

Development of a cloud-point extraction method for copper and nickel determination in food samples

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Abstract

A new, simple and versatile cloud-point extraction (CPE) methodology has been developed for the separation and preconcentration of copper and nickel. The metals in the initial aqueous solution were complexed with 2-(2'-benzothiazolylazo)-5-(*N,N*-diethyl)aminophenol (BDAP) and Triton X-114 was added as surfactant. Dilution of the surfactant-rich phase with acidified methanol was performed after phase separation, and the copper and nickel contents were measured by flame atomic absorption spectrometry. The variables affecting the cloud-point extraction were optimized using a Box–Behnken design. Under the optimum experimental conditions, enrichment factors of 29 and 25 were achieved for copper and nickel, respectively. The accuracy of the method was evaluated and confirmed by analysis of the followings certified reference materials: Apple Leaves, Spinach Leaves and Tomato Leaves. The limits of detection expressed to solid sample analysis were $0.1 \mu\text{g g}^{-1}$ (Cu) and $0.4 \mu\text{g g}^{-1}$ (Ni). The precision for 10 replicate measurements of $75 \mu\text{g L}^{-1}$ Cu or Ni was 6.4 and 1.0, respectively. The method has been successfully applied to the analysis of food samples.

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1. Introduction

Copper and nickel combined with other elements occurs naturally in the earth's crust. Copper is an essential nutrient, while nickel has no known beneficial health effects. However both metals may be harmful if eaten in excessive amounts. The most common harmful health effect of nickel in humans is an allergic reaction. The main route of intake for these elements is from foods. Copper and nickel can be present in foods naturally, as a result of pollution, or from the storage or processing of foods, such as when tin migrates from cans into the contained foods [1,2]. These metals normally occur at very low levels in the environment, so sensitive methods are needed to detect them in most environmental and food samples. The determination of copper and nickel in these matrices is usually carried out by flame atomic absorption spectrometry (FAAS), electrothermal

atomic absorption spectrometry (ETAAS), spectrophotometry, inductively coupled optical emission spectrometry (ICP OES), chemiluminescence and electrochemical methods. FAAS is a powerful detection technique for determining trace elements. The advantages of FAAS include well-known interferences, low operator skill required for operation, and comparatively low cost instrumentation and operation. However, there are some drawbacks; most of environmental samples cannot be directly processed with FAAS because this technique has not enough sensitivity. Therefore, preconcentration and separation of analyte are needed before measuring. Successful preconcentration can be achieved by various methods, such as precipitation [3,4], liquid–liquid [5], solid-phase [6,7] or cloud-point extraction (CPE) [8–10]. Cloud-point extraction is based on the property that a solute present in aqueous solution of non-ionic surfactant is distributed between two phases. Recently great attention has been attracted for its great potential in separation of toxic solutes from several matrices [11–14].

Procedures for preconcentration of metal ions using CPE has been based on the extraction of these metallic substances as

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sparingly water-soluble chelate complexes [15]. Pyridylazo and thiazolylazo reagents have been widely employed for cloud-point extraction of metals. These ligands have a great capacity to form complexes with many metals. Several pyridylazo and thiazolylazo reagents such as 1-(2-thiazolylazo)-2-naphthol (TAN) [16,17], 4-(2-pyridylazo)resorcinol (PAR) [18,19], 1-(2-pyridylazo)-2-naphthol (PAN) [18,19] and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) [18,20,21] have been used for cloud-point extraction of metals in several procedures.

The aim of this work is to apply a thiazolylazo reagent, 2-(2'-benzothiazolylazo)-5-(*N,N*-diethyl)aminophenol (BDAP) in a CPE procedure for determination of copper and nickel in food samples. Some analogous compounds of BDAP such as 2-(6-methyl-2-benzothiazolylazo)-5-diethylaminophenol (MBTAE) [22–24] and 2-(2-thiazolylazo)-5-diethylaminophenol (TADAP) [25–27] have been applied as a precolumn derivatizing reagent in high-performance liquid chromatography (HPLC). Another analogue, 2-(6-bromo-2-benzothiazolylazo)-5-diethylaminophenol, was synthesized and applied to the spectrophotometric determination of nickel [28] and zirconium [29]. According our knowledge, the use of BDAP in analytical procedures has not been reported before.

2. Experimental

2.1. Apparatus

A PerkinElmer Instruments (Shelton, USA) model AAAnalyst 200 flame atomic absorption spectrometer was used for the determination of copper and nickel in the surfactant-rich phase. Copper and nickel hollow cathode lamps were used as the radiation source at the wavelengths of 324.8 and 232.0 nm, respectively. Nebulizer flow rate was 5.0 mL min⁻¹. Cloud-point preconcentration experiments were performed using a thermostated bath (Soc. Fabbe LTDA, São Paulo, Brazil), maintained at the desired temperature. A centrifuge (BIO ENG model BE 5000, São Paulo, Brazil) was used to accelerate the phase separation process. A Digimed DM 20 (Santo Amaro, Brazil) pH meter was used for all pH measurements. Digestion of certified reference material was carried out in a Parr Instrument 4749 (Moline, IL, USA) Acid Digestion Bomb enclosing a chemically inert Teflon sample cup of 23 mL. Melting point of BDAP was determined by using DIGIMEC BTC 9090 equipment.

2.2. Chemicals

All chemicals and reagents used in this study were of analytical-reagent grade. Deionized water was used to prepare all solutions. The laboratory glassware was kept in dilute nitric acid at least overnight and subsequently washed with deionized water. Solutions of the non-ionic surfactant Triton X-114 (Sigma–Aldrich, Milwaukee, USA) were prepared in high purity deionized water. BDAP solutions were prepared by dissolving appropriate amounts of 2-(2'-benzothiazolylazo)-5-(*N,N*-diethyl)aminophenol laboratory-prepared in absolute ethanol (Merck, Darmstadt, Germany). One thousand mil-

ligrams per liter stock standard solutions of Cu and Ni were purchased from Merck. Nitric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions (Merck). Methanol (Merck) was used to decrease the viscosity of surfactant-rich phase. Acetate (4.6), phosphate (6.3) and borate (7.5 and 8.0) buffers were used to adjust the sample pH. Sodium carbonate (Vetec, Rio de Janeiro, Brazil), 2-aminobenzothiazole (Sigma–Aldrich), sodium nitrite (Vetec), *N,N*-diethyl-3-aminophenol (Merck) and ethanol (Merck) were used for synthesis of BDAP. The accuracy of the method was assessed by analysing the following certified reference materials (CRM): NIST 1515 Apple Leaves, NIST 1570a Spinach Leaves and NIST 1573a Tomato Leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.3. Synthesis of BDAP

An amount (3.0 g) of 2-aminobenzothiazole was stirred in 40 mL of hydrochloric acid at room temperature for 2 h. Deionized water (20.0 mL) was added slowly and under mechanical stirring and the mixture was cooled to 0–5 °C. Then 20.0 mL of a 3.6-mol L⁻¹ sodium nitrite solution were added dropwise and the reaction mixture was stirred for 2 h at 0–5 °C. For coupling, 3.3 g of *N,N*-diethyl-3-aminophenol was added to 20 mL of a 1.0-mol L⁻¹ sodium carbonate solution and the mixture was cooled to 0–5 °C. This solution was added dropwise to the above-diazotized solution with vigorous stirring for 45 min. The system was allowed stand overnight in refrigerator at 0–5 °C. Afterwards, the product was filtered and rinsed with cold water. The dark-brown precipitate resulting was purified by recrystallization with ethanol and active carbon.

2.4. Samples and sample pretreatment

Food samples were purchased from local supermarkets at Jequié, Bahia state in Brazil. For decomposition of these samples, a simplified digestion procedure was used. Accurately known mass of approximately 0.15 g of food or CRM was placed in PTFE vessel and 4.0 ml of 1:1 (v/v) nitric acid solution were added. Afterwards the Teflon vessel was closed and put into a pressurized digestion system. The thermal heating was carried out in a stove at 150 °C for 6 h. The resultant solution was allowed to cool. After cooling at room temperature these solutions were adjusted to pH with a 10% (w/v) sodium hydroxide. The solution was made up to required volume with deionized water into a 50-mL volumetric flask. The same procedure was used for the blank solutions. Spiked samples were also prepared in order to calculate the recovery of the digestion procedure.

2.5. Cloud-point extraction procedure

An aliquot (10 mL) of a copper or nickel buffered solution was transferred to a 15 mL centrifuge tube. Appropriate amounts of BDAP and Triton X-114 solutions were added. The sample solution was left to equilibrate in a thermostated bath for 15 min at 40 °C. The system was then centrifuged at 3500 rpm for 20 min to achieve complete separation of the two phases. The phases

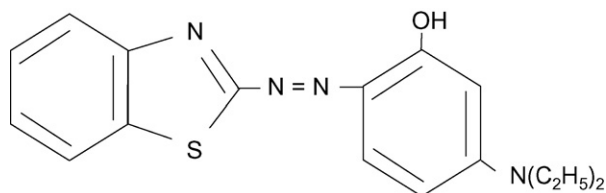


Fig. 1. Proposed structure for BTAP.

were cooled down in an ice bath in order to increase the viscosity of the surfactant-rich phase. After the cloud-point extraction, the aqueous phase was decanted by inverting the tube. Later 200 μL of a 1:1 (v/v) methanol; 1 mol L⁻¹ HNO₃ solution was added to the surfactant-rich phase. The resultant solution was directly introduced into the FAAS by conventional aspiration and the copper or nickel content was measured.

3. Results and discussion

3.1. Characterization of BDAP

The BDAP reagent was characterized by means of solubility tests, melting point and IR instrumental techniques. The solubility of BDAP was tested and it was found that the reagent is soluble in strongly acid solution, acetone, chloroform, ether and ethanol, partly soluble in water and insoluble in basic solution. Melting point was determined seven times and varied in the range of 210–212 °C. The IR spectrum of the dried product showed bands in the region ranging from 3400 to 3100, 1650 and 1150 cm⁻¹ corresponding to –OH, –N=N– and –C–N frequencies. Fig. 1 shows a proposed structure for BDAP.

3.2. Optimization of the experimental conditions for CPE

In order to investigate the influence of the main variables in CPE procedure, a Box–Behnken design was employed [30]. The variables: pH, BDAP concentration (BC) and surfactant concentration (SC) were optimized. Table 1 shows the experiments executed for this design. The data in Table 1 are described by a

quadratic model in the three factor variables. The equation that represents the relationship among the analytical signal for Cu (RCu) or Ni (RNi) and pH, BDAP concentration and surfactant concentration are the following:

$$\begin{aligned} \text{RCu} = & 0.2227 * + 0.0046 (\text{pH}) - 0.0343 * (\text{pH})^2 \\ & + 0.0019 (\text{SC}) - 0.0158 * (\text{SC})^2 - 0.0136 (\text{BC})^2 \\ & - 0.0035 (\text{pH}) (\text{SC}) + 0.0002 (\text{pH}) (\text{BC}) \\ & + 0.0017 (\text{SC}) (\text{BC}) \end{aligned} \quad (1)$$

$$\begin{aligned} \text{RNi} = & 0.0670 * + 0.0239 * (\text{pH}) - 0.0172 * (\text{pH})^2 \\ & - 0.0095 * (\text{SC}) + 0.0060 (\text{SC})^2 - 0.0006 (\text{RC}) \\ & - 0.0113 * (\text{RC})^2 - 0.0007 (\text{pH}) (\text{SC}) - 0.0220 * \\ & \times (\text{pH}) (\text{RC}) - 0.0028 (\text{SC}) (\text{RC}) \end{aligned} \quad (2)$$

Values marked with * are significant. Considering Eq. (1), a maximum point is predicted for the codified factor levels of 0.065 for pH, 0.052 for surfactant concentration and 0.0039 for BDAP concentration. Corresponding real values from data of copper are: 6.4 (pH), 1.53% (v/v) (surfactant concentration) and 1.84×10^{-3} mol L⁻¹ (BDAP concentration). The results from mathematical adjustment by surface response graphs can be seen in Fig. 2.

The critical point of surface response from data of nickel was characterized as a saddle point. This point is a stationary point of a surface response which presents the maximum response for the levels of some variables and simultaneously the minimum response for the levels of other variables of the system [31]. Surface responses for nickel are presented in Fig. 3. Real values of maximum point for nickel are the following: 7.5 (pH), 1.0% (v/v) (surfactant concentration) and 1.23×10^{-3} mol L⁻¹ (BDAP concentration). The results obtained separately for copper and nickel agree with the results calculated using the multiple response function which were: 7.5 (pH), 1.0% (v/v) (surfactant concentration) and 1.9×10^{-3} mol L⁻¹ (BDAP concentration) [31,32].

Table 1
Variables for the Box–Behnken design with real and coded values

Experiment	pH	SC (% v/v)	BC (mol L ⁻¹)	RCu	RNi
1	4.6 (–1.0)	1.0 (–1.0)	1.84×10^{-3} (0.0)	0.1700	0.045
2	8.0 (1.0)	1.0 (–1.0)	1.84×10^{-3} (0.0)	0.1800	0.093
3	4.6 (–1.0)	2.0 (1.0)	1.84×10^{-3} (0.0)	0.1720	0.020
4	8.0 (1.0)	2.0 (1.0)	1.84×10^{-3} (0.0)	0.1680	0.065
5	4.6 (–1.0)	1.5 (0.0)	1.23×10^{-3} (–1.0)	0.1660	0.000
6	8.0 (1.0)	1.5 (0.0)	1.23×10^{-3} (–1.0)	0.1810	0.093
7	4.6 (–1.0)	1.5 (0.0)	2.46×10^{-3} (1.0)	0.1680	0.028
8	8.0 (1.0)	1.5 (0.0)	2.46×10^{-3} (1.0)	0.1840	0.033
9	6.3 (0.0)	1.0 (–1.0)	1.23×10^{-3} (–1.0)	0.1900	0.058
10	6.3 (0.0)	2.0 (1.0)	1.23×10^{-3} (–1.0)	0.1990	0.052
11	6.3 (0.0)	1.0 (–1.0)	2.46×10^{-3} (1.0)	0.1840	0.077
12	6.3 (0.0)	2.0 (1.0)	2.46×10^{-3} (1.0)	0.2000	0.060
13	6.3 (0.0)	1.5 (0.0)	1.84×10^{-3} (0.0)	0.2160	0.068
14	6.3 (0.0)	1.5 (0.0)	1.84×10^{-3} (0.0)	0.2240	0.070
15	6.3 (0.0)	1.5 (0.0)	1.84×10^{-3} (0.0)	0.2280	0.063

SC: surfactant concentration; BC: BDAP concentration; RCu: analytical signal for Cu; RNi: analytical signal for Ni.

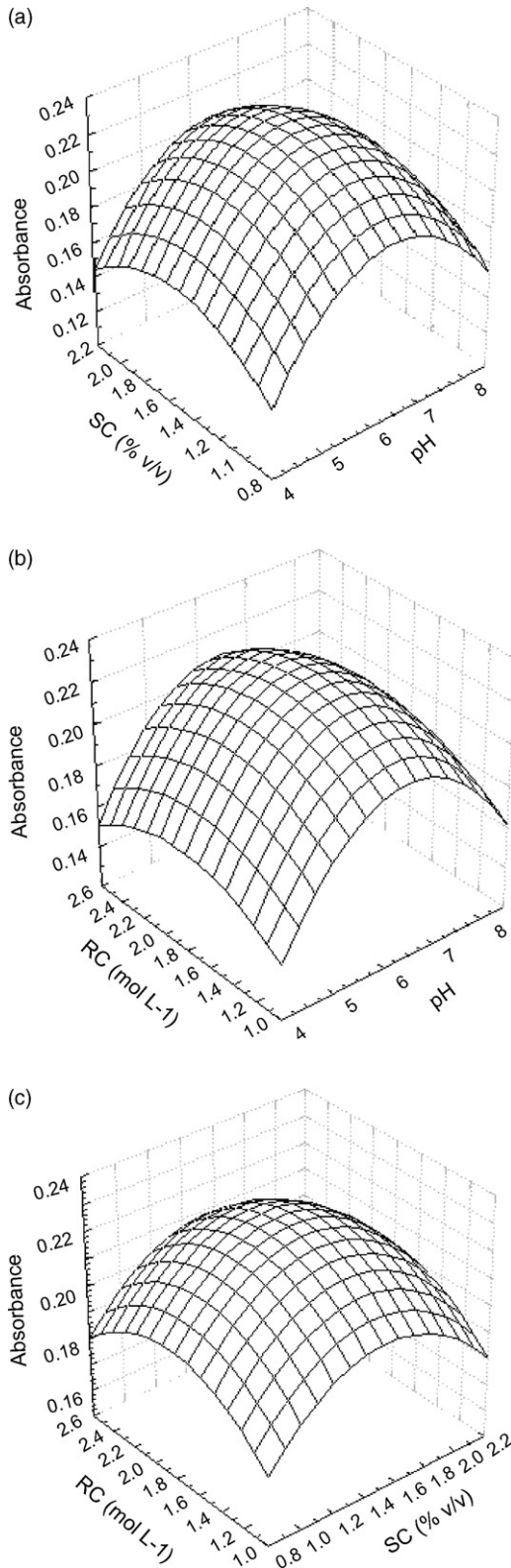


Fig. 2. Response surface plot of the copper analytical signal as a function of (A) pH and surfactant concentration, (B) pH and reagent concentration and (C) surfactant concentration and reagent concentration.

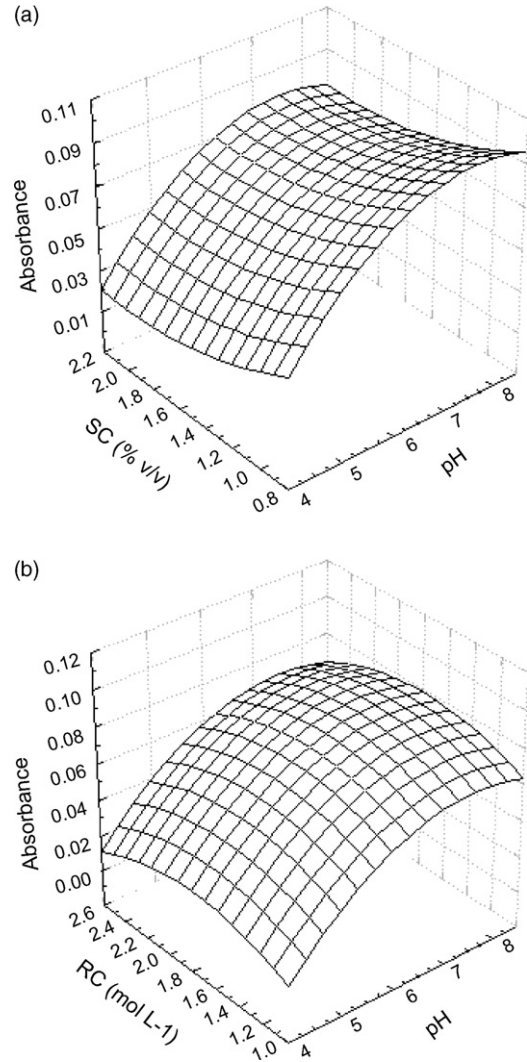


Fig. 3. Response surface plot of the nickel analytical signal as a function of (A) pH and surfactant concentration and (B) pH and reagent concentration.

3.3. Analytical features

Calibration graphs obtained with pre-concentration gave good linearity over the concentration range of $1.0\text{--}100.0\ \mu\text{g L}^{-1}$ of copper ($\text{Abs} = 8.67 \times 10^{-3} + 2.84 \times 10^{-3} C$) and $5.0\text{--}100.0\ \mu\text{g L}^{-1}$ of nickel ($\text{Abs} = 8.05 \times 10^{-3} + 1.34 \times 10^{-3} C$). Abs is the absorbance and C is the metal concentration, in $\mu\text{g L}^{-1}$. By using metal standard solutions with Cu or Ni concentrations in the range from 50.0 to $2000.0\ \mu\text{g L}^{-1}$, calibration graphs for metals without pre-concentration were also obtained. These calibration graphs were: $\text{Abs} = 2.20 \times 10^{-3} + 9.80 \times 10^{-5} C$ and $\text{Abs} = 4.53 \times 10^{-3} + 5.30 \times 10^{-5} C$ for copper and nickel, respectively.

The enrichment factors of metals were based on matching the slopes of calibration graphs of pre-concentration procedure and those by a conventional FAAS nebulization method. The enrichment factors of copper and nickel were 29- and 25-fold, respectively.

Table 2
Effect of foreign ions on the cloud-point extraction of 100.0 $\mu\text{g L}^{-1}$ Cu or Ni

Substance	Concentration	
	Copper	Nickel
Al ³⁺	300.0 mg L ⁻¹	500.0 mg L ⁻¹
Ba ²⁺	30.0 g L ⁻¹	30.0 g L ⁻¹
Br ⁻	40.0 g L ⁻¹	40.0 g L ⁻¹
Cd ²⁺	500.0 mg L ⁻¹	700.0 mg L ⁻¹
Cl ⁻	50.0 g L ⁻¹	40.0 g L ⁻¹
Co ²⁺	200.0 mg L ⁻¹	300.0 mg L ⁻¹
Cr ₂ O ₇ ²⁻	10.0 mg L ⁻¹	10.0 mg L ⁻¹
CrO ₄ ²⁻	10.0 mg L ⁻¹	20.0 mg L ⁻¹
Cu ²⁺	–	1.0 mg L ⁻¹
Fe ³⁺	10.0 mg L ⁻¹	80.0 mg L ⁻¹
K ⁺	60.0 g L ⁻¹	50.0 g L ⁻¹
Mg ²⁺	40.0 g L ⁻¹	30.0 g L ⁻¹
Na ⁺	50.0 g L ⁻¹	60.0 g L ⁻¹
Ni ²⁺	2.0 mg L ⁻¹	–
NO ₃ ⁻	50.0 g L ⁻¹	40.0 g L ⁻¹
Pb ²⁺	500.0 mg L ⁻¹	400.0 mg L ⁻¹
SO ₄ ²⁻	60.0 g L ⁻¹	50.0 g L ⁻¹
Zn ²⁺	400.0 mg L ⁻¹	300.0 mg L ⁻¹

The limit of detection (LOD) was calculated based on three times (3s) of standard deviation of blank signal by 11 replicate measurements [33]. LODs were 0.4 and 1.2 $\mu\text{g L}^{-1}$ for copper and nickel, respectively. The limit of quantification (LOQ) is the concentration that gives a response equivalent to ten times the standard deviation of blank signal ($n = 11$), and define the lower limit of the range. LOQ was also calculated for Cu (1.5 $\mu\text{g L}^{-1}$) and Ni (3.9 $\mu\text{g L}^{-1}$). The precision (determined as the relative standard deviation) for 10 replicate measurements of 75 $\mu\text{g L}^{-1}$ Cu or Ni was 6.4 and 1.0, respectively.

Table 3
Metal determination in certified reference materials using proposed methodology ($n = 4$), confidence interval 95%

Sample	Copper amount ($\mu\text{g g}^{-1}$)		Nickel amount ($\mu\text{g g}^{-1}$)	
	Certified	Found	Certified	Found
NIST 1515 Apple Leaves	5.64 ± 0.24	5.5 ± 0.1	–	–
NIST 1570a Spinach Leaves	12.2 ± 0.6	12.2 ± 0.4	2.14 ± 0.10	2.0 ± 0.1
NIST 1573a Tomato Leaves	4.70 ± 0.14	4.6 ± 0.4	1.59 ± 0.07	1.4 ± 0.2

Table 4
Metal determination in real food samples using proposed methodology ($n = 4$), confidence interval 95%

Sample	Copper amount ($\mu\text{g g}^{-1}$)		Recovery (%)	Nickel amount ($\mu\text{g g}^{-1}$)		Recovery (%)
	Added	Found		Added	Found	
Maize starch 1	0	7.5 ± 0.3	–	0	8.3 ± 0.3	–
	10	18.2 ± 0.3	105	10	18.5 ± 0.3	101
Maize starch 2	0	7.9 ± 0.1	–	0	10.1 ± 0.3	–
	10	17.7 ± 0.1	99	10	20.2 ± 0.3	100
Rice flour 1	0	7.2 ± 0.5	–	0	9.4 ± 0.2	–
	10	17.2 ± 0.5	100	10	19.4 ± 0.2	100
Rice flour 2	0	5.2 ± 0.2	–	0	9.6 ± 0.3	–
	10	15.3 ± 0.2	100	10	19.6 ± 0.3	100
Potato starch	0	8.1 ± 0.3	–	0	4.8 ± 0.1	–
	10	18.2 ± 0.3	100	10	14.9 ± 0.1	100

3.4. Interference

The interference of foreign ions on the CPE determination of 100.0 $\mu\text{g L}^{-1}$ Cu or Ni was studied. The tolerance limits of various foreign species on the sorption of the metal ions are given in Table 2. These tolerance limits were taken as that value which caused an error of not more than 5% in the absorbance reading. Most of the metal ions are tolerated up to 400 mg L⁻¹. The potential interferences from some common matrix cations such as Na(I), K(I) and Mg(II) were also investigated. These substances are tolerated at concentrations at least up to 30 g L⁻¹. The results obtained in these experiments demonstrate that the presence of large amounts of species commonly present in food samples have no significant effect on the CPE of copper and nickel.

3.5. Application

To evaluate the accuracy of the proposed CPE preconcentration procedure for the determination of trace copper and nickel, three certified reference materials were analysed. Table 3 reports the concentrations of Cu and Ni in the CRM's. The obtained analytical values for copper and nickel by the present methodology were in good agreements with the certified values. The results demonstrate the applicability of the method for interference-free determination of the metals.

Applicability of the method to real samples was checked by the determination of copper and nickel in foods. The results of this investigation are given in Table 4. It can be seen that the recovery of spiked samples is good. The results indicate that the proposed method is applicable for routine monitor-

Table 5
 Procedures using cloud-point extraction prior copper and nickel determination by flame atomic absorption spectrometry; EF: enrichment factor; LOD: limit of detection; 1,2-*N,N*: 1-nitroso-2-naphthol; PONPE 7.5: polyethylene glycol-*p*-nonylphenylether; APDC: ammonium pyrrolidinedithiocarbamate; Me-BDBD: 6-[2'-(6'-methyl-benzothiazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid; Me-BTABr: 2-[2'-(6-methyl-benzothiazolylazo)]-4-bromophenol; *O,O*-DDTP: *O,O*-diethyldithiophosphate; TAN: 1-(2-thiazolylazo)-2-naphthol; PAN: 1-(2-pyridylazo)-2-naphthol; BDAP: 2-(2'-benzothiazolylazo)-5-(*N,N*-diethyl)aminophenol

Reagent	Surfactant	Element	EF	Sample volume (mL)	LOD ($\mu\text{g L}^{-1}$)	Sample	Reference
Me-BTABr	Triton X-114	Cu	17	10	1.08	River and well water	[9]
		Ni	23	10	1.1	Water	[38]
<i>O,O</i> -DDTP	Triton X-100	Cu	33.3	10	0.94	Drinking and rainwater, serum and human hair	[10]
TAN	Triton X-114	Cu	64.3	50	0.27	Standard reference material	[16]
		Ni	65	50	0.44	Water	[17]
APDC	Triton X-114	Ni	20	10	11.0	Water	[37]
Dithizone	Triton X-114	Ni	39	10	1.2	Water	[39]
1,2- <i>N,N</i>	PONPE 7.5	Ni	29	10	1.09	Water	[40]
Me-BDBD	Triton X-114	Cu	14	10	1.5	Water	[41]
PAN	Triton X-114	Ni	25	10	6.0	Water	[42]
Pyrogallol	Triton X-114	Cu	85	60	0.05	Water	[43]
BDAP	Triton X-114	Cu	29	10	0.4	Food	[This work]
		Ni	25	10	1.2		

ing of copper and nickel in these matrices. The limits of detection and quantification expressed to solid sample analysis were: Cu (LOD = $0.1 \mu\text{g g}^{-1}$, LOQ = $0.5 \mu\text{g g}^{-1}$) and Ni (LOD = $0.4 \mu\text{g g}^{-1}$, LOQ = $1.0 \mu\text{g g}^{-1}$).

4. Conclusion

The reagent BDAP was successfully employed in a CPE procedure for determination of copper and nickel in food samples by FAAS. This study allowed the development of a rapid, easy to use, safe, environmentally friendly and inexpensive methodology for the preconcentration and separation of trace metals. The method significantly improved the performance of the FAAS detection for Cu and Ni. The proposed preconcentration method allows Cu and Ni determination in food samples at $\mu\text{g kg}^{-1}$ levels. Table 5 shows a comparison of the proposed procedure with other CPE methods for determination of copper and nickel. The obtained detection limits by the proposed procedure are comparable to most of those reported in the literature. Due to good analytical characteristics, the proposed CPE procedure has been demonstrated to be very interesting for trace copper and nickel analysis [34–43].

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