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Extraction and Stripping of Copper(I) as a Neocuproine Complex in a Surfactant System and Determination of Copper in Steel

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An aqueous solution containing surfactants exhibits the property of being separated into two phases due to a temperature change or an addition of salts. The extraction and stripping of copper(I) as a neocuproine complex were investigated between the anionic surfactant of sodium dodecylsulfate (SDS) and aqueous phases. When the surfactant was separated by the addition of NaCl, the copper complex was extracted into the SDS phase. The stripping of copper(I) into the aqueous phase was maintained by phase separation, which was achieved by cooling the solution. Since neocuproine is a highly specific chromogen for copper(I), iron(II) could not form a complex with neocuproine, and was scarcely extracted into the SDS phase. This selective extraction was applied to the separation of copper from iron and the determination of copper in steel samples by a spectrophotometric method and/or an atomic-absorption spectrometric method (AAS).

The surfactant-extraction technique was investigated with a renewable interest in chemical analyses involving the separation and quantitative determination of a large number of metal ions.[1—6] Traditionally, such organic solvents as benzene or chloroform have been used for the extraction of metal complexes; however, these solvents are often carcinogenic, toxic and cause environmental pollution. The surfactant-extraction method is excellent because surfactants have a nonvolatile nature and are relatively harmless reagents.[7]

The extraction was mainly combined with a spectrophotometric measurement of metals as a colored complex in the surfactant phase. Since the surfactant phase exhibits high viscosity and a large matrix influence, determinations in the aqueous phase are suitable for other measurements, such as AAS. There has been a few investigations concerning the recovery of metals into aqueous solution from the surfactant phase. The stripping of Cd(II) was attempted in order to recover it as a water-soluble complex of $[Cd(EDTA)]^{2-}$ (ethylenediaminetetraacetic acid, EDTA) from the SDS phase into water.[8] This process corresponds to back- or reverse-extraction in the conventional liquid–liquid extraction system. The stripping method can be applicable to the recover of metals. We investigated the extraction and stripping of copper(I) in forms of the cationic complex of $[CuL_2]^+$ with neocuproine (L) between the anionic surfactant of SDS and the aqueous phases. This surfactant extraction-striping method was combined with AAS and spectrophotometric determinations of copper in steel.

Experimental

Reagents. The 0.10 mol dm^{-3} stock solution of copper(II) was prepared by dissolving a weighed amount of copper(II) sulfate (Kanto Chemicals) in 0.1 mol dm^{-3} sulfuric acid, and then titrimetrically standardized with EDTA. A 0.01 mol solution of iron(II) was prepared by dissolving iron(II) sulfate in 1.0 mol dm^{-3} sulfuric acid. We prepared 20% (w/v) SDS (Merck), 25% (w/v) NaCl and 5.0% (w/v) ascorbic acid solutions by dissolving the respective weighed amounts in water. A 2.0×10^{-3} mol dm^{-3} neocuproine (2,9-dimethyl-1,10-phenanthroline, Kanto Chemicals) solution was prepared by dissolving 0.105 g in 200 cm^3 of water. An acetate buffer solution was prepared by mixing the same volume of 0.30 mol dm^{-3} acetic acid and 0.10 mol dm^{-3} sodium acetate. All other chemicals were of analytical grade.

Apparatus. AAS measurements were made using a Shimadzu AA-625 flame atomic-absorption spectrometer. The absorbance was measured using a Hitachi U-2000 spectrophotometer with 1.0 cm quartz cells. All pH measurements were made with a Horiba F-11 pH meter and a combination glass electrode. A Hitachi centrifuge (CF7 D2) was used for phase separations.

Procedure for Extraction of Copper. A solution containing copper(II) was transferred to a 10 cm^3 centrifuging tube with a graduation line. To reduce the copper(II) to copper(I), 1.0 cm^3 of ascorbic acid was added. After the successive addition of 2.0 cm^3 of a buffer, 1.0 cm^3 of SDS and 1.0 cm^3 of neocuproine, the solution was diluted to 6.0 cm^3 with water. After shaking the solution, 4.0 cm^3 of NaCl was added. By a salting-out effect, SDS was deposited in the solution. This solution was centrifuged at 4000 rpm for 5 min. About 1 cm^3 of the SDS phase was obtained at the bottom of the tube. This phase separation is briefly termed salting-out separation.

Procedure for Stripping of Copper. The upper aqueous phase was discarded after a salting-out separation. After the addition of 2.0 cm^3 of the buffer and 1.0 cm^3 of neocuproine, it was diluted to the proper volume with water and cooled in an ice-water bath. In this case, the SDS gel was generated by a cooling effect. After centrifugation, the SDS phase settled to the bottom of the tube. This cooling separation was available for the stripping of copper(I).

In the aqueous phase, the remaining SDS concentration was 1.4×10^{-3} mol dm^{-3}, or 0.040%, which was determined by an extraction method with ethyl violet,[9] and was under the critical micelle concentration (CMC). The CMC value and Krafft point are 8.2×10^{-3} mol dm^{-3} (at 25 °C) and 16 °C, respectively, for pure SDS in water.[10] The Krafft point changes with various factors, such as the addition of electrolytes; therefore, we tried cooling of the solution to under 5 °C for complete phase separation. The concentration of copper(I) in the aqueous phase was determined by a spectrophotometric measurement at 457 nm and/or the AAS method.

Results and Discussion

Extraction and Stripping of Copper. Neocuproine produces intense color with copper(I), owing to the formation of a water-soluble complex. This complex was extracted into the SDS phase by salting-out separation with an addition of NaCl. The SDS phase began to deposit at 3.0% NaCl concentration. The phase separation and extraction of the complex were completed at a NaCl concentration of over 8% when using a solution containing 2.0% SDS.

The extraction of copper(I) was independently examined by salting-out separation and by the cooling separation. Figure 1 shows the effect of the SDS concentration on the percent extraction of copper(I). By salting-out separation, the extraction of copper(I) was completed at an SDS concentration greater than 0.2%. By cooling separation, on the other hand, 95% of the copper(I) remained in the aqueous phase. Based on this poor extractability, the cooling separation was used to strip copper(I) from the SDS phase to the aqueous phase.

Figure 2 shows the effect of the neocuproine concentrations on the extraction and stripping of copper(I). By a salting-out separation, the complex of copper(I) was completely extracted into the SDS phase at more than 2.0×10^{-4} mol dm^{-3} of neocuproine. By cooling separation, the extraction of copper(I) decreased with increasing the neocuproine concentrations. These extraction phenomena indicate that the copper(I)–neocuproine complex was the species being extracted and stripped. First, 2.0×10^{-4} mol dm^{-3} of neocuproine was added to form the complex in solution. More than 1.0×10^{-4} mol dm^{-3} of neocuproine was needed to strip the copper(I). However, since the percent extraction of the ligand of neocuproine was only 20% in the SDS phase by the salting-out separation, it was necessary to again add the ligand into the solution before stripping by cooling separation.

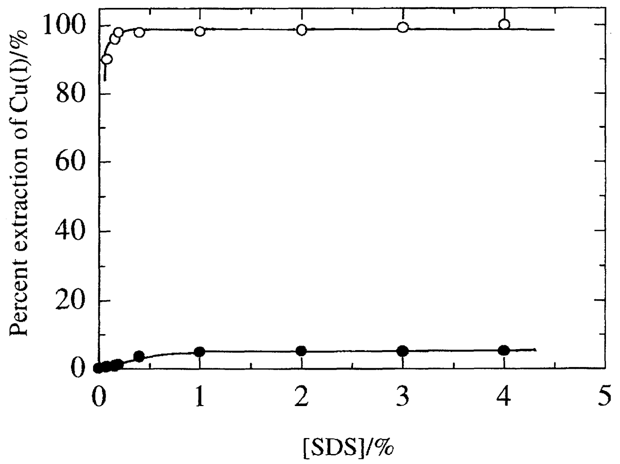

Fig. 1. Effect of the SDS concentration on the extraction of copper(I). (○) salting-out separation, (●) cooling separation, [NaCl] = 10.0%, [Cu] = 4.0×10^{-5} mol dm^{-3}, [neocuproine] = 2.0×10^{-4} mol dm^{-3}, pH = 3.8.

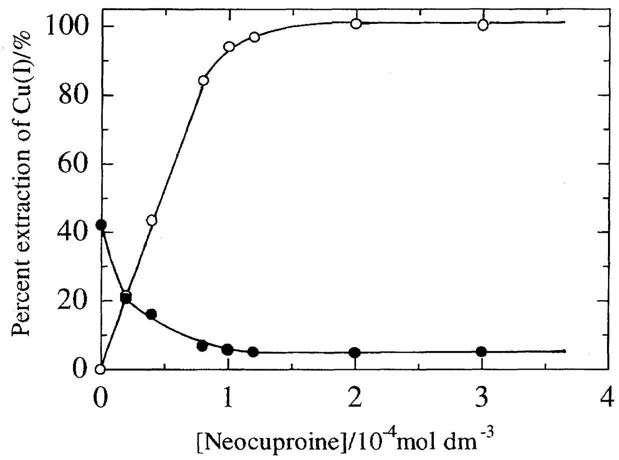

Fig. 2. Effect of the neocuproine concentration on the extraction of copper(I). (○) salting-out separation, (●) cooling separation.

Figure 3 shows the effect of the pH on the extraction of copper(I). At higher than pH = 3, the formation and extraction of the copper(I) complex were complete by salting-out separation; however, the extraction of copper(I) increased along with decreasing the proton concentrations by cooling separation. The detailed mechanism of this pH dependence on the stripping of copper(I) is unknown. The extraction and stripping were performed at pH = 3.8.

Removal of Iron. Neocuproine is a highly specific chromogen for copper(I), and fails to give complex formation with iron(II). The selectivity for copper(I) can be understood to be due to a steric hindrance of the methyl groups.[11] Figure 4 shows the effect of the neocuproine concentration on the percent extraction of iron(II) by salting-out separation. The concentration of iron(II) in the phases was spectrophotometrically determined at 510 nm by the addition of 1,10-phenanthroline. The extraction of iron(II) was independent of the neocuproine concentrations. Such extraction reflected the lack of the complex formation of iron(II) with neocuproine.

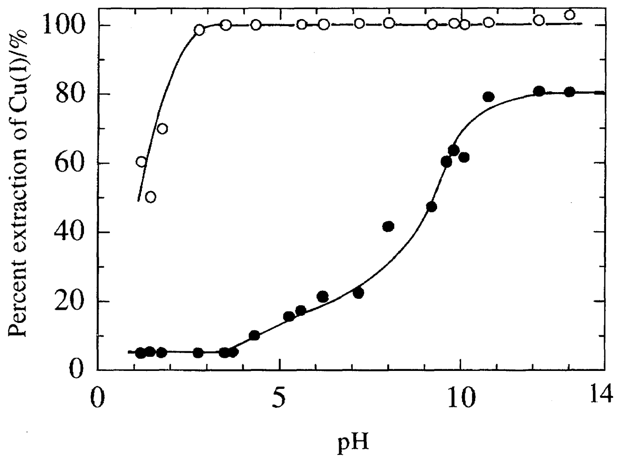

Fig. 3. Effect of the pH on the extraction of copper(I). (○) salting-out separation, (●) cooling separation.

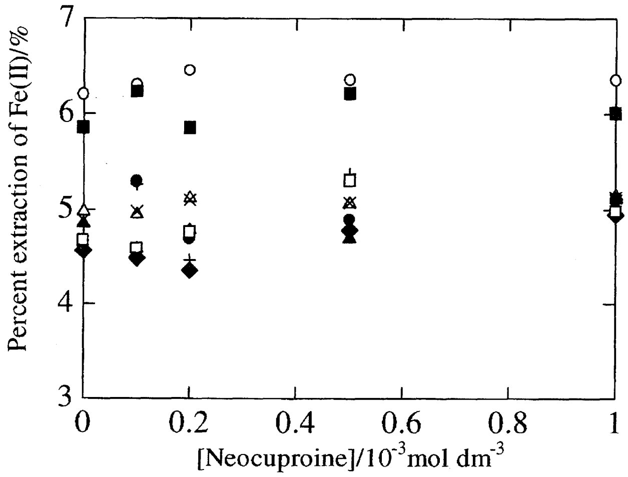

Fig. 4. Effect of the neocuproine concentration on the extraction of iron(II) by the salting-out separation. [Fe(II)]/mol dm^{-3}: (○) 2.0×10^{-5}, (■) 4.0×10^{-5}, (×) 2.0×10^{-4}, (●) 4.0×10^{-4}, (◆) 8.0×10^{-4}, (+) 2.0×10^{-3}, (△) 4.0×10^{-3}, (▼) 8.0×10^{-3}, (□) 4.0×10^{-2}.

The iron(II), about 5% of the initial concentrations, was extracted into the SDS phase by salting-out separation. An aqua-cation of iron(II) can be electrostatically interacted with the anionic charge of the surfactant, and was extracted. The percent of extraction was constant and independent of the initial concentrations of iron(II) between the wide ranges of 2.0×10^{-5} to 4.0×10^{-2} mol dm^{-3}; therefore, more than 99% of the iron was removed from the SDS phase by twice extraction.

Determination of Copper in Steel. A pre-treatment of the samples was carried out as follows. About 100 mg of the sample was decomposed with 20 cm^3 of (1+1) hydrochloric acid and 5 cm^3 of (1+2) nitric acid. The solution was heated and evaporated to dryness. The residue was dissolved with 10 cm^3 of 6 mol dm^{-3} hydrochloric acid and diluted with water to 100 cm^3. The determination of copper was performed after a reduction of the metals by the addition of ascorbic acid.

Sample steels (The Japanese Standard of Iron and Steel, JSS) containing various metals are listed in Table 1. The recovery of copper(I) was 95% in the aqueous phase with once stripping by cooling separation; therefore, more than 99% of the copper(I) was recovered by twice stripping. Table 2 gives the interference of diverse ions on the spectrophotometric determination of copper(I) after successive single extraction and twice stripping. An increase of 200-fold of metals that are minor components of steel and the 1000-fold of the iron(II) did not interfere.

The copper contents in steel was determined by the AAS method after acid-attack dissolution with aqua-regia and perchloric acid.[12] This standard method was applied to samples involving 0.003% to 1.0% copper with calibration curves that were prepared in the presence of iron. On the other hand, after salting-out extraction the remaining iron was less than 5% and did not interfere with the determination of copper using the ordinary calibration curve prepared in the absence of iron.

The concentrations of copper were measured in the aqueous phase by both the AAS and spectrophotometric methods. The obtained analytical results were in good agreement with the certified values (Table 1). The combination of extraction and stripping steps, exploiting the nature of the separated phases, seems to be a reasonable alternative to the traditional

Table 2. The Influence of Diverse Ions on the Spectrophotometric Determination of Copper[a)]

Ion	Added as	[M]/[Cu]	Cu(I) found/%
Mn(II)	$MnSO_4$	20	99.1
		100	99.9
		200	99.5
Ni(II)	$NiSO_4$	20	100.1
		100	99.7
		200	101.3
Cr(III)	$Cr(NO_3)_3$	20	100.3
		100	99.6
		200	100.0
Cr(VI)	K_2CrO_4	20	100.3
		100	100.0
		200	100.2
Mo(VI)	$(NH_4)_6Mo_7O_{24}$	40	98.7
		80	99.8
		200	100.2
V(IV)	$VOSO_4$	20	101.2
		100	99.0
		200	99.9
Fe(II)	$FeSO_4$	100	99.8
		200	100.5
		500	100.1
		1000	100.0

a) 2.5 μg cm^{-3} Cu(I).

Table 1. Analytical Results on the Determination of Copper in Steel Samples

	Metal contents certified/%						Copper contents/%	
Sample	Cu	Mn	Ni	Cr	Mo	V	Found[a,c)]	Found[b,c)]
JSS 151-4	0.46	1.51	2.92	0.15	0.054	0.052	0.465±0.008	0.458±0.010
JSS 152-4	0.45	0.42	1.95	0.52	1.02	0.11	0.462±0.010	0.461±0.018
JSS 153-4	0.17	0.83	0.96	1.01	1.33	0.22	0.172±0.007	0.172±0.004
JSS 154-4	0.21	1.14	0.50	2.04	0.71	0.33	0.219±0.006	0.203±0.007
JSS 155-4	0.30	0.27	0.04	3.08	0.39	0.43	0.296±0.008	0.298±0.009

a) By spectrophotometric determination. b) By Atomic absorption spectrometric determination.
c) Average of 6 determinations, and errors shown are within 95% confidence limits.

extraction procedures using organic solvents. Removal of metals from the surfactant phase is also available to recycle the surfactant.

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