Solid phase extraction of ultra traces copper (II) using octadecyl silica membrane disks modified by a new Schiff base ligand prior to determination by furnace atomic absorption

Mahmood Payehghadr[1]*, Nahid Satei[2], Lotf Ali Saghatforoush[3]

[1]Department of Chemistry, Payame Noor University (PNU), Karaj, (IRAN)
[2]Department of Chemistry, Payame Noor University (PNU), Abhar, (IRAN)
[3]Department of Chemistry, Payame Noor University (PNU), Khoy, (IRAN)
E-mail : mpayehghadr@pnu.ac.ir; mahmood_payehghadr@yahoo.com

ABSTRACT

A simple, reliable and rapid method for pre-concentration and determination of ultra trace copper using octadecyl silica membrane disk modified by a recently synthesized new Schiff base ligand (5-Nitro-N(2-pyridylethyl Sulfanyl Ethyl) Salisyl Salysilyden Imine), and furnace atomic absorption spectrometry is presented. Various parameters including pH of aqueous solution, flow rates, the amount of ligand and type of stripping solvents were optimized. The breakthrough volume is greater than 2000 ml with an enrichment factor of more than 400 and 3.4 ngL^{-1} detection limit. The capacity of the membrane disks modified by 5 mg of the ligand was found to be 327.38μg copper. The effects of various cationic interferences on percent recovery of copper ion were studied. The method was successfully applied for the determination of copper ion in different cow milk samples.
© 2011 Trade Science Inc. - INDIA

INTRODUCTION

Copper are widespread anthropogenic pollutant of environment and the determination of this metal ion is an actual problem. Environmental pollution is the main cause of heavy metal contamination such as cadmium, lead, and copper in the food chain. All foodstuffs, especially products of animal origin, such as milk, present the problems of hygienic safety with increasing environmental pollution[1]. Milk is a complex, bioactive substance to promote growth and development of the infant mammals. Cow's milk is widely consumed by human children and adults after the age of weaning. In fact, milk is an ideal source of macroelements, such as, calcium, potassium, phosphorus. Moreover, microelements and even heavy metals can be found in milk. Microelements, also called trace elements such as copper, iron, selenium, and zinc are known to be essential for normal growth[2]. Excessive accumulation of dietary heavy metals in human body may cause serious health problems, and there is growing concern about the effects of dairy food contaminants on human health. Therefore, it is of prime importance to determine the concentrations of essential and toxic elements in foods[1].

The determination of copper is usually carried out by Flame[3-5] and graphite[6,7] atomic absorption spec-

trometry (AAS), as well as spectrophotometry[8,9], chemiluminescence[10] and electrothermal methods[11,12]. However, due to presence of copper in low levels in environmental samples and the matrix effects, different separation and pre-concentration techniques such as liquid-liquid extraction[13], precipitation[14], ion exchange[15], solid phase extraction[16,17] and membrane filtration[18] 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 pre-concentration factor, rapid phase separation, time and cost saving[19,20]. A number of supports have been widely used for the pre-concentration and separation of trace metal ions from various matrices. Among the absorbents, silica with chemically bonded alkyl chains such as octadecyl bonded silica (C_{18}), modified by the use of suitable ligands has been an excellent used extractor of metal ions[21-25].

The Schiff's bases as poly dentate ligands are known to form very stable complexes with transition metal ions[26,27]. In this work a newly synthesized Schiff base ligand, 5-nitro-N-(2-pyridylethyl sulfanyl ethyl) salisyl salysilyden imine[27] (Figure 1), is studied as an disk modifier for Cu(II). Extraction and pre-concentration of copper (II) from milk samples and determination by furnace atomic absorption spectrometry have been reported.
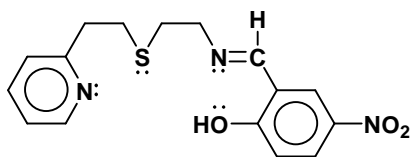
Figure 1 : Chemical structure of 5-Nitro-N(2-pyridylethyl Sulfanyl Ethyl) Salisyl Salysilyden Imine

EXPERIMENTAL

Instrumentation

The Cu^{2+} determination were performed on a BRAIC-WFX-130 furnace atomic absorption spectrometer 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. The determination of all

other ions was carried out with same furnace atomic absorption spectrometer under the recommended conditions for each metal ion. A model Metller-Tolido pH meter equipped with a combined glass-calomel electrode was used for the pH adjustments.

Chemicals and reagents

Methanol, acetonitrile, and other organic solvents used were of spectroscopic grade from Merck, and all acids used were of pro analysis from Merck. Analytical grade standard stock of copper(II), sodium hydroxide, and nitrate or chloride salts of magnesium, zinc, cobalt, nickel, sodium, potassium and calcium (all from Merck) were of the highest purity available. The new synthesized Schiff base (Figure 1) with highest purity was used as the chelating ligand[27]. Working standards were prepared by appropriate dilution of the stock solution with deionized water was prepared by Millipure apparatus.

Sample extraction

Extraction were performed with 47 mm diameter × 0.5 mm thickness, Empore high performance extraction membrane disk containing octadecyl-bonded silica (8 ìm particles, 6 nm pore size) from 3M company. The disks were used in conjunction with a standard Schott 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 minute, a solution of 5mg Schiff base 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 Schiff base ligand is now ready for sample extraction.

Then 100 ml of the sample solution containing 10 μg Cu^{2+} was passed through the membrane (flow rate = 3.5 ml/minute). 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 0.1 M Nitric acid). This step was done

with 5 ml eluent solution and the Cu^{2+} was determined with furnace atomic absorption spectrometer.

RESULTS AND DISCUSSION

Choice of effluent

In order to choose the most effective eluent for quantitative stripping of the retained ions from the modified disk after extraction of 10 µg Cu^{2+} from 100 ml sample (in the presence of 5 mg ligand), the Cu^{2+} ions were stripped with 5 ml of different inorganic solution, and the resulting data are listed in TABLE 1.

From the data given in TABLE 1, it is immediately obvious that among the different solutions, 5 ml 0.1M Nitric acid can accomplish the quantitative elution of copper from the membrane disk, while other solutions are ineffective for the complete elution of copper.

TABLE 1 : Percent recovery of copper from the modified membrane disk using 5 ml of different stripping solutions

Stripping solution Concentration (M)	Recovery %					
	0	0.07	0.05	0. 1	0.5	1
HCl	0	80.6	74.2	81.1	73.4	92.6
HNO₃	0	93.7	95.2	100.0	98.9	93.4
H₂SO₄	0	67.6	68.7	67.4	66.2	65.1
EDTA	0	64.3	62.4	68.9	70.1	----

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
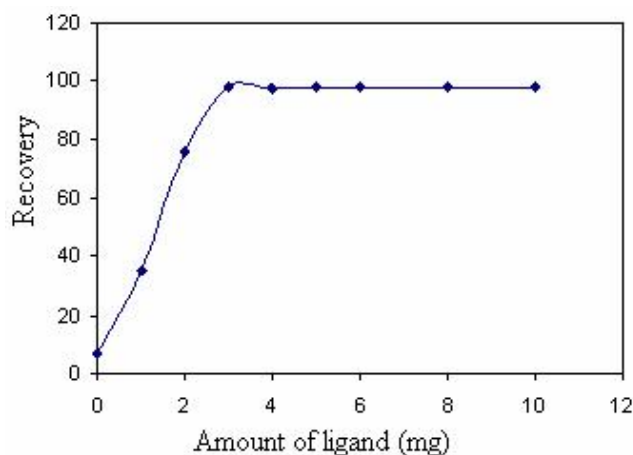

Figure 2 : Ligand amount effect on extraction efficiency of copper ion

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 0-10 mg using 100 ml solution containing 10 µg copper ions. The recoveries of copper ion increased when increasing the amount of ligand and reached to 100% with at least 3 mg of ligand (Figure 2). On this basis, in all studies were carried out with 5 mg of Schiff base ligand.

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 2.0–30 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[28]. In this work quantitative stripping of copper ion from the disk was achieved in a flow rate of 2.0 – 20 ml.min⁻¹, using 5 ml of 0.1M Nitric acid.

Most chelating ligands (such as Schiff bases) 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[29]. Owing to the presence of one hydroxyl group on the Schiff
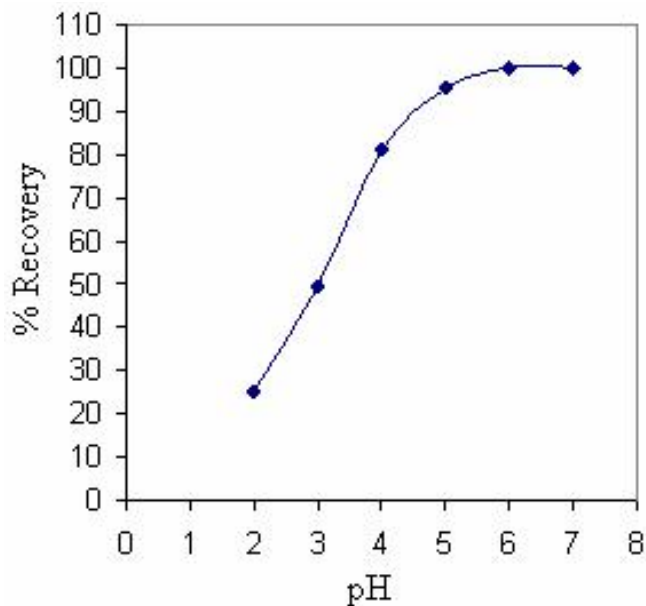
Figure 3 : Effect of aqueous phase pH on extraction of copper (II)

Full Paper

base ligand structure, it is expected that the extent of its complexation is sensitive to pH. In order to investigate the effect of pH on the SPE of copper ion, the pH of aqueous samples was varied from 1–7, using different buffers, and the recommended procedure was followed. Figure 3 indicates that the Cu^{2+} ion can be retained quantitatively in the pH range 5.0-7.0. For subsequent experiments, pH = 7 was chosen as working pH. It is found that the percentage recovery is nearly independent of pH. Higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.

ANALYTICAL PERFORMANCE

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 Schiff base ligand, followed by determination of the retained ions using furnace atomic absorption spectrometry. The maximum capacity of the disk was found to be 327.38 (±13.31) μg copper ion per 5 mg of ligand.

Breakthrough volume

The breakthrough volume of sample solutions, was tested by dissolving 10 μg copper ion in 25, 50, 100, 250, 500, 1000, 1500, and 2000 ml water and the solutions was passed through the modified disk. In all cases, the extraction by membrane disk was found to be quantitative (recovery 100 %). Thus, the breakthrough volume for the method should be greater than 2000 ml. Consequently, and with respect to final elution volume of 5 ml and the sample solution volume of 2000 ml, an enrichment factor of 400 was easily achievable.

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 based on 3σ of the blank, 3.4 ng per 1000 ml.

Effect of diverse ions on sorption of copper

In order to investigate the selective separation and determination of copper ion from its binary mixtures

with diverse 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 2. The results show that the copper ion in the binary mixtures are retained almost completely by the modified membrane disk, even in the presence of up to about 100 mg of the diverse ions. It is interesting to note that retention of other cations by the disk is negligible and they can be separated completely from the copper ion.

TABLE 2 : Effect of diverse ions on the recovery of 10 μg copper ion.

Ion	Amount taken (mg)	Recovery of copper ion (%)
Na^+	100	97.3
K^+	100	98.8
Ca^{2+}	40	97.1
Mg^{2+}	40	99.4
Ni^{2+}	2	99.2
Co^{2+}	2	99.8
Zn^{2+}	2	99.8

Analysis of artificial and natural samples

In order to assess the applicability of the method to real samples with different and complex matrices containing varying amounts of variety ions, it was applied to the separation and recovery of copper ions from four different milk samples. The results are summarized in TABLE 3. As seen, the results of all sample analysis show that, in all cases, the copper recovery is quantitative.

TABLE 3 : Recovery copper added to 100 ml solution of the milk samples.

Milk samples	Added Cu^{2+} (μg)	Determined Cu^{2+} (μgL^{-1})
Sterilized	0	37.29
	5	43.12
Pasteurized, High fat (3%)	0	35.17
	5	40.73
Pasteurized (2.5% fat)	0	20.07
	5	30.42
Pasteurized, low fat (1%)	0	205.31
	5	218.00

CONCLUSION

A simple, precise and accurate method was de-

Full Paper

veloped for selective separation, pre-concentration and determination of copper from various complex matrices such as milk samples. Comparison of our work with some studies on preconcentration of heavy metals and copper by various techniques for the figure of merits, shown that the detection limit and preconcentration factor of analyte ion are superior to those of preconcentration technique for analysis[30-33]. 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 when they are present at much higher concentrations. The method can be successfully applied to the separation and determination of copper in complex real such as milk samples.

REFERENCES

[1] G.Xiang, Y.Huang, Y.Luo; Microchim.Acta, **165**, 237-242 **(2009)**.

[2] L.Q.Qin, X.P.Wang, W.Li, X.Tong, W.J.Tong; J.Health Sci., **55**, 300-305 **(2009)**.

[3] P.Hashemi, S.Bagheri, M.R.Fat'hi; Talanta, **68**, 72-78 **(2005)**.

[4] P.Ashtari, K.Wang, X.Yang, S.Huang, Y.Yamini; Anal.Chim.Acta, **550**, 18-23 **(2005)**.

[5] R.J.Cassella, O.I.B.Magalh˜aes, M.T.Couto, E.L.S.Lima, M.A.F.S.Neves, F.M.B.Coutinho; Talanta, **67**, 121-128 **(2005)**.

[6] O.Acar; Talanta, **65**, 672-677 **(2005)**.

[7] J.Y.Cabon; Spectrochim.Acta B, **57**, 939-950 **(2002)**.

[8] P.Rumori, V.Cerd'a; Anal.Chim.Acta, **486**, 227-235 **(2003)**.

[9] J.J.Pinto, C.Moreno, M.Garc´ya-Vergas; Talanta, **64**, 562-565 **(2004)**.

[10] S.M.Lioret, P.C.Falc´o, S.C´ardenas, M.Gallego, M.Valc´arcel; Talanta, **64**, 1030-1035 **(2004)**.

[11] Z.Szigeti, I.Bitter, K.Toth, C.Latkoczy, D.J.Fliegel, D.Gunther, E.Pretsch; Anal.Chim.Acta, **532**, 129-136 **(2005)**.

[12] M.P.Hurst, K.W.Bruland; Anal.Chim.Acta, **546**, 68-78 **(2005)**.

[13] P.B.Barrera, A.M.Pi˜neiro, R.G.Iglesias, A.B.Barrera; Spectrochim.Acta B, **57**, 1951-1966 **(2002)**.

[14] M.Soylak, S.Saracoglu, U.Divrikli, L.Elci; Talanta, **66**, 1098-1102 **(2005)**.

[15] S.Scaccia, G.Zappa, N.Basili; J.Chromatogr.A, **915**, 167-175 **(2001)**.

[16] E.Kend¨uzler, A.R.T¨urker; Anal.Chim.Acta, **480**, 259-266 **(2003)**.

[17] V.A.Lemos, P.X.Baliza; Talanta, **67**, 564-570 **(2005)**.

[18] U.Divrikli, A.A.Kartal, M.Soylak, L.Elci; J.Hazard. Mater., **145**, 459-464 **(2007)**.

[19] M.Ghaedi, K.Niknam, A.Shokrollahi, E.Niknam, H.R.Rajabi, M.Soylak; J.Hazard.Mater., **155**, 121-127 **(2008)**.

[20] A.B.Tabrizi; J.Hazard.Mater., **B139**, 260-264 **(2007)**.

[21] M.Shamsipur, A.R.Ghiasvand, Y.Yamini; Anal. Chem., **71**, 4892-4897 **(1999)**.

[22] A.R.Khorrami, T.Hashempur, A.Mahmoudi, A.R.Karimi; Microchemical Journal, **84**, 75-79 **(2006)**.

[23] A.R.Khorrami, H.Naeimi, A.R.Fakhari; Talanta, **64**, 13-17 **(2004)**.

[24] Y.Yamini, N.Alizadeh, M.Shamsipur; Anal.Chim.Acta, **355**, 69-73 **(1997)**.

[25] M.Shamsipur, A.Avanes, M.K.Rofouei, H.Sharghi, Gh.Aghapour; Talanta, **54**, 863-869 **(2001)**.

[26] M.Calligaris, R.Randaccio, G.Wil;inson, R.D.Gillard, Mc Cleverty (Eds); Comertensive Coordination Chemistry, Oxford, London, Chap. 20, **2**, **(1987)**.

[27] N.Daneshvar, A.A.Entezami, A.A.Khandar, L.A.Saghatforoush; J.Polyhedron., **22**, 1437-1445 **(2003)**.

[28] M.Shamsipur, A.R.Ghiasvand, H.Sharghi, H.Naeimi; Anal.Chim.Acta, **408**, 271-277 **(2000)**.

[29] F.Poole, S.K.Poole, D.S.Seibert, C.M.Champman; J.Chromatogr.B, **689**, 245-259 **(1997)**.

[30] M.Tuzen, K.O.Saygi, M.Soylak; J.Hazard.Mater., **152**, 632-639 **(2008)**.

[31] V.A.Lemos, P.X.Baliza; Talanta, **67**, 564-570 **(2005)**.

[32] E.Birlik, A.Ers¨oz, A.Denizli, R.Say; Anal.Chim. Acta, **565**, 145-151 **(2006)**.

[33] M.H.Mashhadizadeh, M.Pesteh, M.Talakesh, I.Sheikhshoaie, M.Mazloum Ardakani, M.A.Karimi; Spectrochim.Acta, Part B, **63**, 885-888 **(2008)**.