

# Determination and Pre-concentration of Copper(II) with *N,N'*-Bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine by Flame Atomic Absorption Spectrophotometry

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A water-insoluble chelate reagent, *N,N'*-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine (Schiff base A) has a character to form a macrocyclic metal complex due to an intra-hydrogen-bonding and a  $\pi$ - $\pi$  interaction. A new analogue of *N,N'*-bis[2-(benzylideneamino)ethyl]ethane-1,2-diamine (Schiff base B) also has a character to form a macrocyclic metal complex due to only the  $\pi$ - $\pi$  interaction without the intra-hydrogen-bonding interaction. Determination and pre-concentration of Cu(II) with the Schiff bases A and B in nitrobenzene were investigated. The Schiff base A extracted Cu(II) with one picrate ion. On the other hand, the Schiff base B extracted Cu(II) with two picrate ions. This caused that a proton was dissociated from one phenolic hydroxyl group in the Schiff base A in a carbonate buffer at pH 10. An enrichment factor of Cu(II), 116, was obtained in this method. A detection limit of Cu(II) was  $8 \times 10^{-9}$  M and a linear range of a calibration curve was from  $8 \times 10^{-9}$  to  $1 \times 10^{-6}$  M. This method was applied to determinations of copper in river waters and aluminum and duralumin alloys.

## 1. Introduction

Generally, a dissolved copper in natural waters cannot be measured without its pre-concentration by flame atomic absorption spectrometry (FAAS), because its concentration is low. Therefore, it is necessary for its pre-concentration to determine the copper. Some separation and pre-concentration techniques of Cu(II) from some matrix have been achieved by a solvent extraction of a Cu(II)-diethyldithiocarbamate (DDTC) complex into chloroform, carbon tetrachloride, and methyl isobutyl ketone (MIBK) from water samples.<sup>1</sup> A solvent extraction method for a relatively high concentration of Cu(II) (2 mM) with macrocyclic Schiff bases using chloroform has been also reported.<sup>2</sup> However, it would be necessary to exchange a halogenized solvent into a non-halogenized solvent, because of an air pollution for a vaporization of the halogenized solvent and its poor combustion quality for FAAS.

Comparing to a solvent extraction of Cu(II) from a large volume of water into small volumes of MIBK and

chloroform, a volume of nitrobenzene as the solvent can relatively be smaller than those of MIBK and chloroform, because solubilities of MIBK, chloroform and NB in water are 1.70, 0.80, and 0.21%(w/w), respectively.<sup>1</sup> Therefore, NB was chosen as the non-halogenized solvent in this work. When the solvent of a small relative permittivity, such as chloroform (4.9),<sup>1</sup> was used, it was required that almost all chelating reagents for the solvent extraction of a metal ion formed a neutral metal complex, such as Cu(DDTC)<sub>2</sub>. When NB, which has a high relative permittivity (34.8),<sup>1</sup> was used, even the chelating reagents to form an ionic metal complex could be used. A pre-concentration method by the solvent extraction of cadmium with 2,4,6-tri-2-pyridyl-1,3,5-triazine using NB has been reported.<sup>3</sup> The solvent NB was a proper solvent for a direct introduction into a flame of FAAS in the method. A solvent extraction method of transition metal ions with macrocyclic and acyclic Schiff bases including phenolic hydroxyl groups using NB has been also reported.<sup>4,5</sup> These Schiff bases showed a selectivity of

Cu(II) for the solvent extraction and its efficiency of a phenolate ion in the Schiff base moiety, which could behave as a counterion-like anion for the ionic Cu(II)-Schiff base complexes. However, this proposed method needs to re-dissolve the extracted Cu(II)-Schiff base complexes in water in order to introduce them into FAAS after the solvent extraction of Cu(II) from a water sample into NB and then a vaporization of NB.

In the present work, two water-insoluble Schiff bases were chosen as the chelating reagent. One is *N,N'*-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine (Schiff base A), which could form a macrocyclic metal complex due to an intra-hydrogen-bonding and a  $\pi$ - $\pi$  interaction between its phenolic groups, and the other is *N,N'*-bis[2-(benzylideneamino)ethyl]ethane-1,2-diamine (Schiff base B), which could form the macrocyclic metal complex due to only the  $\pi$ - $\pi$  interaction between its benzene rings without the intra-hydrogen-bonding interaction. Both of the Schiff bases could be easily synthesized from triethylene tetramine.<sup>6</sup> It is also interesting to investigate a selectivity change of metal ions for the Schiff bases formed the different macrocyclic metal complexes due to the different intra-interaction in these Schiff bases.

A pre-concentration method of Cu(II) has been recently developed using solid phase extractions on an Amberlite XAD-2 resin,<sup>7</sup> a microcrystalline naphthalene,<sup>8,9</sup> an octadecyl silica membrane desk,<sup>10</sup> and synthetic zeolites.<sup>11</sup> However, an elution of Cu(II) at a high concentrated acid and a dissolution of a Cu(II) complex into an organic solvent have been required for an introduction of an extracted Cu(II) to FAAS in these solid phase extraction methods. Therefore, a liquid – liquid extraction would be better than these solid extraction method with respect to the direct introduction of the extracted Cu(II) to FAAS.

Accordingly, the pre-concentration method of Cu(II) using these Schiff bases A and B for FAAS was investigated.

## 2. Experimental

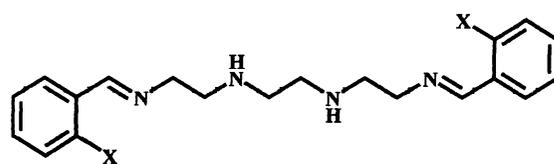
### 2.1. Apparatus

A concentration of Cu(II) was measured by Hitachi Z-6100 Polarized Zeeman Atomic Absorption Spectrophotometer (Tokyo). A FAAS measurement was

conducted according to a recommended method of a manufacturer.

### 2.2. Reagents

The Schiff bases A and B were prepared by stirring a distilled triethylenetetramine (0.05 mol) added salicylaldehyde or benzaldehyde (0.1 mol) in an absolute ethanol for 2 hrs, according to a literature method.<sup>6</sup> Structures of the Schiff bases A and B are illustrated in Figure 1. Sodium acetate, sodium perchlorate, sodium



X = OH : Schiff base A  
X = H : Schiff base B

Fig. 1 Chemical structures of Schiff bases A and B.

1-heptanate, sodium 1-octanate, sodium benzoate, sodium thiocyanate, sodium picrate (Pic<sup>-</sup>), sodium tetraphenylboride (BPh<sub>4</sub><sup>-</sup>), sodium 1-pentanesulfonate, sodium 1-hexanesulfonate, sodium 1-octanesulfonate, copper(II) nitrate and copper(II) perchlorate of reagent grade were purchased from Wako (Osaka, Japan). Buffers of pH 1 – 3, 3 – 6, 6 – 9, 9 – 10, 10 – 11, and 12, were prepared from hydrochloric acid, sodium acetate and acetic acid, sodium dihydroxyphosphate and disodium hydroxyphosphate, sodium tetraborate, sodium hydroxycarbonate and sodium carbonate, and sodium hydroxide (Wako) of the reagent grade, respectively. Sodium tetraborate and NB of the reagent grade were purchased from Nacalai tesque (Kyoto, Japan). Certified reference materials were obtained from Japanese Analytical Chemical Society (JAS0031 and JAS0032) and British Chemical Industry (182/2, 216/2, and 380) for river waters, and aluminum and duralumin alloys, respectively.

### 2.3. Procedure

A 2 mL NB solution of the Schiff base A or B was added into an aqueous Cu(II) sample solution with a 1 M buffer (10 mL) and a 1 M ion-pair formation reagent (10 mL) in 300 mL beaker. A sample volume below ca. 180 mL could be used. A pre-concentration of Cu(II) was

conducted by a stir of a mixture solution. A solvent extraction rate would increase due to the stir, because an apparent surface of a NB phase increased, as a result of producing many small NB drops in a water phase. A phase separation between NB, which has a higher density than water, and the aqueous phase, was very quick. Since a concentration of Cu(II) in the aqueous solution after the solvent extraction was below a detection limit under the optimized conditions, the NB solution with the aqueous phase from the bottom of the beaker without operating any phase separation after the stir could be directly introduced to FAAS.

Aluminum and duralumin alloys were dissolved by heating them in conc. HCl with conc. HNO<sub>3</sub> and HF.

### 3. Results and discussion

#### 3.1. Effect of ion-pair formation reagent

Influences of absorbance of copper with the Schiff base A on some anions for an ion-pair formation reagent at pH 10 after stirring for 90 min are summarized in Table 1.

Table 1 Influences of absorbances of copper on ion-pair formation reagents<sup>a)</sup>

Ion-pair formation reagent	Ratio <sup>b)</sup>
BPh <sub>4</sub> <sup>-</sup>	1.9
Pic <sup>-</sup>	1.8
AcO <sup>-</sup>	1.3
C <sub>8</sub> H <sub>17</sub> COO <sup>-</sup>	1.2
C <sub>7</sub> H <sub>15</sub> COO <sup>-</sup>	1.2
C <sub>8</sub> H <sub>17</sub> SO <sub>3</sub> <sup>-</sup>	1.1
C <sub>6</sub> H <sub>13</sub> SO <sub>3</sub> <sup>-</sup>	1.1
C <sub>5</sub> H <sub>11</sub> SO <sub>3</sub> <sup>-</sup>	1.1
PhCOO <sup>-</sup>	1.1
SCN <sup>-</sup>	0.89
ClO <sub>4</sub> <sup>-</sup>	0.72

<sup>a)</sup> Conditions, buffer: 0.1 M carbonate at pH 10; ion-pair formation reagent: 0.01 M; Cu(II):  $2 \times 10^{-7}$  M; chelate reagent:  $1 \times 10^{-4}$  M Schiff base A; stirring time: 90 min; NB: 2 mL; water: 100 mL.

<sup>b)</sup> Ratio = (absorbance of copper with ion-pair formation reagent) / (absorbance of copper without ion-pair formation reagent).

Its absorbance did not almost increase for the carboxylate

and thiocyanate ions, which would coordinate to a Cu(II)-Schiff base A complex, and for the alkanesulfonate and perchlorate ions of typical ion-pair formation reagents. The largest absorbance of copper was observed for both of Pic<sup>-</sup> and BPh<sub>4</sub><sup>-</sup>, in case of a  $2 \times 10^{-7}$  M Cu(II). However, its absorbance using of Pic<sup>-</sup> was twice larger than that using BPh<sub>4</sub><sup>-</sup>, in case of a  $1 \times 10^{-6}$  M Cu(II) of a sample solution after stirring for 30 min. Therefore, the picrate ion, which always gave a constant high absorbance of copper among these ion-pair formation reagents under the used conditions, was used.

#### 3.2. Effect of pH

Figure 2 shows the dependencies of the absorbance of

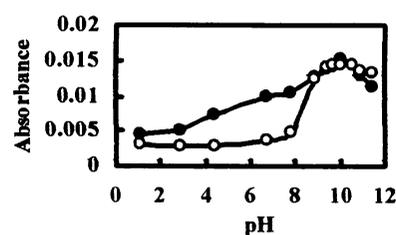


Fig. 2 Dependencies of absorbances of copper with Schiff bases A and B on pH. Conditions, buffer: 0.1 M; stirring time: 90 min; Schiff base:  $1 \times 10^{-4}$  M; NaPic:  $1 \times 10^{-2}$  M; Cu(II):  $2 \times 10^{-7}$  M; NB phase: 2 mL; water phase: 100 mL. ●, Schiff base A; ○, Schiff base B.

copper with Pic<sup>-</sup> on pH after stirring for 90 min. The largest absorbances for Schiff bases A and B were observed in a carbonate buffer at pH 10 and at above pH 8, respectively. The absorbance at the below pH 10 was small, because of protonations of amino groups in the Schiff bases A and B. Therefore, pH 10 was chosen, since the solvent extraction using the Schiff base A could be compared to that using the Schiff base B under the same pH.

#### 3.3. Effects of Schiff base concentration and stirring time

Figure 3 shows the dependencies of the absorbance of copper on concentrations of the Schiff bases A and B after stirring for 90 min. For both the Schiff bases, the largest absorbance of copper was observed at the  $1 \times 10^{-4}$

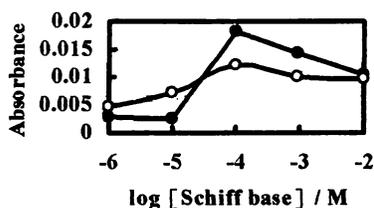


Fig. 3 Dependencies of absorbances of copper on concentrations of Schiff base A and B. Buffer: 0.1 M carbonate buffer at pH 10. Other conditions as in Fig. 2. ●, Schiff base A; ○, Schiff base B.

M Schiff base. The large excess Schiff base would interrupt the complex formation of Cu(II) with the Schiff base due to an inter-hydrogen-bonding interaction between the amino groups of the Schiff base. Also, in case of both the Schiff bases, the absorbance of copper was almost constant at > 60 min for the solvent extraction of Cu(II) from the  $2 \times 10^{-7}$  M Cu(II) aqueous solution into NB.

A theoretical enrichment factor of Cu(II) is 100 in 200-mL-water phase / 2-mL-NB phase system. The enrichment factor of Cu(II) was calculated by a ratio of absorbance of copper(II) perchlorate in a  $1 \times 10^{-2}$  M  $\text{Pic}^-$  NB solution containing the  $1 \times 10^{-4}$  M Schiff base to the observed absorbance of the solvent extracted copper in a range of 1 to  $10 \times 10^{-5}$  M Cu(II). The absorbance of copper for copper(II) perchlorate dissolved in NB was 39% smaller than that in an aqueous solution, because of a poor combustion quality of NB. However, the absorbance of copper for copper(II) perchlorate dissolved in the  $1 \times 10^{-2}$  M  $\text{Pic}^-$  NB solution containing the  $1 \times 10^{-4}$  M Schiff base was 178% larger than that without  $\text{Pic}^-$  and the Schiff base. It is considered that the absorbance of copper in NB was increased by the improved combustion quality of NB in presence of  $\text{Pic}^-$  with the Schiff base, because the absorbances of copper for copper(II) perchlorate in only the  $1 \times 10^{-2}$  M  $\text{Pic}^-$  NB solution and in only the  $1 \times 10^{-4}$  M Schiff base NB solution were similar to that in NB without them. Therefore, the observed absorbance of copper in the NB solution was only 69% smaller than that in the aqueous solution. An extraction

ratio of Cu(II) was 93%. However, the enrichment factor of 116 was found, because only the small volume of NB phase (ca. 1.6 mL) remained in the water phase containing the 0.1 M carbonate buffer at pH 10 with the  $1 \times 10^{-2}$  M  $\text{Pic}^-$ .

#### 3.4. Effect of $\text{Pic}^-$ concentration

Figure 4 shows the dependencies of the absorbances of

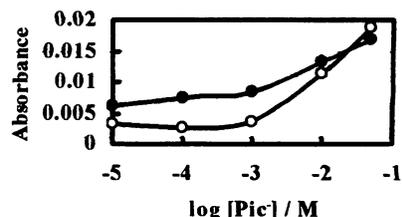


Fig. 4 Dependencies of absorbances of copper on concentration of  $\text{Pic}^-$ . Buffer: 0.1 M carbonate buffer at pH 10. Other conditions as in Fig. 2. ●, Schiff base A; ○, Schiff base B.

copper with the Schiff bases A and B on the  $\text{Pic}^-$  concentration. Although the absorbance of copper increased with increasing concentration of  $\text{Pic}^-$ , the above 0.1 M  $\text{Pic}^-$  could not be dissolved in the carbonate buffer. Therefore, the  $1 \times 10^{-2}$  M  $\text{Pic}^-$  as the ion-pair formation reagent was used.

Accordingly, the optimized conditions were as follows: water phase, 200 mL aqueous sample solution with  $1 \times 10^{-2}$  M NaPic and 0.1 M carbonate buffer at pH 10; NB phase, 2 mL NB with  $1 \times 10^{-4}$  M Schiff base A or B; stirring time, 90 min. The enrichment factor and solvent extraction ratio of Cu(II) were 116 and 93%, respectively. A linear range of the calibration curve for Cu(II) was  $8 \times 10^{-9}$  –  $1 \times 10^{-6}$  M. A detection limit (S/N = 3, the absorbance of copper extracted from a blank buffer solution into NB was used as a signal of noise.) and RSD for Cu(II) was  $8 \times 10^{-9}$  M and 1.7% for this concentration, respectively.

#### 3.5. Interferences of foreign metal ions

Recoveries of copper with the Schiff bases A and B in presence of foreign metal ions are summarized in Table 2. A 1 : 1 ratio of Fe(II) to Cu(II) interfered the absorbance of

Table 2 Recoveries (%) of copper<sup>a)</sup> with Schiff bases A and B in presence of foreign metal ions

[metal ion] / [Cu(II)]	Schiff base A					Schiff base B				
	Fe(II)	Fe(III)	Co(II)	Ni(II)	Zn(II)	Fe(II)	Fe(III)	Co(II)	Ni(II)	Zn(II)
1	58	103	94	98	106	102	93	97	90	100
10	55	98	59	101	104	98	86	98	88	95
100	37	74	58	99	103	107	84	49	39	100
1000	41	60	46	69	84	65	43	26	14	79

<sup>a)</sup> Cu(II) =  $1 \times 10^{-7}$  M.

copper for the Schiff base A. For the Schiff base B, a 1 : 100 ratio of Ni(II) to Cu(II) interfered it. An available macrocyclic coordination site of Cu(II) in the Schiff base A would be formed due to an intra-hydrogen-bond between the phenolic hydroxyl group and the phenolate ion in the Schiff base A at pH 10, as illustrated in Fig. 5.

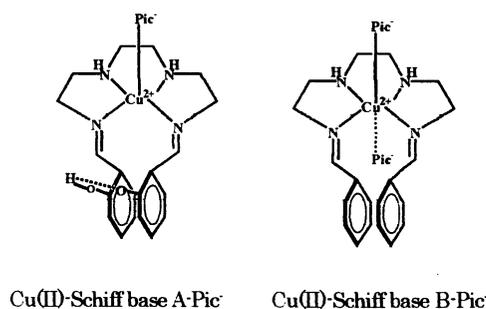


Fig. 5 Structures of Cu(II)-Schiff bases A and B-Pic<sup>-</sup> complexes.

The available macrocyclic coordination site formed by a triethylenetetramine ring in the Schiff base A might give the best fit size for Cu(II) and Fe(II). In case of the Schiff base B, the available macrocyclic coordination site formed by the triethylenetetramine ring would produce due to an intra- $\pi$ - $\pi$  interaction between benzene rings in the Schiff base B. The available macrocyclic coordination site in the Schiff base B would be more flexible than that in the Schiff base A. Therefore, Fe(II) might not interfere the absorbance of copper with the Schiff base B. These structures of the Cu(II)-Schiff base A and B-Pic<sup>-</sup> complexes would be also suggested that a slope for a plot of the absorbance of copper vs. the concentration of Pic<sup>-</sup> for the Schiff base B was larger than that for the Schiff base A in the Pic<sup>-</sup> concentration range of

the above  $1 \times 10^{-3}$  M in Fig. 4. Because it was necessary for an observation of the large absorbance of copper to increase the concentration of Pic<sup>-</sup>, in case of the Schiff base B.

Consequently, a comparison of a selectivity for Cu(II) between the intra- $\pi$ - $\pi$  and the intra-hydrogen-bonding interaction in these Schiff bases would give an important information to make a molecular design for the extractant using these intra-molecular interactions.

### 3.6. Determination of copper

This method using the Schiff base A was applied for determinations of copper in river waters and aluminum and duralumin alloys. These results for the river waters JAC 0031 (certified value,  $0.88 \pm 0.03$  ppb for copper) and JAC 0032 ( $10.5 \pm 0.2$ ) were  $0.87 \pm 0.02$  and  $10.6 \pm 0.2$  ppb, respectively, where errors are standard deviations. These results for the aluminum alloys No. 182/2 (certified value, 0.045%(w/w) for copper) and No. 380 (0.90) and the duralumin alloy No. 216/2 (4.56) were  $0.042 \pm 0.001$ ,  $0.87 \pm 0.01$ , and  $4.39 \pm 0.09\%$ (w/w), respectively. These results agreed with the certified values of copper. An interference of Fe(II) was not found, because the nitrate ion in the dissolved acids generally oxidized Fe(II) to Fe(III) under the heating condition.

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