

A new method for simultaneous determination of trace amounts of Cu(II) and Ni(II) ions by preconcentration and spectrophotometric analysis

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Abstract: Immediate preconcentration and spectrophotometric methods have been developed for the determination of trace amounts of cupric ion (Cu(II)) and nickel ion (Ni(II)) through a solid phase extraction with XAD-4-N,N'-bis-(salicylidene) cyclohexanediamine (XAD-4-SCHD) resin and a complex color reaction of the ions with 2,6-dimethyl-morpholine dithiocarbamate (DMMDTC) in Triton X-100 media. A high preconcentration factor of 125 was achieved. The spectrophotometric method was based on the measurements of the absorption of colored chelates of ions complexing with DMMDTC, and the adsorptions of the complex solutions were measured at their maximum absorption peaks at 460 and 328 nm for Cu(II) and Ni(II) ions, respectively. The impact of the complexing reaction variables including type and amount of surfactant, pH, amount of ligand, and complexation time on the sensitivity of the proposed method was optimized. Calibration graphs were found to be linear in the ranges of 0.02–3 and 0.02–2.5 mg L⁻¹ with detection limits of 5 and 7 µg L⁻¹ for Cu(II) and Ni(II), respectively. The accuracy of the developed method was calculated by recovering all Cu(II) and Ni(II) ions in synthetic and TMDA-70.2 certified reference water samples. Results of the proposed method were also compared with inductively coupled plasma-mass spectrometry results for the determination of trace Cu(II) and Ni(II) ions in water samples.

Key words: Spectrophotometric method development, solid phase extraction, Cu(II), Ni(II), Triton X-100

1. Introduction

Apart from the importance of copper and nickel for the metal industry, these metals also play an important role in biological systems. Copper is an essential micronutrient for animals and humans: it is very active in some biological processes, specifically in the synthesis of hemoglobin molecules. Nevertheless, a heavy dose of copper is harmful to the body because it can accumulate in the brain, liver, pancreas, and myocardium, causing series of systematic toxic effects.¹ Studies have shown that copper can accumulate in surface waters, affecting self-purification of bulk water and disturbing the growth of microbiological organisms, thereby reducing the performance of the treatment of waste waters.²

Nickel is the metal component of the enzyme urease, essential to plants and some domestic animals.³ However, it has been found that accumulated nickel is a moderately carcinogenic element for humans. Trace amounts of Cu(II) and Ni(II) are usually found in most water bodies, making the determination of the metals an important aspect of environmental studies.

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Several methods have been reported in the literature for the direct determination of trace Cu(II) and Ni(II) in environmental water samples using sophisticated instrumental techniques such as inductively coupled plasma mass spectrometry (ICP-MS),⁴ X-ray fluorescence spectrometry (XRF),^{5,6} and stripping voltammetric techniques.⁷ Samples containing high concentrations of foreign ions can cause serious spectral interference; thus, a good background correction system is necessary to overcome the problem of direct determination of Cu(II) and Ni(II) in environmental waters. The preconcentration and selective separation of Cu(II) and Ni(II) from real environmental water samples are very crucial environmental concerns.

Currently, there are numerous analytical methods reported for the preconcentration and selective separation of copper and nickel diffused in the ecosystem; these include liquid-liquid extraction,⁸ ion exchange,⁹ fiber chelation,¹⁰ coprecipitation,¹¹ cloud-point extraction,^{3,12-15} and solid-phase extraction (SPE).¹⁶⁻²⁴

The efficiency and importance of SPE, however, are significant in terms of its ubiquitous and confirmed advantages, such as preconcentration from a larger sample volume forming a higher enrichment factor, removal of potentially interfering matrices, simple storage, high efficiency due to lower consumption of reagents, and less utilization of toxic organic solvents.²³ In SPE, various sorbents such as activated carbon, C-18,¹⁸ silica gel,²⁵ microcrystalline naphthalene,^{22,26} and Amberlite XAD resins have been used. Among them, Amberlite XAD resins were found to be promising neutral media for designing chelating resins because of their useful physical and chemical properties and their effective preconcentration applications to trace metal ions.^{16,17,20,23,27} UV-Vis spectrophotometry based on the use of complex-forming reagents is selective, simple, rapid, versatile, and also a more economical technique as compared with AAS, HPLC, and ICP-MS protocols for the determination of heavy metals.²⁸ The strong metal-binding property of dithiocarbamates (DTCs) produces intensely colored complexes with certain metal ions.^{6,23,29,30} Metal DTC complexes are usually measured by UV-Vis spectrophotometry for determination of DTCs that have strong absorbance in the UV region after solvent extraction with nonpolar organic solvents.^{19,30} However, solvent extraction techniques are time-consuming and demanding, and they usually involve harmful substances.

Thus, ionic as well as nonionic surfactants have been used to replace the solvent extraction process in spectrophotometric determinations because these compounds are stable in aqueous solutions and optically transparent.^{24,31-36} The water-insoluble complexes are stabilized by surfactant systems, and the size of micelles allows equilibrium to be attained quickly with a change in pH, producing the most stable surfactant media complexes of metal ions with the complexing agent.

In this study, XAD-4-(SCHD) resin was used as an adsorbent for enrichment and separation of Cu(II) and Ni(II) ions by SPE under optimal conditions. Accordingly, a spectrophotometric method for the determination of the ions using dimethyl morpholine dithiocarbamate (DMMDTC) in a surfactant medium (Triton X-100) was established and proposed as a SPE-UV-Vis spectrophotometric method aimed at developing a rapid, accurate, and low-cost analytical method at the submilligram per liter level.

2. Results and discussion

2.1. Application of the preconcentration procedure

XAD-4 was functionalized with N,N'-bis-(salicylidene) cyclohexanediamine (SCHD) resin and used in the column mode to preconcentrate and separate trace Cu(II) and Ni(II) from environmental water samples. The sample solution containing 15 μg of Cu(II) and Ni(II) was poured into the XAD-4-SCHD column for adsorption, and then the metal ions were recovered with an elution solution for desorption under optimal conditions. Table

1 shows the optimal adsorption and elution values for both Cu(II) and Ni(II) as follows: pH 4; sample flow rate 2 mL/min; eluent concentration, type, and volume, 1 mol L⁻¹, HNO₃, and 5 mL; and eluent flow rate and volume, 3 mL/min and 5 mL, respectively.³⁷ The recoveries were constant up to 1000 mL of the sample solution. Specific application of this procedure has given approximately 100% adsorption and desorption results. Therefore, a maximum preconcentration factor of 125 was achieved with 1000 mL of sample and 8 mL final volume. The obtained factor improved the selectivity and the sensitivity of the proposed method: that factor had the highest value among the other factor values reported, such as in SPE studies.^{21,38}

Table 1. Identified optimal conditions for the solid phase extraction and preconcentration.

Parameter	Cu(II)	Ni(II)
pH	4	4
Type and concentration of eluent	1 M HNO ₃	1 M HNO ₃
Volume of eluent (mL)	5	5
Maximum volume of sample (mL)	1000	1000
Preconcentration factor	125	125
Flow rate of sample (mL min ⁻¹)	2	2
Flow rate of eluent (mL min ⁻¹)	3	3
Sorption halftimes (min)	10	5
Resin capacity (μg/g)	22.743	11.938

The effects of matrix ions for spectrophotometric determination on the recoveries of Cu(II) and Ni(II) on XAD-4-SCHD column were also investigated. An error of not more than ±5% was set as the allowable limit value in the absorbance for interfering ions that normally exist in water samples during the recovery of metal ions. There was no effect of the interfering ions on the recoveries of Cu(II) and Ni(II) within the allowable limit value in this study.

2.2. Spectrophotometric determination of the metal ions in micellar solution

To find a linear dynamic range of concentrations of Cu(II) and Ni(II), one component calibration was performed for each metal ion. The pH of the elution solution was adjusted to the range of 3 to 7 by addition of 1 M NH₃ and 1 M HCl solutions. Then 0.5 mL of 0.01% potassium 2,6-dimethyl-morpholine dithiocarbamate (KDMMDTC) and 2.0 mL of 1% Triton X-100 solutions were added to the pH-adjusted elution solution and diluted to the mark with distilled water in a 10.0-mL volumetric flask; 8 min of holding was allowed for completion of the complexation reaction that formed Cu(DMMDTC)₂ and Ni(DMMDTC)₂ complexes. The absorption spectra of the complex ions at 25 °C were recorded for the KDMMDTC and Triton X-100 blank solution at 460 (Cu(DMMDTC)₂) and 328 nm (Ni(DMMDTC)₂).

The proposed UV-VIS spectrophotometry method combined with SPE was successfully developed for simultaneous determination of Cu(II) and Ni(II) in environmental water samples; the results were compared with those from ICP-MS.

In the proposed method, the molar absorptivities of the Cu(DMMDTC)₂ and Ni(DMMDTC)₂ complexes were determined in the presence and absence of the nonionic Triton X-100 surfactant. The molar absorptivities were almost two times higher than the value observed without Triton X-100, resulting in an increase in the sensitivity of the method: it is based on the color reactions of Cu(II) and Ni(II) with the 2,6-dimethyl-morpholine dithiocarbamate (DMMDTC) reagent that reacts to form 1:2 brown- and green-colored complexes in Triton X-100 medium.

Cu(II) and Ni(II) ions react with DMMDTC at pH 3–7 to liberate the $\text{Cu}(\text{DMMDTC})_2$ and $\text{Ni}(\text{DMMDTC})_2$ complexes; these were measured at the maximum absorbance wavelengths of 460 and 328 nm, respectively. This method has been shown to have an increased metallic selectivity and low concentration sensitivity with SPE, reaching a high preconcentration factor compared with some common spectrophotometric methods as reported for the determination of trace Cu(II) and Ni(II) ions.

2.3. Determination of the absorption spectra

The absorption spectra of $\text{Cu}(\text{DMMDTC})_2$ and $\text{Ni}(\text{DMMDTC})_2$ complexes in the presence of Triton X-100 were obtained against the KDMMDTC and Triton X-100 blank solution (Figure 1). The spectra of the Cu(II) and Ni(II) complexes have absorbance maxima at 460 and 328 nm. The blank solution of KDMMDTC with Triton X-100 produced a maximum absorption peak at 204 nm, but no absorption peak was observed at either 328 or 460 nm. The molar absorptivities of the complexes calculated from the absorbance data were $1.18 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $2.9 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 460 and 328 nm, respectively.

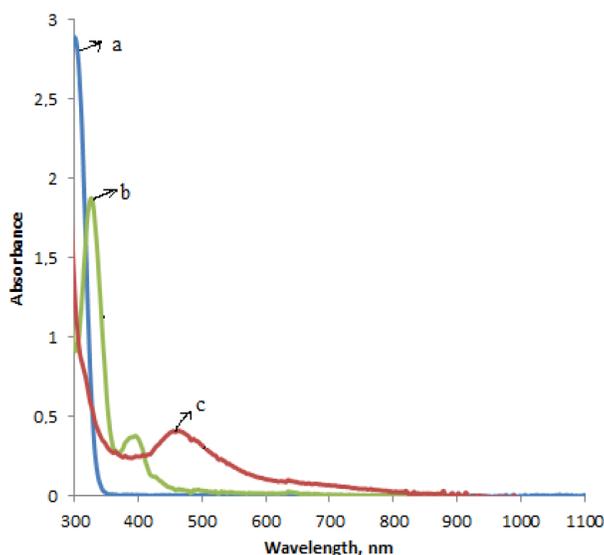


Figure 1. Absorption spectra of (a) DMMDTC solution vs. against water blank, (b) nickel(II)-DMMDTC vs. reagent blank, and (c) copper(II)-DMMDTC vs. reagent blank. Conditions: $[\text{Ni}(\text{II})] = 3.4 \times 10^{-5} \text{ M}$, $[\text{DMMDTC}] = 5 \times 10^{-4} \text{ M}$, $[\text{Cu}(\text{II})] = 3.15 \times 10^{-5} \text{ M}$; pH 5; 1% (v/v) Triton X-100.

2.4. The effect of pH on the absorbance of the $\text{Cu}(\text{DMMDTC})_2$ and $\text{Ni}(\text{DMMDTC})_2$ complexes

The effect of pH on the absorbance of $\text{Cu}(\text{DMMDTC})_2$ and $\text{Ni}(\text{DMMDTC})_2$ in 1% (v/v) Triton X-100 and 0.01% (w/v) DMMDTC was investigated. The results showed that the $\text{Cu}(\text{DMMDTC})_2$ and $\text{Ni}(\text{DMMDTC})_2$ complexes are perfectly formed in the pH range of 3.0–8.0 (Figure 2); therefore, pH 5 was chosen for the further complexing experiments.

2.5. The effect of the surfactants

Many surfactants are offered for scientific use. However, anionic or nonionic surfactants have been used more frequently than cationic surfactants to determine metal ions by UV-Vis spectrophotometry. The surfactant may play the role of a stabilizer and frequently shifts the absorption peak of metal–dye complexes to longer

wavelengths³³. The shift is usually accompanied by an increase in both the molar absorptivity and sensitivity of the UV-Vis method. The complex of the examined metal ion is homogeneously dissolved in surfactant media because the concentration of the surfactant is somewhat less than the micelle concentration.

The various surfactants of nonionic polyoxyethylene dodecyl ether (Brij-35) and Triton X-100, cationic cetyltrimethylammonium bromide (CTAB), and anionic (sodium dodecyl sulfate (SDS) were studied, and among those Triton X-100 was found to be the best surfactant for the complexing systems. The maximum absorbance was observed with 1% Triton X-100 medium. Accordingly, different volumes of 1% Triton X-100 were added to fixed metal ion concentrations, and the absorbances were measured using the standard procedure. At 3 mg L⁻¹ Cu(DMMDTC)₂ and Ni(DMMDTC)₂, complexes were uniquely formed in 1 to 5 mL of 1% Triton X-100 (Figure 3). A solution of 2 mL of 1% Triton X-100 was used for all subsequent absorbance measurements.

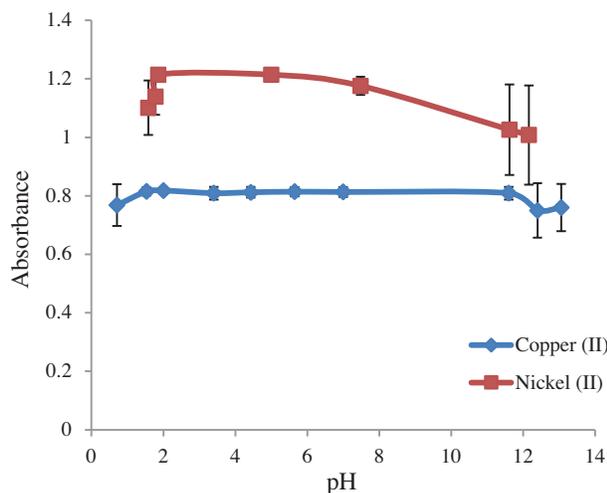


Figure 2. The effect of pH on the absorption of complexes after solid phase extraction. Absorption solution concentrations: 5×10^{-4} M DMMDTC; 2.36×10^{-5} M Cu(II) at 460 nm; 2.55×10^{-5} M Ni(II) in Triton X-100 media at 328 nm.

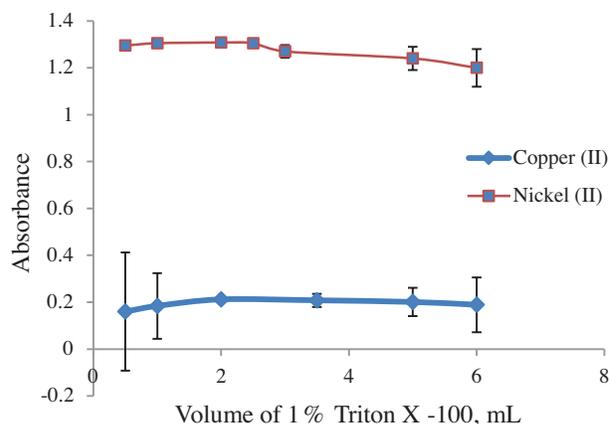


Figure 3. Effect of volume of 1% Triton X-100. The absorption solution concentrations and at pH 5; 5×10^{-4} M DMMDTC; 2.36×10^{-5} M Cu(II), and 2.55×10^{-5} M Ni(II).

2.6. The effect of amount of DMMDTC

An excess of the chelating agent was added to the sample solution for the quantitative formation of the metal complexes. Figure 4 shows the absorbance change of Cu(DMMDTC)₂ and Ni(DMMDTC)₂ complexes with the amount of DMMDTC in 1% (v/v) Triton X-100 in a medium with pH 5; thus, an optimal volume of 0.5 mL of 5×10^{-4} M was used for maximum absorbance readings in the further studies.

2.7. Rate of the stoichiometry and color reaction stability of the complexes

The metal-to-ligand ratio in the complex is 1:2 (M:L), as stated in Job's method. The temporal stability of the Cu(DMMDTC)₂ and Ni(DMMDTC)₂ was investigated at pH 5 in the presence of Triton X-100. Under optimal conditions, the formation of the colored complexes of Cu(II) and Ni(II) with DMMDTC was completed in 5 min. The absorption spectrum was monitored for possible changes, and the readings were recorded as virtually constant for at least 2 h.

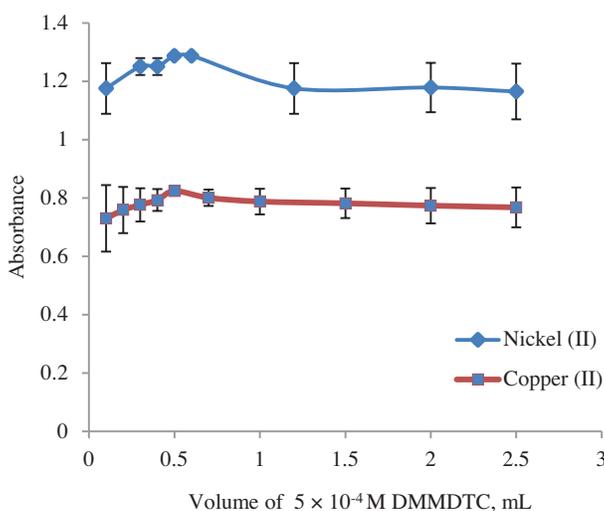


Figure 4. Effect of volume of 5×10^{-4} M DMMDTC. Conditions: in Triton X-100 medium; 2.36×10^{-5} M Cu(II), 2.55×10^{-5} M Ni(II) at pH 5.

2.8. Calibration, sensitivity, and precision

The calibration graphs for the determination of the Cu(II) and Ni(II) ions were prepared using the data obtained from the experiments conducted by the proposed method. The limits of detection and quantification of the proposed method were calculated depending on the concentration corresponding to 3 times and 10 times the standard deviation of blank signals ($N = 20$). The detection limits of the Cu(II) and Ni(II) ions were found to be 5 and 7 $\mu\text{g L}^{-1}$, respectively. Sandell's sensitivity was calculated as 1.47 and 0.6 $\mu\text{g/cm}^2$ for Cu(II) and Ni(II), respectively.

The relative standard deviations for the Cu(II) and Ni(II) ions were found to be 3.8% and 3.3% ($N = 6$) at 15 μg of Cu(II) and Ni(II), providing results that confirm the precision of the proposed method.

2.9. Applicability of the method

The method was initially tested by analyzing TMDA-70.2 certified reference material and the synthetic mixture of Cu(II) and Ni(II); the data are shown in Table 2. The results showed good agreement with the certified and added values for the investigated Cu(II) and Ni(II) ions, which confirms that the proposed method is reliable and accurate for the determination of the metal ions in environmental water samples.

Table 2. Determination of Cu(II) and Ni(II) in a certified reference material and synthetic water sample.

Sample	Certified /added value (mg L^{-1})		Amount found ^a (mg L^{-1})		Recovery \pm s ^b (%)	
	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)
Certified water sample TMDA-70.2	0.409 ± 0.032	0.333 ± 0.022	0.372 ± 0.08	0.365 ± 0.11	90.9 ± 0.8	109.6 ± 1.8
Synthetic sample	1	1	1.10 ± 0.22	0.985 ± 0.05	110 ± 1.2	98.5 ± 0.4

^a Mean of five experiments at 95% confidence level ($x \pm ts / \sqrt{N}$).

^b The measure of precision is the standard deviation (SD).

Furthermore, to evaluate the applicability of the proposed method, the spiked samples of dam, sea, and waste water were analyzed, with recoveries according to the method. The evaluation data are shown in Table

3; these data confirm a significant applicability greater than 90% in recoveries for the determination of Cu(II) and Ni(II) in the water samples using the proposed method.

Table 3. Investigation of Cu(II) and Ni(II) recoveries in the spiked samples.

Element	Gölköy Dam water			Sea water			Waste water		
	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	% Recovery	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	% Recovery	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery $\pm s^b$ (%)
Cu(II)	-	ND	-	-	ND	-	-	600 \pm 0.003	-
	25	22.75 \pm 0.02	91.0	25	22.8 \pm 0.02	91.2	100	695.7 \pm 0.032	95.7 \pm 1.5
Ni(II)	-	0.575 \pm 0.1	-	-	13.1 \pm 0.15	-	-	510 \pm 0.003	-
	25	25.97 \pm 0.12	101.6	25	38.7 \pm 0.11	102.4	100	614.6 \pm 0.048	104.6 \pm 1.1

Sample volume: 200–1000 mL, final volume: 8 mL.

Standard deviation based on three repeated analyses. ND: Not detected.

^bThe measure of precision is the standard deviation (SD).

The other water samples were then analyzed to compare the proposed spectrophotometric method with the ICP-MS method; the results shown in Table 4 confirm excellent agreement between the two methods. Related analytical results show that the Gölköy Lake water samples likely provided the lowest differences between the proposed and ICP-MS methods. The accuracy was verified by the Student t-test. With a calculated Student t-test value of less than the theoretical value (3.18, N = 4) at a confidence level of 95% (P = 0.05), excellent agreement between the spectrophotometric and ICP-MS methods was found.

Table 4. Analytical results for the determination of trace Cu(II) and Ni(II) in environmental water samples with the proposed and ICP-MS methods.

Sample	ICP-MS method ($\mu\text{g/L}$)		Proposed method ($\mu\text{g/L}$)		Student t-test/(3.18) ^b	
	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)
Gölköy Lake water	1.58 \pm 0.0143	3.73 \pm 0.903	1.52 \pm 0.58	4.33 \pm 1.27	0.69	0.5
Mudurnu Creek	0.87 \pm 0.074	4.40 \pm 0.807	0.79 \pm 0.82	3.68 \pm 1.44	2.13	3.05
Left main canal	1.76 \pm 0.055	9.08 \pm 1.00	1.32 \pm 0.53	11.11 \pm 1.53	0.64	1.82
Waste water	110.9 \pm 16.32	883.33 \pm 25.5	117.28 \pm 8.85	920.58 \pm 18.52	1.11	3.5

^bTheoretical value for t-values for three degrees of freedom and 95% confidence limits is 3.18.

DMMDTC is used as a color reagent to obtain a brown color from Cu(DMMDTC)₂ and green color from Ni(DMMDTC)₂ at a specific pH, allowing the complexes to be analyzed suitably by UV-VIS spectrophotometer.

The comparisons of the presented procedure with the previous literature are given in Table 5. Beer's molar absorptivity was found to be higher in the present study than for previous results using UV-Vis spectrophotometric studies.

The present method promises an environmentally friendly process due to using reagents and solutions that are water-soluble, nontoxic organic solutions. When compared to AAS or ICP-based techniques, the present method provides inexpensive and suitable features such as simplicity and rapidity in application. The high stability of XAD-4-(SCHD) resin has made numerous adsorption–elution studies possible that present no substantial decrease in recovery of Cu(II) and Ni(II); the resin has consecutively shown superior chemical stability, excellent regeneration, and reusability. The SPE techniques used have ensured a highly selective removal of trace amounts of the metal ions from water matrices by overcoming the interference effect, and also to achieve an accurate and high-yield preconcentration factor of analyte ions. The preconcentrated Cu(II) and Ni(II) ion complexes reached a maximum absorption peak at 460 and 328 nm, respectively. These color reactions

Table 5. Comparison of characteristic features of reported reagents with proposed reagent for the spectrophotometric determination of copper(II) and nickel(II).

Reagent	Studied metals	Medium	λ_{\max} , nm	Beer's absorptivity, law range, $\mu\text{g mL}^{-1}$	Beer's molar absorptivity $\epsilon \times 10^4$, $\text{L mol}^{-1} \text{cm}^{-1}$	M:L	Reference
2-Amino-cyclopentene-1-dithiocarboxylic acid	Ni(II) and Co(II)	pH 5, Triton X-114	534 and 452	0.02–0.5 and 0.02–0.2		-	3
Benzyl dioxime	Ni(II)	pH 12, SDS	562	0.1–25.0	6.86	-	34
Cefixime	Cu(II)	1,4-Dioxan-distilled water	336	1.015–8.122	0.829	1:1	40
N-Ethyl-3-carbazolecarboxaldehyd-3-thiosemicarbazone	Cu(II)	pH 3.0, n-butanol	380	0.2–5.6	2.243		41
Pyridoxal-4-phenyl-3-thiosemicarbazone	Cu(II)	pH 3.0–5.5, n-butanol	440	0.2–5.0	2.16	1:1	42
2,6-Dimethylmorpholine dithiocarbamate (DMMDTC)	Cu(II) and Ni(II)	pH 5, Triton X-100	460 and 328	0.02–3 and 0.02–2.5	11.8 and 29	1:2	This study

in different wavelengths have been used advantageously for the simultaneous spectrophotometric determination of Cu(II) and Ni(II) in environmental water samples. Beer's molar absorptivity was found to be high for UV-Vis spectrophotometric analyses.

3. Experimental

3.1. Reagents and standards

Analytical reagent-grade 1000 mg L⁻¹ stock standard solutions of Cu(II) and Ni(II) and water-soluble, non-toxic Triton X-100 were supplied by Merck (Darmstadt, Germany). Working solutions used in the experiments were prepared by appropriate dilution of the stock solutions with deionized water. The required pH adjustments of the samples were made by 0.5 mol L⁻¹ ammonia or 0.5 mol L⁻¹ hydrochloric acid solutions. The CH₃COOH/CH₃COONa buffer was prepared by adding an appropriate amount of acetic acid to sodium acetate solutions (Merck) to get pH levels in the 4–6 range; these buffers were used to adjust the pH of the solutions to 5.0. The water standard reference material TMDA-70.2 (Environment Canada) from the environmental matrix reference material was employed to test the proposed method. A synthetic sample mixture containing water matrices was prepared artificially by mixing diverse ions (Merck) of 2 mg per ion of Na⁺, K⁺, Ag⁺, Ca²⁺, Zn²⁺, Cr³⁺, Mn²⁺, Pb²⁺, Cd²⁺, SO₄²⁻, PO₄³⁻, NO₂⁻, CO₃²⁻, F⁻, and Cl⁻ in 0.05 L of synthetic sample.

3.2. Source and preparation of water samples

Real water samples were received from different environments of the Bolu region: industrial waste water, Gölköy Dam water, Gölköy Lake water, Mudurnu Creek, main irrigation canal water, leakage water from the municipal solid waste storing area, and the İzmit shore of the Sea of Marmara. Cu (II) and Ni(II) ions (25 $\mu\text{g/L}$) were added to some of the environmental water samples for preparation of spiked samples for recovery investigations.

For determination of Cu(II) and Ni(II) ions in environmental water samples, a 1000-mL aliquot of the water sample was passed through a 0.45- μm pore cellulose acetate membrane filter (Merck Millipore, mixed cellulose ester gridded) to remove any particles in the sample solution.

3.3. Preparation of XAD-4-SCHD

Amberlite XAD-4 resin was modified with N,N-bis-(salicylidene) cyclohexanediamine (SCHD) as stated in a previous study³⁷ to produce XAD-4-SCHD, which can be used in the column mode as the solid phase in a wide range of pH levels, flow rates, and times for adsorption studies of Cu(II) and Ni(II).

3.4. Synthesis of potassium 2,6-dimethyl-morpholine dithiocarbamate ligand

Potassium 2,6-dimethyl-morpholine dithiocarbamate (KDMMDTC), a novel analytical-class ligand, was synthesized according to the general procedure for dithiocarbamate synthesis^{39,43,44}. Accordingly, 0.1 mol stoichiometric amounts of diethyl ether 2,6-dimethyl-morpholine (Merck), KOH, and carbon disulfide were dissolved in 400 mL of deionized water and mixed, then refluxed for 2 h at 0 °C. The organic phase was separated and the water phase was evaporated. The material remaining in the water was washed with diethyl ether, dried at 90 °C, and then characterized by FT-IR. The spectrum of KDMMDTC showed bands at 1434, 1159, and 1085 cm^{-1} representing $\nu(\text{C-N})$, $\nu(\text{C-O})$, and $\nu(\text{C=S})$, respectively. The FT-IR spectrum and molecular structure of the synthesized KDMMDTC of the ligand are shown in Figures 5 and 6. Elemental composition of synthesized KDMMDTC was determined as the percentages of C (36.60; 36.40), H (5.27; 4.97), and N (6.11; 5.71). In addition, the ¹H NMR spectrum of the synthesized compound obtained from DMSO-*d*₆ gave -CH₂, 6.0–6.02 ppm (4H, doublet peak); -CH, 2.2–2.5 ppm (2H, multiplet peak); and -CH₃, 1.0–1.1 ppm (6H, doublet peak), which confirmed the structure. The KDMMDTC solution was prepared by dissolving 0.0126 g of the reagent in 100 mL (5×10^{-4} M) of water for the spectrophotometric analysis.

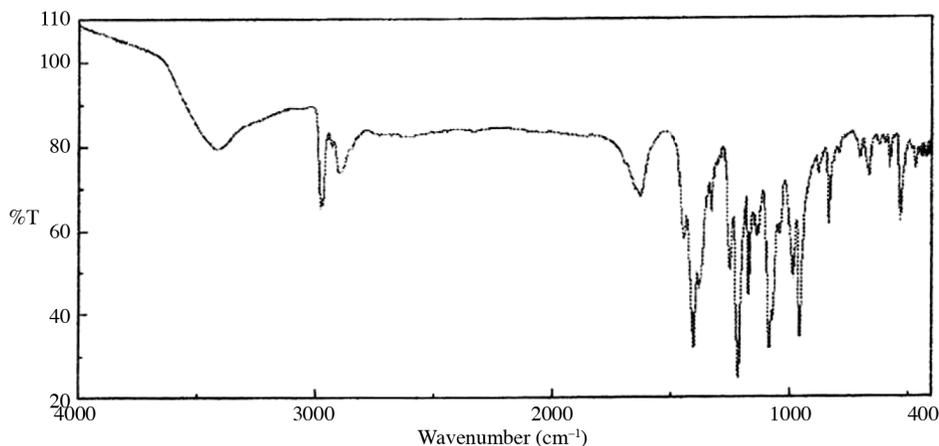


Figure 5. FT-IR spectrum of potassium 2,6-dimethyl-morpholine dithiocarbamate (KDMMDTC).

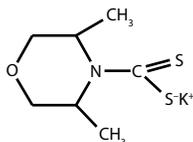


Figure 6. Structure of potassium 2,6-dimethyl-morpholine dithiocarbamate (KDMMDTC).

3.5. SPE column preparation

The bottom of a 10-cm-long SPE column with inner diameter of 1.0 cm was plugged with a piece of clean glass wool and filled with 0.2 g of 24-h water-swollen XAD-4-SCHD resin; the top of the resin was then plugged again with the glass wool. The column was treated with 0.5 M HNO₃ and HCl (50 mL) and double-washed with distilled water until all remaining acid components were removed.

3.6. Instrumental analysis

A Merck Pharo-300 UV-VIS spectrophotometer with a 1.0-cm quartz cell was used for absorbance measurements at the fixed wavelength. A PerkinElmer-SCIEX ELAN DRCe ICP-MS was used to compare the experimental results, and an ISOLab pH meter was used for pH measurements. A flow-rate-adjustable lead fluid BT/101S model peristaltic pump was employed to pump the fluid into the vertically positioned resin column.

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