Trace Analysis of Metals by ESR. III. Determination of Silver by Solvent Extraction with Tetraethylthiuram disulfide Silver(II) Complex[1)]

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A new method was worked out for the determination of silver using ESR. Bivalent complex of silver with tetraethylthiuram disulfide extracted with carbon disulfide, benzene, carbon tetrachloride, xylene, ethylbenzene, toluene, chloroform, and organic solvents was stable. The complex in carbon disulfide gave a very strong ESR signal, the sensitivity being 0.1 ppb. The amount of solution required was 1 m*l*. Colorimetric method can also be applied. However, the sensitivity was lower than that of ESR method. Silver was determined photometrically at 620 nm as a complex with tetraethylthiuram disulfide. The absorption followed Beer's law in the range 10—100 ppm of silver concentration at 620 nm. Bivalent silver complex could be selectively extracted in the presence of several ions, except copper(II) and mercury(II). Results of the continuous variation method indicate that the silver(II) - tetraethylthiuram disulfide ratio in the complex is 1 : 1.

Bivalent silver (Ag(II)) compounds have long been known to be paramagnetic with electron configuration $4d^9$.[2—4)] It is possible to infer the existence of this oxidation state from a study of the ESR spectra. Most measurements were carried out at 77°K under the irradiation of γ-ray or X-ray.[5—9)] Studies of the ESR spectra at room temperature, however, have been only reported by McMillan, Ag^{2+} in nitric solution,[5)] and by Vänngård, Ag(II)-thiuram disulfides.[10—12)]

Many methods have been reported on the determination of silver. A spectrophotometric method using dithizone,[13)] sodium diethyldithiocarbamate,[14)] or *p*-dimethylaminobenzylidenerhodanine[15)] has been reported. The sensitivities were in the order of ppm. The sensitivities of electoanalysis, atomic absorption spectrophotometrical analysis, emission spectrochemical analysis, and activation analysis were in the range 0.1—1 ppm.[16)]

If silver is stable in Ag(II) complex and extracted in organic solvents, a minute amount of silver can be determined by ESR. Thus we attempted to prepare the stable complexes of Ag(II) and to extract them with organic solvents. Various Ag(II) complexes were prepared by oxidation with ammonium persulfate on Ag(I) complex. The ESR spectra of the solid Ag(II) complexes with dithizone, *o*-(1.10)phenanthroline, 8-hydroxyquinoline, picolinic acid, 2-aminopyrimidine, α-nitroso-β-naphthol, or ethylphenyldithiocarbamate could be observed at room temperature. However, these Ag(II) complexes could not be extracted in organic solvents. A Ag(II) complex which can be extracted with organic solvents was reported by Vänngård.[10)] Ag(I) *N*,*N*-dialkyldithiocarbamates were mixed with the corresponding thiuram disulfides in benzene, and Ag(II) complexes were extracted in benzene layer. We found that Ag(II) complexes with tetraethylthiuram disulfide (TET), tetramethylthiuram disulfide (TMT), dipentamethylenethiuram tetrasulfide (DPTTS) and 2,2-dithio-bis-benzothiazole (DBT) prepared by mixing of Ag(I)-diethyldithiocarbamate complex with the above reagents, could be extracted with organic solvents.

Experimental

Reagents. A standard silver solution was prepared by dissolving 0.543 g of a silver nitrate in 100 m*l* of water distilled twice in a quartz apparatus. This solution was then diluted to the required concentration. 10^{-3}M solutions of TET, TMT, DBT, and DPTTS were prepared by dissolving the reagent in organic solvents. The 10^{-3}M solution of sodium diethyldithiocarbamate (DDCNa) was prepared by dissolving DDCNa in 100 m*l* of distilled water. The McIlvaine buffer solution was made from citric acid and Na_2HPO_4. The Menzel buffer solution was made from Na_2CO_3 and $NaHCO_3$. All reagents and organic solvents in the experiments were of JIS special grade and used without further purification.

Apparatus. The ESR spectra were measured in organic solutions at room temperature with a Hitachi X-band ESR spectrometer, Model MPU-3, equipped with a 100 KHz field modulation unit. Absorption spectra were measured with a Hitachi spectrophotometer, Model EPS-3, using a 1 cm glass cell.

Standard Procedure for Extraction. To 1 m*l* of sample

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[2)] G. T. Morgan and S. Sugden, *Nature*, **128**, 31 (1931).

[3)] A. A. Noyes, K. S. Pitzes, and C. L. Dunn, *J. Amer. Chem. Soc.*, **57**, 1299 (1935).

[4)] E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, **1935** 775.

[5)] J. A. McMillan and B. Smaller, *J. Chem. Phys.*, **35**, 1968 (1961).

[6)] J. A. McMillan and W. S. Koski, *J. Amer. Chem. Soc.*, **85**, 2375 (1963).

[7)] F. K. Kneubukl, W. S. Koski, and W. S. Caughey, *ibid.*, **83**, 1607 (1961).

[8)] N. A. Ashford and G. A. Noble, *J. Chem. Phys.*, **49**, 4720 (1968).

[9)] N. A. Ashford and A. Snelson, *ibid.*, **51**, 532 (1969).

[10)] T. Vänngård and S. Akerstron, *Nature*, **187**, 183 (1959).

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

[12)] R. Assa, R. Pettersson, and T. Vänngård, *Nature*, **190**, 258 (1961).

[13)] H. Friedeberg, *Anal. Chem.*, **27**, 305 (1955).

[14)] H. Bode, *Z. Anal. Chem.*, **114**, 164 (1955).

[15)] M. G. Lai and H. V. Weiss, *Anal. Chem.*, **34**, 1012 (1962).

[16)] Ref. L. L. Lewis, *ibid.*, **40**, No. 12, 28A (1968). E. B. Sandell; "Colorimetric Determination of traces of Metals," 3rd ed., Interscience-Wiley, New York, (1959).

solution containing 10^{-6}M of silver were added 1 m*l* of the DDCNa solution and 1 m*l* of the TET (or TMT, DBT, DPTTS) solution. After being shaken for one minute, and left to stand for ten minutes, 0.2 m*l* of the organic solvent layer was drawn off into an ESR cell. The ESR spectrum was measured with sweeping a rate 100 Gauss/15 min. Extraction for the measurement of absorption spectra was carried out in the same way, the volume of each solution being 5 m*l*.

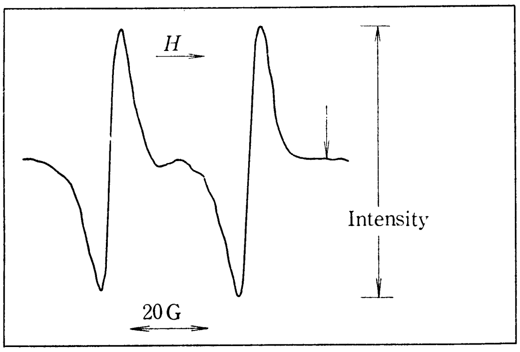


Fig. 1. ESR spectrum of TET-Ag(II) complex in organic solvent at room temperature. The perpendicular arrow in this figure indicates the resonacne filed of solid DPPH.

Results and Discussion

ESR Spectra and Absorption Spectra. Figure 1 shows a typical ESR spectrum obtained from carbon disulfide solution of TET-Ag(II) complex. The two lines of equal intensity ESR spectrum were due to the hyperfine interaction of the nuclear spin of 1/2. Super hyperfine splitting due to magnetic interaction with the nuclei of silver, ^{107}Ag and ^{109}Ag, which have the nuclear magnetic moment of -0.1130 and -0.1299, respectively, was not observed in the case of high field modulation such as 6—10 Gauss. The ESR spectra of the silver(II) complexes with TET, TMT, DBT, and DPTTS were almost the same. The *g*-values were 2.017, and both line widths were 4.7 Gauss. The ESR signal intensity was calculated by the signal height in the high magnetic field as shown in Fig. 1. The ESR signal intensity was proportional to silver concentration.

The typical absorption spectra shown in Fig. 2 were obtained for 10^{-4}M of silver solution. No absorbance maximum of the reagent (curve 2) exists in the wavelength range (Fig. 2). Appearance of the maximum in the absorption spectrum can be attributed to the formation of Ag(II) complex between the reagent cation and the complex anion.

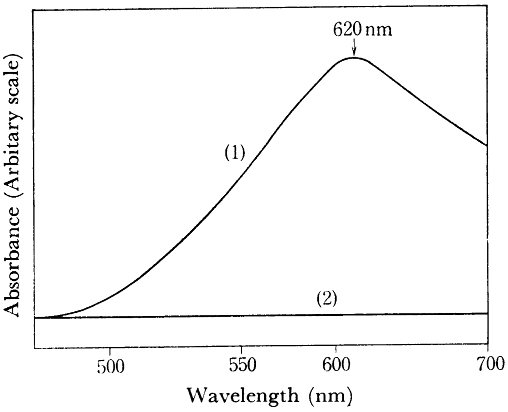


Fig. 2. Absorption spectra.
1) TET-Ag(II) complex in CS_2 solution.
2) TET in CS_2 solution.

Table 1. ESR signal intensities by the different combinations of solvents and reagents

	TET	TMT	DBT	DPTTS
CS_2	100.0	8.9	—	5.0
C_6H_6	27.2	4.4	—	—
CCl_4	12.1	1.3	—	—
$C_6H_5CH_3$	5.3	1.5	—	—
$C_6H_4(CH_3)_2$	4.5	1.1	—	—
$C_6H_5C_2H_5$	4.3	1.1	—	—

Signal intensity of TET-Ag(II) complex in carbon disulfide is taken as 100.0. — shows that ESR signal is obtained only at maximum ESR sensitivity.

Solvents and Reagents. The following solvents and reagents were examined for their ability to extract the Ag(II) complex; carbon disulfide, benzene, carbon tetrachloride, xylene, toluene, and ethylbenzene; TET, TMT, DBT, and DPTTS. The test solutions were made by extracting 10^{-6}M silver nitrate. The results are shown in Table 1. The carbon disulfide and TET pair was found to be the best for extracting the Ag(II) complex, and was thus chosen for the experiments.

Effect of Time of Standing. The stability of the TET-Ag(II) complex in the solvent was determined by measuring the ESR signal intensity. The ESR signal intensity of TET-Ag(II) complex of the solution remained almost constant for at least 8 hr after preparation.

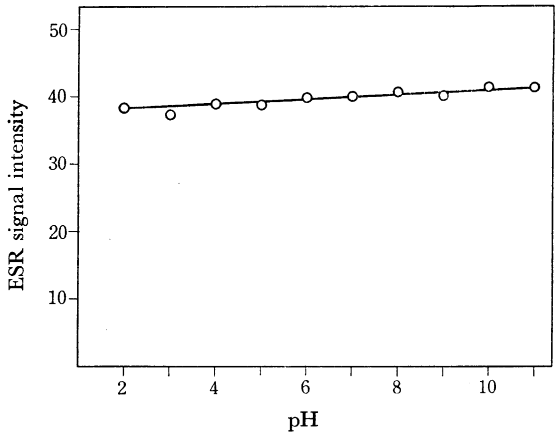


Fig. 3. Effect of pH on ESR signal intensity. Each test solution consists of 5 m*l* buffer solution and 10^{-6}M TET-Ag(II).

Effect of pH. Figure 3 shows a typical pH dependence of the extraction ability. The test solutions were made by extracting 10^{-6}M of silver nitrate in the pH range 2—11. The ESR signals are slightly larger on the alkaline side. The amount of buffer solution per 3 m*l* of the test solution was found to have no effect on the ESR signal intensity over the range 5—10 m*l*.

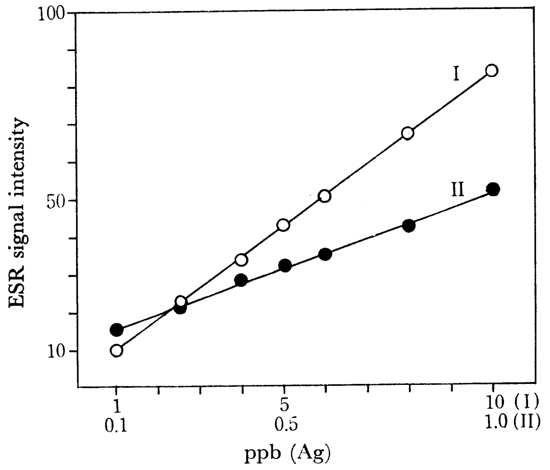


Fig. 4. Calibration curves by ESR method.

Calibration Curve for Silver and Sensitivity of the ESR method. The calibration curve for silver determination was prepared by the ESR signal intensity. Figure 4 shows typical calibration curves. We see that a linear relationship holds between the signal intensity and the silver concentration in the narrow ranges 1—0.1 ppb and 10—1 ppb. The sensitivity of the determination was 0.1 ppb. The total amount of sample solution required was only 1 m*l*.

Beer's Law and Spectrophotometric Sensitivity. The linearity between the absorbance of the TET-Ag(II) complex and silver concentration was examined by varying the silver concentration and by measuring the absorbance at wavelength of 620 nm. The Ag(II) complex was found to follow Beer's law up to the silver concentration of at least 10 ppm at 620 nm.

TABLE 2. EFFECT OF DIVERSE IONS ON EXTRACTION OF Ag(II)

Ion	Added as	10	100	1000
Al^{3+}	$Al_2(SO_4)_3$	—	—	—
Zn^{2+}	$ZnCl_2$	—	—	—
Ba^{2+}	$BaCO_3$	—	—	—
Ni^{2+}	$NiCl_2 \cdot 4H_2O$	—	—	—
Mn^{2+}	$Mn(CH_3COO)_2 \cdot 4H_2O$	—	—	—
Mg^{2+}	$MgCl_2 \cdot 6H_2O$	—	—	—
Cd^{2+}	$Cd(NO_3)_2$	—	—	—
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	—	—	—
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	+	+	+
Hg^{2+}	Hg	—	+	+
I^-	KI	—	—	—
Br^-	KBr	—	—	—
Cl^-	KCl	—	—	—
NO_3^-	KNO_3	—	—	—
CN^-	KCN	—	—	—

Ag: 10^{-6}M, Ions: 10^{-3}M, 10^{-4}M, 10^{-5}M. 10, 100, and 1000 indicate that added diverse ion concentrations are of 10, 100, and 1000 times, respectively, to silver concentration. + Interference, — No interference

Effect of Diverse Ions. The effect of diverse ions was examined for a sample containing 10^{-6}M of silver nitrate. The results are shown in Table 2. Concentrations of the 1000—10 times of silver concentration ion were examined. Ag(II) complex could be selectively extracted in the presence of several ions. Mercury(II) and copper(II) ion interfered with extraction. Copper(II) could be separated, but not mercury(II).

Separation of Copper(II). The large solubility of $(DDC)_2Cu$ and very small solubility of DDC-Ag(I) in benzene were utilized for the separation of copper and silver. To 2 m*l* of the copper-silver mixture were added 10 m*l* of the 2% DDCNa, 20 m*l* of benzene and 1 m*l* of the 1N-HCl. The mixture was then shaken. After the organic layer was separated from the aqueous layer, 1 m*l* of a DDCNa solution and 1 m*l* of a TET-carbon disulfide solution were added to an aqueous solution. In the case of a large amount of copper the procedure was repeated several times. The ESR signal intensity was compared with that of standard TET-Ag(II) complex. The results are shown in Table 3. Copper(II) ion concentrations examined varied from 10000 to 100 times silver concentration. From the standard deviation shown in Table 3, we see that the interference of copper(II) ion diminished to some extent.

Composition of TET-Ag(II) Complex. The composition of the TET-Ag(II) complex was determined by the continuous variation method. The results are

TABLE 3. STANDARD DEVIATION

Ag^+ concn. (ppb)	Cu^{2+} concn. (ppm)	*n*	Standard Dev.
10	0	5	0.775
	10	5	0.894
	100	5	1.732
1.0	0	5	1.414
	1.0	5	2.000
	10	5	3.162
0.1	0	5	2.236
	0.1	5	2.645
	1.0	5	3.873

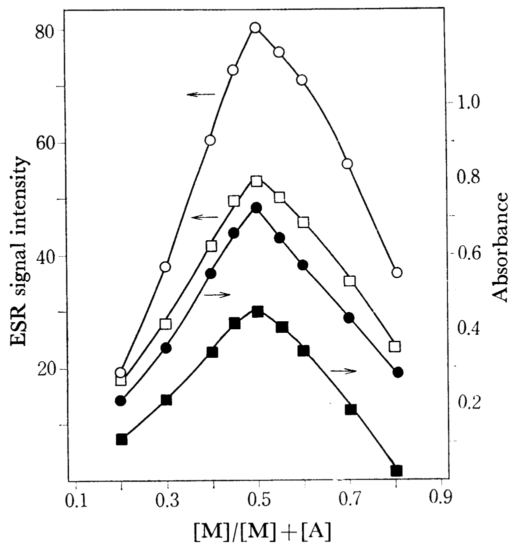
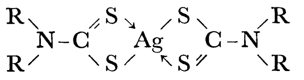


Fig. 5. Continuous variation method.
M: Ag, A: TET or TMT,
○: TET and Ag(II) by ESR,
●: TET and Ag(II) by absorbance at 620 nm,
□: TMT and Ag(II) by ESR,
■: TMT and Ag(II) by absorbance at 620 nm.

shown in Fig. 5. The curves were obtained by measuring the absorbance at 620 nm, and the ESR signal. The resulting curves have a maximum at 0.5 mol fraction of Ag(II), indicating TET-Ag(II) ion ratio 1: 1, and TMT-Ag(II) ion ratio 1: 1. Ag(II) complexes may have the following structure.



$R = C_2H_5$, CH_3

Reaction. When Ag(I) complex with DDC was mixed with TET, TMT, DBT, and DPTTS in organic solvent, the complexes with TET, TMT, DBT, and DPTTS were found to be extractable with organic solvents. Thus we assumed the mechanism of the complex formation. When DDCNa and TET were used, the reactions can be written as follows.

$$\text{DDCNa} + \text{Ag}^+ \longrightarrow \text{DDC-Ag(I)} + \text{Na}^+$$

$$\text{DDC-Ag(I)} + \text{TET} \longrightarrow \text{TET-Ag(II)} + \text{DDC}^-$$

The reaction of DDC-Ag(I) with TMT, DBT, or DPTTS was assumed to be same as that of DDCAg(I) with TET. These Ag(II) complexes gave strong ESR signal intensity.

When DDCNa and EDTA were used, and Ag(I) complexes with 2-aminopyrimidine, 8-hydroxyquinoline, α-nitroso-β-naphthol, dithizone, or *o*-(1.10)phenanthroline were mixed with TET-carbon disulfide solution, the products gave ESR spectra. Thus Ag(II) complexes were assumed to be prepared. Since it requires a long time for Ag(II) complexes to be stabilized and the ESR signal intensity obtained is weak, these complexes could not be used. The reaction, however, may be caused by the existence of DDC acid as impurity during the course of TET production.

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