Flow-Injection Spectrophotometric Determination of Copper (II) Ion at Low µg L⁻¹ Levels

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FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) ION AT LOW $\mu g\ L^{-1}$ LEVELS

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A highly selective, sensitive and fast determination of trace amounts of copper (II) ion is described. The method is based on the formation of the coloured Cu(II)-N,N'-o-phenylenebis(salicylaldimine) (PBS) complex, which is then selectively monitored at 415 nm. To increase the interaction between copper(II) and the colour forming reagent and preconcentrate copper(II), a microcolumn containing strong cation-exchange resins was placed between the injection manifold and the spectrophotometer. The linear range of the proposed method was 25–100 $\mu g\ L^{-1}$, and the limit of detection (signal-to-noise ratio = 2) was < 1 $\mu g\ L^{-1}$ for 20 μL injection volume of copper (II) ion solution at a sampling rate of > 50 h^{-1}. The relative standard deviation at the level of 25–100 $\mu g\ L^{-1}$ was 0.24 % for n = 5. The precision and accuracy of the method was checked by analysis of a certified reference material, and the applied to river and sea water samples.

Keywords: Copper(II) determination; flow-injection; spectrophotometry; N,N'-o-phenylenebis(salicylaldimine)

INTRODUCTION

Flow-injection analysis (FIA) is widely used for the determination of trace metals in environmental samples. The determination of metal ions in flow-injection systems has received a growing attention in recent years since its simplicity, rapidity and versatility which allows the method to be used in conjunction with a variety of detection systems such as spectrophotometry [13], ISE [14], AAS [15], and ICP-MS [16]. Flow-injection systems for the determination of copper (II) ions have been based on atomic absorption spectrometry (AAS)[1–3], inductively-coupled plasma emission spectrometry [4,5], stripping voltametry on a mercury drop [6- 9], UV-Visible spectrophotometric [10–11], and ion-selective electrode [12].

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Chelates of copper ions often absorb at characteristic wavelengths and can be selectively determined spectrophotometrically. Copper (II) has been selectively determined in flow-injection systems by forming coloured complexes with chelating agents which often show a strong absorption at a characteristic wavelength. N,N'-o-phenylenebis(salicylaldimine) (PBS) (Figure 1) has been reported as a complexing agent due to strong chelating ability of the hydroxy groups and nitrogen atoms, forming six- and/or five-membered chelate rings. Most of the copper chelates of PBS were insufficiently water soluble even at trace levels which make difficult their on-line determination in a flow-injection system. In an early work [17] the copper (II) chelate formed with PBS as a colour forming reagent was utilised for RP-HPLC and spectrophotometric determination of copper (II) ion using an aqueous mobile phase. In this paper, a highly sensitive flow-injection spectrophotometric method for copper (II) ions with the use of the tetradentate Schiff-base reagent is described and its practical applicability is suggested.
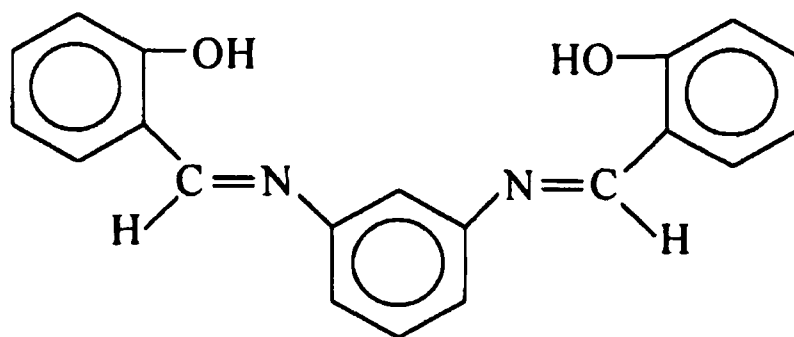

FIGURE 1 Structure of the N,N'-o-phenylenebis(salieylaldimine) (PBS)

EXPERIMENTAL

Reagent and samples

All chemicals were of analytical reagent grade and deionized water was used throughout. A copper (II) stock solution (50 mg L^{-1}) was prepared from $CuSO_4.5H_2O$ (E. Merck) copper working standard solutions were prepared daily.

During the determination of copper (II) in real samples, copper working standard solutions were prepared by several dilution of fresh standard stock solution with deionized water only. Interference studies were carried out by using the chloride or sulphate salts of the metal cations. N,N'-o-phenylenebis(salicylaldimine) is not commercially available, was synthesized according to the method described previously [17]. Stoichiometric amounts of the diamine (0.02 mol in 20 mL of ethanol) and aldehyde (0.04 mol in 40 mL of ethanol) were mixed and refluxed for 1 h. After cooling, the resulting precipitate was collected by filtration and recrystallized twice from hot ethanol. The ligand compounds were characterized by elemental analysis and infrared spectrophotometry. The Cu-PBS complex was prepared by mixing stoichiometric amounts of 0.01 mol L^{-1} copper (II) and 0.001 mol L^{-1} hydrochloric acid with 0.01 mol L^{-1} PBS. The precipitates were filtered, washed with deionized water and ethanol and dried at 80-105°C. When required, the solution of Cu-PBS complex was prepared in aqueous methanol or aqueous acetonitrile solution.

The cation-exchange resin used was the sodium form of A 650 W (100–200 mesh) from BioRad Labs.

Apparatus

A Perkin Elmer (Series 3) high pressure liquid chromatography (HPLC) pump furnished with stainless-steel tubing was used to propel the samples and reagent solutions. Samples (20 µL) were injected into the carrier stream by a Rhodyne injection valve.

The absorbance of the coloured complex formed was measured with a UV-Visible spectrophotometer (Spectra SYSTEM UV 3000 HR, Thermo Separation Products) equipped with a flow-through microcell and connected to a computer (IPX Spectra SYSTEM SN 4000) which was incorporated in a PC 1000 software computer programme. The cation-exchange resin column (25–2 mm i.d.) was machined in a perspect block and was connected to the outlet of the injection valve with the shortest possible length (8 cm × 0.8 mm i.d.) of polyethylene tubing. The resin was held inside the column by plugging the two ends with discs of porous polyethylene held in by O-rings. UV-Visible spectra of Cu-PBS complex was taken using a UV-Visible spectrophotometer (UNICAM UV/VIS, Australia).

Procedure

The FI system used is simple and shown schematically in Figure 2. The sample injected (SI) into the reagent carrier solution (R), soon loads the column filled
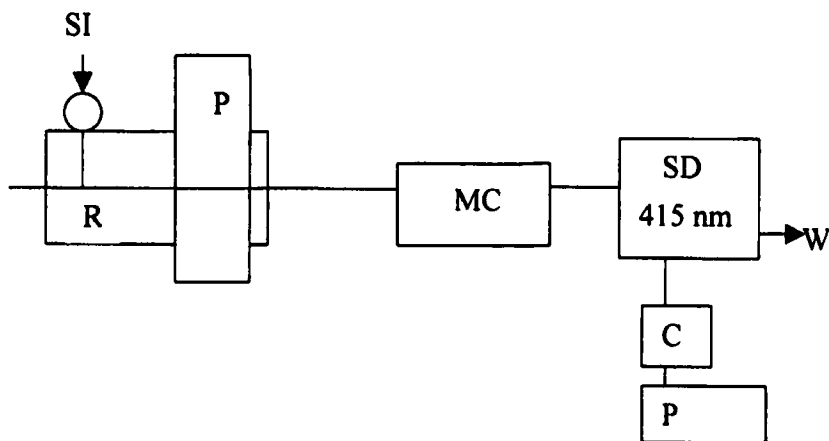
FIGURE 2 Schematic diagram of the flow-injection system used for spectrophotometric determination of copper (II). R, reagent carrier solution PBS in acetonitrile-water-acetate buffer solution in ratio 60:30:10 (v/v), pH:6.5; P, HPLC pump; SI, Rhodyne sample injection valve; MC, microcolumn; SD, spectrophotometric detector (415 nm); C, computer; P, printer; W, waste

with the cation-exchange resin. PBS in the carrier solution interacts with metal ions retained in the microcolumn (MC), and then elutes by coloured complex forming. The interacted zone containing the coloured complex is carried toward the flow-through spectrophotometric detector cell (SD) in which the Cu-PBS complex is selectively monitored at 415 nm and printed (P) continuously on the computer (C).

For the determination of copper (II) in river and seawater samples, 100 mL of undiluted river and seawater samples in Nalgene plastics were filtered over a 0.45 μm filter from Millipore (Bedford, USA), and then 20 μL of each filtered water samples were used as in the procedure described above.

Spectrophotometric studies

Metal ions react with PBS in aqueous medium to form several complexes with different stoichiometry. These complexes are slightly soluble in aqueous medium but fairly soluble in acetonitrile. Absorption spectra of metal complexes corresponding to solutions of 20–100 mg L^{-1} were taken in acetonitrile. They exhibited absorbance maxima at 368 nm and 390 nm for all metal complexes, eventhough the Cu-PBS complex has an absorbance maximum at 415 nm. But Al (III), Ni (II), Fe (II), Co (II))-PBS complexes show negligible absorptions at

this wavelength, so this can specificially be used for the determination of copper (II) ion in solutions.

Cation-exchange resin microcolumn

The cation-exchange resin microcolumn has been employed in FIA for on-line preconcentration and a fast interaction of metal ions with PBS in the carrier solution to develop coloured complexes. A strong cation-exchange resin was selected because metal ions are strongly bound by the resin so that a low amount of the resin can be used. Higher amounts of the resin minimised the use of higher flow-rates due to an increase of hydrodynamic pressure. On the other hand, both the retention time in the cation-exchange microcolumn, and the residence time in the tubing in the flow-path determine the sampling time. At a flow-rate of 0.8 mL min^{-1}, a throughput of > 50 sample analyses per hour was achieved for samples with concentrations ranging from 10 to 300 µg L^{-1} at a 20 µL injection volume.

RESULTS AND DISCUSSION

The specific absorbance maximum of the Cu-PBS complex at 415 nm can be applied for the selective determination of copper (II) in the flow-injection system shown in Figure 2. The Cu-PBS complex was found to be insufficiently soluble even at trace levels for aqueous solutions to be used directly. For the analysis of copper (II), a binary solvent system (acetonitrile+aqueous acetate buffer solution in ratio 60:30:10, pH:6.5) has been developed as a reagent carrier solution. The introduction of copper (II) ion in solution into the reagent carrier solution from the injection valve produces a positive response on the computer, which was free from background absorption from the reagents as illustrated Figure 3 (a). This figure indicates that the flow signals for copper (II) ion show good repeatability. The responses to 20 µL injection volumes of 25–100 µg L^{-1} solutions of copper (II) ions were linear.

For rapid and sensitive continuous spectrophotometric analyses of copper (II) ion in solutions, the use of the cation-exchange microcolumn for on-line preconcentration is satisfactory, providing low concentration ranges to be determined (µg L^{-1}). Such a high sensitivity is well suited to the determination of copper (II) in sea and river waters samples.

(a)   **(b)**
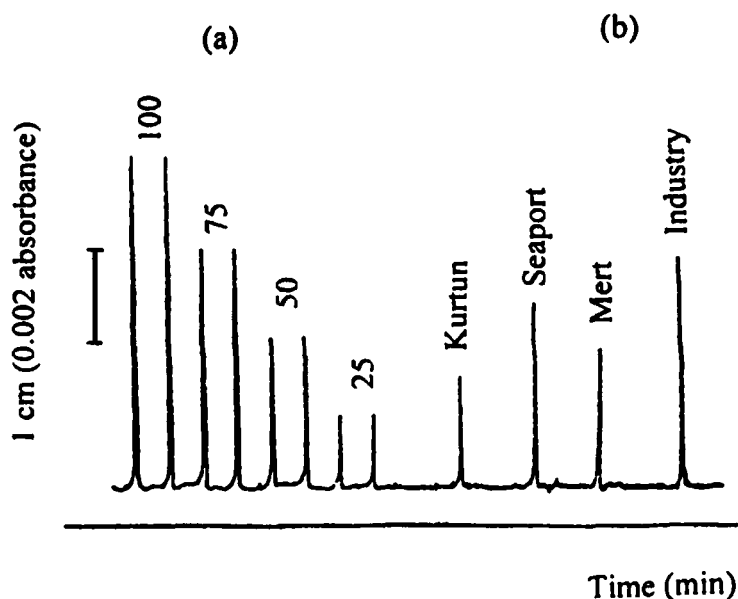

FIGURE 3 Computer outputs obtained with cation-exchange microcolumn in the flow injection system. (a) Standard solution of copper (II) (25–100 µg L^{-1}) injected. (b) Real samples solutions (for concentration see Table II). Figures above the peaks indicate concentrations in µg L^{-1}

Effect of concentration of PBS

The effect of concentration of PBS in the reagent carrier solution on the peak height was examined in the FIA system using 1.2 and 3.8 mg L^{-1} copper (II) solutions. The concentrations of PBS was varied over the range 0.1–1.5 % (w/v), at pH 6.5 and a flow-rate of 0.8 mL min^{-1}. For each concentration level of copper (II) ion, peaks were maximal at a concentration of 0.6 % (w/v). Therefore, a concentration of 0.6 % (w/v) of PBS as colour developing reagent in the carrier solution was chosen (Figure 4).

Effect of flow-rate

The flow-rate of reagent carrier solution was varied from 0.5 to 1.5 mL min^{-1}. The peak height decreased with increasingly flow-rate (Figure 5). Taking into consideration the stability of the pump, peak shape and sampling time, the flow-rate of the reagent carrier solution was adjusted to 0.8 mL min^{-1}.
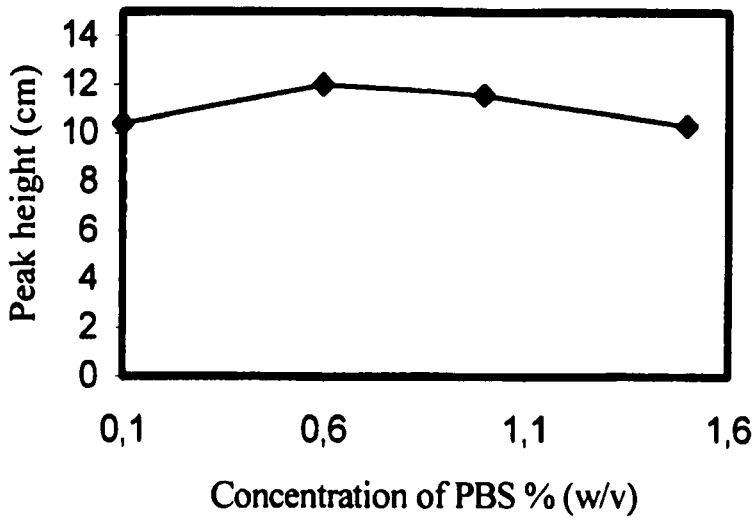
FIGURE 4 Effect of concentration of PBS on the peak height. Flow-rate: 0.8 mL min^{-1}. 3.8 mg L^{-1} of Cu (II)
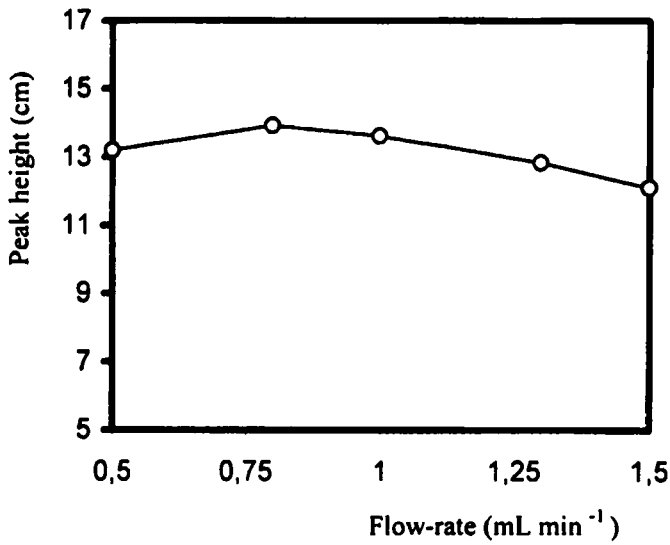

FIGURE 5 Effect of flow-rate of reagent carrier solution on the peak height, 4.2 mg L^{-1} of Cu(II), PBS 0.6 % (w/v)

Effect of foreign ions

The effects of some likely interfering ions were examined. Table I summarizes the tolerance limits of interfering ions on the determination of 80 μg L^{-1} copper (II). Most of the ions examined did not interfere with the copper (II) concentrations up to at least 500-fold excesses. But, Al (III) at the amounts of 800 μg L^{-1} and Fe (III) at the amounts of 1000 μg L^{-1} gave positive interference. They did not interfere at amounts < 500 and 800 μg L^{-1}, respectively.

TABLE I Tolerance limits of foreign ions on the determination of 80 μg L^{-1} copper (II) ion

Tolerance limit (μg L^{-1})	Ion added
Over 150,000	K (I), Na (I), Cl$^-$, Br$^-$, PO$_4^{3-}$, CO$_3^{2-}$
20,000	Co (II), Ni (II), Fe (II), Pb (II), Cd (II), Mn (II)
500	Al (III), Fe (III)

APPLICATIONS

To evaluate the applicability of the proposed flow-injection method, it was applied to the determination of copper (II) in river and seawater samples. The samples collected from different sources were filtered and then directly injected into the FIA system. Both calibration curve and standard addition methods were carried out. The values obtained from the calibration curve and the standard addition methods are in good agreement with each other. Examples of recorded output for different river and sea water samples are shown in Figure 3 (b) The results are summarized in Table II.

The proposed method was also applied to the analysis of copper (II) in solutions obtained conventionally from ore samples. For the copper rich ore sample the results obtained are in good agreement with the certified values (Table II).

TABLE II Determination of copper (II) in different river and sea water samples[a]

Sample	Copper (II) in sample[b] (μg L^{-1})		
	Found[c]	Found[d]	Certified[e]
River water			
Mert	42 22 (0.08)	42.10 (0.03)	
Kurtun	37.17 (0.24)	36.15 (0.09)	

Sample	Copper (II) in sample[b] ($\mu g\ L^{-1}$)		
	Found[c]	Found[d]	Certified[e]
Seashore water			
Baruthane	53.75 (0.11)	53.25 (0.08)	
Seaport	65.38 (0.08)	64.95 (0.10)	
Organized industry	88.15 (0.15)	87.50 (0.06)	
Ore sample[f]			
Copper rich ore	28.65 (0.24)		28.16 (0.18)

a. Samples were collected at Samsun, Turkey.
b. Values in parenthesis are the relative standard deviations for n = 5 with a confidence of 95 %.
c. Calibration curve method.
d. Standard addition method.
e. Provided by copper processing factory body.
f. Values indicated as % (w/w).

References

[1] W.R. Wolf and K.K. Stewart, *Anal. Chem.*, **51**, 1201–1206 (1979).
[2] K. Fukamachi and N. Ishibashi, *Anal. Chim. Acta*, **119**, 383–387 (1980).
[3] Z. Fang, S. Xu and S. Zhang, *Anal. Chim. Acta*, **164**, 41–50 (1984).
[4] A.O. Jacintho, E.A.G. Zagatto, H. Bergamin, F.F.J. Krug, B.F. Reis, R.E. Bruns and B.R. Kowalski, *Anal. Chim. Acta*, **130**, 243–249 (1981).
[5] E.A.G. Zagatto, A.O. Jacintho, F.F.J. Krug, B.F. Reis, R.E. Bruns and M.C. U. Araujo, *Anal. Chim. Acta*, **145**, 169–174 (1983).
[6] J. Ruzicka and E.H. Hansen, *Anal. Chim. Acta*, **99**, 37–41 (1978).
[7] A. Hu, R.E. Dessy and A. Graneli, *Anal. Chem.*, **55**, 320–323 (1983).
[8] L. Anderson, D. Jagner and M. Josefson, *Anal. Chem.*, **51**, 1371–1377 (1982).
[9] J. Janata and J. Ruzicka, *Anal. Chim. Acta*, **139**, 105–108 (1982).
[10] R.M. Smith and T.G. Hurdley, *Anal. Chim. Acta*, **166**, 271–275 (1984).
[11] A. Kojlo and J. Michalowski, *Anal. Chim. Acta*, **228**, 287–291 (1990).
[12] K. Minoura and K. Fukushima, *Chikyu Kagaku*, **22**, 47–53 (1988).
[13] S. Nakano, K. Nakaso, K. Noguchi and T. Kawashima, *Talanta*, **44**, 765–769 (1997).
[14] Yu A. Zolotov, L.K. Shpigun, I. Ya Kolotyrkina, E.A. Novikov and O.V. Bazanova, *Anal. Chim. Acta*, **200**, 21–33 (1987).
[15] E.B. Milosavljevic, J. Ruzycka and E.H. Hansen, *Anal. Chim. Acta*, **169**, 321–329 (1985).
[16] K.K. Falkner and J.M. Edmond, *Anal. Chem.*, **62**, 1477–1483 (1990).
[17] P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *j. Prakt. Chem.*, **149**, 217–224 (1937).