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Simultaneous Spectrometric Determination of Cu(II), Co(II), and Ni(II) in Pharmaceutical and Environmental Samples with XAD-4/DMMDTC Solid-Phase Extraction System

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Abstract

A method for the preconcentration of Cu(II), Co(II), and Ni(II) based on their complex formation with the potassium salt of 2.6-dimethyl-morpholinedithiocarbamate (DMMDTC) and the Amberlite XAD-4 resin as a solid support in a column was suggested. Cu(II), Co(II), and Ni(II) were detected by using the suggested spectrophotometric method in Triton X-100 media. The analytes were adsorbed as DMMDTC complexes on Amberlite XAD-4 column at the pH range of 4–6 and eluted with 0.5 M HNO_3 in acetone. The best possible enrichment factors for trace metal ions were achieved by optimizing the experimental conditions including reagent amount, eluent type, sample and eluent flow rates, sample volume, and the effects of matrix ions. The detection limits of Cu(II), Co(II), and Ni(II) were found to be 11.2, 26.1, and 1.37 μg L^{-1}, respectively. The accuracy of the proposed method was confirmed by determining the analytes in two Certified Reference Materials (TMDA-70.2 Ontario Lake Water and BCR-715 Waste Water) with the recoveries of more than 90%. The proposed method was successfully applied to the environmental and pharmaceutical samples.

Keywords Trace metal · Environmental and pharmaceutical samples · SPE method · Spectrophotometry · 2.6-Dimethyl-morpholinedithiocarbamate

Introduction

The determination of non-biodegradable heavy metals at trace amounts is one of the targets for the researchers around the world, due to their toxicity and accumulation tendency in human vital organs [1–3].

The concentration of heavy metal ions in environmental samples such as waters, biological fluids, and soils is often lower than the detection limit of modern instrumental equipment such as EDXRF, FAAS, inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and NAA. Besides, the main other restriction comes from the matrix effects of the IA (alkaline) and IIA (alkaline earth) metal ions such as Na^+, Ca^{2+}, K^+, Mg^{2+}, Sr^{2+}, and Ba^{2+}.

To determine the low levels of trace metal ions more accurately, sensitively, and selectively using the available techniques, a preconcentration procedure must generally be used [4]. Among the commonly used preconcentration procedures, the solid-phase extraction (SPE) based on solid supports [5–7], functionalized [8, 9] with chelating reagent can easily be applied using a column filled with a solid support without any chemical treatment. The adsorption of trace metal ion complexes with chelating reagent on solid support is auspicious respecting the adsorption capacity because the free chelating reagent is not retained. Especially, complexes of the metal ions can be selectively adsorbed on solid support [10].

Various sorbents have been used as solid supports such as hydrophobic resins (Amberlite XAD derivatives), multiwalled carbon nanotubes (MWCNTs), silica gel, activated carbon [11–15].

Amberlite XAD 4 is known to have high-surface area, uniform pore size distribution, and a promising neutral matrix for designing chelating resins, hence making it an efficient solid support [16, 17].

In recent years, dithiocarbamate (DTC) reagent has been given more attention due to forming stable complexes with heavy metal ions with a wide pH range for the spectrophotometric determination of metal ions [18–20]. DTCs have also

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been used as a chelating reagent for the separation and preconcentration of trace metal ions from various water samples [21–24]. The choice of complexation reagent is based on its fast and effective reaction with metal ions, strength in a wide pH range, and solubility in water. Dithiocarbamates (DTCs) have the advantage of offering remarkable analytical properties, particularly for the separation of the heavy metals. DTCs can form colored chelates with heavy metal ions such as Cu(II), Co(II), Ni(II), and Mn(II), and these chelates are stable during SPE separation procedures. Furthermore, DTCs do not form complexes with the alkali and alkaline earth metals [25]. Therefore, it is a suitable and selective method for heavy metal determinations in environmental water samples including alkali and alkaline earth metals.

The aim of the present work is to investigate the optimal analytical conditions of Amberlite XAD-4 (AXAD-4) with DMMDTC including sample pH and volume and eluent type for the separation and preconcentration of Cu(II), Co(II), and Ni(II) with SPE method before ultraviolet–visible (UV–VIS) spectrophotometric determination.

Experimental

Reagents and Samples

Single standard solutions of Cu(II), Co(II), and Ni(II) (Merck, Darmstadt, Germany) at 1000 µg mL^{-1} in 0.5 mol L^{-1} HNO_3 were used. Working solutions of metal ions were prepared by serial dilutions of the stock standard solution with ultra-pure water (Merck, Darmstadt, Germany). AXAD-4 resin (polystyrene divinylbenzene type, 20–60 mesh, surface area of 725 m^2/g) was obtained from (Sigma, St Louis, USA). It was washed with methanol, water, 1 mol L^{-1} HNO_3 in acetone, water, 1 mol L^{-1} NaOH, and water, respectively, for removing organic and inorganic contaminants.

Dilute solutions (0.1 mol L^{-1}) of either nitric acid or ammonium hydroxide solutions were used to examine the pH effect on sorption efficiency. Na_2HPO_4/KH_2PO_4 (Merck, Darmstadt, Germany) Sorenson's buffer solution (0.133 M, pH 4.0–6.0) was used for keeping the pH constant. Triton X-100 (TX-100, 1%, v/v) was prepared in deionized water.

Table 1 The principal conditions for Cu(II), Co(II), and Ni(II) ions in UV–VIS spectrophotometric measurements in micellar media in the presence of TX-100 at pH interval of 3.0–7.0

Metal ion	Color of metal complexes	Measuring wavelength (nm)
Cu(II)	Brown	460
Co(II)	Dark green	342
Ni(II)	Light green	328

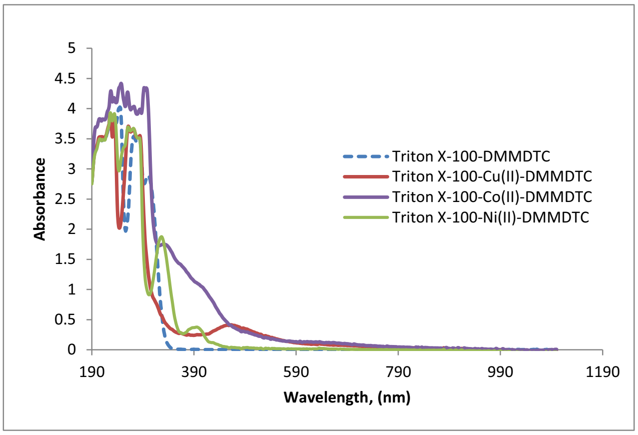

Fig. 1 Absorption spectra of **a** DMMDTC solution vs. against water blank, **b** nickel(II)-DMMDTC vs. reagent blank, and **c** copper(II)-DMMDTC vs. reagent blank. Conditions: [Cu(II)] = 3.15 × 10^{-5} M, [Co(II)] = 3.39 × 10^{-5} M [Ni(II)] = 3.4 × 10^{-5} M, [DMMDTC] = 5 × 10^{-4} M, pH 5 ± 0.2; 1% (v/v) Triton X-100

TMDA-70.2 Ontario Lake (Environment Canada) and BCR-715 Waste Water samples (European Commission-Joint Research Centre-Institute of Reference Materials) Certified Reference Materials were employed to test the accuracy of the proposed method. Before use, all the

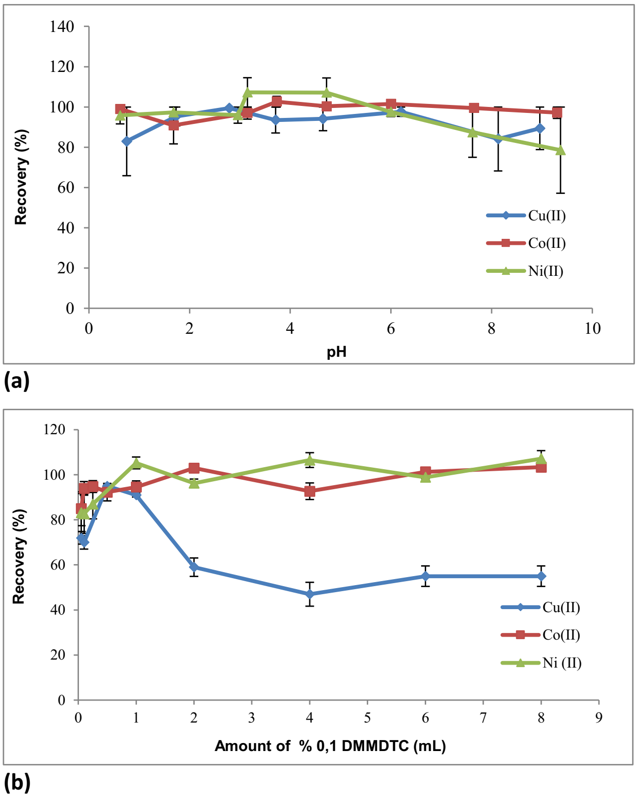

Fig. 2 The influence of **a** pH and **b** DMMDTC concentration on the recovery of Cu(II), Co(II), and Ni(II) by the column SPE procedure. Experimental conditions; sample volume 20 mL, pH = 5, Cu(II), Co(II), and Ni(II) ions concentration 500 µg mL^{-1}, XAD-4 mass 0.200 g, sample flow rate 4.0 mL min^{-1} (*n* = 3)

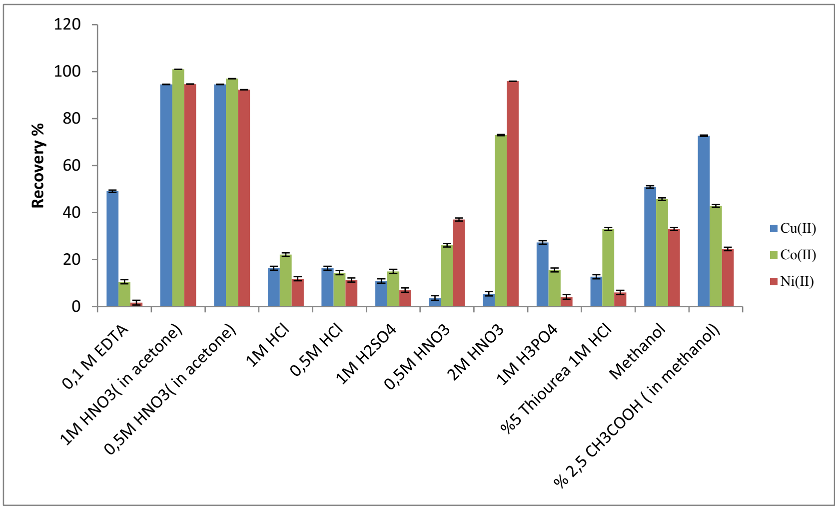

Fig. 3 The effect of eluent type and concentration to the recovery of Cu(II), Co(II), and Ni(II) (sorption conditions: amount of the ions 10 μg, pH 5 ± 0.2, volume of sample 20 mL; $N = 3$)

environmental water samples were filtered through 0.45-μm pore cellulose acetate membrane filters (Merck Millipore, Germany). Potassium salt of 2.6-dimethyl-morpholinedithiocarbamate (KDMMDTC) was synthesized and purified as described in our previous work [26]. All other reagents used were of analytical reagent-grade (Merck, Darmstadt, Germany).

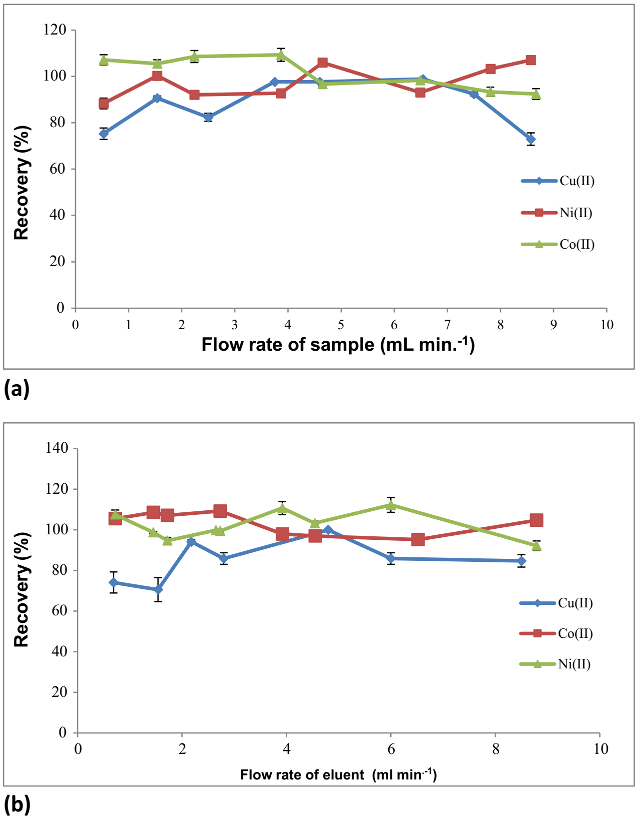

Fig. 4 The effect of **a** sample and **b** eluent flow rate to the recovery of 10 μg Cu(II), Co(II), and Ni(II) conditions: amount of AXAD 0.2 g, 10 mL of 0.5 M of the nitric acid (in acetone) as eluent

Preparation of Water, Fertilizer, and Pharmaceutical Samples

A tap water sample was collected from the research laboratory, a lake water sample was collected from Gölköy in Bolu, and a dam water sample was collected from Yumrukaya Dam in Bolu, Turkey. Water samples were acidified immediately after collection using 1.0 mL of concentrated nitric acid per liter of sample and subsequently filtered through 0.45-μm pore cellulose membrane filter in order to remove the particulate matter.

Fertilizer material was bought from NPK companies. Digestion of the fertilizer was carried out using the method of the Association of Official Agricultural Chemists [26].

Supradyn and Decavit vitamin samples, to be used for the determination of Cu(II) ions, were purchased from a local pharmacy. A known weight of sample was crushed and heated in a furnace at 400 °C for 2 h in nickel crucible. Five-milliliter concentrated HCl was used to dissolve the residue, and the contents were transferred into a 100-mL volumetric flask by filtering through Whatman No. 1 filters, and the residues were washed into a calibrated 100-mL flask [27].

Preparation of the Column

After soaking for 24 h in water, 200 mg of Amberlite XAD-4 resin was transferred into a 10 × 100-mm glass column on glass wool as a plug at one end of the column. Then, another small glass wool plug was placed onto the tap of the adsorbent column. Before each use, 1 mol L^{-1} HNO_3, deionized water, and 1 mol L^{-1} of HCl and deionized water, respectively, were used to clean the column. Subsequently, for obtaining the desired pH, the column was conditioned with proper buffer solutions. In order to prevent the drying of resin, it was kept in ultra-pure water after each use.

Proposed Method

Preconcentrations of Cu (II), Co(II), and Ni(II) ions in real samples were carried out as follows: pH of a known volume of an original sample solution (200 to 1000 mL) was adjusted to pH range of 4–6 with Sorenson's buffer solution. One milliliter of 0.1% DMMDTC ligand solution was added and then the sample solution containing metal-DMMDTC chelate was passed through the preconditioned AXAD-4 column with a flow rate of 4.5 mL min^{-1}. The chelate was sorbed on AXAD-4 column. The sorbed metal-DMMDTC chelates were then extracted from the column by the addition of 8.0 mL of 0.5 mol L^{-1} HNO_3 (in acetone) eluent. One milliliter of 1.0% TX-100 and 0.1% DMMDTC solutions was added on to the eluate which made the final volume 10.0 mL. The eluate was analyzed for Cu(II), Co(II), and Ni(II) ions by using UV–VIS spectrometry according to the proposed method in "Determination of Metal Ions."

Determination of Metal Ions

Cu(II), Co(II), and Ni(II) ions were simultaneously measured by UV–VIS spectrophotometer after elution with 0.5 M HNO_3 (in acetone) from the AXAD-4 column. The principal details of UV–VIS method are listed in Table 1. The absorption spectra of DMMDTC and its Cu(II), Co(II), and Ni(II) chelates in 1% TX-100 medium are shown in Fig. 1.

Results and Discussion

Effects of Sample pH and DMMDTC Concentration

Complexation reaction of DMMDTC with heavy metal ions strongly depends on the pH of the solution. Because DMMDTC forms complexes in the wide pH range (2–10) and the fact that at pH values lower than 2.0 the DMMDTC ligand decomposes and at the pH values higher than 8.0 precipitation of ions as hydroxides develop, optimal pH for extraction procedure needs to be balanced. Thus, the effect of sample pH on the chelate formation of DMMDTC with Cu(II), Co(II), and Ni(II) ions and their following adsorption on AXAD-4 was inspected by changing the pH within the 2–10 range. The pH values were adjusted either by ammonium hydroxide or nitric acid solutions. Figure 2a shows the results of the sample pH influence on the recoveries of Cu(II), Co(II), and Ni(II) metal ions. As shown in Fig. 2a, as the pH increases up to 3, the recovery of the analytes also increases and at this pH, the highest recovery (≥ 95%) was observed. This can be explained by the stabilization of DMMDTC reagent, which is beneficial to the formation of DMMDTC chelates. Further increase of the sample pH causes slight reduction in the recovery due to the precipitation of the ions as hydroxide forms. Thus, since the highest recoveries were obtained for each metal ion at pH 5.0, this sample pH value was selected as the

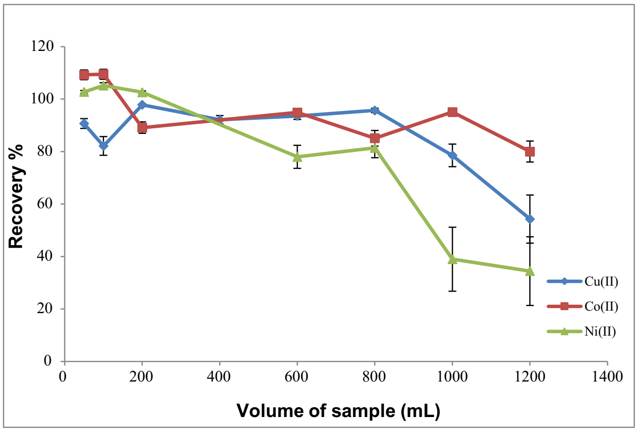

Fig. 5 Effect of the samples volume on the recovery of Cu(II), Co(II), and Ni(II) (pH 5 eluent 10 mL, 0.5 mol L^{-1} HNO3(in acetone) 10 mL, amount of the ions 10 μg; *N* = 3)

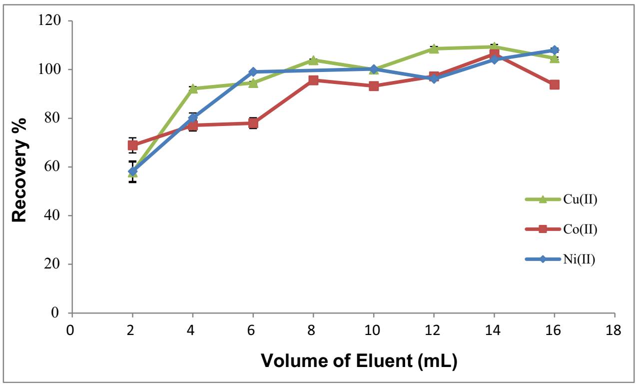

Fig. 6 The effects of volume of eluent solution (0.5 M HNO3 in acetone) on the desorption of Cu(II), Co(II), and Ni(II) ions from AXAD column (*N* = 3)

Table 2 Effect of foreign ions on the determination of 50 ng mL^{-1} of Cu(II), Co(II), Ni(II), and Cu(II) (*N* = 3)

İyon	Amount (μg)	Added	Recovery		
			Cu(II)	Co(II)	Ni(II)
Cl^-	10000	NaCl	102.2	92.8	91.4
NO_3^-	10000	KNO_3	96.8	90.0	92.9
Na^+	10000	NaCI	95.2	91.7	91.9
CO_3^{2-}	10000	Na_2CO_3	103.7	91.1	94.2
SO_4^{2-}	10000	Na_2SO_4	96.0	93.3	100.1
I^-	10000	KI	98.3	95.3	90.2
Ca^{2+}	10000	$Ca(CI)_2.2H_2O$	103.0	89.2	88.6
Mg^{2+}	10000	$Mg(SO_4)_2.7H_2O$	103.7	91.4	97.1
PO_4^{3-}	10000	$Na_2HPO_42H_2O$	92.9	98.6	96.0
Fe^{2+}	1000	$Fe(NO_3)_2$	71.2	96.1	94.0
	100		96.8		

Table 3 The levels of analyte ions in TMDA-70.2 Ontario Lake Water and BCR-715 Waste Water after application of the proposed SPE/UV–VIS method (*N* = 3)

Analyte	Certified samples					
	BCR-715			TMDA-70.2		
	Certified value (mg/L)	Found value (mg/L)	Recovery (%)	Certified value (mg/L)	Found value (mg/L)	Recovery (%)
Cu(II)	0.90 ± 0.140[a]	0.94 ± 0.073	104.4	0.409 ± 0.032	0.412 ± 0.046	100.7
Co(II)	N.I	-	-	0.290 ± 0.021	0.310 ± 0.318	106.8
Ni(II)	1.20 ± 0.090	1.09 ± 0.092	90.8	0.333 ± 0.022	0.359 ± 0.106	107.8

N.I not included

[a] $ts\sqrt{N}$ value of three experiments at 95% confidence level

optimum condition for the column SPE procedure. Therefore, it was concluded that the Cu(II), Co(II), and Ni(II) ions can be simultaneously determined at pH 5.0 with the highest recoveries.

Effective complexation depends on the concentration of DMMDTC as well. In the presence of DMMDTC, formation of hydrophobic complexes of metal ions plays a key role. In this circumstance, Cu(II), Co(II), and Ni(II) are adsorbed on XAD-4 either through van der Waals forces or hydrophobic interaction. Therefore, with the increase of DMMDTC concentration, van der Waals forces or hydrophobic interactions become more important, which is the main cause of very good recoveries for Cu(II), Co(II), and Ni(II) at pH interval of 4.0–6.0. Therefore, the effect of the volume of 0.1% DMMDTC on the quantitative recoveries of the Cu(II), Co(II), and Ni(II) ions was studied in the 0.05–8-mL wide range as given in Fig. 2b. The results indicated that the sorption efficiency was DMMDTC concentration-dependent and the recoveries of Cu(II), Co(II), and Ni(II) ions increased with DMMDTC's volume of up to 0.5 mL. Finally, all the experiments were carried out by using 1 mL vol of 0.1% DMMDTC.

Effect of Eluent Type and Concentration

A series of different elution solutions were applied for the elution of metal-*DMMDTC* complexes from AXAD-4. The results obtained are shown in Fig. 3. It was found that 0.5 mol L^{-1} of HNO_3 (in acetone) was sufficient to have efficiencies of greater than 95% for all the analyte ions, among the elution solutions. Therefore, 0.5 mol L^{-1} of HNO_3 (in acetone) solution was selected and employed as an eluent for all the experiments.

Table 4 The results obtained for the determination of Cu(II) ions in pharmaceutical and fertilizer samples with the proposed method (*N* = 3)

Samples	Cu(II)[a]		Recovery (%)
	Proposed method	Label values	
Supradyn	0.737 ± 0.06	0.752	98.0
Decavit	0.652 ± 0.132	0.635	102.6
Fertilizer	1.872 ± 0.049	1.774	105.5

[a] (mg/g) average of three determinations ± S:D

Effects of Flow Rates of Sample and Eluent Solutions

In solid-phase extraction studies, flow rates of the sample and the eluent solutions are important factors for the quantitative adsorption and desorption of metal chelates. The retention of Cu(II), Co(II), and Ni(II) complexes with DMMDTC on AXAD-4 adsorbent was not affected by sample flow rates in the range of 3.7–7.5 mL min^{-1} for all metal ions (Fig. 4a). Thus, the experiments were performed at a sample flow rate of 7.5 mL min^{-1} which was the maximum flow rate attainable by the peristaltic pump used. High flow rates of a sample solution are advantageous because of saving analysis time. Elution flow rate was also investigated in the flow rate ranges of 0.5–8.5 mL min^{-1} under constant conditions. All further studies were performed at the eluent flow rates of 5.0 mL min^{-1} with over 95% recoveries (Fig. 4b).

Table 5 Analytical results for the determination of Cu(II), Co(II), and Ni(II) in environmental water samples with the proposed method (*N* = 3)

Samples	Proposed method results (μg/L)[a]		
	Cu (II)	Co(II)	Ni (II)
Lake water	7.31 ± 3.95	N.D	12.98 ± 2.68
Irrigation water	6.32 ± 2.38	0.65 ± 0.07	14.87 ± 3.5
Tab water	63.9 ± 27.4	0.73 ± 0.31	22.5 ± 7.65

N.D not detected

[a] Average of three determinations ± S:D

Table 6 Comparison of different extraction techniques for the spectrophotometric determination of Cu(II), Co(II), and Ni(II)

Reagent	Studied metals	Extraction technique	Detection limits ($\mu g\ l^{-1}$)	Sample	Reference
2-Amino-cyclopentene-1-dithiocarboxylic acid	Ni(II) and Co(II)	Cloud point extraction	10 and 7.5	Water	[35]
N-Ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	Cu(II)	Reaction in micellar media	-	Environmental and pharmaceutical	[36]
Pyridoxal-4-phenyl-3-thiosemicarbazone	Cu(II)	Extractive spectrophotometric method	6.5	Leafy vegetable and pharmaceutical	[37]
5-4′-Chlorophenylazo)-6-hydroxypyrimidine-2,4-dione	Ni(II)	Solid phase extraction	3	Water, food, biological and soil samples	[38]
2.6-Dimethyl-morpholinedithiocarbamate	Cu(II), Co(II), and Ni(II)	Solid-phase extraction	11.2, 26.1, and 1.37	Water, pharmaceutical and fertilizer sample	This study

Effect of Sample and Eluent Volume on Preconcentration

For the assessment of the highest enrichment factors, the maximum applicable sample volume must be defined especially in environmental water samples containing very low concentrations of metal ions. The enrichment factors were studied by a proposed column procedure by using the subsequent increased volumes in the range of 50–1200 mL of Cu(II), Co(II), and Ni (II) solutions and keeping the total amount of loaded metal ions constant as 10 μg. The results obtained are presented in Fig. 5. The metal ion adsorptions were quantitative (≥ 95) until 800, 1000, and 200 mL sample volume for Cu(II), Co(II), and Ni(II), respectively. The eluent volume was also studied in a column procedure. The results showed that 8 mL of 0.5 mol L^{-1} of HNO_3 (in acetone) elution solution volume was sufficient for obtaining the recovery of more than 95% (Fig. 6). The preconcentration factor was calculated as the ratio of the highest sample volume (800, 1000, and 200 mL) to the final volume (10 mL) and found to be 80, 100, and 20 for Cu(II), Co(II), and Ni (II), respectively.

Interferences

Some common coexisting ions, including various cations and anions in environmental samples, have been considered as having a potential interfering effect on the preconcentration of Cu(II), Co(II), and Ni(II). In this study, the recoveries of Cu(II), Co(II), and Ni(II) were investigated in the presence of some foreign ions including Cl^{-}, NO_3^{-}, Na^{+}, CO_3^{2-}, SO_4^{2-}, I^{-}, Ca^{2+}, Mg^{2+}, PO_4^{3-}, and Fe^{2+}. The above ions, at various concentrations, were added separately to the sample solution containing 10-μg amounts of analyte. No significant effect on SPE method was observed. Therefore, determination of the analytes with recoveries higher than 90% was achieved with the proposed method as given in Table 2.

Analytical Performance

Analytical characteristics of the present SPE/UV–VIS method were evaluated for the determination of Cu(II), Co(II), and Ni(II) ions. The detection limits (LODs) were defined as the concentration corresponding to three times the standard deviation of ten runs of the blank solution with optimized preconcentration method and calculated as 11.2, 26.1, and 1.37 μg L^{-1}, respectively, for Cu(II), Co(II), and Ni(II) ions. The relative standard deviations (RSDs) were in the range of 3.6–4.8% ($n = 5$, C = 0.5 μg mL^{-1}). The resulting calibration graphs were linear over the concentration ranges of 0.1–3 μg mL^{-1} for Cu(II) ($R^2 = 0.993$), 0.02–4 μg mL^{-1} for Co(II) ($R^2 = 0.998$), and 0.01–1.5 μg mL^{-1} for Ni(II) ($R^2 = 0.992$), respectively.

Application

The method was applied to Standard Reference Materials, namely, TMDA-70.2 Ontario Lake and BCR-715 Waste Water. The results are presented in Table 3. The results are strongly supported by the certified values for the analytes.

The proposed SPE/UV–VIS method for the analyte ions was applied to pharmaceutical and fertilizer samples. These samples were digested by using the procedure given in “Preparation of Water, Fertilizer, and Pharmaceutical Samples” and extracted by using the SPE procedure given in “Proposed Method”. The results are given in Table 4. The observed recoveries of analytes were higher than 95% for pharmaceutical and fertilizer samples. The proposed method was also applied to the preconcentration and determination of Cu(II), Co(II), and Ni(II) content of lake, irrigation, and tap water samples. The 250-mL water samples were treated according to the proposed procedure (Table 5) and it was observed that the method can be used reliably for the analysis of water samples.

Conclusion

A simple, fast, and reliable preconcentration/separation procedure was proposed as a method to determine the Cu(II), Co(II), and Ni(II) ions on Amberlite XAD-4 resin with DMMDTC complexes. The reusability of AXAD-4 was as high as or greater than 100 cycles with over 90% recovery. Developed SPE method achieved the complete removal of chemical interferences in real samples prior to the UV–VIS determination of trace metal ions. In addition, proposed SPE method needs lower time in comparison with the most of the other methods with high sample flow rates and can be combined with atomic spectroscopic methods such as ICP-MS, AAS, ICP-OES, and other electroanalytical techniques as offline or online mode. Many analytical procedures such as polarography [28], voltammetry [29], and ion selective electrode [30, 31] have been suggested for Cu(II), Co(II), and Ni(II) determinations in environmental samples [32, 33]. Many of these methods need more care for sensor preparation, are complicated and time-consuming, and have lower repeatability. However, the spectrophotometric method still has the advantages of the simplicity of procedures and the common availability of the instrumentation and requires no expensive or problematical equipment. For these reasons, UV–VIS spectrophotometry was used for rapid, relatively low cost, and simple determination of the preconcentrated DMMDTC analytes.

The Cu(II), Co(II), and Ni(II) could be determined simultaneously by using UV–VIS spectrophotometry with the detection based on the colored metal-DMMDTC complex formation. Further applications are to be anticipated. All that is necessary is a chemical system in which a selected analyte is exhaustively extracted from XAD-4 resin in a form allowing spectroscopic measurement. The study herein also provided further insight into the SPE mechanism in that DMMDTC–analyte ion complexes must also be pretreated by a nonionic surfactant Triton X-100 in order for the efficient and stable measurement solution to occur. The recoveries of analyte ions were efficiently quantitative and were unaffected by matrix media. The proposed method was successfully applied for the determination of the very low levels of Cu(II), Co(II), and Ni(II) contents in pharmaceutical and environmental samples. Comparison of different extraction techniques for the spectrophotometric determination of Cu(II), Co(II), and Ni(II) is given in Table 6.

As a result, present study developed a simple, efficient, and reliable method for the sensitive determination of Cu(II), Co(II), and Ni(II) ions in the real samples by using DMMDTC/AXAD-4 SPE system with UV–VIS spectrophotometer.

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