Bull. Chem. Soc. Jpn., ***67****, 113—118(1994)*

Determination of Copper(II) Ion by Differential Pulse Voltammetry Used a Glassy Carbon Electrode with a Nafion® Film

Yasuo NAKABAYASHI* and Hiromu IMAI
Faculty of Engineering, Kansai University, 3-3-35, Yamate, Suita 564

(Received July 2, 1993)

The determination of Cu^{2+} by differential pulse voltammetry was carried out using a chemically modified electrode coated with a Nafion® film to the surface of a glassy carbon electrode (GC/NAF electrode). This method, which is based on the principle of ion-exchange equilibria between Nafion® and imidazole–copper(II) complex ions, is applicable to the determination of traces of Cu^{2+} by a measurement of the reduction current of the Cu(II) complex ions incorporated into the Nafion® film. The procedure is as follows: immerse the GC/NAF electrode in 10 cm^3 of a sample solution containing traces (concentration, $<1.0\times10^{-6}$ M) of Cu^{2+}, 1.0×10^{-2} M of imidazole as the complexing agent, and 0.5 M of NaBr as the supporting electrolyte, and record the differential pulse voltammogram after stirring for 15 min at 25 °C. The reduction peak current obtained from this voltammogram was recoganize to be proportional to the Cu^{2+} concentration in the range of 1.0×10^{-7} to 1.0×10^{-6} M at pH 6.0 and 1.0×10^{-8} to 1.0×10^{-7} M at pH 7.0, respectively. The relative standard deviations for the peak currents obtained from four repeated determinations were 1.2 and 1.5% for 5.0×10^{-7} M of Cu^{2+} at pH 6.0 and 5.0×10^{-8} M of Cu^{2+} at pH 7.0, respectively. The diverse metal ions which coexist with Cu^{2+} at pH 6.0 did not interfere up to about a 100-fold excess of Mn^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+}, except for about a 10-fold excess of Fe^{3+}, and about a 50-fold excess of Zn^{2+} for the Cu^{2+} concentration. This method was applied to the determination of Cu^{2+} in both waste- and river-water samples.

Nafion®, which possesses electrical conductance and the chemical stability, is soluble in ethanol, but is insoluble in water. A compound having such properties is applicable to a wide variety of electrochemical fields.[1,2] Since an electrode coated with Nafion® on the surface of a carbon or platinum electrode can easily incorporate organic and metal complex cations; the fundamental behavior of this eleactrode has been reported by numerous investigators.[3—9] In particular, the ion-exchange property of cations for a Nafion® film was quantitatively studied by Szentirmay and Martin.[10] Therefore, the cations existing in the solution can be preconcentrated into the Nafion® film by an electrostatic interaction between the cations and the negatively charged sulfo group of Nafion®.[11—14] If the cations concentrated into the Nafion® film are electoactive, a trace determination of the cations can be carried out from a measurement of the reduction or oxidation current. This method has been called ion-exchange voltammetry by Martin et al.[15] Since the preconcentration of cations into the Nafion® film is due to an inherent thermodynamic driving force, this ion-exchange voltammetry is superior to stripping voltammetry for the selective determination of cations under the optimum condition. We have already reported on the heating decomposition in alcohol[16] and the stability constants[17,18] for imidazoles–copper(II) complex ions. As continuous studies of these complexes, the determination of traces of Cu^{2+} by differential pulse voltammetry was investigated using a glassy carbon electrode coated with Nafion film. This proposed method was applied to the determination of Cu^{2+} in both waste- and river-water samples.

Experimental

Reagents. A 5% solution of Nafion® 117 membrane (registered trademark of E. I. du Pont de Numours & Co., USA) dissolved in a mixture of lower aliphatic alcohols and 10% water was commercially available from Aldrich, and was diluted in ethanol to give a solution of 0.5%.

Imidazole (HIm), 2-methylimidazole (2-CH_3·HIm), 4-methyl-imidazole (4-CH_3·HIm), 2-ethylimidazole (2-C_2H_5·HIm), and 2-isopropylimidazole (2-$(CH_3)_2CH$·HIm) of reagent grade, obtained from Wako Pure Chemical Industries, Ltd. and Tokyo Kasei Kogyo Co., Ltd., were recrystallized from either benzene or benzene–hexane mixed solvents. 1-Methylimidazole (1-CH_3·Im) of reagent grade, obtained from Tokyo Kasei Kogyo Co., Ltd. was distilled under reduced pressure (73.0 °C/10 mmHg, 1 mmHg=133.322 Pa). 0.1 M (1 M=1 mol dm^{-3}) aqueous solutions of imidazoles were prepared from these refined imidazoles.

Each sulfate of manganese(II), cobalt(II), nickel(II), copper(II), zinc, and cadmium, except for iron(III) chloride, was recrystallized from distilled water. About 1×10^{-2} M aqueous solutions of metallic ions were prepared from these salts and were standardized by chelatometric titration with a 1×10^{-2} M solution of EDTA (f=1.003). All other chemicals of analytical reagent grade were purchased from Wako Pure Chemical Industries, Ltd., and were used without further purification.

Preparation of an Electrode Coated with Nafion. A glassy carbon electode (Yanagimoto, GC-P2) of 3 mm diameter was polished with an aqueous slurry of 0.05 µm alumina powder on felt for 5 min. This electrode was then rinsed with distilled water, and after sonicating in distilled water for 5 min, rinsed again with ethanol, and dried in air. An electode coated with a Nafion® film was prepared by drying at room temperature after dropping 1.0×10^{-2} cm^3 of 0.5% Nafion® ethanolic solution onto the surface of a freshly cleaved glassy carbon electrode (abbreviated hereafter as GC/NAF electrode).

Preparation of Sample Solution. The sample solution was prepared as follows: to an aliquot containing Cu^{2+} (concentration, $<1.0\times10^{-6}$ M) in a 20 cm^3 volumetric flask was added 2 cm^3 of 0.10 M imidazoles, 5 cm^3 of 2 M sodium bromide and 2 cm^3 of a 0.5 M sodium dihydrogenphosphate–sodium hydroxide buffer solution. The volume was then adjusted to 20 cm^3 with distilled water.

Procedure. A 10 cm^3 portion of the sample solution prepared as mentioned above was pipetted in a three-electrode cell equipped with a GC/NAF working electrode, a sodium chloride saturated calomel reference electrode and a spiral platinum counter electrode, and was then stirred at a constant rate in order to incorporate imidazoles–copper(II) complex ions into the GC/NAF electrode. The differential pulse voltammograms were measured by using a Yanagimoto polarographic analyzer (P-1100) and a Graphtec X–Y recorder (WX-2400) 1 min after switching off the stirrer at 25 °C under an atmosphere of ordinary air, unless otherwise stated. All pH values were estimated with a Horiba pH meter F-8.

Results and Discussion

Concentration of Imidazoles–Copper(II) Complex Ions. The concentration of imidazoles–copper(II) complex ions into the GC/NAF electrode was confirmed by cyclic voltammetry. The cyclic voltammograms of HIm–Cu(II) complex ions obtained under a nitrogen atmosphere are shown in Fig. 1. The cyclic voltammogram (A) obtained with a naked GC electrode indicated a lower reduction peak current near to 0 V vs. SSCE. On the other hand, multicyclic voltammograms (B), obtained with the GC/NAF electrode, indicated higher peak currents near to the same potential; and the peak current increased with scanning over the potential range +0.5 to −0.7 V vs. SSCE. From these results, it was ascertained that the Nafion film was incorporating the HIm–Cu(II) complex ions from the solution via ion-exchange with the proton of the fixed sulfo group in Nafion.

Concentration Time for Imidazoles–Copper(II) Complex Ions. The electode reaction of HIm–Cu(II) complex ions at the naked GC electode was examined by cyclic voltammetry. The cathodic (E_{pc}) and anodic (E_{pa}) peak potentials were independent of the scan rate (v) over the range 10 to 100 $mV\,s^{-1}$. The separation of the two peaks ($E_{pa}-E_{pc}$) was 60 ± 2 mV, which was in reasonably good agreement with the theoretical value (59 mV) for a one-electron transfer. The peak current divided by the square root of a scan rate ($I_p/v^{1/2}$) was, further, independent of v, and the anodic-to-cathodic peak-current ratio was nearly unity. The electrode reaction of the HIm–Cu(II) complex ions at the naked GC electrode was, consequently, reversible involving a one-electron transfer. The cyclic voltammetric response of HIm–Cu(II) complex ions at the GC/NAF electrode was the same as that at the naked GC electrode, except for ($E_{pa}-E_{pc}$), which was 60 to 105 mV in the 10 to 100 $mV\,s^{-1}$ scan-rate range. Therefore, the charge transfer of the imidazole–copper(II) complex ions at the GC/NAF electrode behaved quasi-reversibly, involving a one-electron transfer. In this research, differential pulse voltammetry with a higher sensitivity was employed in order to achieve the determination of traces of Cu^{2+}. As it became apparent that HIm–Cu(II) complex ions were incorporated into the GC/NAF electrode, the time required to allow sufficient concentration was examined for several imidazoles–copper(II) complex ions. As shown in Fig. 2, the peak currents for the one-electron reduction step of $1\text{-}CH_3\cdot Im$– and HIm–Cu(II) complex ions at pH 6.0 were as high as 4 to 5 times, compared with those of $2\text{-}CH_3\cdot HIm$–, $4\text{-}CH_3\cdot HIm$–, and $2\text{-}C_2H_5\cdot HIm$–Cu(II) complex ions; that of $2\text{-}(C_2H_5)_2CH\cdot HIm$–Cu(II) complex ions was the lowest. These results suggest that the difference in the peak currents may depend on the concentration of imidazoles–copper(II) complex ions formed in aqueous solution.

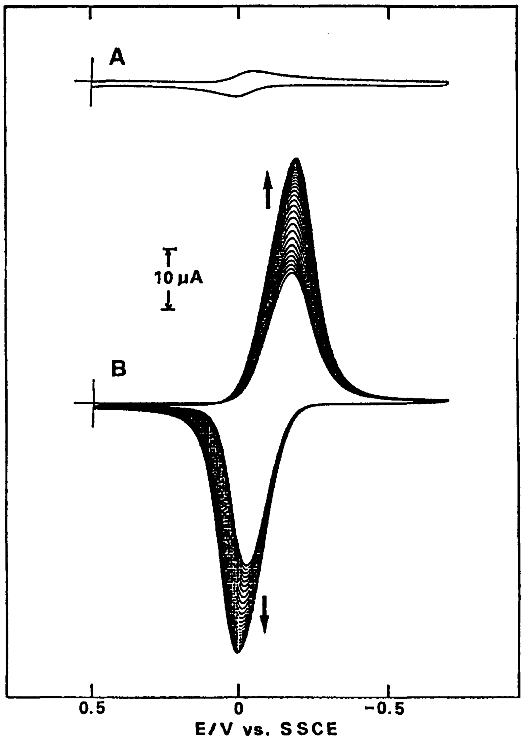

Fig. 1. Cyclic voltammograms of a naked GC electrode (A) and a GC/NAF electrode (B). Scan rate, 50 $mV\,s^{-1}$; Cu^{2+}, 1.0×10^{-4} M; HIm, 1.0×10^{-2} M; NaBr, 0.5 M.

These imidazoles–copper(II) complex ions are classified into two groups from the viewpoint of the reduction peak potentials: that is, group 1 for HIm–, $1\text{-}CH_3\cdot Im$– and $4\text{-}CH_3\cdot HIm$–Cu(II) complex ions, and group 2 for $2\text{-}CH_3\cdot HIm$–, $2\text{-}C_2H_5\cdot HIm$– and $2\text{-}(CH_3)CH\cdot HIm$–Cu(II) complex ions. The reduction peak potentials for the complex ions of group 1 were about 0 V vs. SSCE, while those of group 2 were about +0.1 V vs. SSCE. These results mean that the stability constants for the

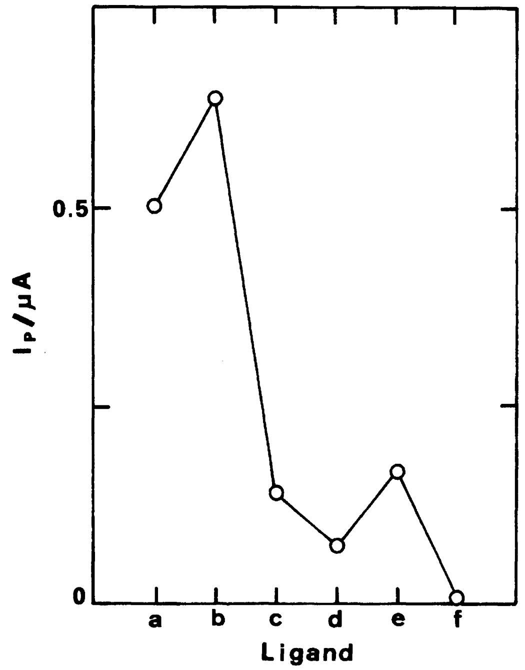

Fig. 2. Peak currents of the differential pulse voltammograms. Cu^{2+}, 2.0×10^{-6} M: HIm and its derivatives, 1.0×10^{-2} M; NaBr, 0.5 M; pH, 6.0; a, HIm; b, 1-CH_3·Im; c, 2-CH_3·HIm; d, 4-CH_3·HIm; e, 2-C_2H_5·HIm; f, 2- $(CH_3)_2CH$·HIm.

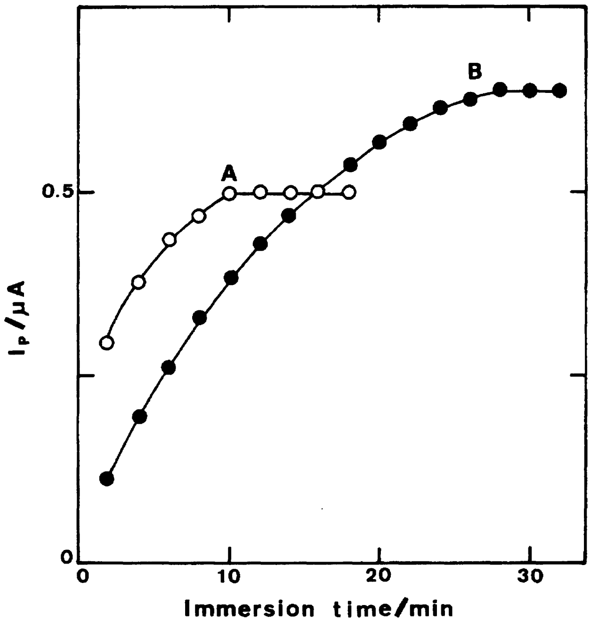

Fig. 3. Effect of the immersion time on the peak currents of the differential pulse voltammograms. Cu^{2+}, 2.0×10^{-6} M; HIm (A) or 1-CH_3·Im (B), 1.0×10^{-2} M; NaBr, 0.5 M; pH, 6.0.

complex ions of group 1 are larger than those of group 2. Then, the percentage of $[Cu(H_2O)_{4-n}L_n]^{2+}$ (L: HIm and its derivatives, n=1—4) formed in aqueous solution of pH 6.0 and 7.0 was evaluated by the use of the stability constants obtained by Imai and Tamura.[18] These obtained results are given in Table 1. The sum of the concentration of complex ions for each ligand of group 1 was higher than that of group 2; this result supported the tendency indicated in Fig. 2. However, 4-CH_3·HIm–Cu(II) complex ions indicated the lower peak current in spite of the higher total concentration of complex ions. It is considered that the equilibrium between 5-CH_3·HIm–Cu(II) and 4-CH_3·HIm–Cu(II) complex ions, which are tautomers,[17] is retained, and the formation of an ion-pair between the sulfo group in Nafion and these complex ions is interfered due to the steric hindrance of the methyl group bonding at the 4- or 5-position. It can therefore be presumed that the lower peak current of 4-CH_3·HIm–Cu(II) complex ions should be attributed to the lower ion-exchange equilibrium constant. From such results, HIm and 1-CH_3·Im, which gave the higher peak currents, were ascertained to be suitable as ligands for the trace determination of Cu^{2+}. Accordingly, the reduction peak current of HIm– or 1-CH_3·Im–Cu(II) complex ions formed was measured for various immersion times. As shown in Fig. 3, at least 10 min were needed to equilibrate with the Nafion® film for HIm–Cu(II) complex ions; on the other hand, 1-CH_3·Im–Cu(II) complex ions required about 30 min to reach euilibrium with the Nafion film. Therefore, HIm as the ligand was used in the following experiment.

Effect of pH on the Peak Currents. As the preconcentration of Cu^{2+} into the GC/NAF electrode is related to the kind of HIm–Cu(II) complex ions formed and these concentrations, and is further based on the ion-exchange equilibrium between the sulfo group in Nafion® and the Cu(II) complex ions, the peak currents are considered to be dependent on the pH. Then, the variation of the peak currents on the pH is shown in Fig. 4. The peak currents increased with increasing pH values over the range 5.8 to 7.3. It was proved that the formation of the Cu(II) complex ions increased as the pH became higher, and these complex ions became liable to be incorporated into the Nafion® film. The Cu(II) complex ions incorporated into the Nafion® film seem to form the ion-pair with the sulfo group in Nafion®. The peak currents decreased further because of a fall in the complexation ability of Cu^{2+} at less than pH 5.8; the formation of complex ions bound hydroxide ion which could not be incorporated into the Nafion® film at more than pH 7.3. Therefore, the optimum pH region for the determination of traces of Cu^{2+} was recognized to be 6.0 to 7.0.

Effect of Diverse Ions on the Determination of Cu^{2+}. Since this method is based on the principle of ion-exchange equilibria between Nafion® and HIm–Cu(II) complex ions, the determination of Cu^{2+} is considered to be interfered with in the presence of diverse ions which form more stable complex ions with HIm. Then, interference of the coexisting ions on the determination of Cu^{2+} was investigated at pH 6.0 and 7.0.

Table 1. Distribution of Imidazoles–Copper(II) Complex Ions in Aqueous Solution
Cu^{2+}: 1.00×10^{-6} M, L: 1.00×10^{-2} M, pH: 6.0 and 7.0

L	pH	$[Cu(H_2O)_{4-n}L_n]^{2+}$(%)				Sum of species concentration
		n=1	n=2	n=3	n=4	%
a. HIm	6.0	14.6	50.9	26.2	7.1	98.9
	7.0	0.6	11.7	34.0	52.0	98.3
b. $1\text{-}CH_3\cdot Im$	6.0	20.3	53.0	20.0	4.7	98.0
	7.0	0.1	15.4	34.8	48.8	99.1
c. $4\text{-}CH_3\cdot HIm$	6.0	39.8	39.8	6.9	0.5	87.0
	7.0	3.4	28.0	39.9	24.9	96.2
d. $2\text{-}CH_3\cdot HIm$	6.0	35.9	10.0	0.5		46.4
	7.0	18.6	47.1	21.2		86.9
e. $2\text{-}C_2H_5\cdot HIm$	6.0	22.5	9.7	0.6		32.8
	7.0	10.4	40.1	23.4		73.9
f. $2\text{-}(CH_3)_2CH\cdot HIm$	6.0	24.7	3.0			27.7
	7.0	27.8	29.4			57.2

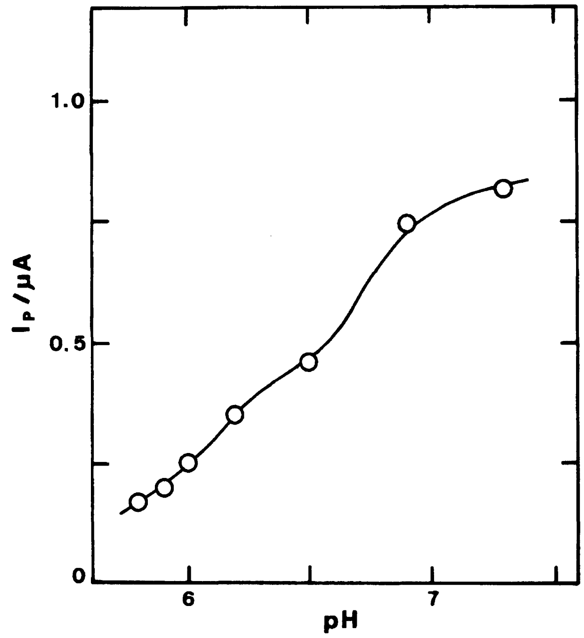

Fig. 4. Effect of the pH on the peak currents of differential pulse voltammograms. Cu^{2+}, 1.0×10^{-6} M; HIm, 1.0×10^{-2} M; NaBr, 0.5 M; pH, 6.0.

Table 2. Effect of Diverse Ions on the Determination of Cu^{2+}
Cu^{2+}: 1.0×10^{-7} M, HIm: 1.0×10^{-2} M, NaBr: 0.5 M

Addition of diverse ions	Molar ratio ($[Ion]/[Cu^{2+}]$)	Relative error/%	
		pH 6.0	pH 7.0
Mn^{2+}	100	+0.46	+0.46
Co^{2+}	100	−0.48	−17
	10	+0.46	−0.48
Ni^{2+}	100	−1.0	−30
	10	−0.48	+0.46
Cd^{2+}	100	−0.48	−5.5
	50	−0.48	−0.48
Zn^{2+} a)	50	+0.77	−15
	10	−0.48	−0.77
Fe^{3+} a)	50	−16	−35
	10	+0.58	−2.5
	5	−0.27	−0.61

a) The precipitate was observed in the presence of a 100-fold excess of diverse ions.

The data are given in Table 2. The negative errors at pH 7.0 were observed in coexisting with Co^{2+}, Ni^{2+}, and Cd^{2+} of a 100-fold excess, Zn^{2+} of a 50-fold excess and $Fe^{3+}$of a 10-fold excess for Cu^{2+} concentration, respectively. However, the presence of Mn^{2+} of a 100-fold over for the Cu^{2+} concentration did not interfere with the determination of Cu^{2+}. On the other hand, the negative error at pH 6.0 was observed only in coexisting with Fe^{3+} of a 50-fold excess; the other diverse ions shown in Table 2, except for Fe^{3+}, did not interfere with the determination of Cu^{2+}. From the data shown in Table 2, it was recognized that the determination of Cu^{2+} was preferable at pH 6.0, which was scarcely subject to the interference of diverse ions, in spite of the lower sensitivity.

Calibration Curve. The relationship between the peak currents and the concentration of Cu^{2+} was examined. Straight lines through the original point were obtained over the range of 1.0×10^{-6} to 1.0×10^{-7} M of Cu^{2+} at pH 6.0, and 1.0×10^{-7} to 1.0×10^{-8} M of Cu^{2+} at pH 7.0, respectively. The relative standard deviations for the peak currents obtained from four repeated determinations were 1.2 and 1.5% for 5.0×10^{-7} M of Cu^{2+} at pH 6.0 and 5.0×10^{-8} M of Cu^{2+} at pH 7.0, respectively. In addition, the HIm–Cu(II) complex ions incorporated into the Nafion® film can be removed by immersion for a few minutes in 5×10^{-2} M H_2SO_4. Therefore, the GC/NAF electrode can be used repeatedly.

Application. The proposed method can be applied to the determination of Cu^{2+} in waste- and river-water samples. Waste water is treated as follows: add 4

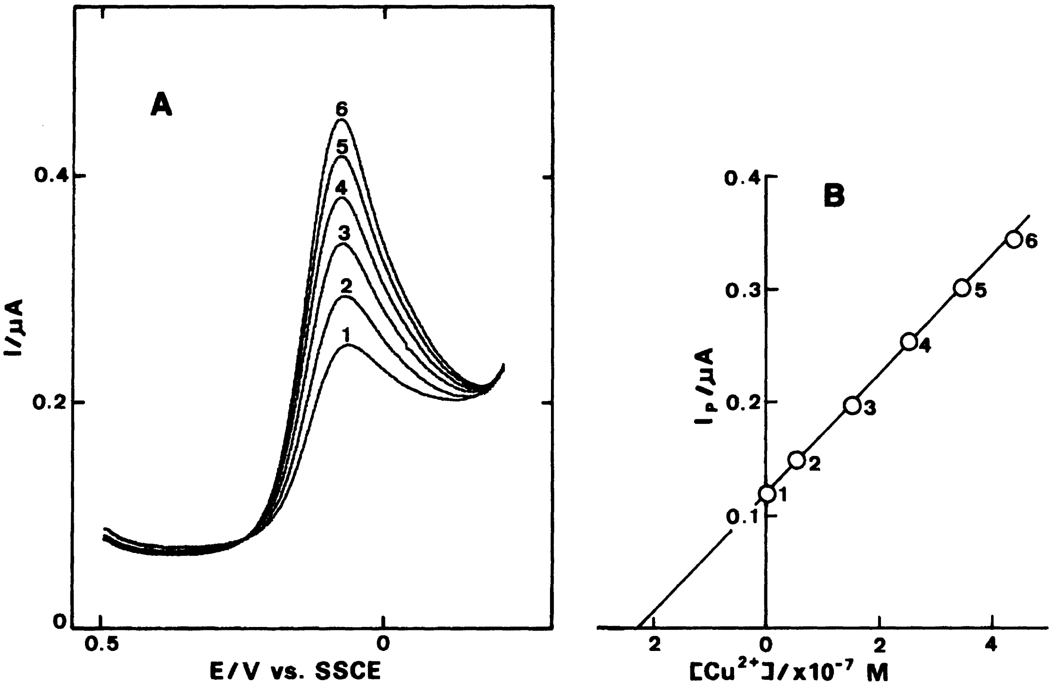

Fig. 5. Determination of Cu^{2+} in waste water by differential pulse voltammetry at a GC/NAF electrode. HIm, 1.0×10^{-2} M; NaBr, 0.5 M; pH, 6.0; Scan rate, 5 mV s^{-1}; pulse amplitude, 50 mV. (A) Differential pulse voltammograms obtained. (1) sample solution; (2)—(6) solution added the known amounts of Cu^{2+} in (1). (B) Regression line for standard addition of Cu^{2+}.

cm^3 of the mixed acid (concd HNO_3 3+concd H_2SO_4 1) in 50 cm^3 of the waste water; after evaporating to near dryness by heating (in order to decompose the organic substances etc.) adjust to pH 6 with 1 M ammonia water, and dilute to 50 cm^3 with distilled water; take an adequate amount from this solution, and prepare a sample solution by the proposed method (pH 6.0). River water is treated as follows: after pipetting 10 cm^3 of the river water, which is filtered through a Toyo Roshi, Ltd. "ADVANTEC" membrane filter (pore size of 0.45 µm), add in a 20 cm^3 volumetric flask, and prepare the sample solution by the proposed method (pH 7.0).

The determination of Cu^{2+} by differential pulse voltammetry was carried out by the standard addition method. Figure 5 shows the differential pulse voltammograms (A) and the regression line (B) for the determination of Cu^{2+} in a waste-water sample. The obtained regression line was a sufficient and satisfactory straight line. The determination of Cu^{2+} in the waste- and river-water samples was then tried. As shown in Table 3, the results obtained by the proposed method were in good agreement with those obtained by atomic absorption spectrometry.[19]

Table 3. Determination of Cu^{2+} in the Waste- and the River-Water Samples

Sample	Cu^{2+}/µg cm^{-3}	
	This method	AAS method[a]
WW1[b]	0.41	0.43
WW2[b]	0.70	0.70
WW3[b]	0.33	0.32
RW[c]	0.012	0.013

a) Atomic absorption spectrometric method. b) Experimental waste water in Kansai University. c) River water (Muko river).

In conclusion, relatively large amounts of diverse ions such as Fe^{3+} must be either masked or removed by means of a proper reagent for the determination of trace amounts of Cu^{2+} (1.0×10^{-8}—1.0×10^{-6} M) by this proposed method. However, the presence of other coexisting ions does not interfere with the determination of Cu^{2+}. This method consequently has the advantages of simplicity and rapidity compared to atomic absorption spectrometry with solvent extraction. In addition, it is worth noting that the values of the peak potentials for the reduction of Cu(II) to Cu(I) complex ions with imidazole were more positive than that of dissolved oxygen; namely, electroanalytical measurements of the system employed can be carried out under an atmosphere of ordinary air.

References

1) F. G. Will, *J. Electroanal. Chem.*, **126**, 35 (1979).

2) R. S. Yeo and D. -T. Chin, *J. Electroanal. Chem.*, **127**, 549 (1980).

3) I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **102**, 6641 (1980).

4) T. P. Henning, H. S. White, and A. J. Bard, *J. Am.*

Chem. Soc., **103**, 3938 (1981).

5) H. S. White, J. Leddy, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4811 (1982).

6) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **104**, 4824 (1982).

7) T. P. Henning, H. S. White, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 5862 (1982).

8) Y.-M. Tsou and F. C. Anson, *J. Phys. Chem.*, **89**, 3818 (1985).

9) N. Oyama, T. Ohsaka, T. Ushirogouchi, S. Sanpei, and S. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 3103 (1988).

10) M. N. Szentirmay and C. R. Martin, *Anal. Chem.*, **56**, 1898 (1984).

11) C. R. Martin, I. Rubinstein, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4817 (1982).

12) C. R. Martin and K. A. Dollard, *J. Electroanal. Chem.*, **159**, 127 (1983).

13) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **106**, 59 (1984),

14) T. Matsue, U. Akiba, and T. Osa, *Anal. Chem.*, **58**, 2097 (1986).

15) M. W. Espenscheid, A. R. Ghatak-Roy, R. B. Moore, III, R. M. Penner, M. N. Szentirmay, and C. R. Martin, *J. Chem. Soc., Faraday Trans.*, **82**, 1051 (1986).

16) H. Imai, H. Ohno, and H. Tamura, *Nippon Kagaku Kaishi*, **1987**, 667.

17) H. Imai, H. Ochiai, and H. Tamura, *Nippon Kagaku Kaishi*, **1989**, 2022.

18) H. Imai and H. Tamura, *Bull. Chem. Soc. Jpn.*, **64**, 2077 (1991).

19) A. Hulanicki, *Talanta*, **12**, 1371 (1967).