Solid Phase Extraction of trace Cu(II) Using N,N′-disalicylideneethylenediamine Modified Graphene to Determination by FAAS

Ali Moghimi1*, Sahar Pourhossein Akbarieh2

1Department of Chemistry, Varamin (Pishva) branch, Islamic Azad University, Varamin Iran
2Department of Chemistry, Shahre Rey branch, Islamic Azad University, Shahre Rey, Iran
*Corresponding author; e-mail: alimoghimi@iauvaramin.ac.ir; kamran9537@yahoo.com

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Abstract. A simple, reliable and rapid method for preconcentration and modification of Graphene with N,N′ -disalicylideneethylenediamine in order to prepare an effective sorbent for the preconcentration and determination of copper. The sorption capacity of N,N′ -disalicylideneethylenediamine -modified Graphene was 50 mg.g⁻¹ and the optimum pH for the quantitative recovery of copper was found as 5.3. The optimum flow rate, sorbent amount and sample volume were 1.0 mL.min⁻¹, 300 mg and 50 mL, respectively. 5 mL of 4 mol.L⁻¹ HNO₃ 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 4.6ng 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 0.7%.

Keywords: Solid phase extraction; copper; N,N′ -disalicylideneethylenediamine -modified Graphene; FAAS

1. 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. The direct determination of trace metals especially toxic metal ions such as Cu, tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden et al., 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones et al., 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar et al., 1998; Caroli et al., 1991). The application of solid phase extraction technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova et al., 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpajian et al., 1997), filter paper (Leyden et al., 1975), cellulose (Gennaro et al., 1983) and ion exchange resins (Grote et al., 1985). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau et al., 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitak et al., 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al., 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as
oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1997; Mahmoud et al., 1997; Tong et al., 1990; Dadler et al., 1987). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields.

Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Cu(II) (Mahmoud, 1998; Mahmoud, 1999) and pre-concentration of various cations (Leyden et al., 1976; Narin et al., 2000; Akama et al., 2000; Ohta et al., 2001; Cuculic et al., 1997; Moghimi et al., 2009; Tehrani et al., 2005; Thurman, 1998; Pawliszyn, 1997; Izatt et al., 1996; Hagen et al., 1990; Krueger, 1995; Yamini et al., 1994; Shamsipur et al., 1999; Shamsipur et al., 2001; Brunner et al., 2003; Zelder et al., 2004; Boll et al., 2005; Nayebi et al., 2006; Moghimi et al., 2007; Moghimi, 2006; Moghimi, 2007; Moghimi, 2008) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng et al., 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova et al., 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi et al., 2010). Sorption of Cu(II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini et al., 2010) was also reported. 2-Amino-1-cyclopentene-1-dithiocabonyl acid (ACDA) for the extraction of silver(I), Cu(II) and palladium(II) (Moghimi et al., 2009), 2-[2-triethoxyxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin et al., 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros et al., 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin et al., 2000) are also sulfur containing silica gel phases.

This work preconcentration of Cu²⁺ based on the adsorption of its N,N’-disalicylideneethylenediamine complex on an Graphene. The adsorbed complex could be eluted using environmentally and the concentration of Cu²⁺ 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.

2. EXPERIMENTAL

2.1. Instrumentation

Determination of Cu²⁺ 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 a pH meter (sartorius model PB-11).

**Synthesis of SALEN**

SALEN [N,N'-bis(salicylidene)ethylenediamine] was prepared according the literature Methods (Harvey et al.1950) by using Schiff base reaction .the condensation ethylenediamine (0.1 mole) with (0.2 mole ) Salicylicaldehyde in ethanol the ratios 1:2 of ligand, the mixture was refluxed for 2hr after cooling .A yellow colour solid was precipitated ligand was filtered and recrystallized from hot ethanol and dried (Kaiss et al., 2007) . Melting point was 122-125 °C, the percentage yield 78%. The reaction procedure is shown schematically in scheme 1

![Calibration curve of Copper(II) measured by SPE-AAS](image_url)
2.2. Chemicals and reagents

N,N’-disalicylideneethylenediamine and sodium dodecyl sulfate (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\(^{-1}\) 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\(^{-1}\) was prepared by suitable dilution. About 0.01 g of N,N’-disalicylideneethylenediamine was dissolved in minimum amount of HNO\(_3\) 4M of deionized water. 1 g graphene (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\(^{-1}\) was prepared by diluting 55.5 mL of concentrated sulfuric acid with 1 L of de-ionized water. Water samples (Pilani, India) were collected, acidified and stored in polythene bottles.

2.3. Preparation of Graphene 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 Graphene 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 Graphene cartridge to settle properly. The column was packed up to a height of 3 cm.

2.4. Procedure for preconcentration

A 50 mg SDS and 30 mg N,N’-disalicylideneethylenediamine was dissolved in 50 mL of water. To the column of neutral Graphene cartridge maintaining a flow rate of 5 mL min\(^{-1}\). Then, 250 mL volume of 10 µg Cu(II) solution was loaded on to the column. The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was eluted using 10 mL of HNO\(_3\) 4M at a flow rate of 0.5 mL min\(^{-1}\) and the concentration of Copper(II) was determined by FAAS.

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

Schematic 1 Synthesis and Molecular structure of N,N’-disalicylideneethylenediamine
3. RESULTS AND DISCUSSIONS

3.1. Effect of acidity

The effect of acidity plays a significant role in the preconcentration studies. The volume of 0.5 mol L$^{-1}$ 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$^{-1}$ sulfuric acid. Beyond 6 mL, there was no change in the recovery of Copper(II).

3.2. 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, $\text{H}_3\text{PO}_4$ 1M, and Acidified methanol (Acidified solvents obtained by addition of HNO$_3$ 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 HNO$_3$ 4M as eluting agents. However, HNO$_3$ 4M was preferred owing to its non-inflammability and less toxicity (Mahmoud et al., 1997). It was observed that when the ratio of HNO$_3$ 4M a recovery of 99.7% could be attained.

3.3. Effect of sample volume

The effect of sample volume on the recovery of the analyte was investigated in the range 100–1500 mL maintaining an overall concentration of 0.025 mol L$^{-1}$ sulfuric acid. The resulting complex was eluted using 10 mL of 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 250 mL sample volume. A preconcentration factor of 170 could be attained for quantitative recovery (>97%) of Cu(II) when the sample volume was 250 mL.

3.4. Effect of flow rate

The flow rate of 1–7 mL min$^{-1}$ was found to be suitable for optimum loading of Cu(II) N,N’-disalicylideneethylenediamine complex on the Graphene 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 Graphene cartridge. A flow rate of 5 mL min$^{-1}$ was maintained for the elution of Copper(II) Fig 2.

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

<table>
<thead>
<tr>
<th>Ions</th>
<th>Amount (mg)</th>
<th>Recovery of found ion(%)</th>
<th>Recovery of Copper(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>10.00</td>
<td>1.16(1.7)$^a$</td>
<td>100(0.5)</td>
</tr>
<tr>
<td>K$^+$</td>
<td>10.00</td>
<td>0.22(2.5)</td>
<td>99.0(0.3)</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>10.00</td>
<td>1.18(1.1)</td>
<td>102.4(1.3)</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>10.00</td>
<td>0.28(1.6)</td>
<td>102.0(0.2)</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.80</td>
<td>2.18(2.3)</td>
<td>99.1(1.7)</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}$</td>
<td>0.80</td>
<td>1.88(1.5)</td>
<td>99.1(1.4)</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.80</td>
<td>1.95(2.3)</td>
<td>96.5(0.7)</td>
</tr>
<tr>
<td>$\text{Co}^{3+}$</td>
<td>0.50</td>
<td>1.52(0.5)</td>
<td>97.5(1.5)</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.50</td>
<td>0.52(2.3)</td>
<td>101.2(2.0)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.50</td>
<td>0.18(0.8)</td>
<td>99.9(1.0)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.50</td>
<td>0.11(0.5)</td>
<td>99.1(1.1)</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.05</td>
<td>0.48(2.3)</td>
<td>98.6(1.5)</td>
</tr>
<tr>
<td>$\text{F}^-$</td>
<td>0.05</td>
<td>1.95(0.5)</td>
<td>101.7(0.8)</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.05</td>
<td>0.25(0.2)</td>
<td>101.6(0.6)</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.05</td>
<td>0.75(1.2)</td>
<td>103(1.2)</td>
</tr>
</tbody>
</table>

3.5. Effect of the amount of Graphene silica cartridge

The amount of Graphene 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 Graphene cartridge. For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

3.6. Precision studies and limit of detection

The precision studies were carried out at 10 µg 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 1.48%. 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 Graphene cartridge is not perceptibly seen. The limit of detection was found to be 0.78µgL\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu(II) added (µg)</th>
<th>Found of Cu(II) with FAAS (µg)</th>
<th>GF-AAS (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water</td>
<td>0.00</td>
<td>N.D(^a)</td>
<td>N.D</td>
</tr>
<tr>
<td></td>
<td>30.00</td>
<td>30.06(0.4)(^b)</td>
<td>29.85(1.9)</td>
</tr>
<tr>
<td>Ground water</td>
<td>0.00</td>
<td>35.00(1.3)</td>
<td>38.18(2.2)</td>
</tr>
<tr>
<td>Waste water</td>
<td>0.00</td>
<td>52.3(1.3)</td>
<td>51.52(2.5)</td>
</tr>
<tr>
<td>Synthesis sample</td>
<td>30.00</td>
<td>44.07(1.0)</td>
<td>44.30(1.3)</td>
</tr>
<tr>
<td>0.2mg of Co(^{2+}), Cd(^{2+}), Na(^{+})</td>
<td>64.09(1.5)</td>
<td>64.18(2.1)</td>
<td></td>
</tr>
</tbody>
</table>

| Table 2: Analytical results for the recovery of Cu(II) in water samples |
|------------------|------------------|-----------------|--------|
|                  | Cu(II) added (µg) | Found of Cu(II) | GF-AAS |
| Tap Water        | 0.00              | N.D\(^a\)       | N.D    |
| Ground water     | 30.00             | 30.06(0.4)\(^b\) | 29.85(1.9) |
| Waste water      | 0.00              | 35.00(1.3)      | 38.18(2.2) |
| Synthesis sample | 30.00             | 52.3(1.3)       | 51.52(2.5) |
| 0.2mg of Co\(^{2+}\), Cd\(^{2+}\), Na\(^{+}\) | 44.07(1.0) | 44.30(1.3) |

| Table 3: The operational conditions of flame for determination of Copper |
| Slit width        | 0.7 mm            |                |
| Operation current of HI-HCL | 5.0 mA          |                |
| Resonance fine    | 283.3 nm          |                |
| Type of background correction | Deuterium lamp |                |
| Type of flame     | Air/acetylene     |                |
| Air flow          | 7.0 mL.min\(^{-1}\) |                |
| Acetylene flow    | 1.7 mL.min\(^{-1}\) |                |

3.7. Stability of the column

The stability of the column was tested using 10µg Cu(II) maintaining a sample volume of 50 mL. The adsorbed Cu(II) N,N’-disalicylideneethylenediamine complex on SDS was eluted using 6mL of 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).

3.8. 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 10µg Cu(II) maintaining a sample volume of 100 mL. The studies indicated that Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\), Mg\(^{2+}\), Cd\(^{2+}\), Cl\(^{-}\), Br\(^{-}\), Fe\(^{3+}\), NO\(_3^{-}\), Zn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), 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.

3.9. 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, 2013) 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.

3.10. 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 (Moghimi 2006; Choi et al, 2003; Saber...
Tehrani et al., 2005). As can be seen from the references, it is evident that the preconcentration factor obtained with Graphene 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 HNO₃ 4 M for the elution of the complex.

3.11. Calibration curve

The calibration curve of Copper(II) solutions is represented in Fig.1 and the related regression is Y=0.0227X-0.0009 providing a correlation coefficient of R²=0.9987.

4. CONCLUSION

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 HNO₃ 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 dithizones is avoided in this methodology. The highest preconcentration factor attainable was 36 for a 250mL 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 1.48% 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 (Moghimi, 2006; Choi et al., 2003; Saber Tehrani et al., 2005).

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Associate Professor Dr Ali Moghimi obtained his first degree from Analytical Chemistry Ph.D., Faculty of Science, Science and Research branch, Islamic Azad University, Tehran, Iran in 2005. Currently, Dr Moghimi serves head department of chemistry, Varamin (Pishva) Branch Islamic Azad University. He has published numerous refereed articles in professional journals. Dr Moghimi field of expertise’s are solid phase extraction, separation and chromatography. Dr Moghimi also has conducted numerous consultancies and research works at national and international level. He has published over 150 refereed articles in professional journals/proceedings and currently sits as the Editorial Board Member for 12 International journals.

Sahar Pourhossein Akbarieh obtained her M.Sc degree in Analytical Chemistry from Islamic Azad University, Shahre Rey Branch, Tehran, Iran in 2013. She has published 3 refereed articles in professional journals/proceedings.