Scientific Research

Spectrophotometric Complexation Studies of Some Transition and Heavy Metals with a New Pyridine Derivative Ligand and Application of It for Solid Phase Extraction of Ultratrace Copper and Determination by Flame Atomic Absorption Spectrometry

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ABSTRACT

A new pyridine derivative ligand, (E)-(Pyridine-2-ylmethylidene) ({2-(E)-(Pyridine-2-ylmethylidene) amino] ethyl} has been synthesized and k_f value of it's complexes with Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Hg^{2+} and Ag^+ has been determined spectrophometrically. The stability of the complexes to vary in acetonitrile solvent was in the order of $Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Hg^{2+} > Ag^+$, thus because this ligand have good selectivity to copper ion, a simple, reliable and rapid method for preconcentration and determination of the ultratrace amount of copper using octadecyl silica membrane disk modified by this ligand, and determination by flame atomic absorption has been presented. Various parameters including pH of aqueous solution, flow rates, the amount of ligand and the type of stripping reagent were optimized. Under optimum experimental conditions, the breakthrough volume is greater than 2000 ml with an enrichment factor of more than 400 and 0.054 $\mu g \cdot L^{-1}$ detection limit. The capacity of the membrane disks modified by 6 mg of the ligand has been found to be 330.17 g of copper. The effects of various cationic interferences on the percent recovery of copper ion were studied. The method has been successfully applied for the determination of copper ion in different water samples.

**Keywords:** Copper; SPE; C18; Oyridine; FAAS; Spectrophotometry; Formation Constant

1. Introduction

The coordination chemistry of pyridine, bipyridine (bipy), terpyridine (terpy), phenantroline (phen), naphthyridine (naphthy) and pyridine-pyridazine (pyridaz) have received more and more attention since the late 19th century [1-3]. Coordination chemistry of these ligands with different metal to ligand ratio results in different geometries, such as tetrahedral [4], squar plannar, pentagonal bipyramidal [5], or octahedral [6,7]. These organic ligands containing unsaturated nitrogen atoms can be regarded as soft Lewis bases [8].

As such compounds may reveal high tendency for stable coordination complexes with numerous transition metal ions, particularly those that can be regarded as soft Lewis acids such as Cu 1) and Cu 2). The polyimine ligands (**Figure 1**) were chosen as suitable building blocks for these complexation reaction. These compounds are flexibile about the central C-C bond. Each of these ligands contains four potential sites for coordina-

tion to metal ions, the peripheral pyridyl-N as well as the inner imino N-atoms. In this work we focus on a series of new 2,2'-bipyridyle-type organic ligands with added matal coordination functionality along the molecular backbone. The complexation process has been monitored by UV/Vis absorption spectroscopy.

Among the chemical species copper has a biological action at low doses and a toxic effect when ingested in larger quantities. A concentration more than 1 $\mu g \cdot mL^{-1}$ of copper can impart a bitter taste to water. Large oral doses can cause vomiting and may eventually cause liver damage. Copper concentration in potable water is usually very low (20 $\mu g \cdot L^{-1}$) [9]. Determination of copper isusually carried out by flame [10-12] and graphite [13,14] atomic absorption spectrometry, as well as spectrophotometry
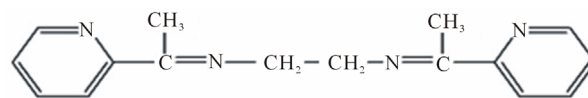
Figure 1. Chemical structure of BPYMH.

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[15,16], chemiluminescence [17] and electrothermal methods [18,19]. However, due to presence of copper in low levels in environmental samples and the matrix effects, different separation and preconcentration techniques such as liquid-liquid extraction [20], precipitation [21], ion exchange [22], solid phase extraction [23,24] and membrane filtration [25] improve the analytical detection limit, increase the sensitivity by several orders of magnitude, enhance the accuracy of the results and facilitate the calibration. Among these techniques, solid phase extraction is preferred by many researchers on account of the fast, simple and higher preconcentration factor, rapid phase separation, time and cost saving [26,27]. A number of supports have been widely used for the preconcentration and separation of trace metal ions from various matrices. Among the absorbents, silica with chemically bonded alkyl chains such as octadecyl bonded silica (C18), modified by suitable ligands has been an excellent used extractor of metal ions [28-32]. In this work a newly synthesized ligand, ((E)-(Pyridine-2-yl-methylidene) ({2-(E)-(Pyridine-2-ylmethylidene) amino] ethyl}) (BPYMH) (**Figure 1**), is studied as a disk modifier for Cu 2) ion. Also, we report on extraction and preconcentration of copper 2) from water samples and determination by atomic absorption spectrometry.

2. Experimental

2.1. Instruments

All UV-Vis Spectra recorded on a computerized double-beam 2550 Shimadzu spectrophotometer, using two matched 10 mm quartz cell. In a typical experiment, 2.0 ml of ligand solution (5.0×10^{-5} mol·L^{-1}) in acetonitrile was placed in the spectrophotometer cell and the absorbance of solution was measured. Then a known amount of the concentrated solution of metal ions in acetonitrile (1.3×10^{-3} mol·L^{-1}) was added in a stepwise manner using an l0 μl Hamilton syringe. The absorbance of the solution was measured after each addition. The metallic ions solution was continually added until the desired metal to ligand mole ratio was achieved.

The determinations of copper were performed on a GBC Sens AA flame atomic absorption spectrometer (air-acetylene flame) with Hollow Cathode Lamp (HCL) and equipped with a deuterium background corrector. The absorbance wavelength was set at 324.7 nm and the spectral bandwidth at 0.5 nm. A Metrohm 827 pH meter was used to measure pH values.

The modified C18 extraction disks were used in conjunction with a standard 47 mm filtration apparatus (Schleicher and Schüell, Dassel, Germany) connected to a vacuum.

2.2. Chemicals

Methanol, acetonitrile and other organic solvents were used spectroscopic grade from Merck. All mineral acids were of pro analysis from Merck. Analytical grade standard stock of copper 2), sodium hydroxide and nitrate or chloride salts of magnesium, zinc, cobalt, manganese, lead, nickel, cadmium, silver, mercury, sodium, potassium and calcium (all from Merck) were of the highest purity available. The new synthesized BPYMH ligand with the highest purity was used as a chelating ligand. Working standards were prepared by appropriate dilution of the stock solution with deionized water.

2.3. Estimation of Formation Constants

The formation constant (kf) and the molar absorptivity (ε) of the resulting 1:1 complexes between the BPYMH ligand and different metallic ions in acetonitrile at 25˚C were calculated by fitting the observed absorbance, Aobs, at various metallic ion/ligand mole ratios to the previously derived equations [33,34] (Equation (1)), which express the Aobs as a function of the free and complexed metal ions and the formation constant evaluated from a non-linear least-squares program KINFIT [35].

2.4. Sample Extraction

Extraction were performed with a 47 mm diameter × 0.5 mm thickness, Empore high performance extraction membrane disk containing octadecyl-bonded silica (8 μm particles, 6 nm pore size) from 3 M company. The disks were used in conjunction with a standard Scott Duran 47 mm filtration apparatus.

After placing the membrane in the filtration apparatus, it was washed with 10 ml methanol and then with 10 ml deionized water to remove all contaminations arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, a solution of 6 mg BPYMH ligand dissolved in 3 ml acetonitrile was introduced to the reservoir of the apparatus and was drawn slowly through the disk by applying a slight vacuum. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25 ml deionized water and dried by passing the air through it. The membrane disk modified by the BPYMH ligand was then ready for sample extraction. It is important to note that the surface of the disk was not left to become dry from the methanol was added until the extraction of Cu^{2+} ions from water were completed [36].

Then 100 ml of the sample solution containing 10 μg Cu^{2+} was passed through the membrane (flow rate = 5 ml/min). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted copper was stripped from the membrane disk using appropriate amounts of suitable eluent (the best eluent was 1 M nitric acid). This step was done with 5 ml eluent solution and the Cu^{2+} was determined with flame

atomic absorption spectrometer.

3. Result and Discussion

3.1. Spectrophotometric Studies

Spectrophotometric studies of complexation reaction between the BPYMH ligand and metallic ions in acetonitrile solution revealed that ligand can form stable 1:1 (metallic ion to ligand) complexes with different metallic ions.

The electronic absorption spectra of BPYMH ligand (5 × 10^{-5} mol·L^{-1}) in the presence and increasing con cen-tration of Cu^{2+} (1.3 × 10^{-3} M) ions were recorded (**Figure 2**) in acetonitrile at 25°C. The resulting complexe of Cu^{2+} with BPYMH ligand are distinguished by a little spectral shift toward longer wavelength.

The stoichiometry of the metal complexes was examined by the mole ratio method. Sample of the resulting plots for all M^{n+}-L complexes are shown in **Figure 3**, at 297 nm, and it is evident that 1:1 (metallic ion to ligand) complexes are formed in solution. The formation constants of the resulting 1:1 metallic ions to the BPYMH complexes were obtained at 25°C by absorbance measurements of solutions in which varying concentrations of metallic ions were added to fixed amounts (5.0 × 10^{-5} mol·L^{-1}) of ligand solution. All the resulting absorbance-mole ratio data were best fitted to Equation (1), which further supports the formation of ML in solution.

$$K_f[L]^2 + (1 + K_f C_M - K_f C_L)[L] - C_L = 0 \qquad (1)$$

For evaluation of the formation constants and molar absorptivity coefficients from absorbance vs. [M]/[L] mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the absorbance-mole ratio data is shown in **Figure 4**. All of the logK_f values evaluated from the computer fitting of the corresponding absorbance-mole ratio data at 25°C are
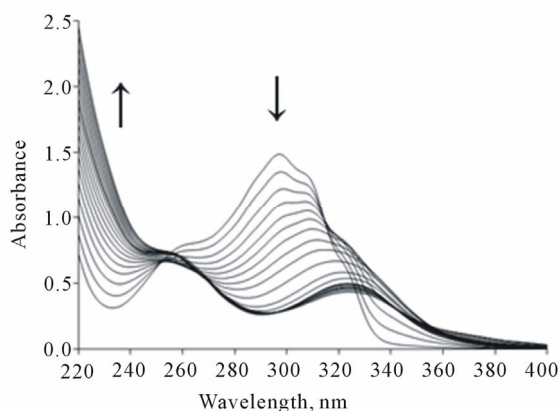
listed in **Table 1**. The data given in **Table 1** revealed that, at 25°C, the stabilities of the complexes varies in the order $Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Hg^{2+} > Ag^+$.

Thus, considering the observed stability, we decided to use ligand as a suitable modifier for the selective con-centration and extraction of Cu^{2+} ions on the octadecyl silica membrane disks. Some preliminary experiments were undertaken in order to investigate ligand retention of copper ions by the membrane disk in the presence of ligand, after the recommended washing, wetting and conditioning procedures were carried out. It was found that, the membrane disk modified by the BPYMH ligand is capable to retain Cu^{2+} ions in the sample solution quantitatively (the test solution used contained 10 μg copper in 100 ml water at pH 7.0).

3.2. Solid Phase Extraction

3.2.1. Choice of Eluent

In order to choose the most effective eluent for quantitative stripping of retained ions from the modified disk-after extraction of 10 μg Cu^{2+} from 100 ml sample (in the presence of 6 mg ligand), the ions were stripped with 5 ml of different inorganic solution and the resulting data are listed in **Table 2**.
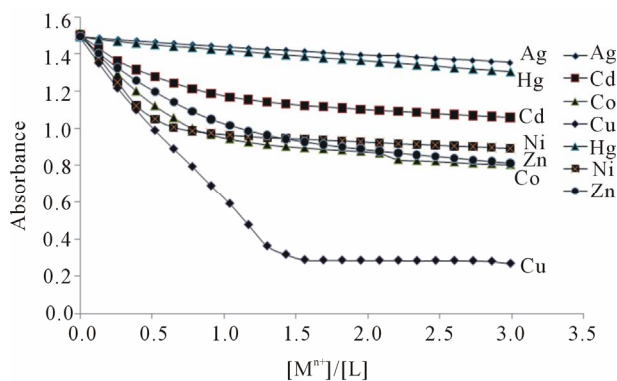
From the data given in **Table 2**, it is immediately obvious

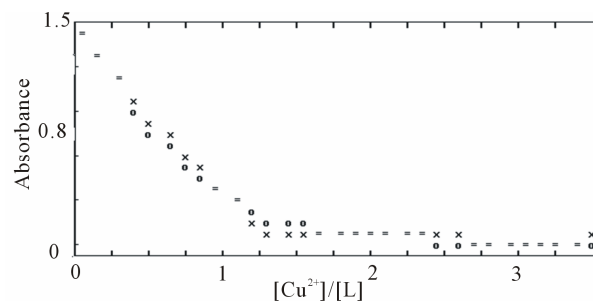**Figure 3. Mole ratio plots of absorbance as [M^{n+}]/[L] at 297.**

Figure 4. Computer fit of absorbance versus [Cu^{2+}]/[L] mole ratio plot in acetonitrile at 25°C, (×) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

Figure 2. The spectrum of ligand solution (5.00 × 10^{-5} M) in acetonitrile and increasing concentration of Cu^{2+} ion solu-tion (1.30 × 10^{-3} M).

that among the different solutions, 5 ml 1 M nitric acid can a accomplish the quantitative elution of copper from the membrane disk, while other solutions are ineffective for the complete elution of copper.

3.2.2. Effect of Ligand Amount

The optimum amount of the ligand for the membrane disks was studied. The results of the amount of ligand play an important role in obtaining quantitative recoveries of metal ions, because in its absence, the disk does not retain the metal ions. Therefore, the influence of the amount of ligand on recovery of the copper ion was examined in the range of 5 - 15 mg using 100 ml solution

Table 1. Formation constants of different ligand-M^{n+} complexes.

Metallic ion	$K_f \pm$ SD
Cu^{2+}	5.24 ± 0.02
Ni^{2+}	4.98 ± 0.01
Cd^{2+}	4.75 ± 0.01
Zn^{2+}	4.56 ± 0.01
Co^{2+}	3.91 ± 0.01
Hg^{2+}	2.95 ± 0.02
Ag^{+}	1.44 ± 0.02

Table 2. Percent recovery of copper from the modified membrane disk using 5 ml of different stripping solutions.

Stripping solution and it's concentration	% Recovery
HCl (0.05 M)	49.5
HCl (0.10 M)	76.5
HCl (0.50 M)	78.5
HCl (1.00 M)	82.0
HNO_3 (0.05 M)	84.5
HNO_3 (0.10 M)	96.5
HNO_3 (0.50 M)	98.5
HNO_3 (1.00 M)	99.6
H_2SO_4 (0.05 M)	41.5
H_2SO_4 (0.10 M)	55.0
H_2SO_4 (0.50 M)	72.0
H_2SO_4 (1.00 M)	54.0
EDTA (0.05 M)	50.5
EDTA (0.10 M)	61.0
EDTA (0.50 M)	74.0

containing 10 μg copper ions. The recoveries of copper ion reached to 100% with 6 mg of ligand (**Figure 5**). On this basis, in all studies were carried out with 6 mg of BPYMH ligand.

3.2.3. Effect of Flow Rate and pH

The effect of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of copper ion was investigated. It was found that, in the range of 5.0 - 20 ml·min^{-1}, the retention of copper by the membrane disk is not affected by the sample solution flow rate considerably. Similar results for extraction metal ions have already been reported [37]. In this work quantitative stripping of copper ion from the disk was achieved in a flow rate of 2.0 - 5 ml·min^{-1}, using 5 ml of 1 M Nitric acid.

Most chelating ligands are conjugate bases of weak acid groups and accordingly, have a very strong affinity for hydrogen ions. The pH therefore, will be a very important factor in the separation of metal ions by chelating, because it will determine the values of the conditional stability constants of the metal complexes on the surface of the sorbent [38]. In order to investigate the effect of pH on the SPE of copper ion, the pH of aqueous samples was varied from 2 - 9, using different buffers, and the recommended procedure was followed. As shown in **Figure 6** the Cu^{2+} ion can be retained quantitatively in the pH range of 7.0 - 8.0. For subsequent experiments, pH = 7 was chosen as a working pH. Higher pH values (>9) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

3.2.4. Analytical Performance
3.2.4.1. Sorption Capacity
The maximum capacity of the disk was determined by passing 50 ml portions of an aqueous solution containing 500 μg copper ion, through the modified disk with BPYMH ligand, followed by determination of the retained ions using FAAS. The maximum capacity of the disk was found to be 330.2 (±8.1) μg copper ion per 6 mg of ligand.

3.2.4.2. Breakthrough Volume
Since Breakthrough volume represents the sample volume that can be pre-concentrated without the loss of analyte during elution of the sample, the measurement of breakthrough volume is important in solid phase extraction. The breakthrough volume of the sample solution was tested by dissolving 10 μg of copper ion in 50, 100, 250, 500, 1000 and 2000 ml water and the recommended procedure was followed. In all cases, the extraction by modified disks was found to be quantitative. Thus, the breakthrough volume for the method should be greater than 2000 ml. Consequently, by considering the final
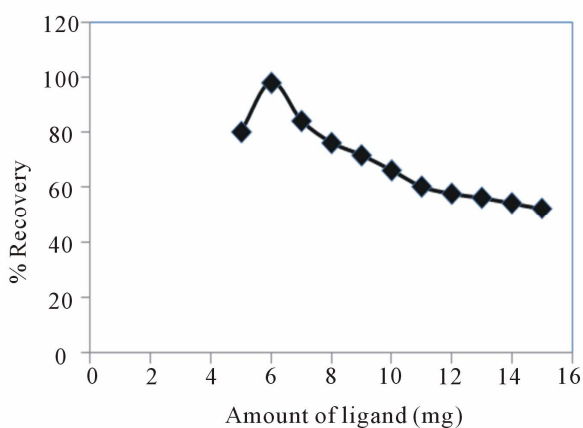
Figure 5. Effect of ligand amount on extraction recovery of copper ion.
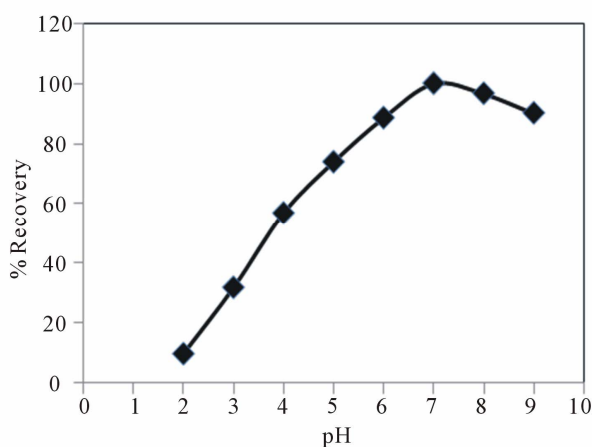
Figure 6. Effect of pH on copper(II) extraction. Copper(II) = 10 μg, aqueous phase volume = 100 ml.

elution volume of 5 ml and the sample solution volume of 2000 ml, an enrichment factor of around 400 was easily available.

3.2.4.3. Limit of Detection
The limit of detection (LOD), of the proposed method for the determination of copper ion was studied under the optimal experimental conditions. The LOD obtained from $CLOD = K_b S_b$ m^{-1} for a numerical factor $K_b = 3$ is 0.054 μg per 1000 ml.

3.2.4.4. Effect of Diverse Ions on Sorption of Copper
In order to investigate the selective separation and determination of Cu^{2+} ion from its binary mixtures with divers metal ions, a 100 ml aliquot solution containing 10 μg Cu^{2+} and milligram amounts of other cations was taken and the recommended procedure was followed. The results are summarized in **Table 3**. The results show that the copper ions in the binary mixtures are retained almost completely by the modified membrane disk.

3.2.4.5. Analysis of Artificial and Natural Water Samples
To test the applicability of the developed procedure, it was applied to the extraction and determination of copper ions from some water samples. Tap water of Abhar and Zanjan cities, two fountains in Tarom city and synthetic water samples were analyzed. The results for this study are presented in **Table 4**. The recovery of samples is satisfactory reasonable and was confirmed using addition method, which indicates the capability of the system in determination of ions. A good agreement was obtained between the added standards and measured analyte amounts. The recovery values calculated for the added standards were always higher than 90%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 3. Effect of divers ions on the recovery of 10 μg copper ion[1].

% Copper recovery	Amount taken, mg	Diverse ions
98.3	100	Na^+
98.8	100	K^+
Precipitated	20	Ca^{2+}
99.6	20	Mg^{2+}
97.2	1	Ni^{2+}
99.8	1	Co^{2+}
96.4	1	Zn^{2+}
98.6	1	Mn^{2+}
Precipitated	1.5	Pb^{2+}
98.5	20	Na^+, K^+, Mg^{2+}
99.1	0.5	$Ni^{2+}, Co^{2+}, Zn^{2+}$

[1]Initial samples contained 10 μg Cu^{2+} and different amounts of various ions in 100 ml water.

Table 4. Determination of copper ions in real water samples. Aqueous phase. 100 ml sample solution pH = 7 (with 0.01 M of phosphate buffer), amount of ligand = 6 mg, eluent = 5 ml (1 M HNO₃).

Copper recovery (μg·L^{-1})	Cu^{2+} added (μg)	Water samples
30.6	0	Fountain water 1
41.2	10	
61.2	0	Fountain water 2
70.8	10	
260.8	0	Tap water of Zanjan
272.8	10	
252.5	0	Tap water of Abhar
265.2	10	

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3.3. Conclusion

A simple, precise and accurate method was developed for selective separation, pre-concentration and determination of copper from various complex matrices. The time taken for the separation and analysis of copper in 100 ml sample is at the most 20 min. It can selectively separate Cu^{2+} ions from various metal ions even they are present at much higher concentrations. The method can be successfully applied to the separation and determination of copper in real samples.

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