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The Selective Extraction and Spectrophotometric Determination of Copper and Silver by the Use of a Thiocrown Compound 1,4,8,11-Tetrathiacyclotetradecane

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A highly selective solvent extraction and spectrophotometric determination of copper and/or silver is proposed; it is based on the extraction of the ion-pair formed by the copper(I)- or silver(I)-thiocrown ether complex cation and the appropriate dye anion. A comparative study of Bromocresol Green (BCG), Thymol Blue (TB), and picrate ions as the pairing ions for the extraction of copper using a 1,4,8,11-tetrathiacyclotetradecane (TTCT) solution of 1,2-dichloroethane is described. The use of BCG gave the highest sensitivity among these three kinds of anions and made it possible to determine copper in the range of 0.6—3.2 $\mu g\,ml^{-1}$. The interferences of six kinds of cations and four kinds of anions were examined; only Ni^{2+} and ClO_4^- interfered, and they slightly. The separation by the extraction of silver and/or copper with TTCT solution of 1,2-dichloroethane from an aqueous solution containing seven kinds of metal ions (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag^+) in the presence of picrate ion (Pic^-) was also examined. Silver was first extracted quantitatively as the ion-pair compound, $[Ag(ttct)_2]^+Pic^-$, and then copper as $[Cu(ttct)]^+Pic^-$ after having been reduced to copper(I). The absorption maximum of both extracted species lies at 378 nm (ε: 1.8×10^4), and the spectrophotometric determination of these metals is possible. This method was successfully applied to the determination of copper and silver in standard samples of steel.

Although the solvent extraction of alkali metals using crown-ether compounds has been widely studied,[1—7] there have been few studies of metals using thiocrown ether compounds.[8—10] We tried to examine the solvent extraction of various metal ions with TTCT, which is a typical thiocrown ether.[11] Consequently, it was found that the Class *b* metals classified by Ahrland,[12] in particular copper(I) and silver(I), are extracted; on the other hand, the Class *a* metals are not extracted at all, and the Class *ab* metals are practically not extracted at all.

In the present study, the extraction-spectrophotometric determination of copper and silver using TTCT as the ligand, the dye anion(BCG or picrate) as the pairing anion, and 1,2-dichoroethane as the extracting solvent, was examined. Therefore, it was confirmed that TTCT is a useful selective reagent to separate the Class *b* metals, especially copper and silver, from other metals. It was also found that the use of the dye anion makes the spectrophotometric determination of copper and/or silver possible. Hitherto,such reagents as neocuproine, diethyldithiocarbamic acid (DDTC), and dithizone for copper and those such as *p*-dimethylaminobenzidinerhodanine and dithizone for silver have usually been employed as the spectrophotometric reagents in the routine analysis of these metals. By comparing the proposed method with conventional methods, it was found that the proposed method is more sensitive than the neocuproine method and more selective than the DDTC and dithizone methods for copper, and is more reproducible than the *p*-dimethylaminobenzidinerhodanine method and more selective than the dithizone method for silver.

Experimental

Reagents. The TTCT was synthesized by the method described by Rosen and Bush[13] and recrystallized three times from ethanol. A 5×10^{-5} M (1 M=1 mol dm^{-3}) TTCT 1,2-dichloroethane solution was prepared; it was stable for a week at least. After we had prepared the 1×10^{-2} M copper(II) and silver(I) sulfate solutions, we determined their concentrations by EDTA titration and by potentiometric titration with sodium chloride respectively. The 1,2-dichloroethane was shaken three times with 2 M potassium hydroxide and then with distilled water. After drying with calcium chloride anhydride, it was distilled. The other reagents used were of analytical-reagent grade.

Apparatus. A Taiyo M incubator was used for shaking a 50-ml glass cylindrical tube equipped with a glass stopper. An Iwaki KM-shaker was used for shaking a 100-ml separatory funnel. A Seiko SAS-725 atomic absorption spectrophotometer was used for the determination of the copper and silver concentrations. The absorption spectra were measured with a Hitachi 124 double-beam spectrophotometer and a Shimadzu UV-240 self-recording spectrophotometer. The pH of the aqueous phase was measured with a Hitachi-Horiba H-5 PH meter.

Solvent Extraction of Copper(I). An aqueous solution containing 5×10^{-5} M copper(II) sulfate, the 5×10^{-5} M dye anion(BCG, TB or picrate), a 1×10^{-2} M buffer, and 0.1 M hydroxylammonium sulfate was prepared; its ionic strength was kept at 0.1 with sodium sulfate. The buffer solutions were prepared with acetic acid–sodium acetate in the weak acidic region and sodium tetraborate and sodium hydroxide in the weak basic region. Ten ml of this aqueous solution was placed in a 50-ml glass cylindrical tube equipped with a glass stopper. After the addition of 10 ml of the 5×10^{-3} M TTCT solution of 1,2-dichloroethane, the mixture was shaken for 30 min at 200 strokes/min at 25±0.1 °C and then centrifuged for 5 min at 2000 min^{-1}. The absorption spectra of the 1,2-dichloroethane phase were measured against a reagent blank in the range from 250 to 550 nm. The pH of the aqueous phase was measured, and the copper concentration of the aqueous phase was measured by means of atomic-absorption spectrophotometry. The copper concentration of the 1,2-dichloroethane phase was determined as follows: a five ml portion of the organic phase was placed in a beaker and allowed to evaporate. The residue was dissolved in concentrated nitric acid and diluted to 25 ml or 10 ml with water. The copper concentration was determined by means of atomic-absorption spectrophotometry.

Separation of Silver and Copper from a Mixed Solution Containing Various Metal Ions. An aqueous solution containing various metal ions(Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag^{+}), a picrate (1×10^{-3} M), and an acetic acid–sodium acetate buffer (1×10^{-2}M, pH 5.4) was prepared. Ten ml of this aqueous solution was introduced into a 50-ml glass cylindrical tube equipped with a glass stopper, and then 10 ml of the 5×10^{-3} M TTCT solution of 1,2-dichloroethane was added. The mixture was shaken for 30 min at 200 strokes/min at 25±0.1 °C and then centrifuged for 5 min at 2000 min^{-1}. A 5 ml portion of the aqueous phase was introduced into a 50-ml glass cylindrical tube equipped with a glass stopper, and then 5-ml of an aqueous solution containing 0.2 M hydroxylammonium sulfate,the 1×10^{-3} M picrate, and the 1×10^{-2} M acetic acid–sodium acetate buffer were added. After the addition of 10 ml of the 5×10^{-3} M TTCT solution of 1,2-dichloroethane, the mixture was shaken for 30 min at 200 strokes/min at 25±0.1 °C and then centrifuged for 5 min at 2000 min^{-1}. All the metals were determined by means of atomic-absorption spectrophotometry. The concentration of the metal ion in the organic phase was determined as has been described above.

Preparation of a Standard Sample Solution of Steel. A standard sample of steel (0.1 g) was dissolved in 20 ml of (1+4) nitric acid by heating. After the addition of 10 ml of (1+9) sulfuric acid, the solution was heated gently until fumes of sulfuric acid had been evolved. The residue was cooled to room temperature, and then the walls of the beaker were washed with a small portion of water. After the addition of several drops of a hydrogen-peroxide solution (30%), the solution was heated gently until fumes of sulfuric acid had been evolved. The residue was cooled and then dissolved in water. Finally the solution was diluted to 100 ml with water.

Recommended Procedure for the Determination of Copper and Silver. *(I) Determination of Copper in a Standard Sample of Steel in the Absence of Silver:* Pipette an aliquot of a sample solution containing up to 32 μg of copper(II) into a 100-ml separatory funnel. Add 5 ml of 1 M hydroxylammonium sulfate and 5 ml of a 1×10^{-2} M picric acid or 2.5×10^{-3} M BCG solution. Adjust the pH in the range of pH 4—5 with a 1.5 M sodium acetate solution, and then dilute with water to 50 ml. After the addition of 10 ml of the TTCT solution of 1,2-dichloroethane, shake for 10 min. Allow it to stand and the layers to separate, and then place the yellow extract in a 1-cm cell. Measure the absorbance at 378 nm for picrate or at 408 nm for BCG against the reagent blank as the reference solution.

(II) Determination of Silver and Copper in a Standard Sample of Steel in the Presence of Silver and Copper: Pipette an aliquot of a sample solution containing up to 54 μg of silver(I) into a 100-ml separatory funnel. Add 5 ml of 1×10^{-2} M picric acid, and then adjust the pH in the range of pH 4—6 with 1.5 M sodium acetate. Dilute it with water to 50 ml, and then shake with 10 ml of the TTCT solution of 1,2-dichloroethane for 10 min. Allow it to stand and the layers to separate, and then place the yellow extract in a 1-cm cell. Measure the absorbance at 378 nm against the reagent blank. Pipette an aliquot of the aqueous phase containing up to 32 μg of copper(II) into a 100-ml separatory funnel. Finally, add 5 ml of 1 M hydroxylammonium sulfate and the 1×10^{-2} M picric acid solution to make a 1×10^{-3} M. The subsequent procedure was the same as that used for the determination of copper in a standard sample of steel in the absence of silver.

Results and Discussion

Extraction Behavior of Copper(I) with TTCT in the Presence of BCG, TB, or Picrate. The extraction of copper(I) with TTCT from the aqueous solution in the presence of BCG, TB, or picrate ions into 1,2-dichloroethane was examined in the pH range from 3—8. Plots of the logarithm of the distribution ratio of copper(I) (log D) *vs.* the pH of the aqueous solution are shown in Fig. 1. For the extraction of copper(I) in the presence of BCG, TB, or picrate ions, almost the same pH dependence was observed. Each extractability is kept constant at a value of more than 99% (log $D>2$) in the pH range from 4 to 6, but it decreases with the decrease in pH value below 4 and with the increase above 6. It is considered that the decrease in the extraction on the acidic side is due to the decrease in the amount of copper(I), accompanied by the decrease in the reducing power of hydroxylammonium sulfate; on the other hand, the decrease in the extraction on the basic side is considered to be due to the hydrolysis of copper(I).

It was found in the previous study[11] that copper(I) was extracted with TTCT into organic solvents by forming an ion-pair compound, $[Cu(ttct)]^{+}Pic^{-}$, in the presence of picrate. In the present study, the composition of the extracted species in the presence of BCG or TB was checked. The logarithmic plot of the distribution ratio of copper(I) *vs.* the concentration of TB in the aqueous phase, which was determined by means of the absorbance at 431 nm, is shown in Fig. 2.

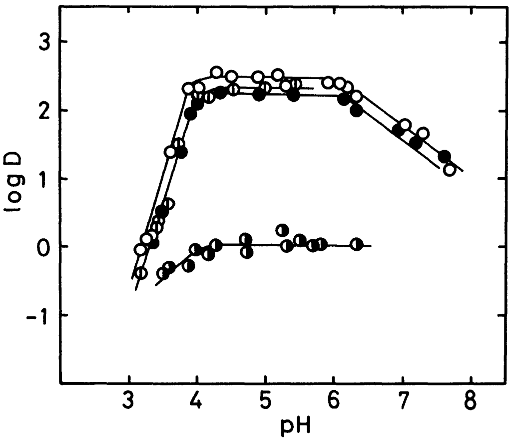

Fig. 1. Plots of log D *vs.* pH. Initial concentration; TTCT: 5×10^{-3}M.
-○-; $[Cu^{+}]_i=5\times10^{-5}$M, $[BCG]_i=5\times10^{-4}$M. -●-; $[Cu^{+}]_i=5\times10^{-5}$M, $[TB]_i=5\times10^{-4}$M. -◐-; $[Cu^{+}]_i=5\times10^{-5}$M, $[Pic]_i=5\times10^{-4}$M. -◑-; $[Cu^{2+}]_i=5\times10^{-5}$M, $[BCG]_i=5\times10^{-4}$ M.

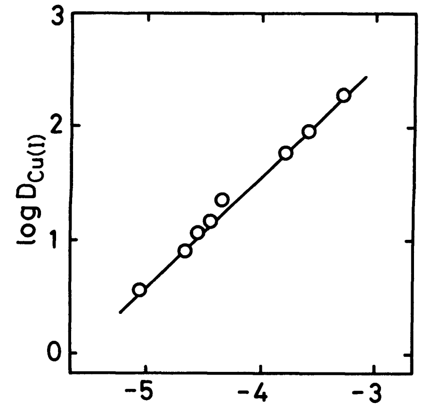

Fig. 2. Plot of log $D_{Cu(I)}$ *vs.* log $[TB^{-}]$. pH 4.5. Initial concentration; copper(I): 5×10^{-5}M, TTCT: 5×10^{-3}M.

The straight line with the slope of +1 thus obtained, indicates the 1 : 1 ratio of copper to TB. The molar ratio of copper to BCG was examined by the continuous-variation method; the results are shown in Fig. 3. As may be seen in Fig. 3, the maximum absorbance is found at the 1 : 1 molar ratio of copper to BCG. These results suggest that the species extracted into 1,2-dichloroethane are $[Cu(ttct)]^+A^-$, where A^- is the TB or BCG anion.

Absorption Spectra. The absorption spectra of the organic extracts, as measured against a reagent blank, are shown in Fig. 4. It was found that the absorption maxima lie at 408, 391, and 378 nm for BCG, TB, and picrate ions respectively. BCG exhibited the maximum absorbance among these three kinds of pairing ions. Although the extracted complexes are stable, the absorbance of the organic phase was measured within 4 h after the extraction.

Effect of pH. The effect of the pH of the aqueous phase was also examined. Plots of the absorbance at the maximum wavelength of the organic phase *vs.* the pH of the aqueous phase are shown in Fig. 5. As is shown in Fig. 5, the absorbance is constant over the pH range from 4.0 to 5.0 for BCG, from 3.8 to 7.0 for TB, and from 4.0 to 5.5 for picrate in the examined pH. It seems that the decreases in absorbance in the range of pH 5—6 for BCG is related to the pH range of color change interval of BCG from pH 3.7 to 5.4. Figure 5 also shows that among the three kinds of pairing ions, BCG is most favorable for the spectrophotometric determintion of copper.

Calibration, Sensitivity, and Precision. When the procedure described for the solvent extraction of copper(I) (Experimental section) was used, Beer's law was followed in the range of 0.6—3.2 μg Cu ml^{-1}. When BCG or picrate ions were used, the molar absorptivity was 2.01×10^4 or 1.80×10^4 l $mol^{-1}cm^{-1}$ respectively. These values are higher than the molar absorptivity for the neocuproine method; 7.95×10^3 at 454 nm in isoamyl alcohol, bathocuproine method; 1.42×10^4 at 479 nm in *n*-hexyl alcohol and diethyldithiocarbamic acid method; 1.42×10^4 at 432 nm in chloroform. The sensitivity for the 0.001 absorbance was 3.16 or 3.53 ng cm^{-2} respectively. When 10 solutions containing 15.9 μg of copper were deter-

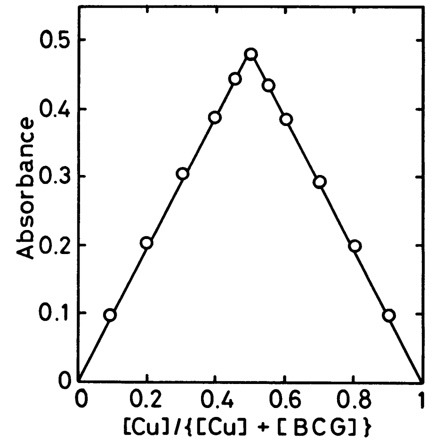

Fig. 3. Continuous variation method.
$[Cu]+[BCG]=2.5\times10^{-5}M$, $[TTCT]_0=5\times10^{-3}M$.
Wavelength; 408 nm. Reference; reagent blank.

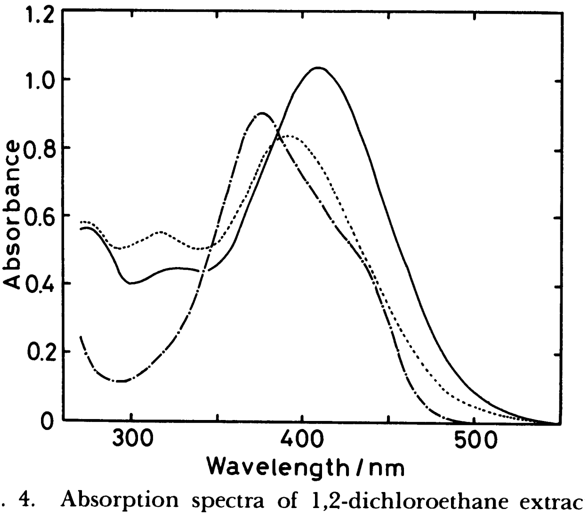

Fig. 4. Absorption spectra of 1,2-dichloroethane extracts from aqueous solution containing $5\times10^{-4}M$ BCG^- (—), TB^-(····), or Pic^-(-·-). Initial concentration; copper(I): 5×10^{-5} M, TTCT: 5×10^{-3} M.

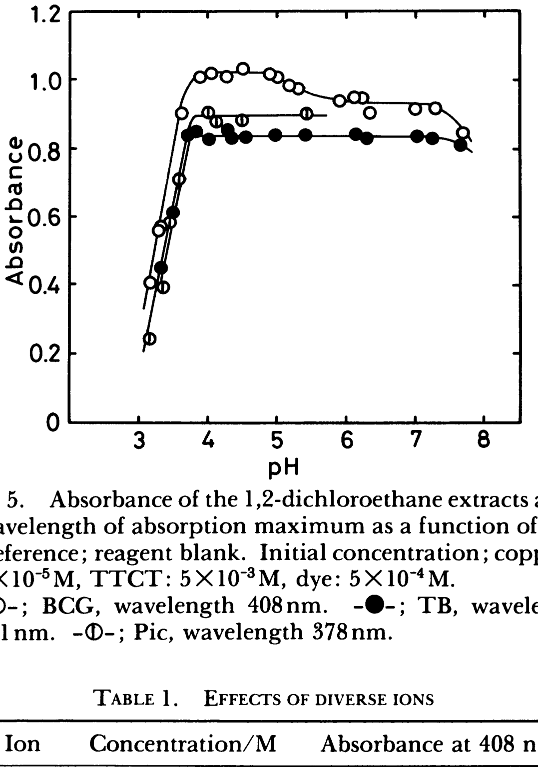

Fig. 5. Absorbance of the 1,2-dichloroethane extracts at the wavelength of absorption maximum as a function of pH. Reference; reagent blank. Initial concentration; copper(I) $5\times10^{-5}M$, TTCT: $5\times10^{-3}M$, dye: $5\times10^{-4}M$.
-○-; BCG, wavelength 408 nm. -●-; TB, wavelength 391 nm. -⦶-; Pic, wavelength 378 nm.

Table 1. Effects of diverse ions

Ion	Concentration/M	Absorbance at 408 nm
None	—	0.505
Mn^{2+}	2.5×10^{-2}	0.050
Fe^{2+}	2.5×10^{-2}	0.504
Co^{2+}	2.5×10^{-2}	0.510
Ni^{2+}	2.5×10^{-2}	0.535
	2.5×10^{-3}	0.507
Zn^{2+}	2.5×10^{-2}	0.504
Cd^{2+}	2.5×10^{-2}	0.510
ClO_4^-	5.0×10^{-2}	0.482
	2.5×10^{-2}	0.491
	5.0×10^{-3}	0.495
NO_3^-	0.1	0.493
Cl^-	0.1	0.502
SO_4^{2-}	0.1	0.508

Concentration of copper(I) in each case: 2.5×10^{-5} M. Reference: reagent blank.

mined using the BCG or the picrate as the pairing ion, the relative standard deviation was 1.5% or 0.6% respectively.

Effect of Foreign Ions. The interference from the following metal ions and anions were examined by using BCG; Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+}, ClO$_4^-$, NO$_3^-$, Cl$^-$, and SO$_4^{2-}$. All the metal ions were added as sulfates, while all the anions were added as their sodium salts. The results are shown in Table 1. Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} in a 1000-fold excess over the copper concentration did not interfere, whereas Ni^{2+} in a 1000-fold excess serves to increase the absorbance by 5.9%. However, Ni^{2+} in a 100-fold excess did not interfere with the determination of copper. The presence of 0.1 M sulfate, chloride, and nitrate ions did not affect the determination of copper significantly, whereas the perchlorate ion when present in a quantity of more than 2.5×10^{-3} M gave a negative error.

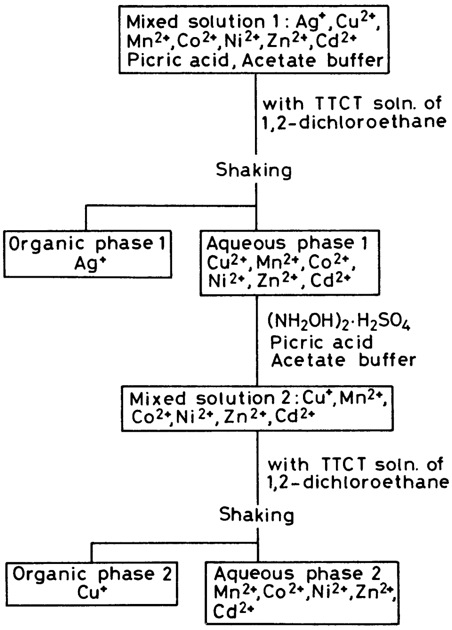

Fig. 6. Procedure of separation for silver and copper.

Separation of Silver and Copper from Aqueous Solution Containing Various Metal Ions. As has been mentioned above, it seems that among the dye anions examined, the BCG is most advantageous for both the ion-pair extraction and the spectrophotometric determination. However, from the fact that about 50% of the copper(II) was extracted when the BCG was used as the pairing ion (Fig. 1), it seems that the selectivity for silver(I) toward copper(II) decrease. Little copper(II) is extracted with TTCT in the presence of the picrate, whereas silver(I) is completely extracted.[11] Consequently a procedure was devised for separating silver and copper from an aqueous solution containing various metal ions using the picrate as the pairing ion. This separation scheme is shown in Fig. 6. Silver was first extracted as the ion-pair compound, [Ag(ttct)$_2$]$^+$Pic$^-$, the composition of which will be clarified in another paper, and then copper was extracted as [Cu(ttct)]$^+$Pic$^-$ after reducing the copper(II) to copper(I) with hydroxylammonium sulfate. The results are shown in Table 2. Silver(I) in a mixed solution containig Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag$^+$ (each metal ion concentration: 5×10^{-5} M) was more than 99% extracted by a single extraction. The other metal ions remained in the aqueous phase. In the case of the extraction from an aqueous solution containing 5×10^{-5} M Ag$^+$ and 1×10^{-2} M of other metal ions, almost the same results were obtained except that only a little copper(II) was extracted (3.8×10^{-6} M). The ion-pair compound, [Ag(ttct)$_2$]$^+$Pic$^-$, was completely back-extracted with 3 M HCl into the aqueous phase. In order to reduce copper(II) to copper(I), a hydroxylammonium sulfate solution was added to an aqueous phase into which silver(I) was extracted into the 1,2-dichloroethane phase, and then the extraction of copper(I) with TTCT was carried out. Ninety-nine percent of the copper(I) in the mixed solution was extracted by the single extraction in this procedure. All the other metal ions remained in the aqueous phase.

TABLE 2. RESULTS OF THE SEPARATION OF Ag$^+$ AND Cu$^+$

Mixed solution 1		Organic phase 1		Recovery of Ag
Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	Ag$^+$	Cu^{2+}	Ag$^+$	%
5×10^{-5} M	5×10^{-5} M		4.98×10^{-5} M	99.6
1×10^{-2} M	5×10^{-5} M	3.8×10^{-6}	4.99×10^{-5} M	99.8
Mixed solution 2		Organic phase 2		Recovery of Cu
Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}	Cu$^+$	Cu$^+$		%
2.5×10^{-5} M	2.5×10^{-5} M	2.48×10^{-5} M		99.2
5×10^{-3} M	2.5×10^{-5} M	2.46×10^{-5} M		98.4

TABLE 3. ANALYTICAL VALUES OF STANDARD STEEL SAMPLES

Sample	Chemical composition (wt%)[a]										
	C	Si	Mn	Ni	Cr	S	Cu	P	V	Mo	Ag
No. 1	0.35	0.61	0.10	0.064	3.00	0.033	0.30	0.016	0.43	0.42	—
No. 2	0.521	0.258	0.807	0.137	1.00	0.027	0.181	0.036	0.054	0.414	0.090

[a] Cited from standard values of JSS 155-1 for Sample No. 1, and from standard values of NBS 159 for Sample No. 2.

TABLE 4. ANALYSIS OF STANDARD STEEL SAMPLES FOR COPPER AND SILVER

Sample	Cu(wt%)			Ag(wt%)	
	Standard value	Present work		Standard value	Present work
		BCG	Pic		Pic
No. 1	0.30	0.30	0.31	—	—
No. 2	0.181	—	0.181	0.090	0.093

The absorption spectrum of the extracted species of silver(I) was almost the same as that of copper(I) in Fig. 4, and the absorption maximum lay at 378 nm.

These results show that the selective extraction-spectrophotometric determination of silver and copper from an aqueous solution containing first-transition metal ions (Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}) and post-transition metal ions (Zn^{2+}, Cd^{2+}) is possible.

Practical Application. Two kinds of standard samples (No. 1 and 2) of steel were used in this study. Sample No. 1 contains copper, but no silver, while sample No. 2 contains both copper and silver. The chemical compositions of these samples are shown in Table 3. Sample No. 1 was analysed for copper using the BCG or picrate as the pairing anion (Table 4). The values in Table 4 are the averages of five measurements. The results show a reasonable agreement with the standard values. This sample contains a relatively large percentage of copper, so that 5 ml of the sample solution is sufficient for the determination of the copper. Therefore, the determination of copper is possible according to the procedure described in the solvent extraction of copper(I) (Experimental section), in which the volume of the aqueous phase is 10 ml. However, in the case of a sample containing a small percentage of copper, we adopted the recommended procedure for the determination of copper and silver, in which the volume of the aqueous phase was 50 ml. The absorbance of the organic phase did not change, although the volume of the aqueous phase increased from 10 to 50 ml.

Sample No. 2 was analyzed for copper and silver according to the procedure described for the separation of silver and copper from a mixed solution containing various metal ions (Table 4). The values in Table 4 are the averages for five measurements. The copper and silver contents (0.181% and 0.093% respectively) obtained by proposed method compare reasonably well with the standard values of 0.181 and 0.090% for copper and silver respectively.

The proposed method is so selective that the determinations of copper(I) and silver(I) are not interfered with the first-transition metal ions even when no masking reagent is present.

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