was refluxed for 12h at 90°C. The solid precipitate was filtered and washed with water and $2\,mol\,l^{-1}$ NaOH solution. The amino resin was first washed with $2\,mol\,l^{-1}$ HCl and finally with distilled water to remove the excess of HCl. It was suspended in an ice-water mixture (150 mL), $1\,mol\,l^{-1}$ HCl and $1\,mol\,l^{-1}$ $NaNO_2$. The diazotized resin was filtered, washed with ice-cold water, and reacted with α-nitroso-β-naphthol (3.0 g in 250 mL of 5% w/v NaOH solution) at 0–5°C for 24h. The resulting dark-brown-colored resin was filtered, washed with water, and dried in air.

2.4. Sample Preparation

Natural waters were sampled from lagoons, rivers, and wells at Salvador, Brazil. For these samples, the only pretreatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the Co (II) ions on the flask walls. The samples were filtered through a Millipore cellulose membrane of pore size 0.45 μm. A volume of 80 mL of the filtrate was added to a 100 mL volumetric flask and the pH was adjusted by addition of 5 mL of buffer solution. Co(II) addition was carried out, and the flask volume was completed with ultrapure water.

At least one blank solution was run for each sample in order to evaluate cobalt contamination by the reagents used.

2.5. On-line Preconcentration System

A diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was operated in a time-based mode. A sample solution (S) containing cobalt was kept at convenient pH with a buffer solution and was percolated through a minicolumn that retained the cation. Thus, cobalt(II) ions are retained onto the minicolumn and the remaining solution was discharged (W). By switching the six-port valve (V), a stream of eluent (E) displaces cobalt ions. This eluate reacted with Nitroso R Salt (R) and the absorbance of the complex was read at 510 nm in a spectrophotometer. Signals were measured as peak height by using instrument software. It was read four times (four preconcentration steps) and averaged. Peak height was used because it resulted in precision better than peak area. Achieved sampling

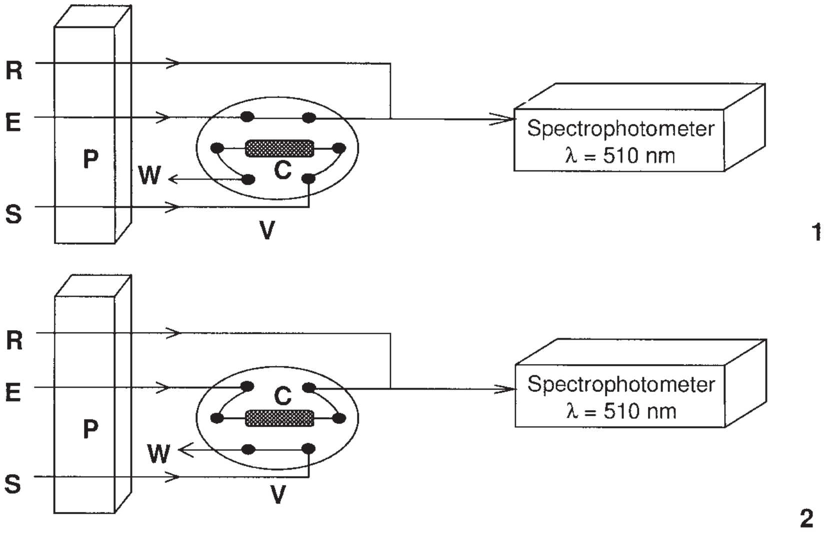

Figure 1. Schematic diagram of the flow system used to preconcentration and determination of cobalt. S: sample; E: eluent; P: peristaltic pump; C: N,N-XAD minicolumn; W: waste; V = six-port valve; R: Nitroso Salt R. 1 = six-port valve in preconcentration position and 2 = six-port valve in elution position.

rate was 45 h^{-1}, when used preconcentration time of 60 sec and considering elution time of 20 sec.

3. RESULTS AND DISCUSSION

3.1. Resin Characterization

Elemental analysis (found: C, 69.9%; H, 5.0%; N, 13.1%; calculated for $C_{18}H_{13}N_3O_2$: C, 71.3%; H, 4.3%; N, 13.9%) shown that on an average one α-nitroso-β-naphthol molecule is present in the resin per repeat unit of the polymer. A structure according with elemental analysis is shown in Fig. 2. Infrared spectrum of NN-XAD is compared with that of free Amberlite XAD-2. There are additional bands at 3500-3400, 1535, 1450, 1390, and 1335 cm^{-1}, which appear to originate due to modification of resin by the ligand and are characteristic of O–H, $-N=N-$, C-N, N═O and C–OH vibrations, respectively.

3.2. Chemical and Flow Variables

To determine the best chemical and hydrodynamic conditions for cobalt determination the continuous flow system was optimized. A cobalt solution containing 100.0 μg l^{-1} was employed for these studies.

Influence of the temperature in absorbance of Co(II)-NRS system was studied. A reaction coil (L), situated before the cuvette, was placed in an adiabatic receptacle with thermometer. Temperature was varied in the range of 25 to 60°C, with increments of 5°C. There was not any change in analytical signal by the temperature range studied. Only a little fall in the absorbance was observed when the used temperature was 60°C. Temperatures higher than

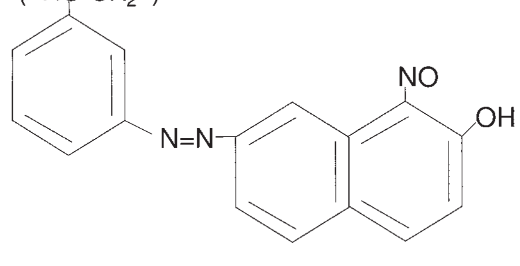

Figure 2. Proposed structure for NN-XAD.

60°C were not considered due to formation of air bubbles inside the reaction coil. These air bubbles prejudiced the detection. So in subsequent experiments the room temperature of 25°C was used.

The reaction coil length was changed from 0 to 200 cm. It was observed that this parameter does not influence the analytical signal. So, it was not used in any coil length in subsequent studies.

The lifetime of column packed with N,N-XAD resin was monitored. It was made measuring the signal of a $100.0\,\mu g\,l^{-1}$ cobalt solution at the end of each day of work and counting the number of cycles. Results show that the column showed good performance for at least 400 cycles. This indicates that material is very stable even under rough changes of pH conditions.

The influence of the eluent composition in the preconcentration system was studied testing solutions of 0.01 to $0.10\,mol\,l^{-1}$ of hydrochloric acid. Analytical signals are maximum at concentrations of acid bigger than $0.025\,mol\,l^{-1}$. It also tested mixtures of hydrochloric acid with the solvents ethanol and acetone. Addition of these solvents have not resulted in any significant increase of analytical signal. In subsequent studies eluent $0.05\,mol\,l^{-1}$ hydrochloric acid solution was used.

The effect of the sample pH on the cobalt response was investigated within the range of 3.5–9.25. Maximum retention occurred within the pH range of 7.0–8.5 Then, pH range of 6.5–7.0 was selected for subsequent work, because the use of lower pH values causes more selective determinations. This selectivity is induced to a fact of α-nitroso-β-naphthol reacting with a major number of metals at weakly alcaline conditions.[41] Cobalt solutions and samples were buffered with borate buffer pH 7.0.

Co (II)-NRS complex is formed under weakly acidic or alkaline conditions.[40] So, NRS solution should be buffered due to contact with the strongly acid eluent. Several buffers and pH values were tested. Best results were obtained using borate buffer pH 7.0–8.0.

The concentration of NRS solution was also studied and best results were obtained for 0.025% (w/v) or higher. The influence of NRS solution flow rate in the cobalt desorption from the minicolumn was tested. Results showed that the analytical signal is maximum at flow rates within the range of 1.50 to $6.00\,mL\,min^{-1}$. Analytical signal decreased at flow rates higher than $6.00\,mL\,min^{-1}$. So, a flow rate of $5.5\,mL\,min^{-1}$ was selected in the subsequent studies.

Sample flow rate can affect the analytical signal in the proposed system. The effect of this parameter was also studied by varying flow rates from 1.50 to $16.00\,mL\,min^{-1}$. As the amount of sample varies with flow rate if preconcentration time is constant, for this experiment, a volume of 3.00 mL of a cobalt solution was pumped in order to maintain the sample amount invariable. Analytical signals decreased slightly at high flow rates, upper

5.60 mL min^{-1}. These results indicate that the cobalt sorption is minor at high flow rates because Co(II) ions pass by the column so quickly that the contact time between the phases is not sufficient for a significant retention. Moreover, high flow rates increase back-pressure and this could cause leakage. Thus, a flow rate of 5.0 mL min^{-1} was chosen for posterior experiments as a compromise between efficiency and stability of the system.

The effect of the eluent flow rate in the step of cobalt desorption from the minicolumn was also investigated. Results showed that the analytical signal is maximum at eluent flow rates within the range of 1.50 to 5.80 mL min^{-1}. At flow rates higher than 5.80 mL min^{-1} the analytical signal decreased considerably. Thus, a flow rate of 5.5 mL min^{-1} was selected in the subsequent studies.

3.3. Effect of Foreign Ions

Solutions containing cobalt (100 μg l^{-1}) and other ions in order to etermine the selectivity of analytical system were prepared and the developed procedure was applied. The effect of each species was considered interference when the signal in the presence of the species resulted in a deviation of the peak height by 5%. Considered substances and their maximum amounts tolerable are shown in Table 1.

3.4. Analytical Features

The solid-phase flow system allowed the determination of cobalt in the concentration range of 6 to 300 μg l^{-1} for 1 min of preconcentration time. The calibration graph under the optimum chemical and flow conditions with

Table 1. Maximum tolerable ratios of other ions for the online system using NN-XAD minicolumn (cobalt concentration = 100 μg l^{-1}).

Substance	Maximum tolerable amount
NO_3^-, Cl^-, SO_4^{-2}, Br^-	100 mg l^{-1}
Al^{+3}, Pb^{+2}, Zn^{+2}	10 mg l^{-1}
Fe^{+3}	4 mg l^{-1}
Ni^{+2}	500 μg l^{-1}
Cu^{+2}	200 μg l^{-1}
Fe^{+2}	100 μg l^{-1}

the manifold depicted in the Figure 1 was given as $A = 0.0091 + 0.0007C$ in the interval of 6 to 300 $\mu g\,l^{-1}$ (C is cobalt concentration in solution, $\mu g\,l^{-1}$). The precision of the procedure, determined as the relative standard deviation in sample solutions containing between 10 and 300 $\mu g\,l^{-1}$ of cobalt was in the range of 6.1 to 1.9%, respectively, calculated by seven measurements. The detection limit (LOD), defined as the cobalt concentration that gives a response equivalent to three times the standard deviations of the blank ($n = 11$), was found to be 6.0 $\mu g\,l^{-1}$ in 5.0 mL of sample solution.

3.5. Application

The analytical system was used for cobalt determination in natural water samples. The results are described in Table 2. Recoveries (R) of spike additions (10, 25, or 50 $\mu g\,l^{-1}$) to several water samples were quantitative (92–106%). R was calculated as follows: $R\ (\%) = \{(C_m - C_o)/m\} \times 100$.

Table 2. Results obtained for cobalt determination in water samples ($n = 4$).

Sample	Added ($\mu g\,l^{-1}$)	Cobalt found by proposed methodology* ($\mu g\,l^{-1}$)	Recovery (%)
Lagoon water	0	<LOD	—
	25	24.0 ± 0.6	96
	50	49.6 ± 0.8	99
River water 1	0	<LOD	—
	25	25.9 ± 0.4	104
	50	48.5 ± 1.3	97
River water 2	0	<LOD	—
	25	26.6 ± 0.8	106
	50	47.0 ± 1.5	94
River water 3	0	<LOD	—
	10	9.2 ± 0.7	92
	25	25.9 ± 0.6	104
Well water	0	<LOD	—
	25	24.7 ± 0.8	99
	50	49.9 ± 1.3	100
Well water 2	0	<LOD	—
	10	9.4 ± 0.6	94
	25	24.3 ± 0.9	97

*Confidence interval 95%.

LOD: Limit of detection.

Where C_m is a value of cobalt in a bland sample (a spike sample), C_o is a value of cobalt in a sample and m is the amount of cobalt spike. These results proved also that the procedure can be applied satisfactorily for cobalt determination in natural water.

4. CONCLUSION

Flow-injection systems using polimeric resins functionalized with complexing reagents can be a promising way for preconcentration and determination of cations in a wide range of samples. The proposed flow injection system with on-line preconcentration by minicolumn packed with NN-XAD was sucessfully applied to the on-line determination of cobalt. Combination of spectrophotometry with flow-injection system resulted in a simple, relatively sensitive, and robust analytical procedure. Simplicity of the manifold is a great advantage of this procedure if compared to many methods existing in cobalt preconcentration.

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