Successive Determination of Copper and Iron by a Flow Injection-Catalytic Photometric Method Using a Serial Flow Cell

Shinsuke OHNO, Miho TANAKA, Norio TESHIMA, and Tadao SAKAI[†]

Department of Applied Chemistry, Aichi Institute of Technology, 1247 Yachigusa, Yakusa-cho,
Toyota, Aichi 470-0392, Japan

A flow injection-catalytic spectrophotometric method using a serial flow cell was proposed for the successive determination of trace amounts of copper and iron. This method is based on the oxidation coupling of *p*-anisidine with *N,N*-dimethylaniline in the presence of hydrogen peroxide to form a dye, which has an absorption maximum at 740 nm. In this indicator reaction, ligands such as 1,10-phenanthroline (phen) and diphosphate were achieved to improve the sensitivity and selectivity. Under the optimal experimental conditions, the determinable ranges were 0.05–5 ppb for copper and 0.5–100 ppb for iron, respectively. The RSDs ($n = 10$) were 0.78% for 0.5 ppb copper(II) and 0.5% for 200 ppb iron(III). The sample throughput was 30 h⁻¹. The present flow-injection method was applied to the determination of copper and iron in standard river water, tap water, and other natural water samples, and also to the analysis of labile and inert complexes in synthesized samples containing humic acid with copper(II) or iron(III).

(Received August 21, 2003; Accepted October 17, 2003)

Introduction

Trace amounts of copper and iron exist widely in river, tap, pond, well, and underground water. These metals are essential trace elements for biological systems. Numerous dissolving chemical forms, such as aqua ions, complexes and colloids, are observed in natural water. In general, the toxicity of dissolved copper(II) is considered to be much less than that of mercury, but greater than that of cadmium, silver, lead, and zinc.¹ However, it has been reported that chelating agents, such as nitrilotriacetic acid and ethylenediaminetetraacetic acid, decreased the toxicity of copper.² The concentration levels of these metals existing in natural water are trace and/or ultratrace. Therefore, a highly sensitive analytical method for the determination of copper and iron is required to investigate water pollution.

Kinetic-catalytic methods based on catalyzed reactions have been developed for the determination of manganese, chromium, cobalt, and vanadium ions at trace and ultratrace levels.^{3–6} Kawashima *et al.* have determined ppb levels of iron in tap and hot-spring water samples.⁷ Recently, the present authors also reported a catalytic method for the determination of copper using a flow-injection system.⁸ On the other hand, adsorptive cathodic stripping voltammetry (ACSV) was proposed to measure copper in seawater at trace levels.⁹ However, one of the major problems in ACSV is the adsorption of organic compounds on the electrode.¹⁰

The kinetic-catalytic methods require a controlled reaction temperature, time, and constant mixing of the reagents. Thus, flow injection analysis (FIA), which has advantages of rapidity and easy assembly, is efficient to control serious experimental conditions. However, it is difficult to successively determine

several analytes by an FIA system equipped with a conventional flow cell. Recently, Sakai and his co-workers designed two-channel double and serial flow cells¹¹ and a twin flow cell¹² for the simultaneous determination of copper and iron with 2-(5-bromo-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]aniline, sodium salt (5-Br-PSAA) or 2-(5-nitro-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]phenol, disodium salt, dihydrate (Nitro-PAPS). However, these methods using chromogenic reagents were not sufficient for the determination of sub-ppb levels of copper and iron. Also, it is difficult to analyze the complexation reactions of ppb levels of copper and iron with ligands, such as humic and fulvic acids. During the recent decade, some researchers have reported on catalytic methods for binary metal mixtures, such as silver(I)-mercury(II),¹³ chromium(VI)-tungsten(VI),¹⁴ and iron(II)-antimony(III).¹⁵ However, there are few reports on kinetic-catalytic methods for the determination of two catalysts using a single indicator reaction.

In the presence of hydrogen peroxide, *p*-anisidine reacted with *N,N*-dimethylaniline (DMA) to form a dye ($\lambda_{\text{max}} = 740 \text{ nm}$). Although the oxidative coupling reaction was slow, the reaction rate was accelerated in the presence of copper(II)¹⁶ or iron(III).¹⁷ Since the absorbance of the dye formed at a fixed time was proportional to these metal concentrations, it was possible to determine copper(II) and iron(III). In a previous paper,¹⁸ this kinetic-catalytic analysis was performed to determine copper(II) and iron(III) selectively by a batchwise method.

This paper describes a catalytic method using an FIA system equipped with a serial flow cell for the successive determination of copper(II) and iron(III) at sub-ppb levels in natural water samples, because the sensitivity and selectivity can be improved. The proposed method can be applied to the determination of trace amounts of copper(II) and iron(III), and also to the determination of labile and inert complexes in synthesized samples involving humic acid and copper(II) or iron(III).

[†] To whom correspondence should be addressed.
E-mail: tadsakai@aitech.ac.jp

Fig. 1 Schematic diagram of a flow-injection system equipped with a serial flow cell: C, carrier solution (0.5 M hydrogen peroxide at pH 2); R₁ (0.08 M *p*-anisidine, 0.06 M DMA, 0.2 M acetate buffer (pH 3.1), 2×10^{-3} M diphosphate); R₂ (0.06 M *p*-anisidine, 0.06 M DMA, 0.2 M acetate buffer (pH 3.1), 2×10^{-3} M diphosphate, 2×10^{-3} M phen); P₁ and P₂, pumps; SL, sample loop (2 m $\times$ ϕ 0.5 mm); RC, reaction coil (8 m $\times$ ϕ 0.5 mm, 90°C); CC, cooling coil (1 m $\times$ ϕ 0.5 mm); BPC, back pressure coil (35 cm $\times$ ϕ 0.25 mm); D, double beam spectrophotometer equipped with a serial flow cell (740 nm); R, recorder; W, waste; S, sample; R₃, 3 M hydrogen peroxide at pH 2; P₃ and P₄, peristaltic pumps.

Experimental

Reagents

All of the reagents were of analytical-reagent grade and were used without further purification. All solutions were prepared with deionized water purified with an Advantec Aquarius GSH-210 system.

Commercially available 1000 ppm copper(II) and iron(III) standard solutions for atomic absorption spectrophotometry (Wako, Osaka) were used. Working solutions of copper and iron were prepared by appropriate dilution of the standard solutions with 0.01 M (= mol dm⁻³) hydrochloric acid.

A 0.25 M *p*-anisidine solution was prepared by dissolving 15.4 g of *p*-anisidine (Wako) in 150 ml of conc. hydrochloric acid and made up to 500 ml with water.

A 0.6 M DMA solution was prepared by dissolving 36.4 g of DMA (Wako) in 90 ml of 4 M hydrochloric acid and made up to 500 ml with water.

A 2 M acetic acid solution was prepared by diluting 60 ml of acetic acid (Sigma Aldrich Japan, Tokyo) to 500 ml with water. A 2 M sodium acetate solution was prepared by dissolving 27.2 g of sodium acetate trihydrate (Nacalai Tesque, Kyoto) with water and made up to 100 ml with water. These solutions were mixed to prepare a buffer solution (pH 3.1).

A 0.1 M diphosphate solution was prepared by dissolving 2.23 g of sodium diphosphate decahydrate (Wako) with 50 ml of water.

A 0.25 M 1,10-phenanthroline (phen) solution was prepared by dissolving 4.96 g of 1,10-phenanthroline monohydrate (Dojindo Laboratories, Kumamoto) with 8 ml of 4 M hydrochloric acid.

Hydrogen peroxide solutions (0.5 and 3 M) were prepared by diluting appropriate amounts of 30% hydrogen peroxide with 0.01 M HCl.

Apparatus

Figure 1 shows a schematic diagram of a flow-injection system using a serial flow cell for the successive determination

Fig. 2 Flow signals for copper(II) and iron(III) using a serial flow cell: (a) and (a'), blank peaks for copper(II) and iron(III); (b) and (b'), 0.5 ppb copper(II) and 20 ppb iron(III); (c) and (c'), 1 ppb copper(II) and 50 ppb iron(III); (d) and (d'), 2 ppb copper(II) and 100 ppb iron(III). Other conditions are the same as in Fig. 1.

of copper(II) and iron(III). The system consisted of two double-plunger pumps (DMX-2000, Sanuki Kogyo, Tokyo and Type DUAL PUMP201, F-I-A Instrument, Tokyo), two six-way injection valves (SVM-6M2, Sanuki Kogyo), two thermostated baths (R-3000C, Sanuki Kogyo and Type 521, F-I-A Instrument), a spectrophotometer (S-3250, Soma Optics, Tokyo) equipped with a serial flow cell (cell volume, 4 μ l; path length, 5 mm),¹¹ two peristaltic pumps (U4-8R, Alitea, Sweden) and a recorder (EB22005, Chino, Tokyo). All connecting lines and reaction coils were made from 0.5 mm i.d. Teflon tubing. A Horiba Model F-22 pH/mV meter was used for pH adjustment.

Procedure

A carrier solution (C, 0.5 M hydrogen peroxide at pH 2) and a R₁ solution (0.08 M *p*-anisidine, 0.06 M DMA, 0.2 M acetate buffer at pH 3.1 and 2×10^{-3} M diphosphate) were delivered at 0.65 ml min⁻¹ by pump 1 (P₁). The carrier solution (described above) and an R₂ solution (0.06 M *p*-anisidine, 0.06 M DMA, 0.2 M acetate buffer at pH 3.1, 2×10^{-3} M diphosphate and 2×10^{-3} M phen) were delivered at 0.70 ml min⁻¹ by pump 2 (P₂). The sample (S) and 3 M hydrogen peroxide (pH 2, R₃) solutions were delivered by two peristaltic pumps (P₃, P₄). These mixed solutions were loaded in two sample loops (2 m) attached to valves V₁ and V₂, and these solutions were injected into the carrier solutions. The absorbance of the dye formed in the reaction coil (RC) and the cooling coil (CC) was monitored at 740 nm using a double-beam spectrophotometer equipped with a serial flow cell and recorded on a recorder. Figure 2 shows flow signals for copper(II) and iron(III) obtained using a serial flow cell.

Results and Discussion

Effects of activators on the catalytic reactions

The use of a suitable activator in the kinetic-catalytic methods can enhance the catalytic effect of specific metal ions, and then the selectivity and sensitivity can be also improved.

The activating effects of several polypyridines, such as phen, 2,9-dimethyl-1,10-phenanthroline (neocuproine), batho-phenanthroline disulfonate (BPS), and bathocuproine disulfonate (BCS), were investigated. Figure 3 (a) shows the effects of the phen concentration on the copper- and iron-catalyzed reactions in the range from 0 to 1×10^{-2} M. Phen enhanced the catalytic action of iron(III) and acted as an inhibitor for copper(II). The conditional redox potential of the Fe(III)/Fe(II) system increased in the presence of phen; the overall formation

Fig. 3 Effects of the activator concentrations of (a) phen and (b) neocuproine on the copper(II) and iron(III) determination: (●), 50 ppb iron(III); (○), blank for iron(III) determination system; (▲), 5 ppb copper(II); (△), blank for copper(II) determination system. Other conditions are the same as in Fig. 1.

Fig. 4 Dependences of copper(II) and iron(III) signals on the hydrogen peroxide concentration of (a) sample and (b) carrier: (▲), 50 ppb iron(III); (△), blank for iron(III) determination system; (●), 5 ppb copper(II); (○), blank for copper(II) determination system. Other conditions are the same as in Fig. 1.

constant of the Fe(II)-phen complex ($\log \beta_3 = 21.3$) is larger than that of the Fe(III)-phen complex ($\log \beta_3 = 14.1$).¹⁹ Therefore, it was obvious that the coexisting phen enhanced the oxidation power of Fe(III). The absorbance of the produced dye in the presence of iron(III) increased up to 2×10^{-3} M phen, and then the absorbance gradually decreased over that concentration. It seems that the activator was attributable to form ternary complexes of the activator-metal-substrate;²⁰ phen-iron-*p*-anisidine and/or phen-iron-DMA. Similarly, the effect of BPS was also studied on the iron-catalyzed dye-formation reaction. However, the absorbance in the presence of BPS was lower than that of phen, because BPS might cause a steric hindrance on the ternary complex formation. Thus, a 2×10^{-3} M phen concentration was selected in the iron(III) determination system.

The effects of neocuproine concentrations were investigated on each metal determination system. Neocuproine did not act as an effective activator for copper(II) and iron(III) in the range from 0 to 1×10^{-2} M. This result is shown in Fig. 3 (b). Although neocuproine acted as an activator for the copper-catalyzed reaction,¹⁸ the same result could not be observed in this study. Neocuproine acted as an activator for a copper-catalyzed reaction when the DMA concentration was 0.02–0.03 M and the *p*-anisidine concentration was 0.01 M. On the other hand, neocuproine acted as an inhibitor for copper(II) if the concentration of *p*-anisidine was more than 0.02 M. Thus, the activator for copper(II) determination was not used in the present FIA study.

Table 1 Recoveries of copper(II) and iron(III) with and without diphosphate

Added, ppb		Found, ppb (Recovery, %)			
		Cu		Fe	
Cu	Fe	With	Without	With	Without
5	50	5.16(103)	6.01(120)	51.3(103)	63.7(127)
1	20	0.99(99)	1.06(106)	20.1(101)	28.8(144)
1	50	1.04(104)	1.11(111)	49.5(99)	65.2(130)

Effect of diphosphate on the determination of copper(II) and iron(III)

In a previous study,¹⁸ diphosphate was effective as a masking agent to determine copper(II) and iron(III) successively. The effects of diphosphate for copper(II) and iron(III) were investigated using the FIA system. The recoveries are given in Table 1. The recoveries in the absence of diphosphate were over 100%. This is because copper(II) and iron(III) catalyze in the same indicator reaction. In the presence of diphosphate, the recoveries of copper(II) and iron(III) were around 100%, because all catalytic actions were slightly inhibited.

The effect of the diphosphate concentration on the copper- and iron-catalyzed dye formation was investigated. The interferences on each element were restricted with increasing the diphosphate concentration. It seems that the complex formation of these metals with diphosphate occurred. In addition, the peak heights of the reagent blank were depressed in the presence of diphosphate. Thus, 2×10^{-3} M diphosphate was selected for each determination of copper(II) and iron(III).

Optimization of the hydrogen peroxide concentration

The hydrogen peroxide concentration in samples was varied from 0 to 4 M. The absorbance of the dye increased with increasing the hydrogen peroxide concentration. Therefore, 3 M hydrogen peroxide was selected for the determinations of copper(II) and iron(III). However, the peak heights of the reagent blank became high with an increase in the concentration of hydrogen peroxide. Consequently, hydrogen peroxide was added to each carrier solution (pH 2) to reduce blank peak heights. The concentration was varied from 0 to 1 M. The results are shown in Figs. 4 (a) and (b). All blank peak heights were reduced with increasing the concentration in the carriers. Thus, the hydrogen peroxide concentrations in the carriers and sample solution were selected to be 0.5 and 3 M, respectively.

Optimization of the pH

The effects of the pH were investigated over the range of 2.1–3.5 for copper(II) and 2.3–3.4 for iron(III). The pH was measured after merging in the tube. In both catalysts, the highest peak height was obtained at around pH 2.8. Therefore, the reaction pHs were fixed at pH 2.8.

Optimization of the reaction temperature

The effects of the reaction temperature on the dye formation in both the absence and presence of copper(II) and iron(III) were studied in the range from 24 to 95°C. The peak heights increased with an increase in the temperature in the presence of catalysts. On the other hand, the peak heights in the absence of catalysts were low. Thus, the reaction temperature was selected to be 90°C.

Table 2 Experimental conditions by the proposed FIA method

Cu	Fe
0.08 M <i>p</i> -Anisidine	0.06 M <i>p</i> -Anisidine
0.06 M DMA	0.06 M DMA
0.2 M Acetate buffer (pH 3.1)	0.2 M Acetate buffer (pH 3.1)
2×10^{-3} M Diphosphate	2×10^{-3} M Diphosphate
	2×10^{-3} M Phen
0.5 M H ₂ O ₂ at pH 2 (carrier)	0.5 M H ₂ O ₂ at pH 2 (carrier)
3 M H ₂ O ₂ at pH 2 (inject)	3 M H ₂ O ₂ at pH 2 (inject)
RC 8 m, 90°C, ϕ 0.5 mm	RC 8 m, 90°C, ϕ 0.5 mm
CC 1 m, ϕ 0.5 mm	CC 1 m, ϕ 0.5 mm
SL 2 m, ϕ 0.5 mm	SL 2 m, ϕ 0.5 mm
BPC 35 cm, ϕ 0.25 mm	BPC 35 cm, ϕ 0.25 mm
Flow rate, 1.4 ml min ⁻¹	Flow rate, 1.3 ml min ⁻¹
$\lambda_{\max}$, 740 nm	$\lambda_{\max}$, 740 nm

Table 3 Recovery tests of copper(II) and iron(III) in mixed solutions

Added, ppb		Found, ppb		Recovery, %	
Cu	Fe	Cu	Fe	Cu	Fe
0.5	20	0.51	19.6	101	98
0.5	50	0.52	52.0	104	104
0.5	100	0.50	95.7	100	96
1	10	0.99	9.76	99	98
1	100	0.96	99	96	99
1	200	1.05	—	105	—
2	100	2.10	99	105	99
2	200	2.09	—	105	—

Optimization of other variables

The effects of other reagent concentrations were examined. The *p*-anisidine concentration was varied from 0 to 0.1 M. The absorbance increased with increasing its concentration. The 0.1 M and 0.08 M *p*-anisidine concentrations were selected for copper(II) and iron(III), respectively. The DMA concentration was varied from 0 to 0.08 M. In this study, 0.06 M DMA was used. The reaction coil length was varied from 2 to 10 m on the copper-(or iron)-catalyzed dye-forming reaction. When the length became longer than 6 m for copper(II) and 8 m for iron(III), the absorbance of the dye increased. Thus, a reaction coil length of 8 m was selected for the determination of copper(II) and iron(III). The slower flow rate resulted in an increase of the absorbance because the reaction time was longer. Flow rates of 1.3 and 1.4 ml min⁻¹ were used for the copper(II) and iron(III) determination, respectively. The sample loops (0.5 mm i.d.) for the copper- and iron-assay system were varied from 0.5 to 3 m. Taking into account the sensitivity and repeatability, sample loops of 2 m were selected.

Calibration curves for copper(II) and iron(III)

The calibration curves for copper(II) and iron(III) were prepared under the optimum conditions (Table 2). The dynamic ranges were 0.05–5 ppb for copper(II) and 0.5–100 ppb for iron(III), respectively. The sampling rate was 30 sample h⁻¹ for each analysis. The repeatabilities by the FIA system were 0.96% and 0.46% for 0.5 and 2 ppb copper(II), 0.78% and 0.45% for 20 and 50 ppb iron(III), respectively. The detection limits ($S/N = 3$) were 10 ppt for copper(II) and 100 ppt for iron(III).

Table 4 Interference of foreign ions in the successive determination of 2 ppb copper(II) and 50 ppb iron(III)

Added ^a /ppb	Cu	Fe
50000	K(I), Mg(II), SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻	K(I), Na(I), SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻
20000	Na(I), Ca(II)	
10000	BO ₃ ³⁻ , Cd(II)	Cd(I), BO ₃ ³⁻ , Mg(II), Ca(II)
5000		Zn(II)
1000	Co(II),	Mn(II), Co(II)
500	Mn(II), Zn(II), Al(III)	Pb(II)
200	Pb(II), Cr(VI), Ni(II)	Cr(VI), Al(III), Ni(II)

a. Tolerable concentration with the tolerance range 95–105%, which means within 5% error in analysis.

Table 5 Simultaneous determination of copper and iron in standard river water^a

Sample	Found ^b , ppb		Certified value, ppb	
	Cu	Fe	Cu	Fe
JAC 0031	0.91 ± 0.03 ^c	7.5 ± 0.2 ^c	0.88 ± 0.3	6.9 ± 0.5
JAC 0032	10.4 ± 0.1 ^c	56 ± 1 ^c	10.5 ± 0.2	57 ± 2

a. Purchased from the Japan Society for Analytical Chemistry.

b. Average value for 10 determinations.

c. The river water was diluted 5 times.

Successive determinations of copper(II) and iron(III) in artificial mixtures were studied. The results are given in Table 3. An error of 5% was considered to be tolerable. The concentration ranges were 0.5–2 ppb for copper and 10–200 ppb for iron. The 100 ppb iron(III) showed no interference in the determination of 0.5 ppb copper(II). On the other hand, 10 ppb iron(III) did not interfere in the determination of 1 ppb copper(II).

Interferences of foreign ions in the determination of copper(II) and iron(III)

The interferences of foreign ions in the determination of a mixture of 2 ppb copper(II) and 50 ppb iron(III) were examined. The results are summarized in Table 4, where the tolerable concentrations of foreign ions are shown in each case. An error of 5% was considered to be tolerable. Most of the metal ions and inorganic anions did not interfere in the determinations of copper(II) and iron(III) for concentrations of up to at least 200 ppb.

Application to standard river water samples and real samples

The proposed method using a serial flow cell was applied to the successive determination of copper(II) and iron(III) in standard river water samples (JAC 0031 and 0032) issued from the Japan Society for Analytical Chemistry. These samples were diluted 5 times with water. Since the pH of the diluted river water was 1.9, it was no problem to determine copper and iron. The results are given in Table 5. Copper and iron obtained by the proposed method were in good agreement with the certified values.

To examine the applicability of the proposed method, copper(II) (0–0.5 ppb) and iron(III) (0–5 ppb) standard solutions were added to tap, rain, and well water samples. These real samples were acidified by adding conc. hydrochloric

Table 6 Determination of copper and iron in tap and natural water samples

Sample	Dilution		In sample, ppb	
	Cu	Fe	Cu	Fe
Tap	5	5	1.36 ± 0.06	63.4 ± 0.6
Rain	1.25	1.25	0.35 ± 0.00	1.78 ± 0.02
Well 1	20	20	5.05 ± 0.19	82.4 ± 0.8
Well 2	20	50	73.8 ± 0.5	43.0 ± 3.4

Table 7 Measurement of labile and inert complexes at pH 5.6 and 1 in artificial samples containing humic acid with copper(II) or iron(III)

Added, ppb		Cu found, ppb		Fe found, ppb	
Cu:Hu ^a	Fe:Hu ^a	pH 5.6	pH 1	pH 5.6	pH 1
4:100	100:500	2.5 ± 0.0	3.5 ± 0.1	47.1 ± 0.8	89.5 ± 1.0
4:200	100:1000	1.9 ± 0.0	3.2 ± 0.1	24.8 ± 1.1	85.2 ± 0.4

a. Humic acid.

acid to pH *ca.* 2 after filtering through a Millipore membrane filter (0.45 µm pore size). The results are given in Table 6. In these experiments, good recoveries of copper(II) and iron(III) were obtained, ranging from 94 to 104% (mean 99%).

Measurement of labile and inert complexes at pH 5.6 and 1

Artificial samples containing humic acid and copper(II) (or iron(III)) were prepared. The copper(II) concentration was 4 ppb and that of iron(III) was 100 ppb. Then, the labile and inert complexes at pH 5.6 and 1 were analyzed using the proposed method. The results are given in Table 7. The recoveries of copper(II) and iron(III) at pH 5.6 were smaller than their added amounts. The results indicate that copper(II) and iron(III) may form inert complexes with humic acid. However, the recovered amounts of copper(II) and iron(III) at pH 1 were larger than those at pH 5.6, which suggests the dissociation of each humic acid complex at a lower pH.

Conclusion

Trace amounts of copper(II) and iron(III) could be successively determined by the proposed FIA system equipped with a serial flow cell, based on their catalytic effects. The proposed FIA system has wider determinable ranges of 0.05 – 5 ppb copper(II) and 0.5 – 100 ppb iron(III), respectively. This method was successfully applied to the determination of copper(II) and

iron(III) in standard river water samples as well as tap, rain, and well water samples without any preconcentration or separation. Also, it was useful to assay labile copper(II) and iron(III) complexes in natural water.

Acknowledgements

This work was partly supported by a Grant of the Science Research Promotion Fund from the Promotion and Mutual Aid Corporation for Private Schools of Japan.

References

1. T. M. Florence and G. E. Batley, *Talanta*, **1977**, *24*, 151.
2. J. B. Sprague, *Nature*, **1968**, *220*, 1345.
3. Y. Miyata, T. Hirano, S. Nakano, and T. Kawashima, *Anal. Sci.*, **1991**, *7*, 97.
4. S. Nakano, S. Hinokuma, and T. Kawashima, *Chem. Lett.*, **1983**, 357.
5. Z. Yu, N. Teshima, S. Nakano, and T. Kawashima, *Talanta*, **1996**, *43*, 1519.
6. S. Nakano, M. Tago, and T. Kawashima, *Anal. Sci.*, **1989**, *5*, 69.
7. T. Tomiyasu, N. Yonehara, N. Teshima, and T. Kawashima, *Anal. Chim. Acta*, **1999**, *394*, 55.
8. J. Wei, N. Teshima, S. Ohno, and T. Sakai, *Anal. Sci.*, **2003**, *19*, 731.
9. G. Scarano, E. Morelli, A. Seritti, and A. Zirino, *Anal. Chim. Acta*, **1990**, *62*, 943.
10. K. Yokoi, T. Tomisaki, T. Koide, and C. M. G. van den Berg, *Fresenius' J. Anal. Chem.*, **1995**, *352*, 547.
11. T. Sakai, Y. Maeda, and N. Ura, *Talanta*, **1999**, *49*, 989.
12. S. Gotoh, N. Teshima, T. Sakai, K. Ida, and N. Ura, *Anal. Chim. Acta*, in press.
13. J. Wang and R. He, *Anal. Chim. Acta*, **1994**, *294*, 195.
14. Z. Zhu, C. Han, Z. Gu, and R. Chen, *Analyst*, **1994**, *119*, 2251.
15. W. Jianhua and H. Ronghuan, *Mikrochim. Acta*, **1994**, *117*, 23.
16. S. Nakano, K. Kuramoto, and T. Kawashima, *Chem. Lett.*, **1980**, 849.
17. T. Kawashima, Y. Kozuma, and S. Nakano, *Anal. Chim. Acta*, **1979**, *106*, 355.
18. S. Ohno, N. Teshima, H. Zhang, and T. Sakai, *Talanta*, **2003**, *60*, 1177.
19. W. A. E. McBryde, "A Critical Review of Equilibrium Data for Proton- and Metal Complexes of 1,10-phenanthroline, 2,2'-Bipyridyl and Related Compounds", **1978**, Pergamon Press, Oxford.
20. P. R. Bontchev, *Talanta*, **1972**, *19*, 675.