A preconcentration system for determination of copper and nickel in water and food samples employing flame atomic absorption spectrometry

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ABSTRACT

A separation/preconcentration procedure using solid phase extraction has been proposed for the flame atomic absorption spectrometric determination of copper and nickel at trace level in food samples. The solid phase is Dowex Optipore SD-2 resin contained on a minicolumn, where analyte ions are sorbed as 5-methyl-4-(2-thiazolylazo) resorcinol chelates. After elution using $1\,mol\,L^{-1}$ nitric acid solution, the analytes are determinate employing flame atomic absorption spectrometry. The optimization step was performed using a full two-level factorial design and the variables studied were: pH, reagent concentration (RC) and amount of resin on the column (AR). Under the experimental conditions established in the optimization step, the procedure allows the determination of copper and nickel with limit of detection of 1.03 and $1.90\,\mu g\,L^{-1}$, respectively and precision of 7 and 8%, for concentrations of copper and nickel of $200\,\mu g\,L^{-1}$. The effect of matrix ions was also evaluated. The accuracy was confirmed by analyzing of the followings certified reference materials: NIST SRM 1515 Apple leaves and GBW 07603 Aquatic and Terrestrial Biological Products. The developed method was successfully applied for the determination of copper and nickel in real samples including human hair, chicken meat, black tea and canned fish.

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1. Introduction

Trace heavy metals are essential micro-nutrients and have a variety of biochemical functions in all living organisms [1–3]. While trace elements are essential, they can be toxic when taken in excess. Trace metals are ubiquitous environmental contaminants. Environmental sample take up trace metals from soils, fertilizers, air, industrial process and transportation. Heavy metals are mobile and easily taken up by plants in the environment [1–4]. Due to these important points, the accurate determinations of trace heavy metals are important part of the studies in analytical chemistry [5–8]. Flame atomic absorption spectrometry (FAAS) is relatively simple and available technique in many laboratories for heavy metal determinations [9–12]. However the conventional determinations of elements at $\mu g\,L^{-1}$ range by flame atomic absorption spectrometry frequently are not possible. To solve this problem, preconcentration/separation procedures have been proposed. Preconcentration is a very important issue for achievement of low detection limits [13–16]. Solid phase extraction is a very important place in preconcentration studies due to its simplicity, high preconcentration factors, environmental friendly, etc. [17–19].

In the recent years the multivariate techniques have been used for optimization of analytical methods [20–25]. Several review papers [24–26] have been published at this subject. The multivariate techniques have some advantages: a reduction in the number of experiments that need be executed resulting in lower reagent consumption and considerably less laboratory work. Furthermore these methods allow the development of mathematical models that permit estimate the relevance as well as statistical significance of the factor effects on the processes and also evaluate the interaction effects between the factors [22–26].

In this paper, a preconcentration procedure using solid phase extraction has been proposed for the determination of copper and nickel in food samples employing flame atomic absorption spectrometry. The extraction step is performed using a minicolumn of Dowex Optipore SD-2 resin, where metal ions are pre-concentrated as 5-methyl-4-(2-thiazolylazo) resorcinol chelates. A full two-level factorial design was used for to evaluate the variables including pH, reagent concentration and amount of Optipore SD-2 resin, considering the experimental domain.

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2. Experimental

2.1. Instruments

A PerkinElmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. PerkinElmer single-element hollow cathode lamps were used in the AAS measurements. All measurements were carried out in an air/acetylene flame. The operating conditions adjusted in the atomic absorption spectrometer were carried out according to the standard guidelines of the manufacturers. A 10-cm long slot-burner head, a lamp and an air/acetylene flame were used.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.2. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute HNO$_3$ (1 + 9) and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg L^{-1} of the given element supplied by Sigma (St. Louis, MO, USA) and Aldrich (Milwaukee, WI, USA). Stock solutions of diverse elements that were the matrix components of the natural water samples and/or have interfering effects in flame atomic absorption spectrometric determinations were prepared from their high purity compounds.

5-Methyl-4-(2-thiazolylazo) resorcinol (Sigma, St. Louis, USA) solution (0.1%, w/v) was prepared by dissolving the requisite amounts of 5-methyl-4-(2-thiazolylazo) resorcinol in water/ ethanol (75%/25%, v/v) mixture.

Sodium phosphate buffer (0.1 mol L^{-1}) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol L^{-1}) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 6. Ammonium chloride buffer solutions (0.1 mol L^{-1}) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8.

Dowex Optipore SD-2 (Sigma, St. Louis, USA) is a macroporous divinylbenzene copolymer with tertiary amine functional group. Its surface area is 800 m^2 g^{-1} [27]. It is specially designed for decolorization as well as taste and odor removal in sweetener applications [20]. It was washed successively with methanol, water, 1 mol L^{-1} HNO$_3$ in acetone, water, 1 mol L^{-1} NaOH, and water, sequentially.

A glass mini column containing 0.45 g of Dowex Optipore SD-2 in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was approximately 2.0 cm.

2.3. Analytical procedure

Test solutions containing 10 μg copper(II) and 10 μg of nickel(II) were prepared in 30–40 mL. 5.0 mL of buffer solution to give the desired pH and 2 mL of 0.1% (w/v) 5-methyl-4-(2-thiazolylazo) resorcinol solution were added. Dowex Optipore SD-2 column was preconditioned with buffer solution. Metal-5-methyl-4-(2-thiazolylazo) resorcinol solution was passed through the column. The test solutions were gravitationally passed through a column at a flow rate of 5 mL min^{-1}. The analytes on the resin were eluted by 5 mL of 1 mol L^{-1} HNO$_3$ at a flow rate of 5 mL min^{-1}. The flow rates were controlled by a stopcock of the column. The analyte ions in the final solution were determined by using flame atomic absorption spectrometry.

2.4. Applications

The digestion conditions for microwave system for the solid samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, ventilation: 8 min [28–30]. Total time to digest a sample in the microwave system was 31 min.

NIST SRM 1515 Apple leaves and GBW 07603 Aquatic and Terrestrial Biological Products standard reference materials (250 mg) were digested with 6 mL of HNO$_3$ 65% (m/v), 2 mL of H$_2$O$_2$ 30% (v/v) in closed microwave digestion system and diluted to 50.0 mL with deionized water. Then the preconcentration procedure given above was applied to the final solutions.

Human hair, chicken meat, black tea and canned fish samples were digested according to procedure given in literature [28–30]. 1.0 g of sample was digested with 6 mL of concentrated HNO$_3$ and 2 mL of H$_2$O$_2$ in microwave system. After digestion of the samples, the volume of the digested sample was made up to 50.0 mL with distilled water. The preconcentration procedure given above was applied to the samples.

The blanks were prepared in the same way as the sample, but omitting the sample. The concentrations of the analytes on the blanks were always below the detection limits of this preconcentration/separation system.

3. Results and discussions

3.1. Optimization of the experimental conditions using factorial design

The optimization step for quantitative extraction of copper and nickel was performed using a full two-level factorial design, involving the followings factors: pH (from 2.0 to 8.0), reagent concentration (from 4.0 to 8.0 μg mL^{-1}) and amount of resin on the column (AR) varying of 0.3 at 0.6 g, having as response the metal recoveries (%). Replicates of central points were done for determination of the experimental errors and curvature tests. The experimental conditions for volume, concentration and flow rate of the nitric acid as eluent were fixed in: 5 mL, 1 mol L^{-1} and 5 mL min^{-1}, respectively, considering results of previous experiments. The sample volume for solid phase extraction studies was fixed in 250 mL. All the two experiments were carried out in random order. The experimental data were processed using the STATISTICA software [31].

The results of the factorial design for copper demonstrate that all the factors studied are significant for the experimental conditions established. However, the pH effect is considerably higher than the effects of reagent concentration and resin mass. It can be seen in Fig. 1 and Table 1. The curvature test was also performed. The result shows that it is significance. It means that there is an experimental region for maximum extraction of copper from its central point to the value that presents the pH variable is at its high level (Table 2).

Table 1
Factors and levels used in the factorial design for the present work

Variable	Low (−)	Central point (0)	High (+)
Reagent concentration (RC)[a]	0.5	1.5	2.0
pH	2.0	5.0	8.0
Amount of resin (AR) (g)	0.3	0.45	0.6

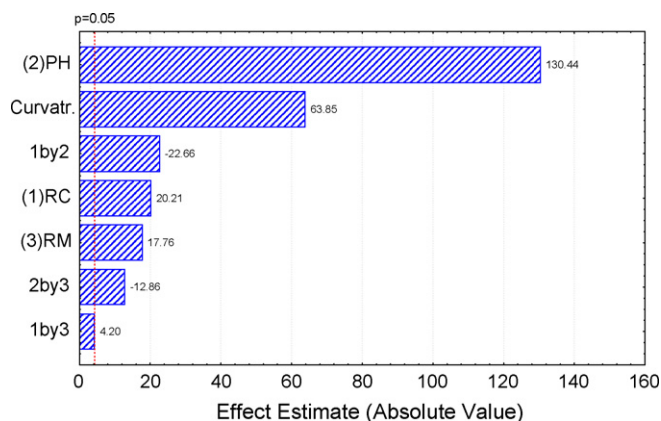[a] mL of 0.1% (w/v) complexing reagent.

Fig. 1. Pareto chart of standardized effects for variables for copper extraction.

Table 2
Design matrix and the results of the factorial design ($N = 4$)

Experiment	RC	pH	AR	Cu, recovery (%)	Ni, recovery (%)
1	+	+	+	98	97
2	+	+	−	95	85
3	+	−	+	60	10
4	+	−	−	45	25
5	−	+	+	98	97
6	−	+	−	97	95
7	−	−	+	40	30
8	−	−	−	30	20
CP[a]	0	0	0	95	95
CP	0	0	0	96	95
CP	0	0	0	95	96

[a] Central point.

The results of the factorial design for the nickel extraction are practically the same found for the copper extraction. The main factor is pH. This can be observed in Pareto chart as Fig. 2. Considering all these information's, the experimental conditions established for the simultaneous extraction of copper and nickel are: pH 8.0, reagent concentration 8.0 μg mL^{-1} and resin mass in 0.6 g. The sample volume was 250 mL. The linear working ranges for nickel and copper were 0–5.0 mg L^{-1} and 0–5.0 mg L^{-1}, respectively.

3.2. Effect of divers ions

The effects of possible matrix ions were also examined. The results are given in Table 3. The tolerance limit is defined as the
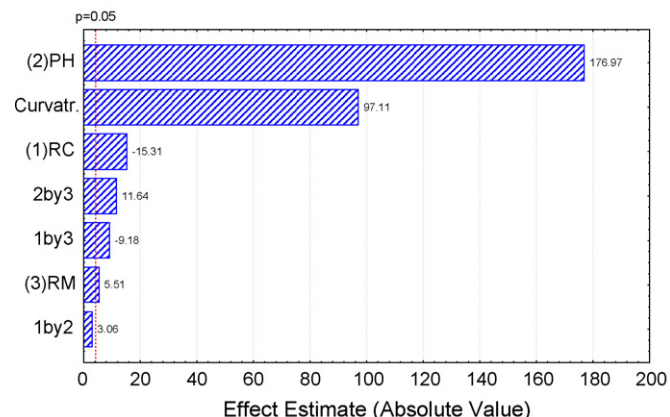

Fig. 2. Pareto chart of standardized effects for variables for nickel extraction.

Table 3
Effects of concomitant ions on the recoveries of analytes ($N = 3$)

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)	
			Cu	Ni
Na^+	NaCl	20000	99 ± 2	95 ± 3
K^+	KCl	3000	96 ± 2	97 ± 2
Ca^{2+}	CaCl$_2$	5000	98 ± 3	99 ± 3
Mg^{2+}	MgCl$_2$	5000	95 ± 2	98 ± 2
Cl^-	NaCl	30000	95 ± 3	99 ± 2
F^-	NaF	1000	95 ± 2	95 ± 3
NO_3^-	KNO$_3$	3000	95 ± 2	95 ± 3
SO_4^{2-}	Na$_2$SO$_4$	3000	98 ± 2	97 ± 2
PO_4^{3-}	Na$_3$PO$_4$	2000	95 ± 2	95 ± 2
Cr^{3+}	Cr(NO$_3$)$_3$	25	98 ± 2	98 ± 1
Cd^{2+}	Cd(NO$_3$)$_2$	25	97 ± 3	96 ± 3
Fe^{3+}	FeCl$_3$	25	96 ± 2	96 ± 3
Pb^{2+}	Pb(NO$_3$)$_2$	25	97 ± 1	95 ± 2
Zn^{2+}	ZnSO$_4$	25	95 ± 3	95 ± 3
Mn^{2+}	MnSO$_4$	25	95 ± 2	95 ± 2
Co^{2+}	CoSO$_4$	25	95 ± 2	95 ± 3

ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of analyte ions. The ions normally present in water do not interfere under the experimental conditions used. Also, some of the transition metals at mg L^{-1} levels were not interfered on the recoveries of the analyte ions. This results show that the proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals given in Table 3 at mg L^{-1} levels.

3.3. Adsorption capacity

In order to study the adsorptive capacity of Dowex Optipore SD-2, 0.1 g resin was added 50 mL of solution containing 1.0 mg of analyte ion at pH 8.0. After shaking for 1 h, the mixture was filtered. 10 mL of the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. This procedure was separately repeated for each analyte ions. The capacity of sorbent for copper(II) and nickel(II) was found to be as 12.0 and 11.5 mg metal/g resin, respectively.

3.4. Figures of merit

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the solid phase extraction procedure to blank solutions. The limits of detection for nickel(II) and copper(II) based on three times the standard deviations of the blank ($k = 3$, $n = 21$) were 1.03 and 1.90 μg L^{-1}, respectively. The limit of qualification values were 5.15 μg L^{-1} for nickel and 9.50 μg L^{-1} for copper. A preconcentration factor of 50 for both analyte ions was obtained for an initial volume of 250 mL.

The presented solid phase extraction method was evaluated using the standard reference materials (NIST SRM 1515 Apple leaves and GBW 07603 Aquatic and Terrestrial Biological Products). The results were given in Table 4. The obtained results were in good agreement with the certified values.

3.5. Application

Tests of addition/recovery in the experiments for copper and nickel determination by the presented method were performed various samples given in Table 5. Good agreements for copper and nickel ions were obtained between spiked and measured analyte amounts. The recovery values calculated for the spiked standards were always higher than 95%. In the light of these results, the

Table 4
The results for reference standard materials after application of presented procedure ($N = 4$)

Element	NIST SRM 1515 Apple leaves ($\mu g\,g^{-1}$)		GBW 07603 Aquatic and Terrestrial Biological Products ($\mu g\,g^{-1}$)	
	Certified value	Presented method	Certified value	Presented method
Cu	5.64	5.57 ± 0.32[a]	6.6	6.80 ± 0.40
Ni	0.91	0.94 ± 0.07	1.7	1.65 ± 0.10

[a] Mean expressed as 95% tolerance limit.

Table 5
The results for tests of addition/recovery for Cu and Ni determination in natural water samples (sample volume: 250 mL, final volume: 10 mL ($N = 4$))

Element	Added ($\mu g\,L^{-1}$)	Tap water		Spring water		River water	
		Found ($\mu g\,L^{-1}$)	Recovery (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)	Found ($\mu g\,L^{-1}$)	Recovery (%)
Cu	–	8.5 ± 0.4[a]	–	10.2 ± 0.5	–	3.4 ± 0.1	–
	5	13.4 ± 0.8	98	15.1 ± 0.8	98	8.1 ± 0.5	94
	10	18.3 ± 0.9	98	20.1 ± 0.9	99	12.9 ± 0.8	95
	20	28.3 ± 0.9	99	29.8 ± 1.1	98	23.1 ± 1.2	99
Ni	–	12.5 ± 0.7	–	9.3 ± 0.6	–	8.7 ± 0.5	–
	5	17.2 ± 0.9	94	14.1 ± 0.8	96	13.4 ± 0.8	94
	10	22.1 ± 1.2	96	18.8 ± 0.7	95	18.4 ± 0.9	97
	20	31.8 ± 1.5	97	29.1 ± 1.6	99	27.5 ± 1.3	94

[a] Standard deviation.

Table 6
Concentration of analyte ions in some real samples after application presented solid phase extraction procedure ($N = 4$)

	Concentration ($\mu g\,g^{-1}$)	
	Cu	Ni
Human hair	3.24 ± 0.10[a]	2.21 ± 0.11
Chicken meat	1.32 ± 0.06	2.85 ± 0.15
Black tea	4.67 ± 0.19	4.45 ± 0.27
Canned fish	0.49 ± 0.02	<LOQ

[a] Mean expressed as 95% tolerance limit; LOQ: lower than quantification limit.

proposed solid phase extraction procedure could be applied satisfactorily for analysis of these samples.

The method has been combined with the microwave assisted digested samples. The results are given in Table 6.

4. Conclusion

Application of two-level full factorial designs allowed the efficient optimization of a solid phase extraction procedure for preconcentration of Cu and Ni in waters and food samples by FAAS after a solid phase extraction using the Dowex Optipore SD-2 resin and 5-methyl-4-(2-thiazolylazo) resorcinol as complexing reagent. Our methodology was shown to be an effective approach for improving the sensitivity of FAAS for Cu and Ni determination. The system is very simple, rapid, easy to use, selective and with a good sensitivity for the determination of Cu and Ni in these samples. Analytical features, such as enrichment factor, limit of detection and accurate are satisfactory and comparable to those presented by methods described in the literature [32–40].

Acknowledgements

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