



## Perconcentration and Determination of copper(II) by 1-(2-Pyridyl Azo)2-Naphtol(PAN) modified Octadecyl Silica

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### ABSTRACT

A simple and reproducible method for the rapid extraction and determination of trace amounts of copper(II) ions using modification of Sodium Dodecyl Sulfonate (SDS) coated for C<sub>18</sub> with and 1-(2-Pyridyl Azo)2-Naphtol(PAN) in order to prepare an effective sorbent for the preconcentration and Atomic Absorption Spectrometry is presented. The sorption capacity of 1-(2-Pyridyl Azo)2-Naphtol(PAN) -modified C<sub>18</sub> was 5.0 mg.g<sup>-1</sup> and the optimum pH for the quantitative recovery of copper was found as 5.0. The optimum flow rate, sorbent amount and sample volume were 1.5 mL.min<sup>-1</sup>, 300 mg and 50 mL, respectively. 5 mL of 4 mol.L<sup>-1</sup> HNO<sub>3</sub> was the most suitable eluent. The recommended method is simple and reliable for the determination of copper without any notable matrix effect and successfully applied to environmental water samples. The limit of detection of the proposed method is 45ng per mL. The method was applied to the extraction and recovery of Cu(II) in different water samples. In this method is relative standard deviation (R.S.D.) of 2%. The method was applied to the extraction and recovery of copper in different water samples.

**Key words:** Copper(II), Solid phase extraction, 1-(2-Pyridyl Azo) 2-Naphtol(PAN)-modified C<sub>18</sub>, Sodium Dodecyl Sulfonate (SDS), FAAS.

### INTRODUCTION

The determination of metal ions in natural samples such as waters, soils and biological fluids is very important part of environmental and public health studies. However, the direct determination of metal ions at trace level is limited due to their low level of concentration and matrix interferences. Flame atomic absorption spectrometry (FAAS) which has been continuously used for the determination of trace metal ions suffers from insufficient sensitivity for direct determination of metal ions in environmental samples. Therefore a

preconcentration or separation step is frequently necessary to improve the detection limit and sensitivity. For this purpose several separation and preconcentration procedures have been developed for trace metal ion determination involving different analytical strategies. These methods include ion exchange<sup>1</sup> liquid extraction<sup>2</sup>, anodic stripping voltammetry<sup>3</sup>, cloud point<sup>4</sup>, coprecipitation<sup>5</sup> and solid-phase extractions<sup>6-10,24</sup>. Among the various methods, solid-phase extraction has received more acceptances due to its simplicity, rapidity and attainability of large preconcentration factor.

A variety of solid materials such as modified ion exchange resins<sup>11-13</sup>, functionalized resins with chelating reagents<sup>14</sup>, activated carbon<sup>15</sup>, zeolites<sup>16</sup>, cellulose<sup>17</sup> and immobilized microorganisms on sepiolite<sup>18</sup> have been used for preconcentration of trace metals. Microcrystalline naphthalene<sup>19-21</sup> and benzophenone<sup>22</sup> have also been used as solid-phase for adsorptive extraction of metal ion complexes.

In this work a simultaneous solid-phase preconcentration method for the determination of copper, iron and copper by atomic absorption is described. Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes.

Cloud point extraction (CPE)<sup>26-31</sup>, homogeneous liquid-liquid extraction (HLLE)<sup>32,33</sup> and single drop microextraction (SDME)<sup>34-38</sup> are fairly new methods of sample preparation which are used in separation and preconcentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous researches, we demonstrated a novel microextraction technique,

named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs), organophosphorus pesticides (OPPs) and chlorobenzenes in water samples<sup>39-41</sup>. DLLME is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of analytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

DLLME is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GF AAS is used. The applicability of the approach has been demonstrated for the determination of copper in water samples. This element was selected for evaluation of the procedure because copper is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations<sup>42,43</sup>.

In our knowledge, SPE and preconcentration by Cu(II)-imprinted diazoaminobenzene-vinylpyridine copolymer packed-bed columns have not been employed for the separation and preconcentration of Cu(II) from aqueous solution. This paper reports the synthesis of Cu(II) imprinted and non-imprinted copolymers by copolymerizing copper chloride (or without it),

diazoaminobenzene (DAAB) and vinylpyridine (VP) using ethyleneglycol dimethacrylate (EGDMA) as cross-linker in presence of 2,2'-azobisisobutyronitrile as initiator and its analytical applications for column preconcentrative separation of Cu(II) from natural water.

This work preconcentration of Cu<sup>2+</sup> based on the adsorption of its 1-(2-Pyridyl Azo)2-Naphtol(PAN) complex on an Sodium Dodecyl Sulfonate (SDS) C<sub>18</sub>. The adsorbed complex could be eluted using environmentally and the concentration of Cu<sup>2+</sup> was determined by FAAS. The influence of various experimental parameters such as acidity, sample volume, flow rate, diverse ions, etc. was examined in detail. The validity of the proposed method was tested in tap water samples and waste water.

## EXPERIMENTAL

### Instrumentation

Determination of Cu<sup>2+</sup> contents in working samples were carried out by a PG-990 flame atomic absorption spectrometer equipped with a high intensity hollow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in( Table 3). The pH measurements were carried out by an pH meter (sartorius model PB-11).

### Chemicals and reagents

1-(2-Pyridyl Azo)2-Naphtol(PAN) and Sodium Dodecyl Sulfonate (SDS) was of analytical grade from E. Merck, D-6100 Darmstadt, F.R. Germany. The solutions were prepared using analytical grade reagents. Triple distilled and deionized water was used for the preparation of solutions. A stock solution of 1000 µg mL<sup>-1</sup> Cu(II) was prepared by dissolving 0.160 g of Copper(II) nitrate (Qualigens Fine Chemicals, Mumbai, India) in 100 mL water. A working solution of 10 µg mL<sup>-1</sup> was prepared by suitable dilution. About 0.01 g of 1-(2-Pyridyl Azo)2-Naphtol(PAN) was dissolved in minimum amount of HNO<sub>3</sub> 4M of deionized water. Neutral C18 (Himedia Research Laboratories, Mumbai, India) of particle size 150 mesh was used as the adsorbent. Sulfuric acid (Qualigens Fine Chemicals, Mumbai, India) of concentration 1 mol L<sup>-1</sup> was prepared by diluting

55.5 mL of concentrated sulfuric acid with 1 L of deionized water. Water samples (Pilani, India) were collected, acidified and stored in polythene bottles.

### Preparation of C<sub>18</sub> cartridge

A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of Copper(II). About 5 g of SDS coated for C<sub>18</sub> cartridge was mixed with 25 mL of HCl 1M to form slurry and then loaded on to the column. Cotton was placed at the bottom for allowing SDS coated for C<sub>18</sub> cartridge to settle properly. The column was packed up to a height of 3 cm.

### Procedure for preconcentration

A 50 mg SDS and 30 mg 1-(2-Pyridyl Azo)2-Naphtol(PAN) of 50 mL was loaded on to the column of neutral C18 cartridge maintaining a flow rate of 5 mL min<sup>-1</sup>. Then 250 mL volume of 10 µg Cu(II) solution was loaded on to the column. The sample solution was loaded on to the column of neutral SDS coated for C<sub>18</sub> cartridge maintaining a flow rate of 0.5 mL min<sup>-1</sup>. The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was eluted using 10 mL of HNO<sub>3</sub> 4M at a flow rate of 0.5 mL min<sup>-1</sup> and the concentration of Copper(II) was determined by FAAS.

## RESULTS AND DISCUSSION

### Effect of acidity

The effect of acidity plays a significant role in the preconcentration studies. The volume of 0.5 mol L<sup>-1</sup> sulfuric acid was varied from 1 to 6 mL in 100 mL sample volume. Quantitative recovery (>97%) was obtained in the range 3.5–6.0 mL of 0.5 mol L<sup>-1</sup> sulfuric acid. Beyond 6 mL, there was no change in the recovery of Copper(II).

### Choice of the eluent

A variety of reagents were tested in order to elute the adsorbed complex from the column. In order to choose the most effective eluent for the quantitative recovery of Copper(II), methanol, ethanol, acetone, HCl 1M, HCl 3M, H<sub>3</sub>PO<sub>4</sub> 1M, and Acidified methanol (Acidified solvents obtained by addition of HNO<sub>3</sub> 4M), were studied. The adsorption studies were carried out maintaining an overall Cu(II) concentration of 10 µg in 100 mL sample

volume. The recovery of Copper(II) was found to be quantitative with ethanol and  $\text{HNO}_3$  4M as eluting agents. However,  $\text{HNO}_3$  4M was preferred owing to its non-inflammability and less toxicity<sup>16,17</sup>. It was observed that when the ratio of  $\text{HNO}_3$  4M a recovery of 99.7% could be attained.

#### Effect of sample volume

The effect of sample volume on the recovery of the analyte was investigated in the range 50–300mL maintaining an overall concentration of  $0.025 \text{ mol L}^{-1}$  sulfuric acid. The resulting complex was eluted using 5mL of  $\text{HNO}_3$  4M. The results are presented in. As can be seen from the figure, it is evident that the recovery of Copper(II) is quantitative (>97%) up to 300mL sample volume. A preconcentration factor of 60 could be attained for quantitative recovery (>97%) of Cu(II) when the sample volume was 300 mL.

#### Effect of flow rate

The flow rate of  $1-7 \text{ mL min}^{-1}$  was found to be suitable for optimum loading of Cu(II) 1-(2-Pyridyl Azo)2-Naphtol(PAN) complex on the Sodium Dodecyl Sulfonate (SDS)  $\text{C}_{18}$  cartridge. At higher flow rates, there was a reduction in the percentage adsorption of Copper(II). This could be probably due to the insufficient contact time between the sample solution and  $\text{C}_{18}$  cartridge. A flow rate of  $2 \text{ mL min}^{-1}$  was maintained for the elution of Copper(II) Fig. 2.

#### Effect of the amount of $\text{C}_{18}$ silica cartridge

The amount of  $\text{C}_{18}$  cartridge loaded was varied from 0.25 to 2.0 g and the preconcentration studies were carried as before. Quantitative recovery of Cu(II) could be attained in the range 0.75–2.0 g of  $\text{C}_{18}$  cartridge. For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

#### Precision studies and limit of detection

The precision studies were carried out at  $10 \mu\text{g}$  level of Copper(II) by carrying out 10 separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 2%. The sensitivity of the developed method is reflected by the limit of detection studies, defined as the lowest concentration of Cu(II) below which quantitative

recovery of the metal ion by C18 cartridge is not perceptibly seen. The limit of detection was found to be  $45 \mu\text{g L}^{-1}$ .

#### Stability of the column

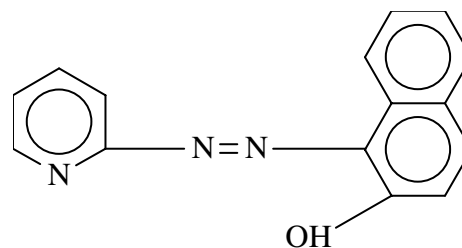
The stability of the column was tested using  $10 \mu\text{g}$  Cu(II) maintaining a sample volume of 50 mL. The adsorbed Cu(II) 1-(2-Pyridyl Azo)2-Naphtol(PAN) complex on SDS was eluted using 6mL of  $\text{HNO}_3$  4M. The column could be used with good precision and quantitative recovery (>97%) for at least 10 cycles. Beyond 10 cycles, there was a significant reduction in the recovery of Copper(II).

#### Effect of other ions

The interfering effect of diverse ions was studied at varying concentrations. The preconcentration studies were carried out as mentioned above using  $10 \mu\text{g}$  Cu(II) maintaining a sample volume of 100 mL. The studies indicated that  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{NO}_3^-$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  did not cause any significant reduction in the recovery of Copper(II). The results are presented in Table 1 showing the recovery of Cu(II) with varying concentrations of metal ions. The recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not interfere significantly, the method was applied to study the recovery of Copper(II) in water samples.

#### Recovery studies in tap water and rain water samples

The validity of the proposed method was tested by spiking known concentrations of Copper(II) to tap water (Tehran, taken after 10 min operation of the tap), and rain water (Tehran, 31 January,



**Scheme 1: Molecular structure of 1-(2-Pyridyl Azo)2-Naphtol(PAN)**

**Table 1: Effect of diverse ions on the recovery of 10 µg Cu(II) in a sample volume of 100 mL**

Ions	Amount (mg)	Recovery of found ion(%)	Recovery of Copper (%)
Na <sup>+</sup>	12.00	1.16(1.2) <sup>a</sup>	98.3 (1.01)
K <sup>+</sup>	11.00	0.22(2.5)	98.6(1.29)
ClO <sub>4</sub> <sup>-</sup>	3.3	1.18(1.1)	97.3(.51)
Mg <sup>2+</sup>	1.05	0.28(1.6)	100.3 (0.88)
Fe <sup>3+</sup>	0.020	2.18(2.3)	98.4(1.19)
Co <sup>2+</sup>	0.90	1.88(1.5)	99.1(1.42)
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	3.10	1.95(2.3)	97.0(1.07)
Ni <sup>2+</sup>	1.30	0.52(2.3)	101.7(1.23)
NO <sub>3</sub> <sup>-</sup>	0.50	0.18(0.8)	99.9(1.0)
Cl <sup>-</sup>	0.50	0.11(0.5)	99.1(1.1)
Br <sup>-</sup>	0.05	0.48(2.3)	98.6(1.5)
F <sup>-</sup>	0.05	1.95(0.5)	101.7(0.8)
Mn <sup>2+</sup>	1.20	0.25(0.2)	98.5(1.06)
Zn <sup>2+</sup>	1.86	0.75(1.2)	97.3(1.32)

**Table 2: Analytical results for the recovery of Cu(II) in water samples**

Sample	Cu(II) added (µg)	Found of Cu(II) with FAAS (µg)	GF-AAS (µg)
River Water	0.00	N.D <sup>a</sup>	N.D
	50.00	50.3(1.13) <sup>b</sup>	50.1(1.25)
Ground water	0.00	35.00(1.3)	38.18(2.2)
	30.00	52.3(1.3)	51.52(2.5)
Waste water	0.00	44.07(1.0)	44.30(1.3)
	30.00	64.09(1.5)	64.18(2.1)
Synthesis sample	0.00	N.D	N.D
0.2ppm of Mg <sup>2+</sup> , Zn <sup>2+</sup> , K <sup>+</sup> Cr <sup>3+</sup> , Pb <sup>2+</sup> , Hg <sup>2+</sup>	50.00	49.1(0.71) <sup>b</sup>	49.3(1.18)

**Table 3: The operational conditions of flame for determination of Copper**

Slit width	0.7 nm
Operation current of HI-HCL	5.0 mA
Resonance fine	283.3nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min <sup>-1</sup>
Acetylene flow	1.7 mL.min <sup>-1</sup>

2011) samples. The water samples were filtered and stored in polythene bottles. The recovery of Copper(II) was found to be satisfactory with a relative standard deviation of 2% for five replicate measurements and the results are shown in Table 2.

#### Comparison with other solid phase adsorbents

The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature. Also, the proposed method was free of interference compared to conventional procedures to determine Copper.<sup>46,51,52</sup> As can be

seen from the references, it is evident that the preconcentration factor obtained with SDS  $C_{18}$  cartridge is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the use of environmentally benign  $HNO_3$  4 M for the elution of the complex.

#### Calibration curve

The calibration curve of Copper(II) solutions is represented in Fig.1 and the related regression is  $Y=0.05372X-0.5931$  providing a correlation coefficient of  $R^2=0.9989$ .

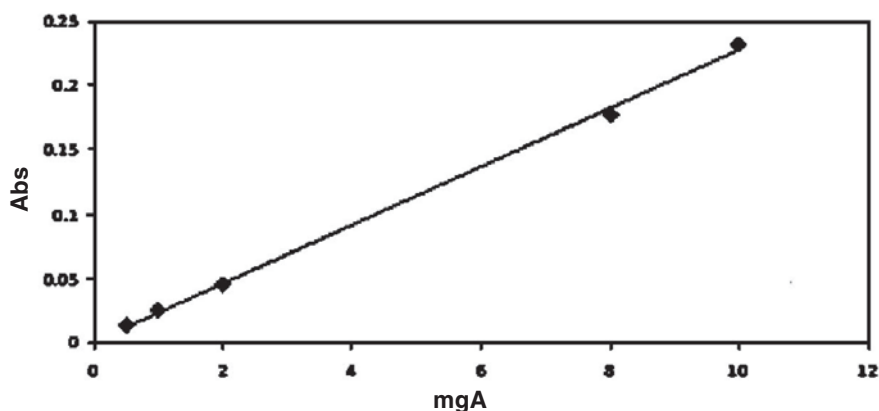


Fig. 1: Calibration curve of Copper(II) measured by SPE-AAS

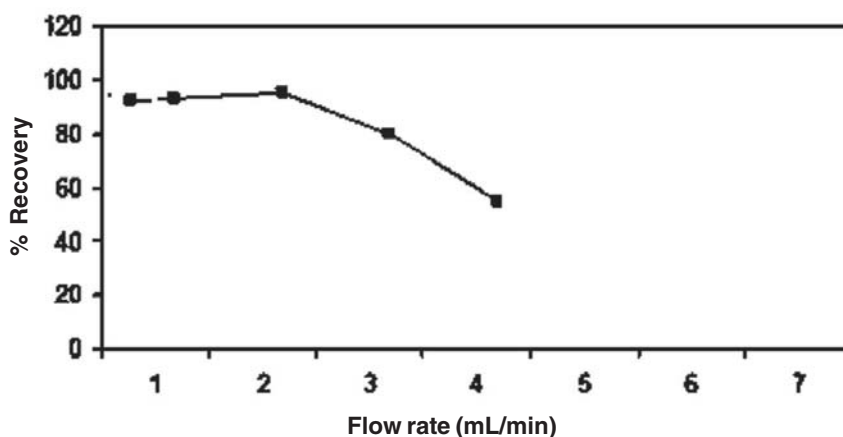


Fig. 2. Effect of flow rates of the sample solutions on the recovery percentage of copper(II)

### CONCLUSIONS

The proposed spectrophotometric method for Copper(II) is simple, sensitive and exhibits good selectivity. The elution of the complex does not involve strong acids or toxic organic solvents. The advantage of using HNO<sub>3</sub> 4 M as the eluent lies in the fact that it is non-inflammable, inexpensive and non-toxic. The conventional solvent extraction procedure associated with metal dithizonates is avoided in this methodology. The highest preconcentration factor attainable was 60 for a 300mL sample volume. The method showed minimum interferences with commonly found ions in water sample and the recovery of copper(II) was quantitative. The important features of the proposed method are its higher adsorption capacity with good preconcentration factor. The developed method is

sensitive in detecting Cu(II) at ppb levels. The column could be used with good precision and quantitative recovery for at least 10 cycles. The quantitative recovery of copper(II) with a low relative standard deviation of 2% reflects the validity and accuracy of the proposed method when applied to real samples. The method developed was simple, reliable, and precise for determining Copper in water. Also, the proposed method was free of interference compared to conventional procedures to determine Copper.<sup>46,51,52</sup>

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