

Synthesis and Application of XAD-2/Me-BTAP Resin for On-Line Solid Phase Extraction and Determination of Trace Metals in Biological Samples by FAAS

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Uma nova resina XAD-2/Me-BTAP foi desenvolvida e aplicada a um sistema em linha para a pré-concentração e determinação de metais por FAAS. O reagente usado na síntese da resina foi o 2-[2'-(6-metil-2'-benzotiazolilazo)-4-aminofenol (Me-BTAP), um composto produzido pela primeira vez para esta aplicação. O reagente e a resina foram caracterizados e o sorvente foi usado como recheio de uma mini-coluna em um sistema de pré-concentração em linha para a determinação de cobalto, cobre e níquel. Os fatores de enriquecimento calculados foram 19 (Co), 12 (Cu) e 12 (Ni), para 60 s de tempo de pré-concentração, e 30 (Co), 30 (Cu) e 24 (Ni), se usados 180 s para a pré-concentração. O procedimento proposto viabilizou a determinação de cobalto, cobre e níquel com limites de detecção de 0,34, 0,87 e 0,81 $\mu\text{g L}^{-1}$, respectivamente, quando usados intervalos de pré-concentração de 180 s. A exatidão do procedimento foi avaliada através da análise de materiais de referência certificados. O método foi aplicado à análise de amostras de alimentos (chá preto e farinha de arroz).

A new XAD-2/Me-BTAP resin has been developed and applied in an on-line system for the preconcentration followed by metal determination by FAAS. The reagent used in the resin synthesis was 2-[2'-(6-methyl-benzothiazolylazo)]-4-aminophenol (Me-BTAP), a compound produced by first time for the application described in this work. The reagent and resin were characterized and the sorbent was used as packing for the minicolumn in an on-line system preconcentration system for cobalt, copper and nickel determination. The enrichment factors calculated were 19 (Co), 12 (Cu) and 12 (Ni), for 60 s preconcentration time, and 30 (Co), 30 (Cu) and 24 (Ni), if used 180 s preconcentration time. The proposed procedure allowed the determination of cobalt, copper and nickel with limits of detection 0.34, 0.87 and 0.81 $\mu\text{g L}^{-1}$, respectively, when used preconcentration periods of 180 s. The accuracy of the developed procedure was evaluated by the analysis of certified reference materials. The method was applied to the analysis of food samples (black tea and rice flour).

Keywords: Me-BTAP, synthesis, metal, Amberlite XAD-2, on-line

Introduction

In recent years, solid-phase extraction (SPE) has become a very important technique for metal, because of its advantages over liquid-liquid extraction such as simplicity, reliability, good metal loading capacity and ability to obtain high enrichment factors.^{1,2} Very versatile systems has been obtained as result of the application of solid supports loaded or functionalized with complexing reagents.^{3,4} These systems could be used for preconcentration and determination of cations in a wide range of samples.⁵⁻⁷ A great advantage of the

incorporation is the reduction of leaching of the ligand from the support.

Many methods have been reported to use combinations of sorbent-ligand to synthesise powerful material for metal preconcentration and determination. Several types of sorbents have been developed, such as chitosan biopolymer/8-hydroxyquinoline,³ acrylic acid grafted PTFE fibers,^{8,9} silica gel/niobium(V) oxide,¹⁰ rice husks/NaOH,¹¹ and Amberlite XAD-2/ α -nitroso- β -naphthol.¹² Amberlite XAD resin series has been functionalized with various ligands in order to develop chelating sorbents for on-line and off-line preconcentration procedures due to its good physical and chemical properties such as porosity, high surface area, durability and purity.^{13,14} Many ligands,

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such as 4,5-dihydroxy-1,3-benzenedisulfonic acid,¹⁵ 1-(2-pyridilazo)-2-naphthol (PAN),^{16,17} 5-palmitoyl-8-hydroxy-quinoline,^{18,19} pyrocathechol violet,²⁰ and 3,4-dihydroxy-benzoic²¹ acid were incorporated in the solid material through a methylene (-CH₂-), azo (-N=N-) or other groups.

Thiazolylazo and benzothiazolylazo reagents have been widely employed in enrichment procedures involving solid-phase extraction due their capacity to form complexes with a large variety of metals.²²⁻²⁴ 1-(2-thiazolylazo)-2-naphthol (TAN) was used in the synthesis of a new chelating resin and its sorption behavior for metal ions was studied.²⁵ TAN was also loaded in activated carbon employed to remove mercury (II) at trace and ultra trace levels from hazardous wastes.²⁶ The reagent 2-(2-thiazolylazo)-p-cresol (TAC) has been loaded in polyurethane foam (PUF) and the resultant material used in a method based on solid sampling to determine lead in saline samples by ETAAS.²⁷ TAC was also successfully used in a flow injection system for cobalt preconcentration.²⁸ We have recently produced new benzothiazolylazo dyes, such as 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTABr)²⁹ and 2-[2'-(6-methyl-benzothiazolylazo)] chromotropic acid (Me-BTANC).³⁰ These reagents were used in cloud point extraction procedures³¹ or loaded on solid supports for on-line preconcentration systems. In continuation of this, it was intended to contribute to the development of new thiazolylazo reagents for use in analytical procedures. The aim of this study is the application of a new XAD-2/Me-BTAP resin in an on-line system for the preconcentration followed by the determination of cobalt, copper and nickel by Flame Atomic Absorption Spectrometry (FAAS). Amberlite XAD-4 (polystyrene-divinylbenzene polymer) was used as a solid sorbent to prepare a ligand-functionalized resin. This sorbent was functionalized with 2-[2'-(6-methyl-benzothiazolylazo)]-4-aminophenol (Me-BTAP), a heterocyclic azo compound capable of forming complexes with metallic cations. This compound was synthesised by first time at our laboratory for the application described in this work. According our knowledge, the synthesis of Me-BTAP and XAD-2/Me-BTAP, as well as its use in analytical procedures has not been reported before. The best conditions for the on-line system, selectivity and analytical features were determined and the proposed procedure was applied to metal determination in food samples.

Experimental

Apparatus

Measurements were performed with a Perkin Elmer Instruments (Shelton, USA) model AAnalyst 200 flame atomic absorption spectrometer equipped with deuterium

lamp background correction and an air-acetylene burner. Perkin-Elmer single-element hollow cathode lamps were also used. The wavelengths used for cobalt, copper and nickel were 240.7, 324.8 and 231.1 nm, respectively. Spectral bandwidth (1.0 nm), acetylene (1.4 L min⁻¹) and nebulizer flow rates (5.0 mL min⁻¹) had conventional values. The output signals were collected as peak height. 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. All pH measurements were performed with a Digimed DM 20 model (Santo Amaro, Brazil) digital pH meter. In the flow system were used two Rheodyne model 5041 six-port rotary valves (Cotati, USA) to select elution and preconcentration steps and an eight-channel multichannel peristaltic pump model 204 from Millan (Colombo, Brazil) furnished with silicone tubes to delivery all solutions. A laboratory-prepared minicolumn packed with XAD-2/Me-BTAP (PVC, 3.50 cm length and 0.4 cm i.d.) was used for on-line preconcentration of the metals. The digestion of food samples was carried out in Parr Instrument 4749 (Moline, Illinois, USA) Acid Digestion Bombs enclosing a chemically inert Teflon sample cup of 23 mL.

Reagents

Sodium nitrite (Vetec, Brazil), 6-methyl-2-amino-benzothiazole (Sigma-Aldrich, Milwaukee, USA), sodium carbonate (Vetec, Brazil), 4-aminophenol (Merck, Darmstadt, Germany) and ethanol (Merck, Darmstadt, Germany) were used for synthesis of Me-BTAP. The resin XAD-2/Me-BTAP was synthesized by using the following materials: Amberlite XAD-2 (specific surface area 330 m² g⁻¹ and bead size 20–60 mesh) purchased from Aldrich (Milwaukee, USA), octanol (Merck, Darmstadt, Germany), methylene chloride (Vetec, Brazil), anhydrous aluminum chloride (Synth, Brazil), dioxane (Synth, Brazil) and Me-BTAP (laboratory-prepared, according section 2.3). Deionized water was used to prepare all solutions. Acetate, borate and ammoniacal buffers³² were used to adjust the sample pH in the range of 4.7–6.0, 7.0–8.0 and 9.2, respectively. Metal working solutions at µg L⁻¹ level were prepared daily by diluting a corresponding 1000 µg mL⁻¹ solution (Merck, Darmstadt, Germany). Hydrochloric and nitric acid solutions used as eluents were prepared by direct dilution with deionized water from the concentrated solutions (Merck). The laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with deionized water and dried. The following certified reference biological

materials were analysed: NIST 1515 Apple Leaves and NIST 1570a Spinach Leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

Synthesis of Me-BTAP

The reagent 2-[2'-(6-methyl-benzothiazolylazo)]-4-aminophenol (Me-BTAP) was produced by coupling diazotized 6-methyl-2-aminobenzothiazole with 4-amino phenol in strongly acidic solution at 0–5 °C as described previously for similar reagents.^{30,33-34} Diazotization was performed as follows: 6-methyl-2-aminobenzothiazole was dissolved (3.0 g) in 50 mL of a 6.0 mol L⁻¹ hydrochloric acid solution; a solution of 2.0 g of sodium nitrite in 20 mL of water at 0–5 °C was added dropwise and the mixture was stirred and kept at 0–5 °C for 1 h. The diazotate mixture was added dropwise to a solution of 3.0 g of 4-aminophenol in 20 mL of an 1.0 mol L⁻¹ sodium carbonate solution at 0–5 °C under vigorous stirring. The system was allowed stand overnight in refrigerator at 0–5 °C. The dark-green precipitate resulting was filtered and purified by recrystallization with ethanol. The solubility of Me-BTAP was tested and it was found that the reagent is soluble in acetone, methanol and ethanol, partly soluble in chloroform and ether and insoluble in water. Melting point was determined seven times and varied in the range of 233–235 °C. Elemental analysis: C₁₄H₁₂ON₄S requires C 59.2%; H 4.2% and N 19.7%; found, C 57.5%; H 5.4% and N 18.9%. The IR spectrum of the dried product showed bands in the region ranging from 3360–3030, 1630, 1540 and 1470 cm⁻¹ corresponding to –OH, –NH, –N=N– and –C=S stretching frequencies, respectively. Figure 1 shows a proposed structure for Me-BTAP.

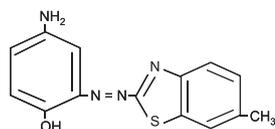


Figure 1. Proposed structure for Me-BTAP.

Synthesis of the resin XAD-2/Me-BTAP

The sorbent was synthesized by two steps from modified procedures, described previously.³⁵⁻³⁷ Amberlite XAD-2 resin (3 g) was treated with 10 mL octanol and 20 mL methylene chloride. Anhydrous aluminum chloride (7g) was added in small increments to the mixture. The system was refluxed for 24 h at 90 °C. The solid precipitate 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 dried

chloromethylated copolymer was suspended in dioxane and stirred for 1 h at room temperature to allow full swelling. To this mixture was added Me-BTAP (0.50 g, 1.76 × 10⁻³ mol) and heated for 72 h at 100 °C with continuous stirring. The mixture was filtered and the resin was washed twice with water and dioxane, respectively. After extraction by heating in dioxane for 48 h, the final product was filtered, washed with diethyl ether and dried in air. Data obtained from elemental analysis (C 70.5%, H 5.1% and N 13.7%) were comparable with the theoretically calculated values (C 69.4%, H 4.5% and N 14.1%).

Infrared spectrum of the resin was compared with that of the free Amberlite XAD-2 and Me-BTAP. These spectra were studied using the potassium bromide technique. Additional peaks in the IR spectrum of the resin that do not appear in the spectrum of the free Amberlite XAD-2 are at 3480–3010, 1530 and 1465 cm⁻¹ which appear to originate due to modification of resin by the ligand and are characteristic of –OH, –N=N– and –C=S vibrations, respectively. The peak corresponding to –NH bending does not appear in the XAD-2/Me-BTAP spectrum. This suggests that the covalent coupling of the copolymer with Me-BTAP occurs through a –C=N– group. So, the proposed structure for XAD-2/Me-BTAP shown in Figure 2 seems to be very reasonable.

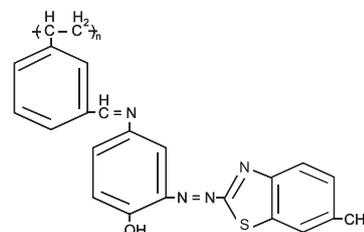


Figure 2. Proposed structure for XAD-2/Me-BTAP.

Procedure

The on-line preconcentration system was operated as follows. With the injection valves in the load position simultaneously, a sample was typically pumped through the XAD-2/Me-BTAP minicolumn. Metal ions were retained on the column surface of the resin either for 60 or 180 s, depending on the calibration mode. The injection valves were then switched on to the elute position and a stream of water carried the acid eluent from the loop and column the ions in order to release metal ions directly into the nebulizer of the spectrometer. The column was arranged in the manifold so that the eluent flowed through it, in reverse direction to that of the sample, minimizing thus the dispersion of the analyte. The injection valves remained in the elute position for 15 s. This time ensured complete elution of the metal ions from minicolumn, because it was

observed that the recorded peaks were sharp and the baseline was stable. The injection valves were then returned to the load position. Total analytical times were 75 or 135s. Signals were measured as peak height (or maximum absorbance) because it resulted in precision better than peak area. The peak height of the signal was proportional to metal concentration.

For analysis of real samples and certified material, a portion of 0.1 g of dry sample (rice flour, black tea or certified reference biological material) was precisely weighted into a Teflon cup, 4.0 mL of 1:1 (v/v) nitric acid solution were added, and the acid digestion bomb was heated in a stove at 150 °C for 5 h.^{21,38} Also a number of sub-samples were spiked with known amount of each analyte. After cooling at room temperature the bomb was opened carefully in a fume cupboard. The pH of the final digests were adjusted by suitable addition of a 10% (m/v) sodium hydroxide solution and an appropriate buffer solution, and the mixture was finally diluted to 25 mL by double deionized water.

Spectral characteristics of Me-BTAP were determined as follows: An aliquot of metal solution containing 0 - 100 µg of metal was placed in a 5 mL volumetric flask; 1 mL of convenient buffer solution, and 1 mL of a 1.0×10^{-3} mol L⁻¹ Me-BTAP solution was added; then the contents were diluted to the mark with 80% (v/v) ethanol solution and mixed thoroughly.

Results and Discussion

Spectral characteristics of Me-BTAP

Reaction of Me-BTAP with some cations, including copper, cobalt and nickel resulted in colored complexes. Table 1 lists the spectral characteristics of Me-BTAP complexes with metallic cations.

Table 1. Spectral characteristics of Me-BTAP complexes with metallic cations

Ion	pH range	λ_{\max} (nm)	Range of Beer's law (µg per 5 mL)	Molar absorptivity $\times 10^4$ (L mol ⁻¹ cm ⁻¹)
Cu (II)	6.0-9.0	560	0-10	1.83
Zn (II)	7.0-8.0	580	0-10	1.42
Ni (II)	7.0-9.0	600	0-10	1.37
Co (II)	8.0-9.0	580	0-10	1.31
Cd (II)	8.0-9.0	530	0-50	0.95
Pb (II)	7.0-9.0	540	0-100	0.52

Optimization of sorption and elution of metal ions

The degree of adsorption of metal ions (100 µg L⁻¹) on the XAD-2/Me-BTAP resin at different pH values was studied by applying the proposed procedure. In order to

evaluate the effect of pH, metal solutions were adjusted to a pH range of 4.7 – 9.2. For this study, 10 mL of acetate, borate or ammoniacal buffers were added to 100 mL calibrated flasks containing the metal and the volume was completed with deionized water. According these experiments, the best pH values for Cu (II), Co (II) and Ni (II) preconcentration are at 8.0, 7.0-9.0 and 7.0-9.0, respectively, as shown in Figure 3. A pH value of 8.0 (borate buffer) was chosen as optimum for Cu, Co and Ni determination. Adsorption of metal ions on minicolumn at acid conditions is negligible. In order to choose the most effective eluent concentration for quantitative stripping of the retained metal ions from the microcolumn, the Cu (II), Co (II) and Ni (II) ions were stripped with nitric and hydrochloric acid solutions. The results showed that both acids used could accomplish the quantitative elution of all metals. Hydrochloric acid solutions at different concentrations were used as stripping agent and the data is given in Figure 4. As can be seen, 1.00 mol L⁻¹ hydrochloric acid is sufficient for quantitative elution of the retained metal ions from the minicolumn. Addition of solvents as ethanol or acetone to acid solution have not

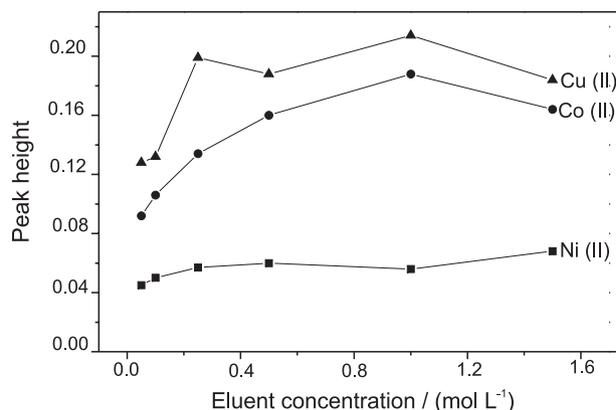


Figure 3. Effect of pH on the preconcentration of Cu, Co and Ni.

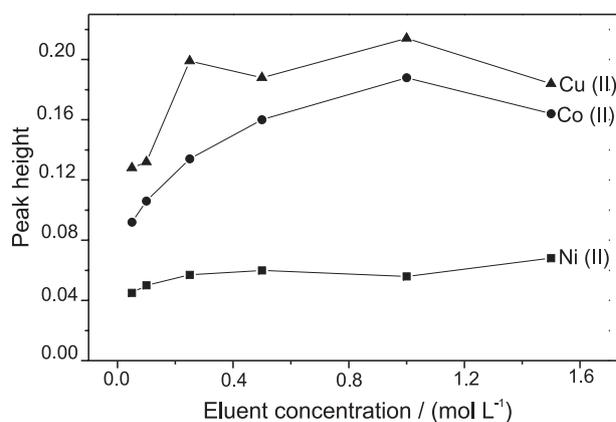


Figure 4. Effect of eluent concentration on the preconcentration of Cu, Co and Ni.

resulted in any increasing of analytical signal. Thus 1.00 mol L⁻¹ hydrochloric acid was used as an eluent for further studies. The effect of the eluent volume was studied using eluent loops. The smallest volume of eluent sufficient for complete recovery of retained metal ions from minicolumn was 150 µL. Volumes above this value also allowed quantitative recovery for all metals. A volume of 200 µL of eluent loop was chosen for copper, cobalt, and nickel in posterior experiments.

FI flow conditions

Sample flow rate is an important parameter in on-line systems because it determines the velocity of the cation on the minicolumn. The effect of the sample flow rate in the proposed manifold was investigated in the range from 4.00 to 10.00 mL min⁻¹. According to Figure 5, the absorption decreased slightly up to the whole examined range, implying that the complexation is complete and the contact time is sufficient and the kinetic properties of the Me-BTAP allow significant retention of the analytes. Optimum flow rate of 5.5 mL min⁻¹ was chosen for all metals in posterior experiments, as a compromise between high sensitivity and low sample consumption. In the proposed procedure, the eluent flow rate is not important, because it is used just to fill the loop (L). The carrier (water) flow rate determinates the speed of the introduction in the nebulizer. Experiments were carried out by pumping carrier in order to achieve an analytical signal as high as possible. Best results were found within the range of 4.0 to 6.0 mL min⁻¹ for the three metals. At flow rates less than 4.0 mL min⁻¹ the analytical signal considerably decreased, resulting broader peaks. Probably, it is due to incompatibility between elution and nebulization flow rates, which cause significant dispersion when eluent flow rate is smaller than nebulizer flow rate. A flow rate of 5.0

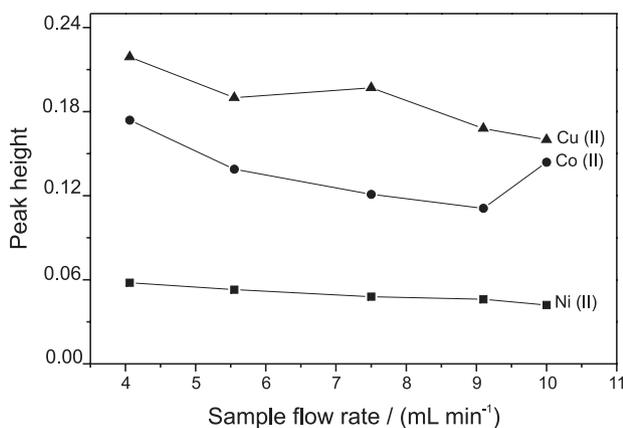


Figure 5. Effect of sample flow rate on the preconcentration of Cu, Co and Ni.

mL min⁻¹ was selected in the subsequent studies, in order to match elution and aspiration flow rates.

Sorption capacity and reusability of XAD-2/Me-BTAP

Sorption capacity studies were carried out by taking 100 mL of 10.0 mg L⁻¹ Cu (II), Co (II) or Ni (II) solutions and 0.10 g of XAD-2/Me-BTAP resin after adjusting the pH to 8.00 with 10 mL of borate buffer and then diluting to 100 mL. These systems were kept for 4 h in separate flasks under vigorous stirring and filtered through a filter paper. Value of 8.0 (borate buffer) was chosen as optimum for Cu, Co and Ni determination. The amount of copper, cobalt or nickel enriched onto polymer particles were determined by FAAS. The retention capacities of XAD-2/Me-BTAP resin were calculated to be 27.5, 31.2 and 28.6 mmol per gram for cobalt, copper and nickel, respectively. Lifetime of the minicolumn packed with XAD-2/Me-BTAP was monitored measuring the signal of 100 µg L⁻¹ copper, cobalt and nickel solutions at end of each day of work and counting the number of runs in that day. Results demonstrated that column shown good performance for at least 500 runs.

Analytical features

Features of the proposed system under the optimum conditions for FAAS determination of copper, cobalt and nickel are given in Table 2. For the three metals, the data are shown for 60 and 180 s preconcentration time. Linear equations obtained for each metal by direct aspiration were $A = -2.06 \times 10^{-2} + 1.31 \times 10^{-4} C$ (Cu 10-1000 µg L⁻¹), $A = -2.98 \times 10^{-2} + 6.06 \times 10^{-5} C$ (Co 50-5000 µg L⁻¹) and $A = -4.70 \times 10^{-4} + 5.09 \times 10^{-5} C$ (Ni 50-5000 µg L⁻¹) for copper, cobalt and nickel, respectively, where A is the absorbance and C is the metal concentration in solution. The detection limits were calculated by the 3s criterion as the concentration that gives a response equivalent to three times the standard deviation (S.D.) of the blank (n=12). The quantification limits were calculated as the concentration that gives a response equivalent to ten times the S.D. of the blank (n=12), and define the lower limit of the range. Other factors that characterize on-line preconcentration systems were also calculated. Enrichment factors were calculated as the ratio of the slopes of the linear section in calibration graphs for preconcentration and direct aspiration, respectively.³⁹⁻⁴¹ Concentration efficiency (CE) is defined as the product of the enrichment factor and the sampling frequency in number of samples analyzed per minute. Consumptive index (CI) reflects the volume of the sample consumed to

Table 2. Analytical characteristics of the on-line copper, cobalt and nickel preconcentration system using XAD-2/Me-BTAP minicolumn (A is absorbance and C is the metal concentration, $\mu\text{g L}^{-1}$)

Element	Copper		Cobalt		Nickel	
Preconcentration time, s	60	180	60	180	60	180
Enrichment factor	12	30	19	30	12	24
Concentration efficiency, min^{-1}	10.0	9.5	16.0	9.5	10.2	7.6
Transfer phase factor		0.91		0.91		0.87
Consumptive index, μL	0.56	0.59	0.35	0.59	0.55	0.74
Sample frequency, h^{-1}	51	19	51	19	51	19
Eluent consumption, μL		200		200		200
Limit of detection, $\mu\text{g L}^{-1}$	0.87	0.34	1.39	0.87	2.52	0.81
Limit of quantification, $\mu\text{g L}^{-1}$	2.90	1.13	4.65	2.90	8.39	2.70
Precision, %	5.1	4.5	3.3	2.2	5.7	5.0
Calibration function	$A = 5.69 \times 10^{-3} + 1.62 \times 10^{-3} C$	$A = -1.70 \times 10^{-2} + 3.98 \times 10^{-3} C$	$A = 2.36 \times 10^{-3} + 1.14 \times 10^{-3} C$	$A = 2.007 \times 10^{-2} + 1.83 \times 10^{-3} C$	$A = 1.15 \times 10^{-2} + 6.08 \times 10^{-4} C$	$A = 3.30 \times 10^{-2} + 1.22 \times 10^{-3} C$

achieve the EF value. It was calculated by the ratio of the sample volume, in milliliters, and EF. The retention efficiency of the minicolumn, also known as transfer phase factor, defined as the ratio between the analyte mass in original sample and that in the concentrate was determined by percolation of 25.0 mL of a $100.0 \mu\text{g L}^{-1}$ copper, cobalt or nickel solution by the minicolumn under optimum conditions. The desorption was carried out with 1.00 mL of 1.00 mol L^{-1} hydrochloric acid solution and the metals were measured by FAAS.

Interference studies

In order to evaluate the selectivity of the proposed on-line preconcentration system the interference of various elements was investigated on the determination of $100.0 \mu\text{g L}^{-1}$ copper, cobalt or nickel. Any deviation of $\pm 5\%$ or more from the standard absorbance value was taken as an interference. The results obtained in these experiments (Table 3) demonstrate that the presence of large amounts of alkali and alkaline earth metals in the sample have no significant effect on the preconcentration of copper, cobalt and nickel. The effects of other ions at given concentrations are also negligible.

Application of the procedure

The accuracy of the developed preconcentration procedure was tested, by determining the copper, cobalt and nickel content in certified reference materials. The

Table 3. Maximum tolerable quantities of other ions for the on-line system using Amberlite XAD-2 / Me-BTAP minicolumn for cobalt ($100 \mu\text{g L}^{-1}$), copper ($100 \mu\text{g L}^{-1}$) and nickel ($100 \mu\text{g L}^{-1}$) determination

Substance	Maximum tolerable amount		
	Copper	Cobalt	Nickel
Al^{3+}	50 mg L^{-1}	0.1 g L^{-1}	0.1 g L^{-1}
Br^{-}	10.0 mg L^{-1}	0.5 g L^{-1}	0.1 g L^{-1}
Ca^{2+}	2.0 g L^{-1}	5.0 g L^{-1}	2.0 g L^{-1}
Cd^{2+}	5.0 mg L^{-1}	5.0 mg L^{-1}	1.0 mg L^{-1}
Ba^{2+}	0.5 g L^{-1}	0.5 g L^{-1}	0.1 g L^{-1}
Cl^{-}	10.0 g L^{-1}	10.0 g L^{-1}	10.0 g L^{-1}
Co^{2+}	0.5 mg L^{-1}	-	0.5 mg L^{-1}
Cu^{2+}	-	1.0 mg L^{-1}	5.0 mg L^{-1}
F^{-}	0.1 g L^{-1}	0.5 g L^{-1}	0.5 g L^{-1}
Fe^{3+}	5.0 mg L^{-1}	1.0 mg L^{-1}	5.0 mg L^{-1}
K^{+}	5.0 g L^{-1}	10.0 g L^{-1}	10.0 g L^{-1}
Mg^{2+}	5.0 mg L^{-1}	0.5 mg L^{-1}	0.8 mg L^{-1}
Na^{+}	10.0 g L^{-1}	10.0 g L^{-1}	10.0 g L^{-1}
Ni^{2+}	0.5 mg L^{-1}	1.0 mg L^{-1}	-
NO_3^{-}	5.0 g L^{-1}	10.0 g L^{-1}	10.0 g L^{-1}
Pb^{2+}	2.0 mg L^{-1}	5.0 mg L^{-1}	5.0 mg L^{-1}
Zn^{2+}	5.0 mg L^{-1}	2.5 mg L^{-1}	2.0 mg L^{-1}

samples were digested by using the procedure already described. The certified values and the obtained analytical results are presented in Table 4. Metal contents established by the present procedure agree well with the certified values. Results indicate the applicability of the developed procedure in copper, cobalt and nickel determination free of interference.

The method was applied to the analysis of rice flour and black tea. Real samples collected from supermarkets of Jequié, Bahia, Brazil were subjected to dissolution,

Table 4. Metal determination in certified reference materials using proposed methodology ($n=4$, confidence interval 95%)

Sample	Cobalt amount ($\mu\text{g g}^{-1}$)		Copper amount ($\mu\text{g g}^{-1}$)		Nickel amount ($\mu\text{g g}^{-1}$)	
	Found	Certified	Found	Certified	Found	Certified
NIST 1515 - Apple Leaves	—	—	5.39 ± 0.18	5.64 ± 0.24	—	—
NIST 1570a - Spinach Leaves	0.35 ± 0.11	0.39 ± 0.05	12.85 ± 0.52	13.15 ± 0.75	2.19 ± 0.07	2.14 ± 0.10

NIST-National Institute of Standards & Technology, USA.

Table 5. Results obtained for metal determination in food samples (n=4, confidence interval 95%)

Sample	Cobalt amount ($\mu\text{g g}^{-1}$)		Recovery (%)	Copper amount ($\mu\text{g g}^{-1}$)		Recovery (%)	Nickel amount ($\mu\text{g g}^{-1}$)		Recovery (%)
	Added	Found		Added	Found		Added	Found	
Black tea	0.0	1.98 \pm 0.05	—	0.0	2.35 \pm 0.12	—	0.0	< LOD	—
	2.0	4.01 \pm 0.13	102	2.0	4.21 \pm 0.08	93	2.0	1.89 \pm 0.07	95
	4.0	5.78 \pm 0.16	95	4.0	6.23 \pm 0.21	97	4.0	3.84 \pm 0.11	96
Rice flour	0.0	1.71 \pm 0.04	—	0.0	1.95 \pm 0.07	—	0.0	< LOD	—
	2.0	3.85 \pm 0.05	107	2.0	3.99 \pm 0.15	102	2.0	2.06 \pm 0.10	103
	4.0	5.91 \pm 0.12	105	4.0	5.94 \pm 0.19	100	4.0	3.72 \pm 0.17	93

LOD: Limit of detection.

preconcentration and metal determination using the proposed procedure. The recoveries of the spiked samples (2.0 or 4.0 $\mu\text{g g}^{-1}$) were determined and results given in Table 5 indicate that the analytes added to the samples were quantitatively recovered. It can be concluded that the described procedure can be successfully applied to these biological matrices for the preconcentration and determination of copper, cobalt and nickel.

Conclusions

The utilisation of XAD-2/Me-BTAP in an on-line preconcentration system provides a simple, easy, accurate and faster procedure for the determination of copper, cobalt and nickel. The functionalization of the reagent on Amberlite XAD-2 results in a powerful support that remains stable even under rough changes of pH and solvent conditions. Functionalization also minimises problems associated with leaching of ligand from minicolumn packed with XAD-2/Me-BTAP, allowing it use for several operational cycles (> 500). Sensitivity obtained for the metals was comparable to those presented by other methods described in the literature. Due to stability of the support, high tolerance to interference from the matrix ions and low detection limits obtained, the proposed procedure has been demonstrated to be promising for routine laboratories in trace element analysis.

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