

# Chelating Polymer Bearing Triazolylazophenol Moiety as the Functional Group

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## Synopsis

The chelating polymer-bearing triazolylazophenol moiety as the functional group was synthesized, its metal adsorption properties for 6 divalent heavy metal ions;  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were investigated. The capacity of the polymer for  $\text{Cu}^{2+}$  achieved 8.7 mEq/g in pH 5.3 solution. The polymer showed remarkable color changes from orange to red violet or blue violet with its chelations to the heavy metal ions. The metal adsorption rates of the polymer were rapid in performing complete capacity saturation of heavy metal ions in about 30 min. The capacities varied little the presence of alkali or alkaline earth metal ions in solutions. The perfect elimination of metals from the polymer- $\text{M}^{2+}$  chelates were performed with mineral acid solutions. The metal ions;  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in plating-process solutions were effectively removed by the chelating polymer, and the polymer can be practically used for the removal of these ions from waste water.

## INTRODUCTION

Pyridylazonaphthols, pyridylazophenols, thiazolylazophenols and some other analogous hydroxyazo compounds<sup>1,2</sup> were commonly used as metallochromic indicators. The chelating property of the polymer-containing pyridylazoresorcinol moiety<sup>3</sup> was investigated, the application of the polymer sheet having thiazolylazophenol group for a metallochromic indicator<sup>4</sup> was examined. The preparation and the chelating ability of the polymer-bearing triazolylazophenol group was previously reported.<sup>5</sup> In the report, poly(vinylalcohol) film containing the triazolylazophenol moiety was prepared, and its coloration reaction with some transition metal ions was investigated.

In the present work, the chelating polymer-bearing triazolylazophenol moiety was synthesized and its capacities for 6 divalent heavy metal ions;  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  were investigated. Compared with the chelating resin containing the iminodiacetic acid group, the polymer with the triazolylazophenol group was expected to form somewhat less stable chelates with heavy metal ions ( $\text{M}^{2+}$ ). The elimination of the metal from the polymer- $\text{M}^{2+}$  chelate was anticipated to be very easy compared with that of the metal from the corresponding  $\text{M}^{2+}$  complex of the commonly used commercial chelating resins bearing iminodiacetic acid moiety as the functional group. The capacities of the chelating resin for heavy metal ions can hardly exceed 2.5 mEq/g because of the difficulties of incorporating the functional group into the resin matrix of styrene-divinylbenzene copolymer. On the other hand, the maximal capacity of the chelating polymer for  $\text{M}^{2+}$  was expected to exceed 2.5 mEq/g.

## EXPERIMENTAL

## Measurement

<sup>1</sup>H-NMR spectra were taken on a Hitachi 90 MHz R-22K high-resolution spectrometer in acetone-d<sub>6</sub> at 35°C by employing TMS as an internal standard. Infrared absorption spectra were measured on a Nihon Bunko IRA-2 spectrometer. Ultraviolet absorption spectra were obtained using a Hitachi 323 spectrophotometer in methyl alcohol at room temperature. Mass spectra were recorded on a Hitachi M-70 gas chromatography-mass spectrometry equipment by the electron impact ionization method. Elemental analyses were performed on a Yanaco MT-3 CHN Corder. A Hitachi 308 atomic absorption spectrometer and chelatometric titrations using EDTA as a titrant were used for the determination of metal concentration. GPC was done with a Gasukurokogyo 570B high performance liquid chromatograph.

## Preparation of the Chelating Polymer

*p*-Vinylphenol was prepared in a similar manner as Sovish's method<sup>6</sup> by employing *p*-hydroxybenzaldehyde as a starting material.

A mixture consisting of 61 g *p*-hydroxybenzaldehyde (0.5 mole), 52 g malonic acid (0.5 mole), 4 ml pyridine, and 4 ml aniline was heated at 116°C for 40 min, during which time the mixture was decarboxylated to a yellowish-orange crude solid. The resultant reaction mixture was dissolved in methyl alcohol, and distilled water was added to 40 v/v % alcohol content(1000 ml). The pale yellowish-white crystalline needles of *p*-hydroxycinnamic acid were obtained: yield 49.3 g(60%); mp 203°C; <sup>1</sup>H-NMR(acetone-d<sub>6</sub>) δ 6.40(d,J=16,1 H), 6.95(d,J=9,2 H), 7.59(d,J=9,2 H), 7.74(d,J=16,1 H); ir(KBr) 1670 cm<sup>-1</sup>(ν<sub>c=0</sub>), 1522(ν<sub>c=c</sub>), 977(δ<sub>CH</sub>), 830(δ<sub>CH</sub>); UV(methyl alcohol) λ<sub>max</sub> 212.5 nm(ε1.08 × 10<sup>4</sup>), 227.5(1.13 × 10<sup>4</sup>), 312.5(2.15 × 10<sup>4</sup>); mass spectrum (70 eV) M<sup>+</sup> at m/e 164(C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>); Anal. Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>: C, 65.85; H, 4.91. Found: C, 65.79; H, 5.00.

A mixture of 30 g *p*-hydroxycinnamic acid, 60 g quinoline, 4 g Cu powder, and a small amount of hydroquinone was poured into a 300 ml flask. The decarboxylation was done at 210-220°C for 25 min under reduced pressure(40-60 mm). A colorless clear distillate was obtained. The distillate was diluted with iced 3 mole/liter HCl solution(150 ml), and *p*-vinylphenol was extracted twice with 50 ml ethyl ether. The ether layer was washed with iced 3 mole/liter HCl solution(50 ml), followed by washing with ice cold water(150 ml). The ether was evaporated to dryness in vacuo(40-50 mm). The obtained crude product was recrystallized from petroleum ether to yield *p*-vinylphenol as white crystalline plates: yield 7.5 g(34%); mp 69°C; <sup>1</sup>H-NMR(acetone-d<sub>6</sub>) δ 5.06(d,J=12,1 H), 5.61(d,J=18,1 H), 6.70(q,1 H), 6.86(d,J=8,2 H), 7.33(d,J=8,2 H), 8.37(s,1 H); ir(KBr) 1510 cm<sup>-1</sup>(ν<sub>c=c</sub>), 1366(ν<sub>c-o</sub>), 1230(δ<sub>OH</sub>), 989(δ<sub>CH</sub>), 897(δ<sub>CH</sub>); uv(methyl alcohol) λ<sub>max</sub> 212.5 nm(ε1.44 × 10<sup>4</sup>), 260.5(1.53 × 10<sup>4</sup>); mass spectrum(70 eV) M<sup>+</sup> at m/e 120(C<sub>8</sub>H<sub>8</sub>O); Anal. Calcd for C<sub>8</sub>H<sub>8</sub>O: C, 79.97; H, 6.71. Found: C, 77.76; H, 6.83.

*p*-Vinylphenol, 20 g, and 0.2 g azobisisobutyronitrile were dissolved in 40 ml methyl ethyl ketone, and the system was sealed in vacuo. The polymerization was carried out in 6 h at 90°C. The resulting reaction mixture was poured into 400 ml petroleum ether to yield a precipitate. The precipitate was dissolved in methyl alcohol and precipitated in water to give glassy polymer: yield 7.3 g (37%);  $^1\text{H-NMR}$ (acetone- $d_6$ ) ca. 1.52(bs,2 H), ca. 1.90(bs,1 H), ca. 6.63(bs, 4 H), 8.05(s,1 H); ir(KBr) 1513  $\text{cm}^{-1}$ ( $\nu_{C=C}$ ), 1366( $\nu_{C-O}$ ), 1230( $\delta_{OH}$ ), 827( $\delta_{CH}$ ); uv (methyl alcohol)  $\lambda_{\text{max}}$  213.5 nm, 225, 279; Anal. Calcd for  $(\text{C}_8\text{H}_8\text{O})_n$ : C, 79.97; H, 6.71. Found: C, 76.09; H, 6.94. The molecular weight distribution of the polymer measured by gel permeation chromatography is shown in Figure 1.

The chelating polymer was prepared by the conventional diazotized-coupling reaction of 3-amino-1,2,4-triazole with *p*-vinylphenol polymer. 3-Amino-1,2,4-triazole, 7.01 g(1/12 mole), was diazotized and coupled with 10 g poly(*p*-vinyl-phenol)(1/12 mole as a monomer unit) to give an orange reaction mixture. The mixture was centrifuged, and the orange polymer was obtained. The obtained chelating polymer was washed repeatedly with a large amount of distilled water by decantation and was used for the experiment as a wet polymer of 90.1% moisture content: yield 12.6 g(70%); Anal. Found for the chelating polymer: C, 61.66; H, 5.29; N, 16.42. This indicates an approximate composition of 36.2 mole % triazolylazo-vinylphenol.

## RESULTS AND DISCUSSION

### Metal Adsorption Ability of the Chelating Polymer

The chelating polymer showed chelate formations with some heavy metal ions accompanying remarkable color changes. Its reversed color change occurred by chelate deformation. The colors and the absorption maxima of the metal chelates are presented (Table I). The elution of the metal ion from the chelate accompanying a back coloration was performed using the solution of a mineral acid or a strong chelating agent (for example EDTA)

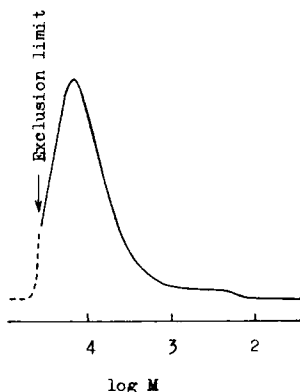


Fig. 1. Molecular weight distribution of poly(*p*-vinylphenol).

TABLE I  
Color and Absorption Maxima of Polymer-M<sup>2+</sup> Chelates

Metal ion	$\lambda_{\max}$	Color
Co <sup>2+</sup>	655	orange red
Ni <sup>2+</sup>	655	red violet
Cu <sup>2+</sup>	700	blue violet
Zn <sup>2+</sup>	660	red violet
Cd <sup>2+</sup>	655	orange red
Pb <sup>2+</sup>	655	red violet

as eluant. This coloration afforded the advantage of easy control of the chelate-forming ability of the polymer with the naked eye.

The effects of pH on the capacities of the chelating polymer for the heavy metal ions are shown (Fig. 2). A solution (100 ml) containing metal ion (ca.  $10^{-2}$  mole/L), the pH of which was controlled with acetate buffer ( $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2$  mole/L), and 2 g wet polymer were placed in a 300 ml flask. The mixture was shaken and equilibrated for 6 h at 23°C, after which time the chelate was excluded immediately by centrifugation. The metal ion concentration of the supernatant was determined by the chelatometric titration, and the capacity of the polymer for the metal ion was evaluated. If a triazolylazophenol moiety of the chelating polymer would form a 1:1 chelate with M<sup>2+</sup>, the maximum capacity for M<sup>2+</sup> was expected to be 4.7 mEq/g according to the elemental analysis. The observed maximum capacity of the polymer for Cu<sup>2+</sup> was 8.7 mEq/g at pH 5.3. The discrepancy between the expected capacity for M<sup>2+</sup> and the observed one for Cu<sup>2+</sup> was based on the effect of another chelating site (for example phenolic OH). In the solutions (pH  $\leq$  5.3), the capacity of the polymer for any one of the other examined metal ions was smaller than a half for Cu<sup>2+</sup>, the capacity was reasonable compared with its expected value. In the heavy

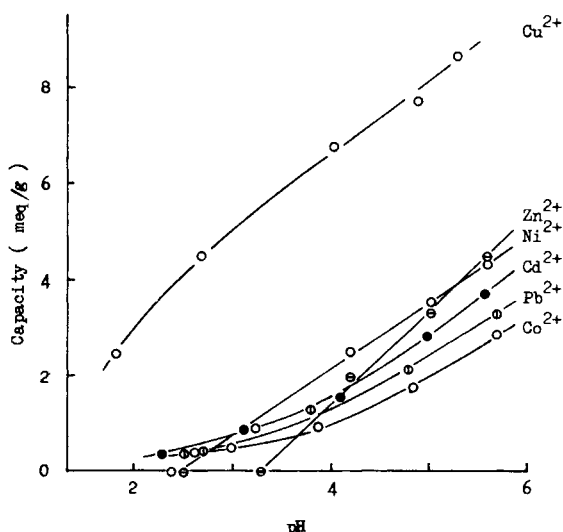


Fig. 2. Effects of pH on the capacities of the chelating polymer for the heavy metal ions at 23°C. Shaking time: 6 hr, Buffer solution:  $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2$  mole/l.

metal ions,  $\text{Cu}^{2+}$  was expected to make a most stable complex with this chelating polymer from the Irving-Williams order, and other chelating sites of the polymer acted effectively only when the metal ion was  $\text{Cu}^{2+}$ .

Solute-adsorbing agents are usually characterized by isotherm adsorption curves. The typical isotherm adsorption curves obtained for the chelating polymer with  $\text{M}^{2+}$  are shown (Fig. 3). The  $1/n$  values of the Freundlich equation ( $\log q = \log k + 1/n \log C$ ) evaluated for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorption by the polymer were 0.207 and 0.227, respectively. These values were in the range of 0.1–0.5. Therefore, these metals were very effectively adsorbed by the polymer.

The measurement of the equilibration rates of the chelating polymer with  $\text{M}^{2+}$  are shown (Fig. 4). A mixture of 2 g wet polymer and a buffered solution (100 ml) containing metal ion (ca.  $10^{-2}$  mole/L) was equilibrated for a definite time, and then capacity was determined. The time needed for perfect saturation of the capacity of the polymer for the heavy metal ion was about 30 min, which was sufficiently a short time for the polymer to be used for the removal of the heavy metal ion.

The effect of the presence of alkali or alkaline earth metal ion on the capacity of the chelating polymer for  $\text{M}^{2+}$  was examined. A mixture of 2 g wet polymer, 100 ml of the buffered solution of  $\text{Cu}^{2+}$  (ca.  $10^{-2}$  mole/L) and a definite amount of  $\text{KNO}_3$  or  $\text{CaCl}_2$  was equilibrated for 6 h, and the capacity was determined as described previously. The chelating site of the polymer suggested that its capacity for the heavy metal ion would be slightly affected by the presence of alkali or alkaline earth metal ion in water. The relationship between the capacity of the polymer for  $\text{Cu}^{2+}$  and the amount of coexisting  $\text{KNO}_3$  (or  $\text{CaCl}_2$ ) is shown (Fig. 5). The capacity of the polymer for the heavy metal ion hardly varied with the presence of these ions.

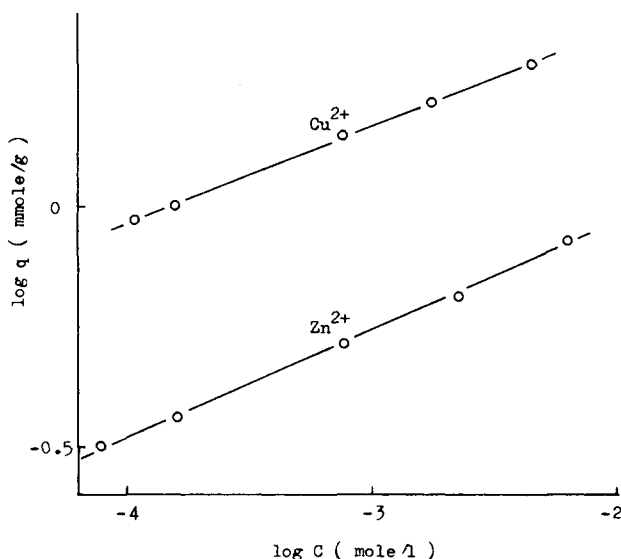


Fig. 3. Isotherm adsorption curves for the adsorptions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by the chelating polymer at 23°C. Shaking time: 6.5 hr, pH: 4.9 ( $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2$  mole/l).

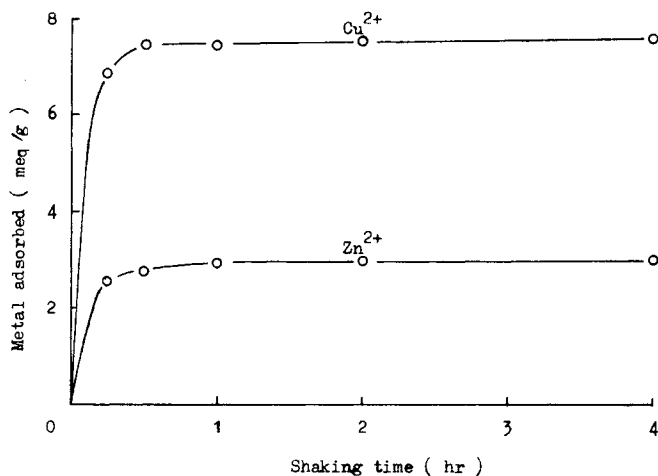


Fig. 4. Effects of shaking time on the adsorptions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by the chelating polymer at  $23^\circ\text{C}$ . pH: 5.10( $\text{Cu}^{2+}$ ) and pH: 5.17( $\text{Zn}^{2+}$ ) ( $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2$  mole/l).

### Eliminations of the Metal Ions from Polymer- $\text{M}^{2+}$ Chelates

The elimination of  $\text{M}^{2+}$  from its chelate was performed by the solution of a mineral acid. The experimental results are shown (Fig. 6). The wet polymer, 2 g, was equilibrated with 100 ml of the buffered solution of  $\text{M}^{2+}$  (ca.  $10^{-2}$  mole/L), and its  $\text{M}^{2+}$  chelate was obtained from the solution by centrifugation. The chelate was washed with 10 ml distilled water, followed by treatment with a mineral acid solution. The metals:  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  were perfectly eluted from the polymer with 1 mole/L HCl solution, but it was very difficult to perform a perfect elimination from  $\text{Cu}^{2+}$  even if the eluant was 4 mole/L HCl solution. The perfect elimination of  $\text{Cu}^{2+}$  required the use of 4 mole/L  $\text{H}_2\text{SO}_4$  solution. The 90% removals of  $\text{Cu}^{2+}$

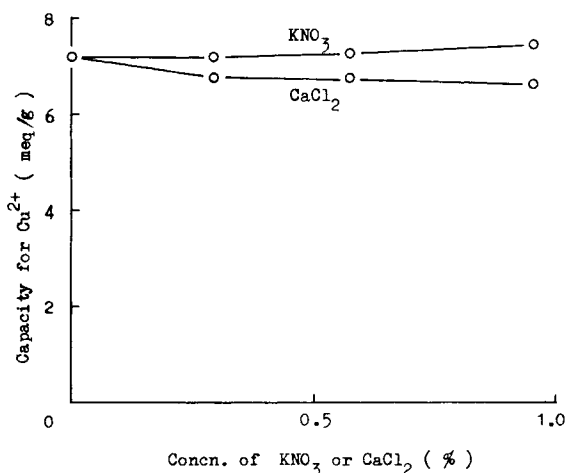


Fig. 5. Effect of the presence of alkali or alkaline earth metal ion on the capacity of the chelating polymer for  $\text{Cu}^{2+}$  at  $23^\circ\text{C}$ . Shaking time: 6 hr, pH: 4.8 ( $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2$  mole/l).

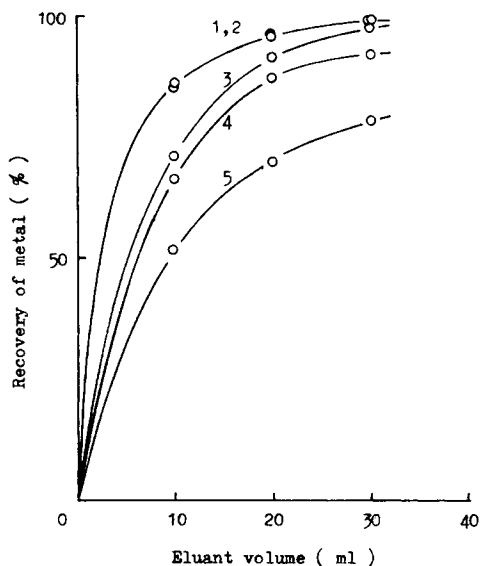


Fig. 6. Elimination of metal ions from the chelating polymer- $M^{2+}$  chelates by mineral acids solutions at 23°C. Initial amount of the adsorbed  $M^{2+}$ :  $Cu^{2+}$ ,  $7.20 \times 10^{-4}$  mole;  $Ni^{2+}$ ,  $3.35 \times 10^{-4}$  mole;  $Zn^{2+}$ ,  $2.75 \times 10^{-4}$  mole. 1:  $Zn^{2+}$  chelate-1 mole/l HCl, 2:  $Ni^{2+}$  chelate-1 mole/l HCl, 3:  $Cu^{2+}$  chelate-4 mole/l  $H_2SO_4$ , 4:  $Cu^{2+}$  chelate-4 mole/l HCl, 5:  $Cu^{2+}$  chelate-1 mole/l HCl.

and the other metal ions from the polymer- $M^{2+}$  chelates, respectively, were performed with 4 mole/L  $H_2SO_4$  solution (ca. 100 times equivalent of adsorbed  $Cu^{2+}$ ) and 1 mole/L HCl solution (ca. 25 times that of adsorbed  $M^{2+}$ ).

### Removal of heavy metal ions from plating process solutions

The chelating polymer was applied to the removal of metal ions from copper solutions from electrolytic-plating processes, the electrolytic-plating processes of nickel and chemical polishing processes of copper-zinc alloy. A mixture of the metal-acetate buffer solution (100 ml), and 2 g wet polymer was equilibrated for 30 min, after which time the remaining concentration of metal was measured using atomic absorption spectrometry. (Table II). In the case of the electrolytic copper-plating process solution, the capacity of the chelating polymer for  $Cu^{2+}$  (5.82 mEq/g) in the buffered solution (pH 5.2) showed a large value compared with that (4.33 mEq/g) in the initial solution (pH 7.5). This result did not agree with the expectation that was produced from the pH dependence of the capacity of the polymer for  $Cu^{2+}$  (Fig. 2). In the electrolytic copper-plating process solution, however, about 3% of  $NH_3$  existed. The conditional stability constant of the polymer- $Cu^{2+}$  chelate was reduced in the presence of  $NH_3$ , therefore, the capacity would likely decrease. In the case of the solution of the chemical polishing process of copper-zinc alloy, as was expected from the result of Figure 2, the selective adsorption of  $Cu^{2+}$  (2.52 mEq/g) was achieved in the initial solution (pH 2.7), and the relatively small amount of  $Zn^{2+}$  (0.28 mEq/g) compared with  $Cu^{2+}$  (3.85 mEq/g) was removed at the same time in the buffered solution (pH 4.7).

TABLE II  
Adsorption of Heavy Metal Ions in Plating-Process Solutions by the Chelating  
Polymer at 23°C

Sample	pH	Metal ion	Initial concn. of metal(mole/L)	Remaining concn. of metal(mole/L)	Capacity (mEq/g)
A	3.27	Ni <sup>2+</sup>	$9.01 \times 10^{-3}$	$8.07 \times 10^{-3}$	0.95
	4.70 <sup>a</sup>	Ni <sup>2+</sup>	$9.01 \times 10^{-3}$	$6.05 \times 10^{-3}$	2.99
B	7.50	Cu <sup>2+</sup>	$9.22 \times 10^{-3}$	$4.93 \times 10^{-3}$	4.33
	5.20 <sup>a</sup>	Cu <sup>2+</sup>	$9.22 \times 10^{-3}$	$3.46 \times 10^{-3}$	5.82
C	2.70	Cu <sup>2+</sup>	$4.41 \times 10^{-3}$	$1.92 \times 10^{-3}$	2.52
		Zn <sup>2+</sup>	$2.44 \times 10^{-3}$	$2.44 \times 10^{-3}$	0
	4.70 <sup>a</sup>	Cu <sup>2+</sup>	$3.92 \times 10^{-3}$	$1.15 \times 10^{-4}$	3.85
		Zn <sup>2+</sup>	$2.17 \times 10^{-3}$	$1.89 \times 10^{-3}$	0.28

A : Solution of the electrolytic-plating process of Ni.

B : Solution of the electrolytic-plating process of Cu.

C : Solution of the chemical polishing process of Cu-Zn alloy.

<sup>a</sup> : pH was controlled with acetate buffer(CH<sub>3</sub>CO<sub>2</sub>H + CH<sub>3</sub>CO<sub>2</sub>Na = 0.2 mole/L).

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### References

1. D. Betteridge and D. John, *Analyst*, **98**, 390 (1973).
2. H. Wada, *Bunseki Kagaku*, **21**, 543 (1972).
3. H. Eccles and F. Vernon, *Analytica Chimica Acta*, **66**, 231 (1973).
4. S. Fruya, *Bull. Res. Inst. Polym. Text. (Japan)*, No. **129**, 5 (1981).
5. Y. Onari, presented in part at the 32nd Annual Meeting of the Chemical Society of Japan, April 1975, Abstracts IV, p. 2050.
6. R. C. Sovish, *J. Org. Chem.*, **24**, 1345 (1959).

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