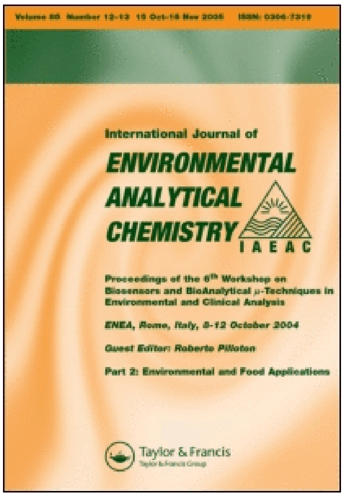

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Pre-concentration of ultra trace amounts of copper, zinc, cobalt and nickel in environmental water samples using modified C18 extraction disks and determination by inductively coupled plasma-optical emission spectrometry

Afshin Rajabi Khorrami[a]; Ali Reza Fakhari[b]; Mojtaba Shamsipur[c]; Hossein Naeimi[d]
[a] Faculty of Sciences, Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran [b] Department of Chemistry, Shahid Beheshti University, Tehran, Iran [c] Department of Chemistry, Razi University, Kermanshah, Iran [d] Department of Chemistry, Kashan University, Kashan, Iran

To cite this Article Rajabi Khorrami, Afshin , Fakhari, Ali Reza , Shamsipur, Mojtaba and Naeimi, Hossein(2009) 'Pre-concentration of ultra trace amounts of copper, zinc, cobalt and nickel in environmental water samples using modified C18 extraction disks and determination by inductively coupled plasma-optical emission spectrometry', International Journal of Environmental Analytical Chemistry, 89: 5, 319 — 329

To link to this Article: DOI: 10.1080/03067310802549953

URL: http://dx.doi.org/10.1080/03067310802549953

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 5, 20 April 2009, 319–329

Taylor & Francis
Taylor & Francis Group

Pre-concentration of ultra trace amounts of copper, zinc, cobalt and nickel in environmental water samples using modified C18 extraction disks and determination by inductively coupled plasma–optical emission spectrometry

Afshin Rajabi Khorrami[a]*, Ali Reza Fakhari[b],
Mojtaba Shamsipur[c] and Hossein Naeimi[d]

[a]*Faculty of Sciences, Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran;* [b]*Department of Chemistry, Shahid Beheshti University, Tehran, Iran;* [c]*Department of Chemistry, Razi University, Kermanshah, Iran;* [d]*Department of Chemistry, Kashan University, Kashan, Iran*

(*Received 9 August 2008; final version received 13 October 2008*)

A highly sensitive and accurate method for pre-concentration and determination of ultra trace amounts of zinc, copper, cobalt and nickel ions in environmental water samples is proposed. The method is based on the solid phase extraction of these ions on C18-bonded silica extraction disks modified with a novel Schiff base 2,2′-[1,6-hexanediyl *bis* (nitriloethylidine)]*bis*-1-naphthol (HDN). The retained ions on the prepared solid phase was eluted with 10 mL 0.01 M nitric acid and measured by inductively coupled plasma–optical emission spectrometry. The extraction efficiency and the influence of the type and least amount of eluent for the stripping of ions from the disks, pH, flow rates of sample solution and eluent, amount of HDN, effect of other ions and breakthrough volume were evaluated. The limits of detection of the method were 0.2, 0.2, 0.8 and 0.6 $\mu g\,L^{-1}$ for zinc, copper, cobalt and nickel, respectively and an enrichment factor of 100 was obtained. The proposed method was applied for determination of zinc, copper, cobalt and nickel ions in some natural and synthetic water samples with satisfactory results.

Keywords: solid phase extraction; trace amounts; zinc; copper; cobalt; nickel; Schiff base; inductively coupled plasma-optical emission spectrometry

1. Introduction

The ultra trace determination of heavy metal ions in environmental samples is very important because they pose undoubtedly a serious potential hazard to living organisms. Consequently, the development of reliable methods for quantifying ultra trace elements is highly required and challenged.

The ability of the inductively coupled plasma–optical emission spectrometry (ICP–OES) to perform multi-element trace analysis has made it an essential tool in many commercial laboratories. However, despite the selectivity and sensitivity provided by this technique, there is a crucial need for the pre-concentration of trace elements before

---

*Corresponding author. Email: chemafshin@gmail.com

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802549953
http://www.informaworld.com

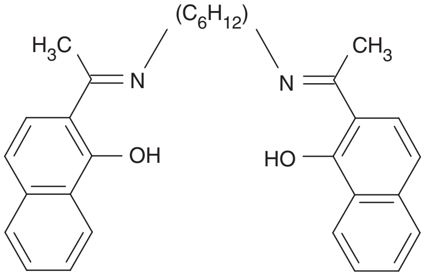

Figure 1. Structure of 2,2′-[1,6-hexanediyl *bis* (nitriloethylidine)]*bis*-1-naphthol (HDN).

their analysis due to their frequently low concentrations in environmental samples. In addition, since ICP–OES is usually susceptible to high levels of interferences that frequently accompany analytes; a clean-up step prior to determination is often required.

Many methods have been developed for the pre-concentration of trace heavy metals from various samples. These include co-precipitation, electrodeposition, liquid–liquid extraction and solid phase extraction. Solid-phase extraction (SPE) has received much attention in recent years for the analysis of trace concentrations in water samples [1–3]. This technique reduces consumption of and exposure to solvent, disposal costs and extraction time [4,5]. Many solid phases, such as activated carbon, polymeric fibres, Amberlite XAD, silica gel, modified alkyl-bonded silica gel have been used to concentrate trace metal ions from various media. Silica with chemically bounded alkyl chains such as C18-bonded silica modified by suitable ligands has been one of the excellent and widely used extractors of metal ions [6–11].

The Schiff bases as polydentate ligands are known to form very stable complexes with transition metal ions [12,13]. The resulting 1:1 complexes have been frequently used as catalysts in such diverse processes as oxygen and atom-transfer [14], enantioselective epoxidation [15] and mediating organic redox reactions [16]. However, despite extensive scientific reports on the synthesis, characterisation and crystalline structure of these complexes, reports on analytical application of these ligands are quite sparse [17].

In this work, a novel Schiff base, 2,2′-[1,6-hexanediyl *bis* (nitriloethylidine)]*bis*-1-naphthol (HDN), with the structure that is shown in Figure 1, is synthesised and used to modify the C18-bonded silica extraction disks as a solid phase. Then, an efficient method for the pre-concentration of ultra trace amounts of zinc, copper, cobalt and nickel in water samples and their simultaneous determination by ICP-OES based on this solid phase is developed.

2. Experimental

2.1 *Apparatus*

An inductively coupled plasma-optical emission spectrometer (ICP-OES, Varian Vista-Pro, Australia) coupled to a V-groove nebuliser and equipped with a charge coupled device (CCD) was used. The operating parameters are listed in Table 1.

The pH was determined with a model 691 Metrohm pH meter with a combined glass-calomel electrode. The modified C18-bonded silica extraction disks were used in conjunction with a standard 47 mm filtration apparatus (Schleicher & Schüell, Dassel, Germany) connected to a vacuum.

Table 1. Instrumental parameters.

Plasma	Argon
Frequency of RF generator	40.68 MHz
RF power	1.0 KW
Plasma gas flow rate	$13 \mathrm{l\,min^{-1}}$
Nebuliser flow rate	$0.8 \mathrm{l\,min^{-1}}$
Sample uptake time	20 s
Integration time	0.5 s
Sample integration number	3
Sample solution flow rate	$4 \mathrm{mL\,min^{-1}}$
Analysis wavelength	
• Zn	213.9 nm
• Cu	324.8 nm
• Co	228.6 nm
• Ni	231.6 nm

2.2 *Reagents*

All metal salts, acids and solvents used were of analytical reagent grade and purchased from Merck (Darmstadt, Germany) and deionised double distilled water was used throughout.

Stock solutions ($1000 \mathrm{mg\,L^{-1}}$) were prepared by dissolving the appropriate amounts of nitrate salts of metals in 100 mL calibration flasks. Working solutions were prepared by appropriate dilution of these stock solutions. Phosphate buffer was prepared by dissolving 1.179 g of potassium dihydrogen phosphate and 4.30 g of disodium hydrogen phosphate in deionised double distilled water to give 1000 mL of solution. The reference water sample, SRM 1640, was obtained from the National Institute of Standards and Technology (NIST), Gaithersberg, MA.

2.3 *Synthesis of 2,2′-[1,6-hexanediyl* bis *(nitriloethylidine)]*bis-*1-naphthol (HDN)*

The target Schiff base, HDN, was synthesised according to the following procedure. To a mixture of 2-ethanoil-1-naphthol (0.93 g, 5 mmol) in methanol was added 1, 6-diaminohexane (0.29 g, 2.5 mmol) by stirring in one portion. The mixture stirring is continued to 25 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, yellow substance was obtained. The solid product was filtered off and washed with cold methanol. The crude product was purified by re-crystallisation in ethanol and the pure Schiff base, was obtained in 95% yield. The Schiff base product was identified by physical and spectroscopic data: m.p. 206–207°C; IR (KBr)/υ ($\mathrm{cm^{-1}}$): 3300–3550(s, br, OH), 3050(m, C–H, Ar), 1600 (s, C = N), 1475, 1540 (Ar), 1270 (C–O); ^{1}H NMR/DMSO/δ ppm 1.6–2.0 (m, 8H), 2.4 (s, 6H), 3.6 (t, 4H), 7.2–8.4 (m, 10H), 8.4 (d, 2H), 16.0 (s, 2H); ^{13}C NMR/DMSO/δ ppm 14.59, 26.82, 28.89, 30.68, 48.70, 110.23, 113.15, 116.68, 118.82, 119.38, 128.95, 132.63, 146.34, 164.09, 172.79; MS: $m/z = 453$ ($M^+ + 1$, 6), 452 (M^+, 36), 284 (40), 168 (45), 127 (100), 112 (54), 84 (30), 41(88), 27(24).

2.4 *Preparation of modified extraction disks*

Extractions were performed with 3M Empore extraction disks (47 mm diameter and 0.5 mm thick) containing C18-bonded silica (8 µm particles, 6 nm pore size). The typical composition of the disks was 90% w/w C18-bonded silica and 10% w/w PTFE fibres. In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use. Thus, after placing the disk in the filtration apparatus, 10 mL methanol was poured onto the disk and immediately drawn through it by applying a slight vacuum to remove all contaminants arising from the manufacturing process and the environment. After all of the solvent passed through the disk, passing air through it for 5 min dried it. This procedure is especially important for the disks, which are used for the first time. After drying the disk, a solution of 6 mg of HDN dissolved in 5 mL chloroform was introduced onto the disk and allowed to penetrate inside the disk completely. Then, the solvent was evaporated at 60°C and the modified disk was washed and preconditioned by passing a 20 mL portion of buffer solution to pre-wet the surface of the disk prior to the extraction of ions from aqueous samples. In order to ensure complete wetting of the disk with the buffer solution it is preferable to leave extra buffer above the disk rather than to allow any air to contact the surface of the disk.

2.5 *Procedure of extraction, elution and determination*

The general procedure for the extraction and determination of analyte ions (zinc, copper, cobalt and nickel) was as follows: A 250 mL volume of multi-elemental solution containing 0.5 µg of each metal was adjusted to the pH 7.0 by the addition of 5 mL phosphate buffer and then passed through the modified disk at 20 mL min^{-1} flow rate. The disk was dried completely by passing air through it for 5 min. After the extraction, a 25 × 200 mm^2 test tube was then placed under the extraction funnel. The extracted ions were stripped from the modified disk using two times 5 mL solution of 0.01 M of nitric acid at 5 mL min^{-1} flow rate. The analyte ion concentrations were then determined at recommended conditions by ICP–OES.

2.6 *Analytical procedure for zinc, copper, cobalt and nickel in water samples*

Water samples were acidified with HNO_3 to 0.5% v/v prior to storage in order to avoid metal adsorption onto the inner bottles walls. A 1000 mL aliquot of water samples were first passed through 2.5 µm pore size Whatman filter paper to remove suspended particulate matter and stored at 6°C in the dark. Then complete the determination as recommended procedure.

3. Results and discussion

3.1 *Effect of pH on the adsorption of metal ions*

The pH of sample solution is one of the influencing factors in SPE process. The analyte solutions were adjusted by the addition of appropriate amounts of 0.1 M either nitric acid or ammonia solutions to a fixed pH and passed through modified C18-bonded silica disks at a flow rate of 20 mL min^{-1}. The pH range studied was between 2.0 and 8.0. Higher pH values (>8) were not tested because of the possibility of the hydrolysis of C18-bonded silica in the disks. Then the metal ions were eluted from the disks and their determination by ICP–OES gave the percentage recoveries of the eluted metal ions at various pHs. Figure 2 shows the effect of pH on the retention of metal ions on the modified C18-bonded

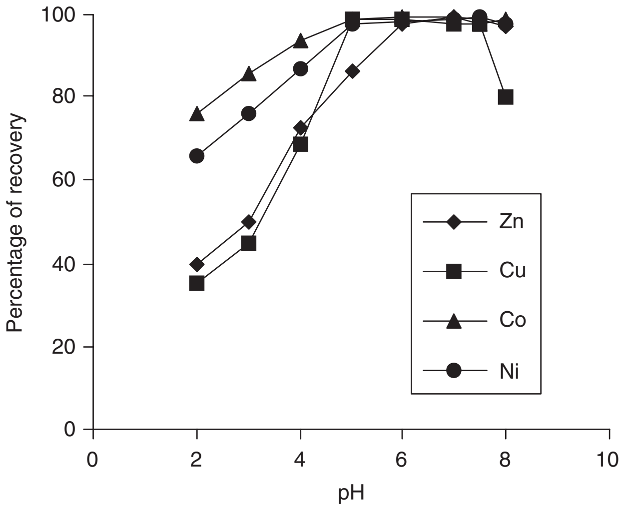

Figure 2. Effect of pH on the recovery of zinc, copper, cobalt and nickel. (Sample solution: 250 mL of multi-element solution containing 0.5 µg of each metal ion at 20 mL min^{-1} flow rate. Eluent: 10 mL of 0.01 M of nitric acid solution at 5 mL min^{-1} flow rate. Amount of ligand: 6 mg).

silica extraction disks. Copper has been quantitatively retained in the pH range of 5.0–7.5. In case of zinc, the pH range was found to be 6.0–8.0. Nickel and cobalt show maximum adsorption in the pH range of 5.0–8.0. For subsequent experiments, pH 7.0 was chosen as working pH. Addition of 5 mL of phosphate buffer was sufficient for achieving this pH.

3.2 *Choice of eluent*

In order to choose a proper eluent for the retained ions after extraction of them, the analyte ions were stripped with varying amounts of 0.01 M concentrations of different acids and the results are summarised in Table 2.

It is seen that the elution of them from the modified membrane disk was quantitative with 10 mL of 0.01 M nitric acid, while this could not be done even with greater than 10 mL volumes of the other acids tested. The eluting volume of 2.5 mL was the lowest volume studied because the ICP–OES used requires at least 2.0 mL to perform the measurements. In other experiments it was found that the lower the concentration of nitric acid, the larger the volume of acid solution needed for the quantitative stripping of the cations. Thus, 10 mL portions of 0.01 M nitric acid were used for further studies. It is noteworthy that when nitric acid of concentrations higher than 0.01 M was used; there was some leaching of HDN from the disk.

3.3 *Effect of amount of ligand*

In order to investigate the optimum amount of HDN on the quantitative extraction of metal ions by the modified extraction disks, extraction from 250 mL solutions containing 0.5 µg of each element under the optimal conditions were conducted by varying the amounts of ligand from 2 to 10 mg. In all cases, the extraction of metal ions found to be quantitative. Hence, subsequent experiments were carried out with 6 mg of the ligand.

Table 2. Percent recovery of zinc, copper, cobalt and nickel from modified C18-bonded silica extraction disks using varying amounts of different 0.01 M of acid solutions.[a]

Volume of acid (mL)		Recovery (%)			
		Acetic acid	Hydrochloric acid	Nitric acid	Hydrobromic acid
2.5	Zn	35.4 ± 2.0	67.5 ± 2.6	73.4 ± 2.3	46.7 ± 0.2
	Cu	22.2 ± 3.1	48.0 ± 0.1	61.3 ± 2.5	33.4 ± 1.9
	Co	47.1 ± 0.9	53.2 ± 1.3	53.3 ± 4.0	43.2 ± 3.2
	Ni	37.2 ± 1.4	54.4 ± 0.4	72.4 ± 3.1	39.4 ± 4.0
6.0	Zn	49.5 ± 1.4	73.4 ± 3.0	88.7 ± 0.3	56.4 ± 0.4
	Cu	43.6 ± 0.3	59.8 ± 0.4	83.4 ± 3.0	65.7 ± 0.4
	Co	53.0 ± 1.5	76.7 ± 1.5	69.8 ± 2.1	77.1 ± 0.4
	Ni	59.3 ± 1.7	67.3 ± 0.8	92.4 ± 0.6	51.4 ± 2.0
10.0	Zn	73.9 ± 0.7	86.7 ± 1.2	100.0 ± 0.1	73.5 ± 0.9
	Cu	66.6 ± 1.5	73.8 ± 0.5	99.8 ± 0.7	83.9 ± 1.6
	Co	60.7 ± 3.0	89.9 ± 0.7	100.0 ± 1.0	80.8 ± 3.0
	Ni	67.4 ± 0.2	76.7 ± 2.4	98.7 ± 0.2	76.1 ± 3.1
15.0	Zn	85.0 ± 1.1	89.9 ± 0.8	100.1 ± 0.9	88.7 ± 0.4
	Cu	73.0 ± 0.4	93.4 ± 1.1	99.7 ± 1.3	93.7 ± 2.7
	Co	85.1 ± 4.5	96.7 ± 0.6	99.9 ± 2.3	99.1 ± 2.7
	Ni	91.2 ± 0.3	89.7 ± 0.4	98.9 ± 0.7	89.7 ± 3.3

[a] Sample solution: 250 mL of multi-elemental solution containing 0.5 µg of each metal (pH = 7.0) at 20 mL min^{-1} flow rate. Eluent flow rate: 5 mL min^{-1}. Amount of ligand: 6 mg.

3.4 *Effect of flow rates*

The dependency of uptake of the metal ions on the flow rate was studied. The flow rate of solution through modified disk was being varied from 10 to 30 mL min^{-1}. Adsorption of cations was quantitative and reproducible in this range and not considerably affected by the sample solution flow rate. Similar results for the extraction of organic [18] and inorganic [6–10] materials by C18-bonded silica extraction disks have been reported in the literature. Thus, the flow rate of sample solution was maintained at 20 mL min^{-1} throughout the experiment. Quantitative stripping of metal ions from the modified disk was achieved in a flow rate range of 1–10 mL min^{-1}, using 10 mL of 0.01 M HNO_3 as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of ions. Hence, subsequent experiments were carried out with a flow rate of 5 mL min^{-1}.

3.5 *Analytical figures of merit*

The measurement of breakthrough volume is important in SPE because breakthrough volume represents the sample volume that can be pre-concentrated without loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 0.5 µg of zinc, copper, cobalt and nickel ions in 500, 750 and 1000 mL of buffered solution and the recommended procedure was followed. In all cases, the extraction by modified disk was found to be nearly quantitative. Thus, the breakthrough

Table 3. Effect of foreign ions on the recovery of zinc, copper, cobalt and nickel ions.[a]

		Recovery (%)			
Ions	Concentration (mg L^{-1})	Zn	Cu	Co	Ni
Zn^{+2}	0.1	–	98.8	101.5	98.0
Cu^{+2}	0.1	100.1	–	99.3	98.6
Co^{+2}	0.1	99.1	98.9	–	101.8
Ni^{+2}	0.1	104.0	103.2	96.8	–
Fe^{+3}	0.5	100.3	99.0	99.5	100.8
Al^{+3}	0.8	98.5	97.8	104.1	102.2
Mn^{+2}	0.8	94.7	96.1	97.0	99.1
Mg^{+2}	500	100.0	97.5	99.0	98.6
Na^{+}	1000	99.2	100.8	96.8	100.4
K^{+}	1000	104.0	100.0	99.1	99.0
Ca^{+2}	500	100.0	101.2	98.0	99.7
Hg^{+2}	0.5	98.3	99.0	98.0	100.0
Cd^{+2}	0.5	100.2	100.8	99.2	99.7
Cr^{+3}	0.8	98.2	99.1	98.4	99.0
Ag^{+}	1	100.5	103.0	99.4	99.9
Pb^{+2}	0.8	97.0	98.4	97.3	99.3
Ba^{+2}	50	98.4	100.6	99.6	101.0
As^{+3}	50	100.4	100.0	96.9	100.7

[a] Sample solution: 250 mL of multi-elemental solution containing 0.5 µg of each metal (pH = 7.0) at 20 mL min^{-1} flow rate. Eluent: 10 mL of 0.01 M of nitric acid solutions at 5 mL min^{-1} flow rate. Amount of ligand: 6 mg.

volume for the method should be around 1000 mL. Consequently, by considering the final elution volume of 10 mL and the sample solution volume of 1000 mL, an enrichment factor of 100 was easily available.

The maximum capacity of the modified disk for each ion was determined by passing 250 mL portions of buffered aqueous solutions through the disk which each of the solutions containing 500 µg of one of the ions. The conditions were as recommended procedure. The maximum capacities of the disks obtained from three replicate measurements were 130 ± 2, 60 ± 3, 120 ± 3 and 46 ± 4 µg for zinc, copper, cobalt and nickel, respectively. The limits of detection (LOD) and the limits of quantification (LOQ) of the proposed method were studied under the optimal experimental conditions. These parameters were calculated by ks_b/m, where k is equal to 3 and 10 according to the confidence level of 95% for LODs and LOQs, respectively. s_b is the standard deviation of the blank signal and m is the slope of the analytical curve. The LODs were 0.2, 0.2, 0.8 and 0.6 µg L^{-1} and the LOQs were 0.7, 0.7, 2.7 and 2.0 µg L^{-1} for zinc, copper, cobalt and nickel, respectively.

The reproducibility of the proposed method for the extraction and determination of 0.5 µg of analyte ions from 250 mL of buffered solution at pH 7.0 was also studied. The results obtained on 10 successive extraction and elution cycles revealed relative standard deviations of 1.2, 2.0, 2.0 and 1.8% for zinc, copper, cobalt and nickel, respectively.

Table 4. Determination of zinc, copper, cobalt and nickel ions in 1000 mL of different water samples and recovery test.[a]

Sample	Element	Added (μg)	Determined ($\mu g l^{-1}$)	Recovery (%)
Seawater	Zn	–	16.1 (1.3)	–
		5	21.3 (1.5)	104
		10	26.0 (1.3)	99
	Cu	–	10.5 (2.1)	–
		5	15.6 (2.0)	102
		10	20.4 (2.3)	99
	Co	–	2.6 (2.1)	–
		5	7.6 (2.0)	100
		10	12.0 (2.5)	94
	Ni	–	5.3 (2.0)	–
		5	10.3 (2.1)	100
		10	15.1 (2.0)	98
River water	Zn	–	13.8 (1.5)	–
		5	18.7 (1.3)	98
		10	23.1 (1.3)	93
	Cu	–	7.3 (2.1)	–
		5	12.0 (2.0)	94
		10	17.4 (2.0)	101
	Co	–	4.3 (1.9)	–
		5	9.2 (1.8)	98
		10	14.0 (2.0)	97
	Ni	–	2.1 (2.5)	–
		5	6.8 (2.2)	94
		10	11.9 (2.5)	98
Synthetic water (K^+, Na^+, Li^+, Mg^{2+}, Ba^{2+}, Na^+, Ag^+, Ca^{2+}, Fe^{3+}, Mn^{2+}, 0.02 mg of each cation)	Zn	–	n.d.	–
		5	4.8 (2.0)	96
		10	9.7 (1.9)	97
	Cu	–	n.d.	–
		5	5.1 (2.1)	102
		10	9.3 (2.5)	93
	Co	–	n.d.	–
		5	4.7 (1.7)	97
		10	9.2 (1.8)	92
	Ni	–	n.d.	–
		5	5 (2.1)	100
		10	10.4 (2.2)	104
SRM 1640[b]	Zn	–	25.0 (2.4)	94
	Cu	–	41.2 (2.0)	97
	Co	–	10.6 (1.8)	105
	Ni	–	12.9 (1.7)	94

[a] Values in parenthesis are RSDs based on three replicate analysis; n.d.: not determined.

[b] Certified values were 26.6, 42.6, 10.14 and 13.7 $\mu g L^{-1}$ for zinc, copper, cobalt and nickel, respectively.

Table 5. Comparison of the proposed method with some SPE methods in literature for preconcentration of metal ions in different water samples.

Metal ions	Chelating agent	Sorbent	Detection	EF[a]	LOD ($\mu g\,L^{-1}$)	R.S.D (%)	Ref.
Cu, Cd, Pb, Zn, Ni, Co	Ammonium pyrrolidinecarbodithioate	Multiwalled carbon nanotubes	FAAS	80	0.30–0.60	<5	[19]
Fe, Cu, Mn, Zn, Co, Ni, Cd, Pb	Diethyldithiocarbamate	Amberlite XAD-2000	FAAS	100	0.15–0.45	–	[20]
Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni, Co	Bathocuproinedisulfonic	Chromosorb 108	FAAS	80	0.16–0.60	1-17	[21]
Cu, Mn, Co, Ni, Cd, Pb	Diethyldithiocarbamate	Amberlite XAD-2010	FAAS	100	0.08–0.26	1.7–5.6	[22]
Cr, Cu, Ni, Pb, Zn	*p*-dimethylaminobenzaldehyde	Silica gel	ICP-OES	125	0.69–6.5	5	[23]
Cu, Fe, Zn	Curcumin	Silica gel	ICP-OES	75	0.12–0.4	<3	[24]
Cu, Zn, Ni, Co	HDN	C18 extraction disks	ICP-OES	100	0.20–0.80	≤2	This work

[a] EF: Enrichment factor.

3.6 *Effect of foreign ions*

The effect of other cations on the determination of analyte ions was studied. Known quantities of the foreign ions were added to 250 mL aliquot of aqueous solution (pH = 7.0) containing 0.5 µg of each analyte ion, and the recommended procedure was followed. As shown in Table 3, most of the examined cations did not interfere considerably with the extraction of analyte ions and their recoveries were nearly quantitative in the presence of other cations.

4. Application

To test the applicability of the developed procedure, it was applied to the extraction and determination of zinc, copper, cobalt and nickel contents from some water samples. River water (Chalous river, 23 October 2007), seawater (taken from Caspian sea, Anzali port, 11 November 2007), synthetic and reference water samples were analysed (Table 4). As can be seen from Table 4, the added analyte ions can be quantitatively recovered from the water samples by the aforementioned procedure, thus being a guarantee of the accuracy of the solid phase extraction and ICP-OES determination of these ions in different water samples.

5. Conclusion

Results presented in this work are well demonstrated the tremendous possibilities offered by SPE of trace amounts of zinc, copper, cobalt and nickel from natural water samples using C18-bonded silica extraction disks, which are modified with a novel Schiff base, 2,2′-[1,6-hexanediyl *bis* (nitriloethylidine)]*bis*-1-naphthol (HDN) and their determination by ICP–OES. Comparative information from some studies on SPE of metal ions from water samples by various methods is given in Table 5. As seen from the data, the proposed method provides a precise alternative for simultaneous determination of trace amounts of these ions in various aqueous samples. In addition, the use of disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes and offer high breakthrough volumes. In general, the proposed method is promising for routine determination of trace amounts of Cu, Zn, Co and Ni in natural water samples because of its simplicity, reproducibility, selectivity, high enrichment factor and low detection limits.

References

[1] I. Narin and M. Soylak, Anal. Chim. Acta **493**, 205 (2003).

[2] Q. Wu, X. Chang, Q. He, Y. Zhai, Y. Cui, and X. Huang, Int. J. Environ. An. Ch. **88**, 245 (2008).

[3] N. Burham, S.M. Abdel-Azeem, and F. El-Shahat, Int. J. Environ. An. Ch. **88**, 775 (2008).

[4] R.E. Majors, LC-GC **4**, 972 (1989).

[5] D.F. Hagen, C.G. Markell, G.A. Schmitt, and D.D. Blevins, Anal. Chim. Acta **236**, 157 (1990).

[6] M. Shamsipur, A.R. Ghiasvand, and Y. Yamini, Anal. Chem. **71**, 4892 (1999).

[7] Y. Yamini, N. Alizadeh, and M. Shamsipur, Anal. Chim. Acta **355**, 69 (1997).

[8] A. Rajabi Khorrami, H. Naeimi, and A.R. Fakhari, Talanta **64**, 13 (2004).

[9] A. Rajabi Khorrami, T. Hashempur, A. Mahmoudi, and A.R. Karimi, Microchem. J. **84**, 75 (2006).

[10] T. Hashempur, M.K. Rofouei, and A. Rajabi Khorrami, Microchem. J. **89**, 131 (2008).

[11] T. Shamspur, A. Mostafavi, and I. Sheikhshoaie, J. AOAC Int. **91**, 865 (2008).

[12] G. Wilkinson, R.D. Gillard, J.A. McCleverty, editors, *Comprehensive Coordination Chemistry*, (Oxford, London, 1987).

[13] D.A. Alwood, Coord. Chem. Rev. **195**, 267 (1997).

[14] B. Rither, S. Srittari, S. Hunter, and J. Masnovi, J. Am. Chem. Soc. **115**, 3918 (1993).

[15] W. Zhang, J.L. Loehach, S.R. Wilson, and E.N. Jacobson, J. Am. Chem. Soc. **112**, 2801 (1990).

[16] A.J. Fry, P.F. Fry, and J. Org, Chem. **58**, 3496 (1993).

[17] A.R. Fakhari, A.R. Khorrami, and H. Naeimi, Talanta **66**, 813 (2005).

[18] D.C. Messer and L.T. Taylor, J. Chromatogr. Sci. **33**, 290 (1995).

[19] M. Tuzen, K.O. Saygi, and M. Soylak, J. Hazard. Mater. **152**, 632 (2008).

[20] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, and M. Tufekci, J. Hazard. Mater. **146**, 155 (2007).

[21] M. Tuzen, M. Soylak, and L. Elci, Anal. Chim. Acta **548**, 101 (2005).

[22] C. Duran, A. Gundogdu, V.N. Bulut, M. Soylak, L. Elci, H.B. Senturk, and M. Tufekci, J. Hazard. Mater. **146**, 347 (2007).

[23] Y. Cui, X. Chang, X. Zhu, H. Luo, Z. Hu, X. Zou, and Q. He, Microchem. J. **87**, 20 (2007).

[24] X. Zhu, X. Chang, Y. Cui, X. Zou, D. Yang, and Z. Hu, Microchem. J. **86**, 189 (2007).