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Highlights

- ▶ We use BTAHNA as a reagent for the determination of trace Cd(II) by SPS method. ▶ Calibration is linear over the range 0.2–3.5 $\mu\text{g L}^{-1}$.
 - ▶ The proposed method has been applied for determination of Cd(II) in food samples.
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Analytical Methods

Utility of solid phase spectrophotometry for the modified determination of trace amounts of cadmium in food samples

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ABSTRACT

A modified selective, highly sensitive and accurate procedure for the determination of trace amounts of cadmium which reacts with 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid (BTAHNA) to give a deep violet complex with high molar absorptivity ($7.05 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$, $3.92 \times 10^7 \text{ L mol}^{-1} \text{ cm}^{-1}$, $1.78 \times 10^8 \text{ L mol}^{-1} \text{ cm}^{-1}$, and $4.10 \times 10^8 \text{ L mol}^{-1} \text{ cm}^{-1}$), fixed on a Dowex 1-X8 type anion-exchange resin for 10 mL, 100 mL, 500 mL, and 1000 mL, respectively. Calibration is linear over the range $0.2\text{--}3.5 \mu\text{g L}^{-1}$ with RSD of $\leq 1.14\%$ ($n = 10$). The detection and quantification limits were calculated. Increasing the sample volume can enhance the sensitivity. The method has been successfully applied for the determination of Cd(II) in food samples, water samples and some salts samples without interfering effect of various cations and anions.

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1. Introduction

Heavy metal ions are increasingly being released into the environment, leading to serious pollution, particularly as a result of industrialization. Cadmium is a very toxic element for animals and human, even at low concentrations. The International Agency for Research on Cancer classified cadmium as a human carcinogen (IARC, 1993). Due to its toxicity both to humans and animals cadmium concentration in the environment should be monitored, hence appropriate guideline values for cadmium content have been introduced; for drinking water they are as follow:

WHO $3.0 \mu\text{g L}^{-1}$ (WHO, 2006), USEPA $5.0 \mu\text{g L}^{-1}$ (USEPA, 2003).

Cadmium enters the organism primarily via the alimentary and respiratory tract. The sources of this metal are food, drinking water and air. Roughly 15,000 t of cadmium is produced worldwide each year for nickel-cadmium batteries, pigments, chemical stabilizers, metal coatings and alloys. So its usage is becoming wider and wider. However, as the levels of cadmium in geological and environmental samples are low, a preconcentrative separation and determination of trace cadmium from the natural water is

essential and needs much more attention (Liu, Chang, et al., 2004; Liu, Yang, et al., 2004).

One of widely used and fast emerging preconcentrative separation techniques for this purpose is the solid-phase extraction (SPE) due to the following advantages. These include: (1) higher enrichment factors; (2) absence of emulsion; (3) safety with respect to hazardous samples; (4) minimal costs due to low consumption of reagents; (5) flexibility; and (6) ease of automation (Daniel, Praveen, & Rao, 2006). An efficient solid-phase extractant should consist of a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with heavy metal ions (Fang, Tan, & Yan, 2005). Solid phase extraction (SPE) of trace metal ions is also an important preconcentration/separation technique (Soylak et al., 2003; Godlewska-Zytkiewicz, 2004). SPE has many advantages: it is a simple technique. Several analytes can be enriched and separated simultaneously. Furthermore, high preconcentration factors can be obtained by using solid phase extraction procedures. Main properties of the solid phases for solid phase extraction should be high surface area, their high purity and good sorption properties including porosity, durability, and uniform pore distribution. A large variety of efficient solid materials like Amberlite XAD resins (Tuzen & Soylik, 2004), silica gel (Sawula, 2004; Yamini, Hosseini, & Morsali, 2004), chitosan (Wang et al., 2004), benzophenone/naphthalene (Preetha & Rao, 2003), Chelex 100 (Soylik, 2004), etc. have been used for solid phase extraction of metal ions at trace levels by various researchers.

Solid-phase spectrophotometry (SPS) combines the preconcentration of the species of interest on a solid matrix, usually an

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ion-exchanger, with the aid of complexing agent and subsequent measurement of the absorbance of the complex in the solid phase. This provides an increase in selectivity and sensitivity with respect to conventional spectrophotometric method (Amin, 2002; Teixeira & Rocha, 2007). 1-(2-benzothiazolylazo)-2-hydroxy-3-naphthoic acid (BTAHNA) is one of the thiazolylazo reagents (Amin, 2000, 2001, 2009; Amin & El-Mossalamy, 2003; Amin & Ibrahim, 2001), it has been successfully used for spectrophotometric determination of Cd(II) (Amin, 2001), Cu(II) (Amin, 2009), Nb(III) (Amin, 2000), Ni(II) (Amin & Ibrahim, 2001) and UO₂(II) (Amin & El-Mossalamy, 2003). Table 1 describes comparison of analytical performance of various spectrophotometric methods for determination of cadmium (II), while Table 2 presents comparison of detection limits of diverse instrumental techniques for the determination of cadmium (II).

The goal of the present work is intended to study the possibilities of using BTAHNA as a reagent for the determination of trace Cd(II) by SPS. The optimum conditions have been established. Cd(II) reacts with BTAHNA to give a colored complex, which is easily sorbed on an anion-exchange resin and provides the basis for a relatively simple, accurate and rapid spectrophotometric method of Cd(II) at sub- $\mu\text{g L}^{-1}$ level, without a previous preconcentration step. The proposed method is free from many interferences and has been applied to the determination of Cd(II) in food samples, water samples and some salts samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Lambda 12 UV-VIS spectrophotometer with a 1.0 mm quartz cell was used for all spectral measurements. A selecta desk centrifuge and an Orion research model 601 A/digital ionalyzer pH meter were used for checking pH of the solutions. A Perkin-Elmer atomic absorption spectrometry model A Analyst 300 was used for all AAS measurements.

The absorbance of the BTAHNA-Cd(II) deep violet complex sorbed on the resin was measured in a 1.0 mm cell at 692 nm (corresponding to the absorption maximum of the colored complex) and 800 nm (in a region where only the resin absorbs light) against a 1.0 mm cell packed with resin equilibrated with a blank solution. The net absorbance (A_c) for the complex was obtained using the following equation (Fernandez-de Cordova, Molina-Diaz, Pascual-Reguera, & Capitan-Vallvey, 1992; Yoshimura & Waki, 1985)

$$A_c = A_{692} - A_{800} \quad (1)$$

Table 1
Comparison of analytical performance of various spectrophotometric methods for determination of cadmium.

Reagent	λ_{max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$) $\times 10^{-5}$	Remarks	Ref.
1-(2-Benzothiazolylazo)-2-hydroxy-3-naphthoic acid	616	1.14	Triton X-100	Amin (2001)
2-[(5-Bromo-2-pyridine)azo]-5-diethylaminopheno	556	1.39	In 50% ethanol medium	Shibata et al. (1976)
2-[2-(5-Bromopyridine)azo]-5-dimethylaminophenol	555	1.41	Low sensitivity, extracting with trimethylbutanol	Shibata et al. (1976)
p-Nitrophenyldiazo aminoazobenzene	480	4.1	Low sensitivity, with very toxic KCN as masking reagent and formaldehyde as demasking reagent	Hsu et al. (1980)
o-Hydroxyphenyldiazo aminoazobenzene	520	1.5	Low sensitivity, extracting with MIBK	Hsu et al. (1989)
2,6-Dibromo-4-nitrophenyldiazo Aminoazobenzene	500	1.52	Many ions interfering with color reaction	Cao and Li (1992)
2-Acetylmercaptophenyldiazo aminoazobenzene	529	2.4	Ions interfering, sodium thiosulfate as masking	Liu et al. (2004)
5-(2-Benzothiazolylazo)-8-hydroxyquinolene (SPS)	667	70.5	10 mL sample	Proposed method
		392.1	100 mL Sample	
		1783	500 mL Sample	
		4102	1000 mL Sample	

2.2. Reagents and solutions

Analytical reagent grade chemicals and doubly distilled water were used throughout the experiments. All experiments were carried out at room temperature. A known amount of cadmium acetate is dissolved in water and then diluted to 100 mL with distilled water. The stock solution is then standardized by EDTA titration (Vogel, 1978) using xylenol orange as an indicator. The working standard solutions were prepared by a suitable dilution of the stock solution.

1-(2-Benzothiazolylazo)-2-hydroxy-3-naphthoic acid (BTAHNA) of high purity used in the present investigation was easily prepared according to the procedure described previously (Amin, 2000). A stock of $1 \times 10^{-3} \text{ mol L}^{-1}$ solution of BTAHNA was prepared by dissolving an appropriate amount of the reagent in a minimum amount of pure ethanol and diluting the mixture to 100 mL with ethanol. The working solution was prepared by its appropriate dilution with the same solvent. Phosphate buffer solutions of pH values ranging from 3.0 to 11.0 were prepared as recommended earlier (Britton, 1952).

Dowex 1-X8 (200–400 mesh) anion-exchange resin (Aldrich) was used in the chloride form. The resin was washed several times with doubly distilled water, treated with 2.0 mol L^{-1} HCl for 4.0 h and finally with doubly distilled water until the washing was free from chloride ions. Then, it was air-dried and stored in a polyethylene container.

2.3. General procedures

2.3.1. For 10 mL samples

An appropriate volume of the sample containing $0.20\text{--}2.4 \mu\text{g}$ of Cd(II) was placed in a 25 mL-measuring flask with a stopper, 0.5 mL of $1 \times 10^{-5} \text{ mol L}^{-1}$ BTAHNA solution and 1.0 mL of pH 8.5 phosphate buffer solution were added, the solution was made up to 10 mL (final concentration of Cd(II) was $20\text{--}240 \mu\text{g L}^{-1}$). Finally, 50 mg of Dowex 1-X8 (200–400 mesh) resin were added. The mixture was mechanically stirred for 5.0 min and the colored resin beads were collected by filtration under suction and, with the aid of a small pipette, packed into a 1.0 mm cell together with a small volume of the filtrate. The cell was centrifuged at 5000 rpm for 2.0 min. A blank solution containing all reagents except cadmium was prepared and treated in the same way as the sample. The absorbance difference between the sample and the blank, measured as described above, provided an estimation of the net absorbance.

2.3.2. For 100 mL samples

An appropriate volume containing $0.2\text{--}4.0 \mu\text{g}$ ($2.0\text{--}40 \mu\text{g L}^{-1}$) of Cd(II) was transferred into a 1 L polyethylene bottle and 0.8 mL of

Table 2

Comparison of detection limits of diverse instrumental techniques for the determination of cadmium (II).

Technique	Conditions	Detection limit	Ref.
Flow injection	Preconcentration and flame atomic absorption spectroscopy (FAAS)	0.11 $\mu\text{g L}^{-1}$	Gawin et al. (2010)
Atomic absorption spectroscopy	Flame atomic absorption spectrometry (FAAS)	0.014 ng mL^{-1}	Shabania et al. (2009)
Atomic absorption spectrometry	Electrothermal atomic absorption spectrometry (ET AAS)	0.333 $\mu\text{g L}^{-1}$	Ferreira et al. (2009)
Cloud Point Extraction	Flame atomic absorption spectrometry (FAAS)	1.0 ng mL^{-1}	Afkhami, Madrakian, and Siampour (2006)
Flow injection Solid phase extraction	Flame atomic absorption spectrometry (FAAS)	0.3 $\mu\text{g L}^{-1}$	Lemos et al. (2008)
Solid phase extraction	Inductively coupled plasma atomic emission spectrometry (ICP-AES)	0.14 $\mu\text{g L}^{-1}$	Zhai et al. (2007)
Solid phase extraction	Inductively coupled plasma optical emission spectrometry (ICP-OES)	0.18 mg L^{-1}	Puzio et al. (2008)
Solid phase extraction	Flame atomic absorption spectrometry	0.028 mg L^{-1}	Yaganas et al. (2008)
Solid phase extraction	Liquid electrode plasma atomic emission spectrometric (LEP-AES)	0.2 μg in 200 mL	Kagaya et al. (2010)
Liquid–liquid extraction	flame atomic absorption spectrometry	6.0 ng g^{-1}	Martinisa et al. (2009)
Complexation	Graphite furnace atomic absorption spectrometry GF-AAS.	0.09 ng L^{-1}	Hata et al. (2008)
Complexation	Solid phase spectrophotometry	53 ng L^{-1}	Proposed method

174 $1 \times 10^{-4} \text{ mol L}^{-1}$ BTAHNA solution and 10 mL of pH 8.5 phosphate
175 buffer solution were added, 50 mg of Dowex I-X8 (200–400 mesh)
176 resin were added after filling the bottle up to 100 mL. The mixture
177 was mechanically shaken for 15 min, and treated as indicated in
178 the above procedure.

179 2.3.3. For 500 mL samples

180 An appropriate volume of sample containing 0.2–4.5 μg (0.4–
181 9.0 $\mu\text{g L}^{-1}$) of Cd(II) was transferred into a 1 L polyethylene bottle
182 and 2.0 mL of $1 \times 10^{-4} \text{ mol L}^{-1}$ BTAHNA solution and 40 mL of pH
183 8.5 phosphate buffer solution were added, 50 mg of Dowex I-X8
184 (200–400 mesh) resin were added after filling the bottle up to
185 500 mL. The mixture was mechanically shaken for 25 min and fur-
186 ther treated as indicated in the above procedure.

187 2.3.4. For 1000 mL samples

188 An appropriate volume of sample containing 0.2–3.5 μg (0.2–
189 3.5 $\mu\text{g L}^{-1}$) of Cd(II) was transferred into a 2 L polyethylene bottle
190 and 3.0 mL of $1 \times 10^{-4} \text{ mol L}^{-1}$ BTAHNA solution and 75 mL of pH
191 8.5 phosphate buffer solution were added, 50 mg of Dowex I-X8
192 (200–400 mesh) resin were added after filling the bottle up to
193 1000 mL. The stirring time was increased to 40 min. Other details
194 were kept as above. Calibration graphs were constructed in the
195 same way using Cd(II) solutions of known concentration.

196 2.4. Food samples treatment

197 The sample was dried in a forced-draft oven at 70 °C to constant
198 mass and then ground to a fine powder. A suitable aliquot was
199 weighed (2.0 g dry material) into a 100 mL Claisen distilling flask,
200 and 10 mL of HNO₃ was added. After that, the flask was put into
201 a model MDS-81D microwave oven and digested for 5.0 min at
202 50% power and continuously for 15 min at 100% power. Then the
203 flask was taken out and cooled to ambient temperature before an-
204 other 10 mL of HNO₃ and 1.0 mL of H₂O₂ were added and left to
205 stand for 20 min. The flask was placed in the microwave oven
206 and irradiated for 40 min at 100% power. Then the flask was taken
207 out and cooled to ambient temperature. The final 1.0 mL of HNO₃
208 was added and again the flask was left to stand for 10 min. The fi-
209 nal solution was neutralized to pH 8.0–9.0 with solid Na₂CO₃ and
210 transferred into a 25 mL calibrated flask. The solutions were fur-
211 ther treated as given in general procedure.

212 2.5. Procedures for tobacco, green and black tea, human hair, spice and 213 river sediment

214 0.25 g of tobacco sample was digested with 4.0 mL of concen-
215 trated HNO₃ and 2.0 mL of concentrated H₂O₂ in microwave sys-
216 tem. Blank digestions were also performed at the same
217 conditions. After digestion, the volume was made up to 25 mL with
218 distilled water. The procedure given above was applied to the sam-
219 ples. The metal concentrations in the final solutions were also
220 determined by AAS.

221 For the digestion of green and black tea samples, 0.25 g of tea
222 was mixed with 6.0 mL of HNO₃:H₂SO₄:H₂O₂ (1:1:1) in microwave
223 system. After digestion, the volume was made up to 25 mL with
224 distilled water. Blanks were prepared in the same way as the sam-
225 ple, but omitting the sample. The preconcentration procedure gi-
226 ven above was applied to the samples.

227 For the microwave digestion of human hair and a spice sample,
228 1.0 g of samples were digested with 4.0 mL of concentrated HNO₃
229 and 2.0 mL of concentrated H₂O₂ in microwave system. After diges-
230 tion, the volume was made up to 25 mL with distilled water. Blanks
231 were prepared in the same way as the sample, but omitting the
232 sample. The general procedure given above was applied to the
233 samples.

234 0.25 g of river sediment was digested with HCl:HNO₃:H₂SO₄
235 (4:2:2) in microwave system. After digestion, the volume was
236 made up to 25 mL with distilled water. Blanks were prepared in
237 the same way as the sample, but omitting the sample. The general
238 procedure given above was applied to the samples. The final vol-
239 ume was 5.0 mL.

240 2.6. Determination of cadmium (II) in water samples

241 A choice of water samples in and around the Shobra-El-Qhema
242 and Benha cities has been made. Each filtered environmental water
243 sample is evaporated nearly to dryness with a mixture of 5.0 mL
244 concentrated H₂SO₄ and 10 mL concentrated HNO₃ in a fume cup-
245 board and then cooled to room temperature. The residue is then
246 heated with 10.0 mL of deionized water, in order to dissolve the
247 salts. The solution is cooled and neutralized with dilute NH₄OH.
248 The resulting solution is filtered and quantitatively transferred into
249 a 25 mL calibrated flask and made up to the mark with deionized
250 water. A known aliquot of the above sample solution is taken into
251 a 25 mL separating funnel and the cadmium content is determined
252 as described in the general procedure.

2.7. Determination of cadmium ions in salt samples

For the determination of analyte ions in alkaline salt samples, 3.0 g of each salt sample was dissolved in 3.0 mL of distilled water and diluted to 100 mL with distilled water. The procedure given above was applied to these solutions. The analyte ions in the final solution were also determined by atomic absorption spectrometry.

2.8. Distribution measurements

BTAHNA solution, buffer solution, and 50 mg of Dowex 1-X8 (200–400 mesh) were added to 100 mL of aqueous solution containing 8.0 μg of Cd(II). After a 30 min equilibration, the resin beads were separated by filtration under suction. Then, the equilibrium concentration of Cd(II) in the solution was determined as described in the 100 mL procedure. The distribution ratio D was calculated from the initial and the equilibrium concentrations in the solution.

3. Results and discussions

3.1. Absorption spectra

Absorption spectra in solid phase BTAHNA was fixed on an anionic resin, giving red color with a $\lambda_{\text{max}} = 554 \text{ nm}$ in the resin phase, compared with $\lambda_{\text{max}} = 562 \text{ nm}$ in the solution. The presence of Cd(II) ion resulted in a deep violet complex which shifted the λ_{max} to 659–664 nm in the solution and to $\lambda_{\text{max}} = 692 \text{ nm}$ in the resin phase (Fig. 1). It is evident that the sensitivity increases when the complex is sorbed on the resin.

3.2. Effect of pH

pH-dependence was studied by applying the 100 mL procedure. The optimum buffer solution was investigated by examining different types of buffer (acetate, borate, phosphate, thiel, and universal) solutions. Phosphate buffer gave the best results. Moreover, optimum pH for the formation and fixation of the species is in the range of 8.3–8.7 (Fig. 2). At pH values below 6.5 or above 9.2, the absorbance decreased significantly. Hence, pH 8.5 was chosen as

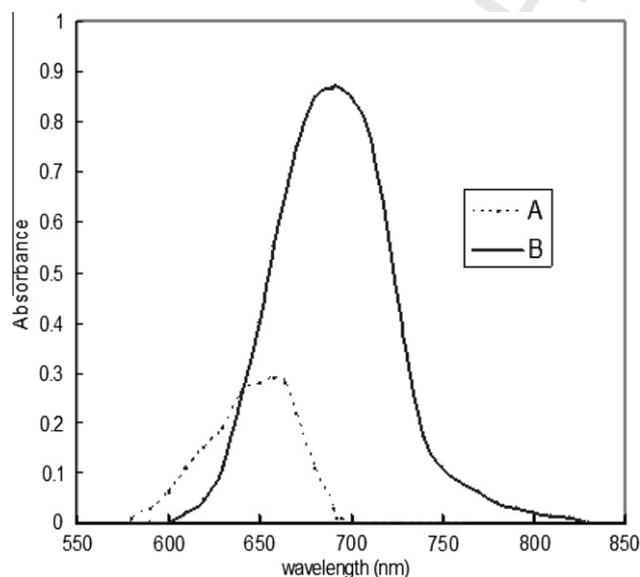


Fig. 1. Absorption spectra of Cd(II)-BTAHNA complex (A) in solution; $[\text{Cd(II)}] = 2.22 \times 10^{-4} \text{ mol L}^{-1}$; $[\text{BTAHNA}] = 8.0 \times 10^{-3} \text{ mol L}^{-1}$; pH 8.5; (B) in the resin $[\text{Cd(II)}] = 2.22 \times 10^{-7} \text{ mol L}^{-1}$; $[\text{BTAHNA}] = 8.0 \times 10^{-5} \text{ mol L}^{-1}$; pH = 8.5.

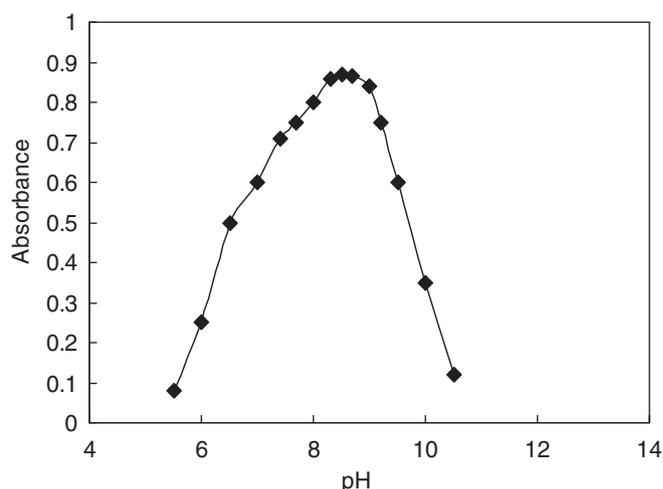


Fig. 2. Effect of pH on the complexation of $2.22 \times 10^{-7} \text{ mol L}^{-1}$ of Cd(II) complexed with $8 \times 10^{-5} \text{ mol L}^{-1}$ BTAHNA for 100 mL sample.

the working pH. The absorbance is independent of the ionic strength (adjusted with the buffer solution) up to the concentration of $8 \times 10^{-2} \text{ mol L}^{-1}$. At higher concentrations, the absorbance decreases quickly, as is usual in SPS studies, probably owing to the competition between the anions of the buffer for the anionic sites of the resin. Moreover, the optimum value of pH 8.5 was selected as recorded for each procedure described in the general procedures.

3.3. Effect of reagent concentration

The absorbance was found to increase with the BTAHNA concentration. The results indicated that the maximum absorbance for the complex fixed on Dowex 1-X8 was found with 0.5, 0.8, 2.0 and 3.0 mL of $1 \times 10^{-5} \text{ M}$ BTAHNA for 10, 100, 500, and 1000 mL sample procedures.

3.4. Effect of shaking time

The optimum stirring times were 5 min, 15 min, 25 min, and 40 min for the 10 mL, 100 mL, 500 mL, and 1000 mL procedures, respectively. The fixed complex was stable for at least 36 h after the equilibration. The complex was completely fixed on Dowex 1-X8 and the extraction coefficient constants in various volumes of the liquid phase were not altered. The sequence of (Cd(II)-BTAHNA-buffer-resin) addition gave the highest absorbance in addition to the stirring time compared with other sequences.

3.5. Effect of amount of resin

The use of a large amount of resin (m_r) lowered the absorbance. Only the amount required to fill the cell and to facilitate handling (i.e. 50 mg) was used for all measurements. The reduction of absorbance is according to the empirical equation

$$A_c = 0.0063 + 0.047/m_r \quad (r = 0.9967) \quad (2)$$

The agreement of the slope with the molar absorbance can be calculated as follows (Yoshimura & Waki, 1985).

$$A_c = \varepsilon_c I_R C_o V 1000 / (m_r + V/D) \quad (3)$$

where ε_c is the molar absorptivity of the sample species in the ion-exchanger phase (21.171), I_R is the mean light-path length through the solid phase, C_o the initial molar concentration of Cd(II), V/L the volume of the sample solution, D the distribution ratio, and m_r/g the

mass of ion exchanger. The fraction Y/D can be neglected when compared with m_r , being 0.125 g or higher and Eq. (4) which relates the absorbance to the mass of ion-exchanger is obtained

$$A_c = 1000\epsilon_c I_R C_0 V / m_r = K / m_r \quad (4)$$

where $K = 1000\epsilon_c I_R C_0 V$, is the slope of the graphic representation of A_c vs. $1/m_r$. Supposing $I_R = 0.1$ cm, the expected value of $K = 1000 \times 21.171 \times 0.1 \times 2.22 \times 10^{-7} \times 0.100 = 0.047$ which is in excellent agreement with the experimental value of 0.0473.

3.6. Fixed complex

The nature of the species fixed on the resin was established at the working pH of 8.5 using the molar ratio and continuous variation methods. The plot A vs. BTAHNA to Cd(II) mole ratio, obtained by varying the BTAHNA concentration, showed an inflexion at the mole ratio of 1.0 indicating the presence of one molecule of BTAHNA in the fixed complex. Moreover, the Job method showed that the BTAHNA to Cd(II) mole ratio was 1.0. Consequently, the results indicated that the stoichiometry was 1:1 (BTAHNA:Cd(II)). The conditional formation constant ($\log K$), calculated using the Harvey and Manning equation, applying the data obtained from the above two methods, was found to be 8.53, whereas the true constant was 8.45.

3.7. Analytical data

Analytical parameters are summarized in Table 3. It was verified that one of the main contributions to the relative standard deviation (RSD) comes from the variability of the ion-exchanger packing. RSD was 6.1% without centrifugation for the 100 mL sample and 10 determinations. When the cells packed with the resin phase were centrifuged for 2.0 min at 5000g before the absorbance measurements were carried out, RSD decreased to 0.93% and the absorbance value increased to about 15%. The results indicate that increasing the sample volume increases the slope of the calibration graph and so increases also the sensitivity of the proposed methods. The increase in sensitivity achieved with the proposed methods is substantial compared with the earlier spectrophotometric methods for the determination of Cd(II) (Table 1), as can be seen from the range of molar absorptivity values of these methods (Cao & Li, 1992; Hsu, Hu, & Jing, 1980; Hsu, Wang, & Yang, 1989; Shibata, Kamata, & Nakashima, 1976). The values of apparent molar absorptivity (absorbance value of the complex sorbed on the resin from an aqueous solution of Cd(II), supposing a measurement in a 10 mm optical path length cell) for the methods proposed are 7.05×10^6 L mol⁻¹ cm⁻¹, 3.92×10^7 L mol⁻¹ cm⁻¹, 1.78×10^8 L mol⁻¹ cm⁻¹, and 4.10×10^8 L mol⁻¹ cm⁻¹ respectively.

In the SPS methods, sensitivity can be enhanced by increasing the sample volume. The increase in sensitivity can be evaluated by measuring the absorbance of the resin equilibrated with different volumes of solutions containing the same concentration of Cd(II) and proportional amounts of the other reagents. The absor-

bance increases with the sample volume (V) till 1.0 L, then the absorbance becomes independent of the sample volume at higher sample volumes (i.e. $V \geq 1.100$ L), as usual in SPS (Fernandez-de Cordova et al., 1992).

In practice, the increase of sensitivity with a higher amount of sample solution can be calculated from the slope of the calibration graphs. The calculated values of the sensitivity ratio S for the samples analyzed are: $S(1000/500) = 2.31$; $S(1000/100) = 10.48$; $S(1000/10) = 58.21$; $S(500/100) = 4.54$; $S(500/10) = 25.20$, and $S(100/10) = 5.55$. The values obtained using the distribution ratio value D are 2.19, 10.35, 58.07, 4.43, 25.07, and 5.47, respectively.

Detection limits of the proposed methods are similar to those obtained by other sensitive techniques such as ET-AAS, AFS and ICP-OES (Table 2) (Ferreira et al., 2009; Gawin et al., 2010; Hata et al., 2008; Kagaya et al., 2010; Lemos, Novaes, Lima, & Vieira, 2008; Martinisa, Olsinab, Altamiranoa, & Wuillouda, 2009; Puzio, Mikula, & Feist, 2008; Shabania, Dadfarniaa, Motavaselian, & Ahmadib, 2009; Yaganas, Efendioglu, & Bati, 2008; Zhai, Liu, Chang, Chena, & Huanga, 2007) and, although the time required for the analysis by these techniques is shorter than in SPS, the costs of the necessary equipments are considerably higher than the corresponding costs for the SPS technique. On the other hand, it can be stated that accuracy and precision of the proposed SPS methods are similar to those obtained by the techniques indicated above.

3.8. Effect of foreign ions on the extraction of the Cd(II)-BDTSC complex

The effect of foreign ions is studied by measuring the absorbance of the reaction mixture containing 25 $\mu\text{g L}^{-1}$ of Cd(II) for 100 mL sample in the presence of different amounts of foreign ions. An error of $\pm 3.0\%$ in the absorbance value caused by foreign ions is considered as a tolerable limit. The interference of metal ions has been tested up to 750-fold excess. The results show that Al(III), Mn(II), W(IV), Mg(II), Pb(II), Co(II), Ca(II), La(III), Ti(IV), Th(IV), and U(VI) do not interfere. The tolerated limits for other metal ions are Fe(III) and Zr(IV) up to 400-fold excess, Cr(III) and Mo(VI) up to 100-fold excess, Cu(II), Ni(II), Ag(I), Pd(II) and Zn(II) less than 50-fold excess. 1.0 mL of 5.0% citrate has been employed as a masking agent for Ni(II), Pd(II), Zn(II). The interference of copper (II) has been eliminated by using 1.0 mL of 2.0% thiosulphate as the masking agent. Ag(I) has to be removed as silver chloride, prior to the extraction of Cd(II). Anions like bromide, chloride, fluoride, iodide, nitrate, sulphate, phosphate, tartrate, citrate, thiocyanate, thiosulphate and thiourea have no effect on the extraction of Cd(II), even when they are present in 250-fold excess or more. However, EDTA, and oxalate interfere seriously.

3.9. Analytical applications

The SPS procedure for cadmium ions was applied to various water samples. The results for natural water samples were given in Table 4. The proposed method has been combined with the

Table 3
Analytical parameters for cadmium (II) determination using the proposed method.

Parameter	Sample volume (mL)			
	10	100	500	1000
Slope	6.27×10^{-3}	3.48×10^{-2}	0.158	0.365
Linear dynamic range ($\mu\text{g L}^{-1}$)	20–240 (40–220) ^a	2.0–40.0 (3.0–37.5) ^a	0.4–9.0 (0.6–8.4) ^a	0.2–3.5 (0.4–3.25) ^a
Correlation coefficient	0.9996	0.9994	0.9992	0.9995
Detection limit ($K = 3$) ($\mu\text{g L}^{-1}$)	5.80	0.553	0.119	0.053
Determination limit ($K = 10$) ($\mu\text{g L}^{-1}$)	19.2	1.85	0.395	0.18
RSD (%) ($n = 10$)	1.14 (100) ^b	0.93 (12) ^b	1.02 (4) ^b	0.88 (2) ^b

^a Evaluated by Ringbom's method (Ringbom, 1938).

^b Cd(II) concentration ($\mu\text{g L}^{-1}$) used for the determination of the reproducibility.

Table 4
Determination of cadmium (II) in water, microwave-digested food and some salt samples.

Sample	Cd(II) found		Standard deviation	RSD (%)
	Proposed method ^a	AAS		
<i>Water samples^b ($\mu\text{g L}^{-1}$)</i>				
River water (Shobra)	2.01	1.95	0.0989	0.74
Waste water (Benha)	2.51	2.55	0.0132	1.07
River water (Benha)	0.91	0.93	0.0197	1.53
Tap water	1.68	1.64	0.0127	1.11
Spring water	1.41	1.45	0.0154	1.29
Fortified water	2.34	2.54	0.0176	1.40
Lake water	2.85	2.82	0.0142	1.26
Bottled mineral water	0.85	0.88	0.0104	0.97
<i>Microwave-digested food samples ($\mu\text{g g}^{-1}$)</i>				
Human hair	0.25	0.24	0.0126	1.50
Tobacco	2.85	2.88	0.0103	1.27
Green tea	0.56	0.55	0.0088	1.01
Black tea	0.74	0.73	0.0097	1.23
Spice	0.23	0.24	0.0118	1.42
River sediment	3.50	3.47	0.0088	1.28
Rice	0.37	0.35	0.0067	0.99
Grain	0.60	0.58	0.0105	1.30
Flour	0.44	0.45	0.0091	1.17
<i>Salt samples^c</i>				
Ammonium chloride (technical grade)	0.40	0.42	0.089	0.74
Sodium chloride (technical grade)	0.32	0.33	0.132	1.07

^a Average of six determinations.

^b Mean expressed as 95% tolerance limit.

^c Mean expressed as 97% tolerance limit.

microwave assisted digested samples including a human hair, a tobacco, a green and black tea, a spice and a river sediment. For this purpose, these samples were digested by closed microwave system. The results are given in Table 4. Concentrations of the investigated ions in our samples were $\mu\text{g g}^{-1}$ level. The proposed method has been applied to the direct determination of cadmium in rice, grain and flour (purchased from Benha, Egypt). The determination was performed using the standard addition calibration graph method (Table 4).

The proposed SPS method is applied for the determination of Cd(II) in some salt samples. The data obtained in the analysis of some salt samples were given in Table 4. The precision shown for the samples studied is also satisfactory.

Performance of the proposed method was assessed using the *t*-value (for accuracy) and *F*-test (for precision) compared with the AAS method. The mean values were obtained by a Student's *t*-test and *F*-tests at 95% confidence limits for five degrees of freedom (Miller & Miller, 2005). The results showed that the calculated values did not exceed the theoretical values. A wider range of determination, higher accuracy, higher stability and lower time demand, are the advantage of the proposed method over other ones.

4. Conclusions

The proposed method has the following characteristics:

- (1) BTAHNA is one of the most easily prepared high purity, sensitive, and selective spectrophotometric reagents for cadmium determination. Molar absorptivity of the chelate was found to be up to $4.10 \times 10^7 \text{ L mol}^{-1} \text{ cm}^{-1}$ in the measured solution.
- (2) Most foreign ions do not interfere with the determination. 1.0 mL of 5.0% citrate has been employed as a masking agent for Ni(II), Pd(II), Zn(II). The interference of Cu(II) has been

eliminated by using 1.0 mL of 2.0% thiosulphate as the masking agent. Ag(I) has to be removed as silver chloride, prior to the extraction of cadmium (II).

- (3) Increasing the sample volume enhances the sensitivity. Detection and quantification limits of the 500 mL sample method are 119 ng L^{-1} and 395 ng L^{-1} , respectively, when using 50 mg of Dowex 1-X8. For the 1000 mL sample, the detection and quantification limits are 53 ng L^{-1} and 180 ng L^{-1} , respectively, using 50 mg of the exchanger.
- (4) Successful application of the proposed method to the determination of low levels of cadmium in food samples, some salts, as well as, water samples with good results.

5. Uncited reference

Szczepaniak et al. (1984).

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