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Trace Analysis of Metals by ESR. I. Microdetermination of Copper by Means of Solvent Extraction of Copper(II) Diethyldithiocarbamate

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A new method was developed for the direct determination of copper using ESR. Cupric diethyldithiocarbamate complex dissolved in benzene shows a unique ESR spectrum. The bivalent complex in benzene gave a very strong ESR signal with intensity sensitive to 0.005 ppm of Cu(II)-ion. Thus the ESR signal can be utilized for the trace analysis of Cu(II)-ion. The ESR signal intensity was linear in the ranges 1.0—0.1 γ/ml and 0.1—0.01 γ/ml of Cu(II)-ion. Mg^{2+}, Fe^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, I^-, Br^-, and NO_3^- did not interfere with the determination, while Hg^{2+} and CN^- did. Comparing this method with photometric determination, we see that a very low content of Cu(II)-ion can be determined with a very small amount of sample.

It is known that Cu(II) forms various paramagnetic Cu(II) complexes which show characteristic ESR spectra.[1-3] In a previous paper, ESR spectra of powder and solution of Cu(II) complexes were reported,[4] for which seventeen samples were prepared by the usual methods. In the present study, a new method was developed for the rapid solvent extraction and direct determination of Cu(II) using ESR. Powdered $(DDC)_2Cu$, the Cu(II) complex, showed the known broad absorption spectrum whereas hyperfine structure was observed in a benzene solution, *i.e.*, the ESR spectrum was split into four lines. In the case of cupric dithiocarbamates the ESR spectra were very narrow and sharp. The second signal, counted from higher magnetic field, was dominant and its height was proportional to the amount of Cu(II) in a certain concentration range. The signal could be found even in the very dilute solution of Cu(II)-ion. Thus the application of ESR signal to the trace analysis of Cu(II)-ion is possible.

Experimental

Apparatus. The ESR measurement was carried out with a Hitachi X-band spectrometer, Model MPU-3. The magnetic field was modulated at 100 kHz. A Hitachi-Perkin Elmer spectrophotometer, Model 139, was used for the absorption spectra and colorimetric analysis. The measurements were carried out with 1 cm glass cell.

Reagents. Sodium diethyldithiocarbamate(DDCNa) was of JIS special grade from Kokusan Kagaku Co., Ltd. A standard solution of Cu(II) was prepared by dissolving 78.592 mg of $CuSO_45H_2O$ of JIS special grade in 200 m*l* twice distilled water. Other reagents were of guaranteed grade from Kokusan Kagaku Co., Ltd. and used without further purification.

Preparation of the Sample Solution. One m*l* of 0.2% aqueous solution of DDCNa was added into 1 m*l* of the solution containing Cu(II)-ion. The pH was regulated to 1—2 with hydrochloric acid, and 1.0 m*l* of benzene was poured into the mixture. After shaking for a few minutes $(DDC)_2Cu$ was extracted entirely into the benzene layer, and 0.1 m*l* of the solution was taken for examination by ESR.

Results and Discussion

ESR spectrum of $(DDC)_2Cu$. $(DDC)_2Cu$ in benzene showed a unique ESR spectrum as shown in Fig. 1. Owing to the existence of nuclear spin (3/2) of ^{63}Cu and ^{65}Cu four splitting absorption bands appeared. The second signal counted from higher magnetic field was dominant, and its height was proportional to the amount of Cu(II)-ion in a certain range. Thus the second signal intensity was used for the determination of Cu(II)-ion concentration.

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[2] R. Rajan and T. R. Reddy, *ibid.*, **39**, 1140 (1963).

[3] B. G. Malmström and T. Vänngård, *J. Mol. Biol.*, **2**, 118 (1960).

[4] D. Yamamoto and T. Fukumoto, *Memoirs of Inst. of Sci. and Tech. Meiji Univ.*, **5**, 251 (1966).

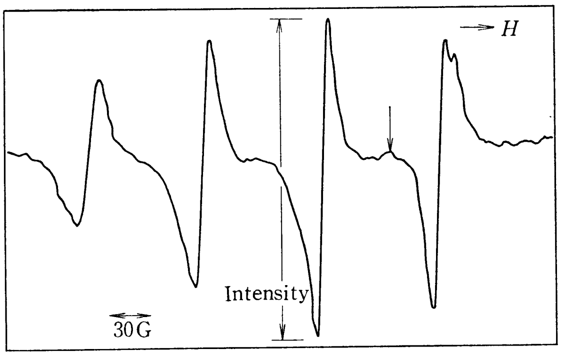

Fig. 1. ESR spectrum of $(DDC)_2Cu$ complex in benzene solution, at room temperature. The arrow indicates the resonance field of solid DPPH.

TABLE 1. COMPARISON OF SIGNAL INTENSITIES IN SOLVENTS

Organic solvent	Signal intensity
Benzene	100
Carbon tetrachloride	96.7
Carbon disulfide	94.8
Ethylbenzene	66.2
Xylene	62.3
Toluene	60.0

Signal intensity of $(DDC)_2Cu$ complex in benzene is taken as 100.

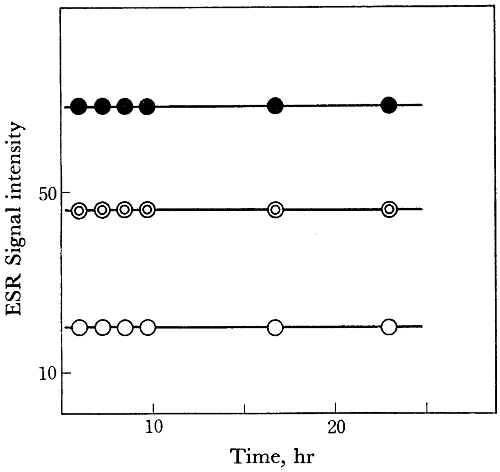

Fig. 2. Effect of time of standing.
●: 10.0γ/m*l*, ◎: 1.0γ/m*l*, ○: 0.1γ/m*l*.

Effect of Organic Solvents on Extraction. Extraction was carried out by the above procedure. ESR spectra of six solutions of $(DDC)_2Cu$ in different organic solvents were measured. The signal intensities are shown in Table 1. We see that the maximum ESR signal intensity is obtained in the benzene solution.

Effect of Time of Standing. The ESR signal intensity of the solution extracted at pH 2.0, was determined as a function of the time elapsed after the preparation of the solution. As shown in Fig. 2, no change was observed in the ESR signal intensities over a period of 24 hr.

Effect of pH on Extraction. The effect of pH on the extraction was examined. The signal intensities obtained from solutions of 0.1 γ/m*l*, 1.0 γ/m*l*, and 10.0 γ/m*l* Cu(II)-ion were constant in the pH range 1.0—7.0 as shown in Fig. 3. However, the range pH 1—2 was chosen to avoid the extraction of other metal ions such as Mn^{2+}, Fe^{2+}, Ni^{2+}.

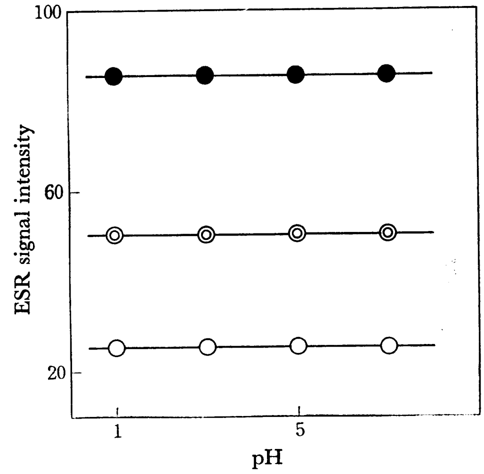

Fig. 3. Effect of pH on extraction.
●: 10.0γ/m*l*, ◎: 1.0γ/m*l*, ○: 0.1γ/m*l*.

TABLE 2. EFFECT OF DIVERSE IONS

Ion	Added as	0.1γ/m*l* Cu taken Cu found	1.0γ/m*l* Cu taken Cu found
Mg^{2+}	$MgCl_2$	—	—
Fe^{2+}	$FeCl_2$	—	—
Ba^{2+}	$BaCl_2$	—	—
Mn^{2+}	$MnCl_2$	—	—
Zn^{2+}	$ZnCl_2$	—	—
Co^{2+}	$CoCl_2$	—	—
Pb^{2+}	$Pb(CH_3COO)_2$	—	—
Ni^{2+}	$NiCl_2$	—	—
Hg^{2+}	$HgCl_2$	+	+
I^-	KI	—	—
Br^-	KBr	—	—
CN^-	KCN	+	+
NO_3^-	KNO_3	—	—

100 γ/m*l* of diverse ions added.
+) Interference —) No interference

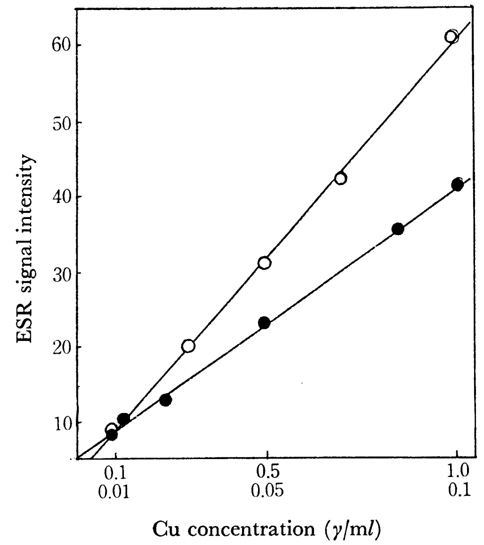

Fig. 4. Calibration curve.
●: 0.01—0.1γ/m*l*, ○: 0.1—1.0γ/m*l*.

Table 3. Comparison of ESR method with photometric method. Cu contents in aluminum foil

Al-foil (g)	ESR method[a)] (ppm)	Photometric method[b)] (ppm)
0.0992	49.3	49.6
0.1014	56.6	56.4
0.1008	64.4	64.6
0.0998	28.0	28.5
0.1017	68.8	69.7

All values are means of five measurements.

a) 0.1 m*l* of 100 times diluted solution

b) 5.0 m*l* of 10 times diluted solution

Effect of Diverse Ions. The effect of 13 ions on the determination of Cu(II) was examined. The results are summarized in Table 2. CN^- and Hg^{2+} interfere with the determination.

Calibration Curve for the Determination of Cu(II). The calibration curve for the Cu(II)-ion was determined from the height of the second signal at different Cu(II)-ion concentrations. In Fig. 4, the ordinate is in an arbitrary scale.

Comparison with usual Photometric Determination. For the sake of comparison, the Cu content in aluminium foil were determined by the usual photometric and ESR methods. About 100 mg of aluminium foil was dissolved in 6N-HCl with a small amount of concd. nitric acid and diluted to 100 m*l* with water. The solution was used as a sample. Determination of Cu content was carried out by the usual photometric method.[5)] Comparison of results from ESR and photometric methods is given in Table 3. We see that the ESR method can be used for the determination of a very low content of Cu(II)-ion with a very small amount of sample.

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5) *Cf.* IUPAC, Spectrophotometric Data for Colorimetric Analysis, Butterworths, London, 1963, pp. 150—156.