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Tween 80 coated alumina: An alternative support for solid phase extraction of copper, nickel, cobalt and cadmium prior to flame atomic absorption spectrometric determination



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KEYWORDS

Coated alumina; Tween 80: Simultaneous; Preconcentration; Tobacco; Brewed tea

Abstract The potential of coated alumina as a sorbent for the simultaneous separation and preconcentration of copper, nickel, cobalt and cadmium ions has been investigated. Copper, nickel, cobalt and cadmium were adsorbed quantitatively on coated alumina in the pH of 6. The main factors such as pH, amount sorbent, sample and eluent flow rate, type and volume of elution solution and interfering ions on the sorption of metal ions have been investigated in detail. Under the optimum experimental conditions, the detection limits (3S_b) of this method for Cu(II), Ni(II), Co(II) and Cd(II) ions were 0.4, 1.0, 1.2 and 0.2 ng mL⁻¹ in the original solution, respectively. Seven replicate determinations of a mixture of 5.0 µg of Cu(II), Ni(II), Co(II) and 1.0 µg of Cd(II) ions in the original solution gave a mean absorbance of 0.093, 0.071, 0.066 and 0.049 with relative standard deviations 1.9%, 2.3%, 2.6% and 2.1%, respectively. The method has been applied for the determination of trace amounts of Cu(II), Ni(II), Co(II) and Cd(II) ions in tobacco, brewed tea and water samples with satisfactory results.

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1. Introduction

Copper, cobalt and nickel are essential trace elements, having an important role in many body functions. These elements are required in small amounts; while they are toxic in large amounts (Mohammadi et al., 2009a, 2010; Hu et al., 2006). Chronic ingestion of cobalt in daily diet can cause some toxicological effects (Felipe-Sotelo et al., 2004). Also, cadmium is well recognized to be a highly toxic and hazardous element to human health (Valerie, 2003). Therefore, sensitive and accurate determination of the levels of heavy metals in the environ-

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Tween 80 coated alumina S1291

mental samples has been continuously carried out on the analytical and environmental laboratories around the world (Tuzen et al., 2008).

Spectrophotometry (Taher and Mohammadi Mobarakeh, 2005), electrothermal and/or flame atomic absorption spectrometry (Salih et al., 2007; Sabermahani et al., 2011), inductively coupled plasma atomic emission spectrometry (Bezerra et al., 2007), inductively coupled mass spectrometry (Liu et al., 2007), voltammetry (Ghiaci et al., 2007) are the main instrumental techniques for the determination of traces of heavy metal ions.

The common availability of the instrumentation, simplicity of the procedure, speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternative (Afzali et al., 2005; Ghaedi et al., 2009a; Soylak et al., 2003; Mohammadi et al., 2009b). However, flame atomic absorption spectrometry (FAAS), suffers from insufficient sensitivity for the direct determination of metal ions in environmental samples and the interfering effects sourced from the matrix of the real samples (Afzali et al., 2005; Ghaedi et al., 2009a; Soylak et al., 2003; Mohammadi et al., 2009b). In order to overcome these difficulties, various methods including, cloud point extraction (Ghaedi et al., 2009a; Mohammadi et al., 2011), coprecipitation (Soylak and Tuzen, 2008a), liquid-liquid extraction (Pena-Pereira et al., 2009), and solidphase extraction (SPE) (Shamspur and Mostafavi, 2009) have been commonly used for the sample pre-treatment.

Solid-phase extraction of heavy metal ions for preconcentration is preferred to other techniques due to simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor (Pena-Pereira et al., 2009). It is commonly acknowledged that the adsorption materials play a very important role in SPE, because adsorption materials determine the analytical sensitivity, precision and selectivity in SPE techniques. The current researches in SPE are mainly focused on the development of new sorbents.

The design of stable and selective solid phase sorbents for separation and preconcentration of target metal ions depends on different factors such as the nature of solid support, its surface area and activity (Ghaedi et al., 2009b). Among the various solid phases, alumina is one of the most widely used adsorbents, as it does not swell and has good mechanical strength, small solubility and stability in a broad pH range (Chibowski et al., 2005). Chemical activation of the alumina with functional groups containing N, S, O, and P atoms is highly efficient for the sorption of several metal ions. Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases toward certain metal ions is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups and the type of the interaction of functional group (Tewari and Singh, 2000).

In this work, the analytical potential of alumina coated with Tween 80 (Fig. 1) was examined for simultaneous separation and preconcentration trace amounts of copper, nickel, cobalt and cadmium ions in tobacco, brewed tea and water samples. The analytical conditions for the preconcentration of analytes were investigated.

2. Experimental

2.1. Instrumentation

A SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with deuterium background correction and air–acetylene burner was used for absorbance measurements. Copper, nickel, cobalt and cadmium hollow cathode lamps were used as light sources at wavelengths of 324.8, 232.0, 240.7 and 228.8 nm, respectively. The operating parameters of elements were set according to the manufacturer recommendations. The acetylene flow rate and burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solutions. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements.

2.2. Reagents and solutions

Deionized water was used throughout the experimental work. Standard solutions of the analyte ions were prepared by diluting stock solutions of $1000.0\,\mathrm{mgL^{-1}}$ supplied by Merck (Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution of the stock standard solutions by serial dilution with deionized water. Al₂O₃ (0.063–0.2 mm) (Merck) was used for the preparation of sorbent. Buffer solution was prepared, from 0.1 mol L⁻¹ acetic acid and the addition of NaOH solution. Before use, all of the glasswares were washed with deionized water and dried. The solutions of alkali metal salts (1% w/v) and various metal salts (0.1% w/v) were used to study the interference of anions and cations, respectively.

2.3. Preparation of the coated alumina with Tween 80

Before use, 5.0 g of the alumina was added to 30 mL of the solution containing 3.0% Tween 80 and the mixture was shaken at room temperature for 2 h. The coated alumina was filtered, washed with water and dried at room temperature for 24 h.

2.4. Preparation of column

Sixty milligram of coated alumina was introduced into a funnel-tipped glass tube (80×10 mm); plugged with a small portion of glass wool, at both ends. Before use, the column was preconditioned by passing a buffer solution at pH \sim 6 through it. After preparation, the column could be used repeatedly up to a maximum of 20 times.

Figure 1 Tween 80.

S1292 S.Z. Mohammadi et al.

2.5. SPE procedure

An aliquot of the sample solution (50 mL) containing analyte ions was taken in a beaker and 2 mL acetate buffer solution with pH 6 was added to it. It was then passed through the column with a flow rate of 3 mL min $^{-1}$. The retained metal ions were eluted from the sorbent with 5.0 mL of a mixture containing 0.5 mol L $^{-1}$ HNO $_3$ and thiourea with a flow rate of 1 mL min $^{-1}$. This solution was aspirated into an air–acetylene flame for the determination of the analyte ions by FAAS.

3. Result and discussion

A large number of studies have been reported on the use of bared alumina for metal ion removal from aqueous solution that were not selective and the recoveries were incomplete (for example Cu: 79%, Ni: 65%, Co: 72%, Cd: 76%, Fe: 90%, Mn: 80%, Zn: 85%, Ag: 30%). By coating of the alumina with Tween 80, only copper, nickel, cobalt and cadmium can be adsorbed in the specific pH. On the other hand, the coating of alumina with Tween 80 increases the adsorption capacity for the analyte ions.

The aim of the described research was to develop a sorbent for simultaneous separation and preconcentration of trace amounts of copper, nickel, cobalt and cadmium. Several factors that may affect the preconcentration and extraction process, including pH, type and volume of elution solution, flow rate of sample and eluent, sample volume and matrix effect were optimized. The optimizations were carried out with an aqueous solution containing 5.0 μ g of Cu(II), Ni(II), Co(II) and 1.0 μ g of Cd(II) ions.

3.1. Characterization of adsorbent

Chemical characterizations were studied by Fourier transform infrared (FTIR) spectroscopy in order to identify the functional groups at the surface of the modified alumina. FTIR study confirmed the presence of oxygenated functional groups in the modified alumina.

3.2. Effect of pH on retention

The influence of pH on the metal ion retention on coated alumina was investigated. In this view, a set of similar experiments

in the pH range of 3–11 was conducted according to the SPE procedure. Diluted HNO $_3$ and NaOH solutions were used for pH adjustments. The results are shown in Fig. 2 and showed that all of the analyte ions were adsorbed on coated alumina in the pH 6.0. Therefore, in subsequent studies, the pH was maintained at approximately 6. The addition of 1–5 mL of buffer did not have any effect on the adsorption. Therefore, 2 mL of the acetic acid and sodium acetate buffer with pH \sim 6.0 was used in all subsequent experiments.

3.3. Effect of eluent

Another important factor which affects the SPE procedure is the type, volume and concentration of the eluent used for removal of the analyte ions from the sorbent. Optimization of the elution conditions was performed in order to obtain the maximum recovery with the minimal concentration and volume of the eluent. Various eluents (5.0 mL) were studied according to the SPE procedure. The results are shown in Table 1. As can be seen, the analyte ions were quantitatively eluted from the sorbent with 5.0 mL of a mixture containing 0.5 mol L⁻¹ HNO₃ and thioure. Therefore, 5.0 mL of 0.5 mol L⁻¹ HNO₃ and thioure was used in all subsequent experiments.

3.4. Effect of the flow rate

The retention of the analyte ions on the sorbent depends on the flow rate of the metal ions solution. For the investigation of this parameter, a set of similar experiments were designed and the flow rate of the sample was varied from 0.5 to 6 mL min⁻¹. It was found that a flow rate of 0.5–4 mL min⁻¹ did not affect retention. Then, the retention of the analyte ions decreased when the flow rate was increased over 4 mL min⁻¹. Therefore, a flow rate of 3 mL min⁻¹ was selected in all experiments.

Effect of flow rate of eluent on desorption of the analyte ions from sorbent was also investigated. For this purpose, a set of similar experiments were designed and the flow rate of eluent was varied from 0.5 to 3 mL min⁻¹. It was found that a flow rate of 0.5–1.5 mL min⁻¹ did not affect desorption. Therefore, a flow rate of 1.0 mL min⁻¹ was selected in all experiments.

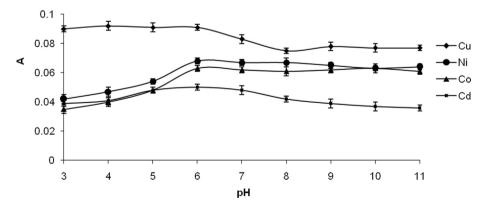


Figure 2 Effect of pH on the SPE procedure of the analyte ions. Conditions: Cu(II), Ni(II) and Co(II) 5.0 μ g; Cd(II), 1.0 μ g; buffer with pH 6, 2 mL; flow rate of sample and eluent, 3.0 and 1.0 mL min⁻¹; final solution, 5.0 mL of a mixture containing 0.5 mol L⁻¹ HNO₃ and thioure; reference, reagent blank.

Tween 80 coated alumina S1293

Table 1 Effect of type and concentration of eluer	nt on the recovery of t	he analyte ions.			
Eluent	A				
	Cu	Ni	Со	Cd	
HCl 1.0 mol L ⁻¹	0.092	0.070	0.059	0.039	
$H_2SO_4 \ 1.0 \ mol \ L^{-1}$	0.086	0.067	0.052	0.043	
$\mathrm{HNO_3}\ 1.0\ \mathrm{mol}\ \mathrm{L}^{-1}$	0.092	0.070	0.056	0.048	
Thiourea $0.5 \text{ mol } L^{-1}$	0.081	0.063	0.067	0.046	
Mixture of HNO ₃ and thiourea 0.5 mol L ⁻¹	0.095	0.074	0.068	0.048	

3.5. Effect of sample volume

Sample volume is one of the important parameters for obtaining high preconcentration factor (Ezoddin et al., 2010). For this purpose a set of similar experiments (5.0 μ g of copper, nickel and cobalt and 1.0 μ g of cadmium ions) in the volume range of 30–1100 were conducted according to the SPE procedure. It was observed that retention of all analyte ions was almost constant up to 1000 mL (preconcentration factor 200). However, for convenience, all experiments were carried out with 50 mL of the aqueous solution.

3.6. Sorption capacity of the coated alumina

The sorption capacity of the coated alumina was also determined by the batch process. In order to, a solution containing 5.0 mg of each analyte ions at pH 6 and 0.1 g of the sorbent were stirred for 1 h to ensure complete equilibration. The mixture was filtered and the concentration of the analyte ions in the supernatant solution was determined by FAAS. The loading capacity of the sorbent for the analyte ions was calculated from the difference between the metal ions concentration before and after sorption. It is found that, the coated alumina has a sorption capacity of 21.5, 24.7, 27.9 and 46.5 mg g⁻¹ for copper, nickel, cobalt and cadmium, respectively.

3.7. Effect of foreign ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the preconcentration step. For this purpose, interference ions in different interfere-to-analyte ratios were added to a solution containing 5.0 μg of Cu(II), Ni(II) and Co(II) and 1.0 μg of Cd(II) and were subjected to the SPE procedure. The tolerance limits were determined for a maximum error of $\pm\,5\%$. The results are given in Table 2. These results demonstrate that the common coexisting ions did not have a significant effect on the determination of the analyte ions.

3.8. Analytical figures of merit

Under the optimized conditions, calibration curves were constructed for the determination of copper, nickel, cobalt and cadmium according to the SPE procedure. Linearity was maintained between 2.0 and 900.0 ng mL $^{-1}$ for copper, 5.0 and 1700.0 ng mL $^{-1}$ for nickel and cobalt and 1.0 and 400.0 ng mL $^{-1}$ for cadmium in the original solution. Detection limits based on three times the standard deviation of the blank

Table 2 Tolerance limit of the foreign ions. Foreign ions Interference/analyte ions(II) ratio Cu(II) Ni(II) Co(II) Cd(II) CH₃COO 5000 5000 5000 5000 Ca²⁺, Mg²⁺ Al³⁺ 2000 2000 1500 2000 75 50 75 100 Ag^+ 400 500 500 500 Mn^{3+} 200 200 150 200 Ba²⁺ 500 400 500 400 Cr^{3+} 900 2.50 250 200 Zn^{2+} 800 450 400 600 Fe^{3+} 300 400 250 300 Pb^{2+} 800 600 600 600 Conditions were the same as Fig. 2.

 $(3S_b)$ for Cu(II), Ni(II), Co(II) and Cd(II) ions were 0.4, 1.0, 1.2 and 0.2 ng mL $^{-1}$, respectively. Seven replicate determinations of a mixture of 5.0 µg of Cu(II), Ni(II), Co(II) and 1.0 µg of Cd(II) ions in the original solution gave a mean absorbance of 0.093, 0.071, 0.066 and 0.049 with relative standard deviations 1.9%, 2.3%, 2.6% and 2.1%, respectively.

The enrichment factor, defined as the ratio of the slope of calibration curve for the SPE procedure to that obtained without preconcentration. In the SPE procedure, enrichment factors were 8.8, 8.5, 8.3 and 9.5 for copper, nickel, cobalt and cadmium, respectively.

3.9. Accuracy and applications of SPE procedure

3.9.1. Analysis of the analyte ions in the standard samples One certified reference material was obtained from the National Institute for Environment Studies (NIES, Tsukuba-City, Japan) No. 1 Pepperbush was analyzed. Approximately 1.0 g of NIES, No.1 was weighed accurately into a beaker and dissolved in concentrated nitric acid (ca. 10 mL) with heating on a water bath. The solution was cooled, diluted to 20 mL with deionized water and filtered. Then, the filtrate was made up to 250.0 mL with deionized water in a calibrated flask. An aliquot of this solution was taken and the analyte ions were determined by the SPE procedure. The results are shown in Table 3 and are in good agreement with the certified values.

3.9.2. Analysis of the analyte ions in the tobacco samples The applicability of the SPE procedure was evaluated in two tobacco samples. For this purpose, approximately 1.0 g of Cigarette's and Hookah's tobacco was weighed accurately into two beakers and dissolved in concentrated nitric acid (ca. 10 mL) with heating on a water bath. The solutions were

S1294 S.Z. Mohammadi et al.

Sample	Certified value (µg g ⁻¹)	Found* ($\mu g g^{-1}$)	Recovery (%)
NIES, No. 1	Ni: 8.7 ± 0.6	Ni: 8.89 ± 0.43	102.2
Pepperbush	Cu: 12 ± 1	Cu: 11.83 ± 0.37	98.6
	Co: 23.0 ± 3	Co: 22.53 ± 0.75	97.9
	Cd: 6.7 ± 0.5	Cd: 6.92 ± 0.22	103.3

cooled, diluted to 20 mL with deionized water and filtered. Then, the filtrate was made up to 250.0 mL with deionized water in two calibrated flasks. An aliquot of these solutions was taken individually and the analyte ions were determined by the SPE procedure. The recovery of the analyte ions from tobacco samples spiked with analyte ions was also studied. The results are given in Table 4. According to this Table, the added analyte ions can be quantitatively recovered from the tobacco samples by the SPE procedure.

3.9.3. Analysis of the analyte ions in water samples

River, well, mineral and Hookah's water samples were collected in acid leached polyethylene bottles. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H₂O₂ and then was acidified to pH 2 with nitric acid. Before the analysis, water samples were filtered through a cellulose membrane (Millipore, Bedford, MA, USA). Also, 0.5 g of Blake tea was weighed accurately into a beaker containing 50 mL of deionized water and heated on a

Table 4 Determination of copper, nickel, cobalt and cadmium in tobacco samples.					
Sample	Found ^a ($\mu g g^{-1}$)	Added (µg g ⁻¹)	Found ($\mu g g^{-1}$)	Recovery (%)	
Cigarette's tobacco	Cu: 7.58 ± 0.37	Cu:10.00	Cu: 17.25 ± 0.88	96.7	
	Co: BLR ^b	Co:10.00	Co: 10.34 ± 0.49	103.4	
	Cd: 3.56 ± 0.18	Cd:10.00	Cd: 13.32 ± 0.61	97.6	
	Ni: 8.33 ± 0.35	Ni:10.00	$Ni:18.47 \pm 0.87$	101.4	
Hookah's tobacco	Cu: 4.97 ± 0.23	Cu:10.00	Cu: 15.14 ± 0.71	101.7	
	Co: BLR	Co:10.00	Co: 10.25 ± 0.51	102.5	
	Cd: 1.78 ± 0.09	Cd:10.00	Cd: 11.64 ± 0.53	98.6	
	Ni: 5.13 ± 0.25	Ni:10.00	$Ni:15.52 \pm 0.74$	103.9	

^a Average of four determination \pm standard deviation.

^b Below of linear range.

Sample	$Found^a \ (ng \ mL^{-1})$	Added (ng mL^{-1})	Found (ng mL ⁻¹)	Recovery (%)
Well water (Payame Noor University of Kerman)	Cu: 3.6 ± 0.2	Cu:10.0	Cu: 13.8 ± 0.6	102
	Co: 5.8 ± 0.4	Co:10.0	Co: 15.5 ± 0.7	97
	Cd: 2.1 ± 0.1	Cd:10.0	Cd: 12.4 ± 0.5	103
	Ni: 7.9 ± 0.3	Ni:10.0	Ni: 18.2 ± 0.9	103
River water (Kohpayeh, Kerman)	Cu: 7.3 ± 0.3	Cu:10.0	Cu: 17.6 ± 0.8	103
	Co: 5.8 ± 0.3	Co:10.0	Co: 15.9 ± 0.7	101
	Cd: 1.5 ± 0.1	Cd:10.0	Cd: 11.6 ± 0.4	101
	Ni: 8.3 ± 0.4	Ni:10.0	Ni: 18.7 ± 0.9	104
Mineral water	Cu: 2.7 ± 0.3	Cu:10.0	Cu: 12.5 ± 0.6	98
	Co: BLR ^b	Co:10.0	Co: 10.5 ± 0.5	105
	Cd: BLR	Cd:10.0	Cd: 9.8 ± 0.4	98
	Ni: BLR	Ni:10.0	Ni: 10.4 ± 0.4	104
Brewed tea	Cu: 5.1 ± 0.7	Cu:10.0	Cu: 14.9 ± 0.7	98
	Co: BLR	Co:10.0	Co: 10.1 ± 0.6	101
	Cd: BLR	Cd:10.0	Cd: 10.2 ± 0.6	102
	Ni: 6.0 ± 0.3	Ni:10.0	Ni: 16.3 ± 0.6	103
Hookah's water	Cu: 9.8 ± 0.4	Cu:10.0	Cu: 19.9 ± 1.0	101
	Co: BLR	Co:10.0	Co: 10.4 ± 0.5	104
	Cd: 2.1 ± 0.1	Cd:10.0	Cd: 12.0 ± 0.6	99
	Ni: BLR	Ni:10.0	Ni: 10.3 ± 0.5	103

 $^{^{\}rm a}$ Average of four determination \pm standard deviation.

b Below of linear range.

Tween 80 coated alumina S1295

System	Analysis method	Sample volume (mL)	RSD (%)	Linear range (ng mL ⁻¹)	$\begin{array}{c} LOD \\ (ng \ mL^{-1}) \end{array}$	Ref.
SPE	FAAS	21	Ni: 1.9	Ni: 2–100	Ni: 0.8	Lemos et al. (2008)
			Cd:3.1	Cd: 0.5-10	Cd:0.3	
Coprecipitation	FAAS	10	_	-	Ni: 3.0	Soylak et al.
· •					Cd:2.0	(2008b)
Coprecipitation	FAAS	25	≤10%		Ni: 0.06	Tuzen and Soylak
•					Cd: 0.34	(2009)
SPE	FAAS	_	Cu: 4.31	Cu:0.4-2600	Cu:0.86	Xie et al. (2008)
			Ni: 5.80	Cd:0.2-1000	Ni:0.92	
			Cd: 3.83	Ni:1.0-5000	Cd: 0.65	
SPE	FAAS	50	Cu:1.9	Cu:2.0-900.0	Cu:0.4	Present work
			Ni:2.3	Ni:5.0-1700.0	Ni:1.0	
			Co:2.6	Co:5.0-1700.0	Co:1.2	
			Cd:2.1	Cd:1.0-400.0	Cd:0.2	

water bath for 20 min. The solution was cooled and filtered. Then, the filtrate was made up to 250.0 mL with deionized water in a calibrated flask. An aliquot of brewed tea was taken and the analyte ions were determined by the SPE procedure. The recovery of the analyte ions from various water samples spiked with analyte ions was also studied. The results are given in Table 5. According to Table 5, the added analyte ions can be quantitatively recovered from the various water samples by the SPE procedure.

3.10. Comparison of SPE procedure with the other methods

A comparison of the SPE procedure with other reported preconcentration methods, for Cu(II), Ni(II), Co(II) and Cd(II) extraction from water samples, is given in Table 6 (Lemos et al., 2008; Soylak et al., 2008b; Tuzen and Soylak, 2009; Xie et al., 2008). The detection limits obtained, using the SPE procedure, was better than some of the other reported preconcentration methods (Soylak et al., 2008b; Xie et al., 2008). Based on the results shown in Table 6, the linear range of the SPE procedure was wider than some of the other reported preconcentration methods (Lemos et al., 2008; Xie et al., 2008). The relative standard deviation of the present work was lower than some of the other reported preconcentration methods (Lemos et al., 2008; Tuzen and Soylak, 2009; Xie et al., 2008).

4. Conclusions

A simple, sensitive and economical method was developed for flame atomic absorption spectrometry determination of trace amounts of copper, nickel, cobalt and cadmium ions after separation and preconcentration by coated alumina. The study demonstrates that coated alumina exhibits many desirable characteristics such as high selectivity, excellent ability to resist interferences, high enrichment factor, easy elution, high adsorption capacity and good reproducibility. In addition, preparation of the sorbent is simple, rapid and low cost. Therefore, this new developed method is feasible for the analysis of trace amounts of copper, nickel, cobalt and cadmium ions in tobacco, brewed tea and water samples with satisfactory results.

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