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Trace Analysis of Metals by ESR. II. Indirect Microdetermination of Mercury(II) with Tetraethylthiuram disulfide Copper(II) Complex[1]

Daijiro YAMAMOTO and Noriaki IKAWA
Faculty of Agriculture, Meiji University, Ikuta, Kawasaki-shi

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A method was devised for the indirect microdetermination of mercury by means of ESR. Tetraethylthiuram disulfide(TET)-Cu(II) complex dissolved in benzene showed a characteristic ESR spectrum. Quantitative determination of a small amount of mercury(II) was made by application of the replacement reaction of TET-Cu(II) by mercury(II)-ion in a benzene solution:

$$\text{TET-Cu} + \text{Hg}^{2+} \rightarrow \text{TET-Hg} + \text{Cu}^{2+}$$

The ratio of metal to ligand was considered to be 1: 1 in the complex. 1.0—0.1 γ/m*l* and 0.1—0.01 γ/m*l* of mercury was determined rapidly in the presence of Mg^{2+}, Fe^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, I^-, Br^-, NO_3^-, and Cl^- ions. CN^- interfered with the determination. From a comparison of this and photometric methods a very small amount of mercury(II) ion can be determined with a very small amount of sample.

Spectrophotometric determination of mercury(II) with dithizone, dithiocarbamates, and cupric diethyldithiocarbamate ($(DDC)_2Cu$)[2,3] has been reported. Determination with $(DDC)_2Cu$ was indirect and the following replacement reaction was used.

$$(DDC)_2Cu + Hg^{2+} \longrightarrow (DDC)_2Hg + Cu^{2+}$$

The decolorization which takes place in the solution by the replacement reaction was utilized in the spectrophotometric measurement. ESR spectra of $(DDC)_2Cu$ complex in various organic solvents have been reported.[4,5] A small amount of copper could be determined by means of ESR. $(DDC)_2Cu$ complex dissolved in benzene showed a characteristic ESR spectrum. The signal intensity was sensitive to 0.005 ppm of copper(II) ion.

In the present study, tetraethylthiuram disulfide (TET) was used in place of DDC, since TET-Cu(II) complex has the same structure as that of DDC-Cu(II),[6] and TET was cheaper than DDCNa. The TET-Cu(II) complex in benzene gave a strong ESR signal

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[1] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966, and the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[2] S. Komatsu and S. Kuwano, *Nippon Kagaku Zasshi*, **83**, 1262 (1962).

[3] Y. Hamamoto and M. Kotaki, *Nippon Nogei Kagaku Kaishi*, **34**, 885 (1960); *ibid.*, **39**, 442 (1965). K. Takehara and T. Takeshita, *Bunseki Kagaku*, **15**, 332 (1966).

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

[5] This Bulletin in press.

[6] R. Petterson and T. Vänngård, *Arkiv. Kemi.*, **17**, 249 (1961).

and its intensity was sensitive to 0.005 ppm of Cu(II) ion. The ESR spectrum was split into four narrow lines. The intensity of 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. Thus the diminution of the ESR signal intensity could be used for the trace analysis of mercury(II).

Experimental

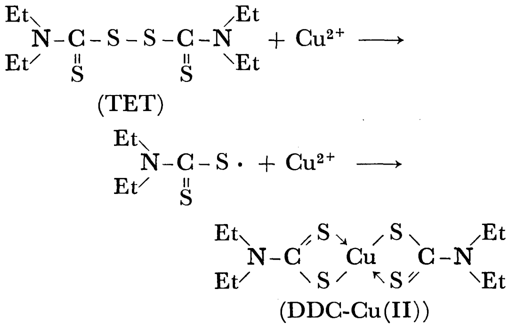
Apparatus. ESR measurements were carried out at room temperature with a Hitachi X-band spectrometer, Model MPU-3. The magnetic field was modulated at 100 KHz. Absorption spectra measurements and colorimetric analysis were carried out with a Hitachi-Perkin Elmer Spectrophotometer, Model 139 using a 1 cm glass cell.

Reagents. TET used in the experiments was of JIS special grade from Tokyo Kasei Kogyo Ltd. A pure TET was prepared by recrystallization in a hot mixture of ethanol and carbon tetrachloride. Standard mercury(II) solution was prepared as follows. Distilled mercury was dissolved in concd. nitric acid and diluted with water to the concentration 10 γ/m*l*. Other reagents were of guaranteed grade from Kokusan Kagaku Co., Ltd. and used without further purification.

Preparation of TET-Cu Complex. The complex was prepared by mixing 1.0% ethanolic solution of TET(ligand) and saturated cupric sulfate solution. Bluish brown precipitate was washed with water-ethanol mixture.

Results and Discussion

ESR Spectrum of TET-Cu Complex. TET-Cu complex in benzene showed a characteristic ESR spectrum.[4] This spectrum was the same as one of $(DDC)_2$-Cu in benzene.[4] The formation of TET-Cu might be as follows;



$$Et_2N\text{-}\overset{\displaystyle S}{\underset{}{C}}\text{-}S\text{-}S\text{-}C(=S)\text{-}NEt_2 + Cu^{2+} \longrightarrow$$

(TET)

$$Et_2N\text{-}C(=S)\text{-}S\cdot + Cu^{2+} \longrightarrow$$

$$Et_2N\text{-}C(S)_2Cu(S)_2C\text{-}NEt_2$$

(DDC-Cu(II))

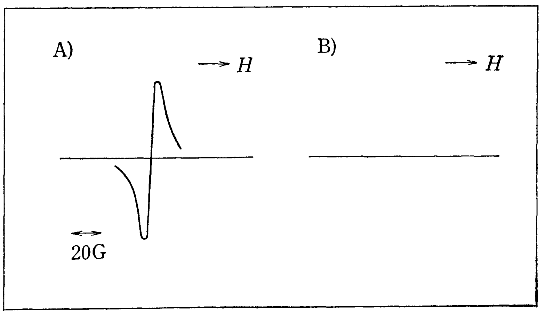


Fig. 1. ESR spectrum after replacement reaction of Hg(II) ion with Cu(II) in TET-Cu complex.
A): Before reaction, B): After reaction.

From the results we see that the second signal, counted from higher magnetic field, was dominant and its height is proportional to the amount of copper in certain

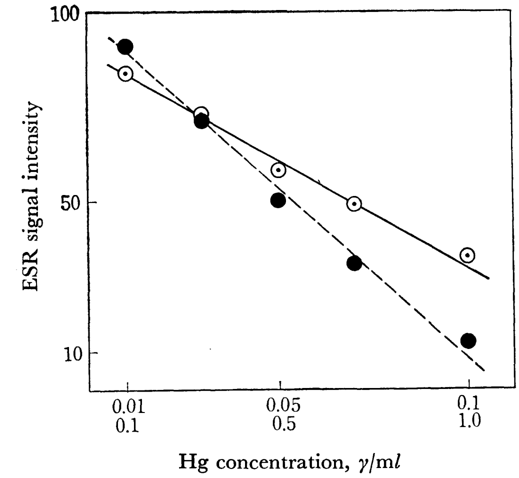


Fig. 2. Relations between mercury concentration and ESR signal intensity, 1.0 m*l* TET-Cu solution in benzene, pH 4.0, 1.0 m*l* mercury sample.
⊙: 1.0—0.1 γ/m*l*, ●: 0.1—0.01 γ/m*l*.

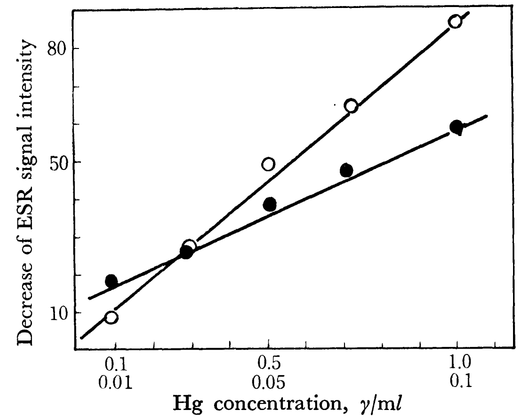


Fig. 3. Calibration curve.
●: 1.0—0.1 γ/m*l*, ○: 0.1—0.01 γ/m*l*.

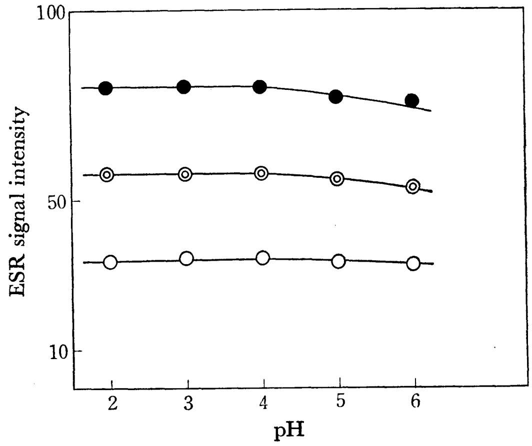


Fig. 4. Effect of pH.
●: 10.0 γ/m*l*, ◎: 1.0 γ/m*l*, ○: 0.1 γ/m*l*.

TABLE 1. EFFECT OF DIVERSE IONS

Ion	Added as	1.0 γ/m*l* Hg taken	100 γ/m*l* Hg taken
Mg^{2+}	$MgCl_2$	—	—
Fe^{2+}	$FeCl_2$	—	—
Ba^{2+}	$BrCl_2$	—	—
Mn^{2+}	$MnCl_2$	—	—
Zn^{2+}	$ZnCl_2$	—	—
Co^{2+}	$CoCl_2$	—	—
Pb^{2+}	$Pb(CH_3COO)_2$	—	—
Ni^{2+}	$NiCl_2$	—	—
I^-	KI	—	—
Br^-	KBr	—	—
CN^-	KCN	+	+
NO_3^-	KNO_3	—	—
Cl^-	NaCl	—	—

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

ranges. Thus the second signal intensity was used for the determination of copper(II) concentration.[5]

Replacement Reaction of Mercury(II) with Copper(II) in TET-Cu Complex. One m*l* of 0.00015M mercury(II) solution was mixed with 1.0 m*l* of 0.00015M TET-Cu benzene solution. After shaking for a few minutes, the brownish yellow benzene layer disappeared completely showing the accomplishment of the replacement reaction.

One tenth m*l* of the benzene layer was taken for examination. The ESR spectrum after replacement reaction of mercury(II) with Cu(II) in TET-Cu complex in benzene (0.00015M, Cu(II) content) showed ESR spectrum as shown in Fig. 1. The spectrum disappeared when the benzene layer was taken. This shows the accomplishment of replacement reaction. The metal to ligand ratio of the complex was considered to be 1 : 1. Therefore, the overall replacement reaction between TET-Cu and mercury(II)-ion can be given by

$$\text{TET-Cu} + Hg^{2+} \longrightarrow \text{TET-Hg} + Cu^{2+}$$

Decrease of TET-Cu Concentration by Mercury(II) Ion. Decrease of TET-Cu concentration due to the replacement by mercury(II) ion was determined by ESR. The original concentration of copper(II) was 1.0 γ/m*l* or 0.5 γ/m*l*, and the mercury(II) concentration ranges were 0.1—0.01 γ/m*l* and 1.0—0.1 γ/m*l*. The intensity of the second signal peak height was used for the measurement. The results are given in Fig. 2.

Calibration Curve for the Determination of Mercury. From the results, calibration curves for the determination of mercury were prepared in the mercury(II) ion concentration ranges 0.1—0.01 γ/m*l* and 1.0—0.1 γ/m*l*, respectively. Figure 3 shows that the ESR signal intensities are linear in the above ranges.

Effect of pH on Solvent Extraction. The effect of pH on the replacement reaction was examined. The signal intensities of the solution of 0.1 γ/m*l*, 1.0 γ/m*l*, and 10.0 γ/m*l* mercury(II) were constant within experimental error in the pH range 1 to 7, as shown in Fig. 4.

Effect of Diverse Ions. The effect of diverse ions on the determination of mercury(II) was examined with 13 different ions. The results are summarized in Table 1. We see that CN^- interferes with determination of mercury(II).

Comparison with the Usual Photometric Method. For the sake of comparison the mercury(II) contents in $HgCl_2$ were determined by the usual photometric[2] and ESR methods. 135.4 mg $HgCl_2$ was dissolved in water and diluted to 100 m*l*. This was used as the sample. Comparison of the ESR and photometric methods is given in Table 2.

TABLE 2. COMPARISON OF ESR METHOD WITH PHOTOMETRIC METHOD

Hg (γ/m*l*)	ESR method[a] (γ/m*l*)	Photometric[b] method (γ/m*l*)
100	102	101
250	252	253
500	503	501

All values are the means of five measurements.
a) 0.1 m*l* of 100 times diluted solution
b) 5.0 m*l* of 10 times diluted solution

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