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2(1*H*)-Quinolinethione Derivatives as Organic Reagents. II.[1,2] Properties of Some 2(1*H*)-Quinolinethione Derivatives and Application to the Potentiometric Titration of the Silver Ion

SABURO NAKANO, TOMOHIKO YOSHIDA, HIROKAZU TANIGUCHI,
and MASANORI YASUKI

Meiji College of Pharmacy[3]

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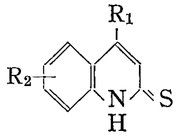
Halogen derivatives of 2(1*H*)-quinolinethione, alkyl derivatives of 1,2-dihydro-2-thioxo-4-quinolinecarboxylic acid, and alkyl 1,2-dihydro-2-thioxo-4-quinolinecarboxylate were synthesized. The detection limits for metal ions with these reagents were examined by spot tests. The metal ions which gave a precipitate with these reagents were the same as those reported previously.[1] iso-Amyl 1,2-dihydro-2-thioxo-4-quinolinecarboxylate (ATQ) forms a 1-to-1 compound with silver, and an ethanolic solution of ATQ was used as a titrant to determine 0.01—0.0001 M silver ions potentiometrically. The coefficient of variation was 1.8% ($n=10$) for 107.4 μg of silver. Silver protein was titrated potentiometrically with ATQ in 50% (v/v) ethanolic solution. The silver content was 8.0%, with a coefficient of variation of 1.8% ($n=5$).

Keywords——2(1*H*)-quinolinethione; organic reagent; potentiometric titration; silver ion; silver protein; iso-amyl 1,2-dihydro-2-thioxo-4-quinolinecarboxylate

In the previous paper,[1] the preparation of alkyl derivatives of 2(1*H*)-quinolinethione (QT) and the results of spectrophotometric investigation of the coloration of these QT derivatives with palladium(II) or copper(I) were reported. In the present work, we prepared halogen derivatives (I—VIII) of QT and 1,2-dihydro-2-thioxo-4-quinolinecarboxylic acid derivatives (IX—XIII) from the corresponding 2-bromo(or 2-chloro)quinoline and 2-bromo-(or 2-chloro)-4-quinolinecarboxylic acid derivatives, respectively, using thiourea. In addition, ester derivatives (XIV—XX) of IX were prepared by a general method of esterification.

TABLE I. 2(1*H*)-Quinolinethione Derivatives (I—VIII) and 1,2-Dihydro-2-thioxo-4-quinolinecarboxylic Acid Derivatives (IX—XX)



Compd. No.	R_1	R_2	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N	UV λ_{max}^{EtOH} nm (log ε)
I	CH_3	6-Cl	98	298—299[a] (dec.)	$C_{10}H_8ClNS$	57.28 (57.56	3.85 4.10	6.68 6.99)	223 (4.67) 287 (4.30) 394 (4.04)
II	CH_3	7-Cl	70	272—273[b] (dec.)	$C_{10}H_8ClNS$	57.28 (57.25	3.85 3.88	6.68 6.68)	224 (4.82) 279 (4.31) 388 (4.10)

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[1] Part I: S. Nakano, T. Yoshida, H. Taniguchi, and N. Suzuki, *Chem. Pharm. Bull.*, **25**, 1658 (1977).

[2] This work was presented at the 85th, 87th, 89th, and 91st Annual Meetings of the Pharmaceutical Society of Japan, Tokushima, 1965, Kyoto, 1967, Nagoya, 1969, and Fukuoka, 1971.

[3] Location: *1-35-23 Nozawa, Setagaya-ku, Tokyo.*

Compd. No.	R_1	R_2	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd (Found) C H N	UV λ_{max}^{EtOH} nm (log ε)
III	CH_3	6-Br	71	294—295 (dec.)	$C_{10}H_8BrNS$	47.26 3.17 5.51 (47.38 3.35 5.29)	226(4.65) 287(4.30) 394(4.00)
IV	CH_3	7-Br	84	251—252 (dec.)	$C_{10}H_8BrNS$	47.26 3.17 5.51 (47.53 2.85 5.27)	227(4.66) 280(4.19) 390(3.90)
V	C_6H_5	6-Cl	77	257—259 (dec.)	$C_{15}H_{10}ClNS$	66.29 3.71 5.15 (66.01 3.41 5.43)	225(4.59) 293(4.40) 402(3.98)
VI	C_6H_5	7-Cl	89	246—248 (dec.)	$C_{15}H_{10}ClNS$	66.29 3.71 5.15 (66.11 3.52 5.25)	225(4.63) 286(4.36) 398(4.04)
VII	C_6H_5	6-Br	54	245—247 (dec.)	$C_{15}H_{10}BrNS$	56.96 3.19 4.43 (56.86 3.16 4.28)	228(4.56) 294(4.40) 403(3.98)
VIII	C_6H_5	7-Br	100	244—245 (dec.)	$C_{15}H_{10}BrNS$	56.96 3.19 4.43 (57.23 3.32 4.54)	227(4.58) 287(4.37) 398(4.03)
IX	COOH	H	95	268—269 (dec.)	$C_{10}H_7NO_2S$	58.52 3.44 6.82 (58.58 3.70 6.95)	221(4.52) 286(4.28) 413(3.95)
X	COOH	5-CH_3	95	250—252 (dec.)	$C_{11}H_9NO_2S$	60.26 4.14 6.39 (60.12 4.11 6.45)	223(4.53) 287(4.42) 392(4.01)
XI	COOH	6-CH_3	97	279—281 (dec.)	$C_{11}H_9NO_2S$	60.26 4.14 6.39 (60.56 4.29 6.07)	222(4.54) 288(4.35) 400(3.98)
XII	COOH	7-CH_3	100	287—288 (dec.)	$C_{11}H_9NO_2S$	60.26 4.14 6.39 (60.00 4.06 6.20)	223(4.64) 282(4.38) 398(4.10)
XIII	COOH	8-CH_3	94	333—334 (dec.)	$C_{11}H_9NO_2S$	60.26 4.14 6.39 (60.39 4.13 6.56)	222(4.50) 284(4.34) 395(3.98)
XIV	$COOCH_3$	H	22	187—188	$C_{11}H_9NO_2S$	60.26 4.14 6.39 (60.42 4.28 6.45)	222(4.49) 289(4.22) 419(3.97)
XV	$COOC_2H_5$	H	62	182—183	$C_{12}H_{11}NO_2S$	61.78 4.75 6.00 (61.57 4.96 5.90)	221(4.53) 288(4.31) 419(3.95)
XVI	$COOCH_2CH_2CH_3$	H	34	156—157	$C_{13}H_{13}NO_2S$	63.14 5.30 5.66 (62.85 5.03 5.54)	222(4.53) 288(4.32) 418(3.99)
XVII	$COOCH_2CH(CH_3)_2$	H	63	168—169	$C_{14}H_{15}NO_2S$	64.34 5.79 5.36 (64.19 5.65 5.17)	221(4.54) 288(4.31) 418(3.96)
XVIII	$COOCH_2CH_2CH_2CH_3$	H	34	116—117	$C_{14}H_{15}NO_2S$	64.34 5.79 5.36 (64.30 5.68 5.56)	222(4.53) 289(4.27) 420(3.97)
XIX	$COOCH_2CH_2CH(CH_3)_2$	H	15	106—107	$C_{15}H_{17}NO_2S$	65.43 6.22 5.09 (65.27 6.15 4.92)	221(4.53) 289(4.31) 418(3.98)
XX	$COOCH_2CH_2CH_2CH_2CH_3$	H	30	108—109	$C_{15}H_{17}NO_2S$	65.43 6.22 5.09 (65.38 5.97 5.27)	221(4.51) 289(4.28) 418(3.98)

a) lit., mp 235°,[4a] mp 273—275°.[4b]

b) lit., mp 275°.[4c]

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4) *a*) Y. Hamada, H. Sugihara, and T. Isobe, *Yakugaku Zasshi*, **82**, 1592 (1962); *b*) D.I. Biskupskaya, A.V. Voropaeva, *Khim. Geterotsikl. Soedin.*, **1973**, 521; *c*) A.G. Renfrew, *J. Am. Chem. Soc.*, **68**, 1433 (1946).

The yields, mp, elemental analyses, ultraviolet absorption maxima, and molecular extinction coefficients of these derivatives are listed in Table I.

Screening tests for 34 kinds of metal ions were carried out by means of spot tests with these reagents (I—XX). The results show that the reactivity of these reagents with metal ions in an acetic acid solution is similar to that in an ethanolic solution. As described previously,[1] these reagents were also useful for palladium(II) and copper(I, II).

Compounds IX—XIII and the ester derivatives were found to be good reagents for silver ions from the results of the spot tests. Consequently, the potentiometric titration of silver ions with these ester derivatives was investigated. This titration procedure could be used to determine silver protein (J.P.IX), using iso-amyl 1,2-dihydro-2-thioxo-4-quinolinecarboxylate (AQT, XIX).

Experimental

Preparation of Reagents——1) Halogen derivatives (I—VIII) of QT were prepared as described previously.[1]

2) 1,2-Dihydro-2-thioxo-4-quinolinecarboxylic acid derivatives (IX—XIII): 2-Bromo(or 2-chloro)-4-quinolinecarboxylic acid (1 mol) was added to an EtOH solution of thiourea (1.2 mol) and the mixture was refluxed on a water bath for 15—30 min. The solution was cooled, diluted to twice its volume with H_2O, and the yellow product obtained was dissolved in 10% NaOH. The yellow filtrate was acidified with 10% HCl and the yellow precipitate obtained was collected by filtration, washed with H_2O, and dried. It was recrystallized from EtOH to give yellowish-orange needles.

3) Ester Derivatives (XIV—XX) were prepared by a general method: refluxing a mixture of IX and a large excess of the appropriate alcohol in the presence of concentrated H_2SO_4.

Apparatus——1) Spectrophotometric measurements were made with a Shimadzu UV-200 spectrophotometer and a Hitachi EPS-3T spectrophotometer.

2) The pH measurements were made with a Tōa HM-20A pH meter.

3) The measurements of electromotive force were made with a Shimadzu 3P potentiometer and a Tōa HM-20A pH meter.

4) Titration was carried out with a microburet (Shibata Co. Ltd.; capacity, 1 ml; smallest subdivision, 0.005 ml).

Stock Solutions of Metal Ions——Stock solutions of palladium(II) and copper(II) were prepared by dissolving weighed amounts of $PdCl_2$ in HCl solution and of $CuSO_4 \cdot 5H_2O$ in 0.1 N H_2SO_4. A stock solution of copper(I) was prepared by reducing a suitable volume of the copper(II) stock solution with $NH_2OH \cdot HCl$. The concentrations of these stock solutions were checked by the method described previously.[1]

Silver(I) Solution: An accurately weighed amount of $AgNO_3$ was dissolved in H_2O and a standard $AgNO_3$ solution (0.01 N) was prepared by diluting this solution with H_2O to the mark in a volumetric flask. The concentration of silver was checked by potentiometric titration with 0.01 N NaCl.

Stock solutions of other metal ions were also prepared: Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, As^{3+}, Sr^{2+}, Cd^{2+}, Sn^{2+}, Sb^{3+}, Ba^{2+}, Ce^{4+}, Pt^{4+}, Au^{3+}, Hg_2^{2+}, Hg^{2+}, Tl^+, Pb^{2+}, Bi^{3+}, Th^{4+} WO_4^{2-}, and UO_2^{2+}.

All chemicals and solvents used were of reagent grade, and redistilled water was used.

Reagent Solution——For the spot tests, these reagents (0.1 g) were dissolved in AcOH or EtOH to make 0.1% solutions. For potentiometric titration, an accurately weighed amount of one of the ester derivatives

Table II. Silver Compounds of Ester Derivatives

Compound No.	Formula	Analysis (%) Calcd C	H	N	Found C	H	N
XIV	$AgC_{11}H_8NO_2S$	40.51	2.47	4.30	40.44	2.22	4.30
XV	$AgC_{12}H_{10}NO_2S$	42.37	2.96	4.12	42.34	3.06	4.21
XVI	$AgC_{13}H_{12}NO_2S$	44.09	3.42	3.96	44.35	3.64	4.02
XVII	$AgC_{14}H_{14}NO_2S$	45.67	3.83	3.80	45.69	3.56	3.92
XVIII	$AgC_{14}H_{14}NO_2S$	45.67	3.83	3.80	45.72	4.07	3.85
XIX	$AgC_{15}H_{16}NO_2S$	47.14	4.22	3.66	46.99	4.35	3.66

(XIV—XIX) was dissolved in EtOH and 0.001 M solution was prepared by diluting this solution with EtOH to the mark of a volumetric flask.

Spot Tests for Metals——1) AcOH or EtOH Medium: A drop of test solution containing a metal ion and a drop of a reagent solution (AcOH or EtOH solution) were placed in the depression of a spot plate and the two drops were mixed with a glass rod. After about 1 min, the color developed was observed against a blank.

2) NH_4OH Medium: A drop of a reagent solution (EtOH solution) was added to a drop of a test solution and a drop of 10% NH_4OH. The mixed solution was observed as described in 1).

Measurement of Molecular Extinction Coefficient——1) A mixture of 2.0 ml of palladium(II) solution (2 or 5 μg/ml), 2.0 ml of AcOH, and 1.0 ml of 0.002 M reagent solution (AcOH) was allowed to stand at 20°, then diluted to 5.0 ml with AcOH. After 10 min, the absorption spectrum of the reaction mixture was measured with a 1 cm cell relative to a reagent blank.

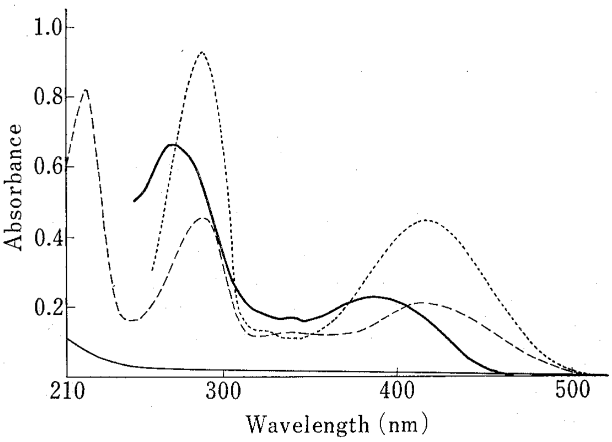

Fig. 1. Absorption Spectra of XIX and the Silver Compound of XIX

——: CH_2Cl_2 solution of XIX-Ag compound (8.0×10^{-5} M).
…………: CH_2Cl_2 solution of XIX (5.0×10^{-5} M).
———: EtOH solution of XIX-Ag compound (saturated solution).
--------: EtOH solution of XIX (2.5×10^{-5} M).

2) The same measurement was made with 2.0 ml of copper(I) solution.

Preparation of Silver Compounds——Each of the ester derivatives (XIV—XIX) (0.00015 mol) was dissolved in 20 ml of EtOH. One ml of 0.1 M $AgNO_3$ (0.0001 mol) was added to the solution. The pale yellow precipitate obtained was collected by filtration, washed with EtOH, and dried. The molar compositions of silver compounds of some ester derivatives were established by elemental analyses. The ratio of silver to XIV—XIX was 1:1. The elemental analysis data of these compounds and the absorption spectra of XIX and XIX-silver compound are shown in Table II and Fig. 1, respectively.

Recommended Procedure for Potentiometric Titration of Silver——First, 1.0 ml of 0.001 M $AgNO_3$, 4 ml of H_2O, and 5 ml of EtOH were placed in a titration vessel. The mixture was titrated potentiometrically with a 0.001 M ethanolic solution of XIX. The titration vessel was assembled with a silver-plate indicator electrode, a saturated calomel electrode, and an agar salt-bridge filled with saturated KNO_3 solution. The end point was determined by the second derivative method.

Results and Discussion

Reaction with Metal Ions

The metal ions which gave a colored precipitate with these reagents in acetic acid solution were described previously.1) In addition, lead(II) (in an ethanolic solution) and thallium(I) (in an ammoniacal solution) reacted with these reagents (except IX—XIII) to form yellow and orange-yellow precipitates, respectively.

The limits of detection by means of this spot test are shown in Tables III and IV. These results show that palladium(II), copper(I), and copper(II) were detected more efficiently than the other metal ions. Compounds IX—XIII and XIV—XX were excellent reagents for silver ion in acetic acid and ethanolic solutions.

Molecular Extinction Coefficients of Palladium(II) and Copper(I) Complexes

The molecular extinction coefficients (Table V) of complexes of palladium(II) and copper(I) with these reagents were calculated from their absorbance in acetic acid solution. It was found that these reagents were no more sensitive than the reagents described previously.1)

Potentiometric Titration of Silver

The ester derivatives (XIV—XIX) were used as titrants for the potentiometric titration of silver ions in 50%(v/v) ethanolic solution.

Selection of Reagent——According to the recommended procedure, 1.0 ml of 0.001 M silver nitrate was titrated potentiometrically with the same concentration of XIV—XIX.

The results indicate that the potential break in the titration curves of silver with XVIII and XIX at the equivalence point was sharper than in the titration curves of silver with XIV, XV, and XVII. In addition, XIX reacts stoichiometrically with silver ions. Consequently, we selected XIX as a titrant for silver ions.

Solubility of the Reagent (XIX) and Effect of Solvents——XIX was readily soluble in N,N′-dimethylformamide, pyridine, and acetone, and soluble in methyl cellosolve, acetic acid, and ethanol.

TABLE III. Detection Limits of Metal Ions in Acetic Acid Solution (μg/ml)

Compound No.	Cu^+	Cu^{2+}	Pd^{2+}	Ag^+	Pt^{4+}	Au^{3+}	Hg_2^{2+}	Hg^{2+}	Bi^{3+}
I	5	10	5	200	30	80	100	100	50
II	5	10	1	200	10	80	100	200	30
III	5	10	1	200	10	80	100	100	50
IV	5	10	1	100	10	80	100	100	30
V	5	5	1	100	30	80	100	100	50
VI	5	5	1	100	50	80	200	200	30
VII	1	1	1	200	30	80	200	100	50
VIII	1	1	1	200	50	80	200	100	30
IX	5	5	5	5	10	30	80	30	—
X	5	1	1	5	10	30	80	30	—
XI	5	5	1	5	10	30	30	10	—
XII	10	5	1	5	10	10	30	10	—
XIII	30	—	5	10	10	10	30	10	—
XIV	5	10	5	5	5	30	50	10	—
XV	5	5	5	5	5	10	30	30	—
XVI	1	1	5	5	1	10	100	30	—
XVII	1	1	5	1	1	10	80	50	—
XVIII	1	1	5	1	1	10	80	30	—
XIX	1	1	5	1	1	10	80	50	—
XX	1	1	5	1	1	10	100	50	—

TABLE IV. Detection Limits of Metal Ions in Ethanolic Solution (μg/ml)

Compound No.	Cu^+	Cu^{2+}	Pd^{2+}	Ag^+	Pt^{4+}	Au^{3+}	Hg_2^{2+}	Hg^{2+}	Bi^{3+}	Pb^{2+}	$Tl^{+a)}$
I	5	1	1	100	50	10	100	30	100	10	30
II	5	0.5	1	100	50	10	200	100	100	10	50
III	5	0.5	1	80	50	10	200	80	100	10	30
IV	5	1	1	80	50	5	30	80	100	10	30
V	5	1	5	100	50	10	80	80	80	10	30
VI	5	0.5	1	100	30	5	100	100	200	10	50
VII	5	1	1	200	50	5	30	80	200	10	30
VIII	1	1	1	200	50	5	100	80	200	10	30
IX	0.5	0.5	1	5	10	10	30	30	30	100	—
X	0.5	0.5	0.5	5	30	10	30	30	30	300	—
XI	0.5	0.5	0.5	5	10	10	30	30	30	100	—
XII	0.5	0.5	1	5	10	5	30	30	30	50	—
XIII	1	1	1	5	30	10	30	30	50	300	—
XIV	1	1	1	10	30	5	50	50	30	1	50
XV	1	1	1	10	30	5	30	30	30	1	30
XVI	1	1	1	10	10	5	30	80	30	1	30
XVII	1	1	1	10	20	5	30	80	30	1	30
XVIII	1	1	1	5	50	10	10	80	30	1	30
XIX	1	1	1	5	30	5	30	30	10	1	30
XX	1	1	1	5	50	30	30	80	10	1	30

a) In ammoniacal solution.

Table V. UV Maxima and log ε Values of Complexes of Pd^{2+} and Cu^{+} with 2(1*H*)-Quinolinethione Derivatives

Compound No.	Pd^{2+} λ_{max}^{AcOH} (log ε)	Cu^{+} λ_{max}^{AcOH} (log ε)
I	422(4.48)	444(3.93)
II	418(4.51)	— —
III	421(4.56)	444(4.07)
IV	420(4.48)	— —
V	434(4.56)	458(3.97)
VI	432(4.57)	459(4.02)
VII	422(4.43)	438(3.82)
VIII	433(4.58)	458(4.01)
IX	457(4.29)	470(3.58)
X	433(4.38)	444(3.68)
XI	465(4.28)	477(3.57)
XII	458(4.37)	465(3.65)
XIII	458(4.09)	470(3.17)
XIV	464(4.25)	474(3.17)
XV	464(4.22)	471(3.28)
XVI	464(4.24)	470(3.39)
XVII	464(4.28)	474(3.47)
XVIII	465(4.25)	473(3.29)
XIX	464(4.29)	472(3.40)
XX	465(4.27)	476(3.41)

The effects of the solvents were observed by means of the recommended procedure. Acetone was not suitable as a solvent for the standard solution because of its volatility. When pyridine or N,N′-dimethylformamide was used as a solvent, the titration curves were not sharp. At the end point, the inflection potential in ethanolic solution was greater than that in acetic acid solution. Thus, ethanol was selected as a solvent for potentiometric titration of silver ions.

The Detection Limit of Silver Ion Concentration——According to the recommended procedure, 1.0 ml of 0.0001 M, 0.001 M, or 0.01 M silver nitrate was potentiometrically titrated with 0.0001 M, 0.001 M, or 0.01 M XIX, respectively. These results, shown in Fig. 2, indicate that the detectable limit of silver ion concentration was 0.0001 M (about 10 ppm).

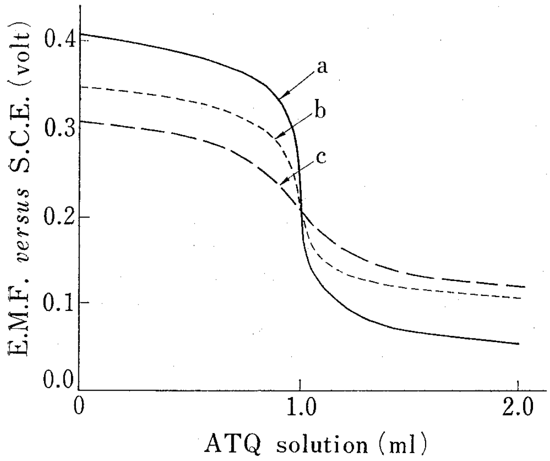

Fig. 2. Potentiometric Titration of Silver Ions with ATQ Solution at Various Concentrations

a: 0.01 M, b: 0.001 M, c: 0.0001 M.

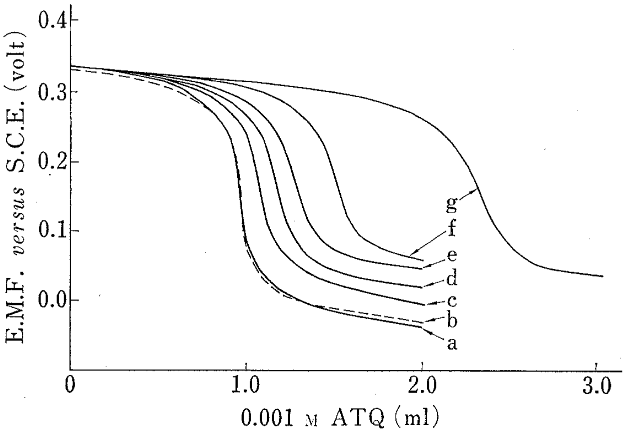

Fig. 3. Effect of Standing Time of 0.001 M ATQ on the Results of Potentiometric Titration of Silver Ions

a: 1 hr, b: 19 hr, c: 45 hr, d: 4 days, e: 7 days, f: 15 days, g: 73 days.

Stability of Reagent Solution——The stability of the reagent solution was examined in the following manner; 0.001 M XIX was allowed to stand in the dark at room temperature and after a certain period, 1.0 ml of 0.001 M silver nitrate was titrated with the reagent solution according to the recommended procedure (Fig. 3). It was found that the reagent solution (0.001 M) was stable for 19 hours.

Effect of pH——The effect of pH on the potentiometric titration was observed as follows: a mixture of 4 ml of a test solution (nitric acid, potassium nitrate, or potassium hydroxide were used), 5 ml of ethanol, and 1.0 ml of 0.001 M silver nitrate was titrated with 0.001 M XIX according to the recommended procedure. As shown in Fig. 4, the potential break at the equivalence point is dependent on the pH of the titrating solution. In a neutral solution, the inflection potential was about 200 mV and in an acid solution, about 150 mV (*vs.* S. C. E.).

Effect of Temperature——The potential of the silver-plate indicator electrode at the equivalence point was measured in a neutral solution. No difference in potential was observed in the range from 10 to 25°.

Table VI. Effects of Foreign Ions on the Determination of 1×10^{-6} mol (107.4 μg) of Silver Ions

Ions	Added ([Ion]/[Ag])	Ag found (μg)	Ions	Added ([Ion]/[Ag])	Ag found (μg)
Na(I)	100	110.0	Cd(II)	10	109.4
Al(III)	10	109.4	Ba(II)	10	109.4
Ca(II)	25	105.7	W(VI)	10	109.0
Cr(III)	20	101.1	Tl(I)	10	104.6
Mn(II)	10	108.6	Th(IV)	10	106.0
Fe(II)	20	112.4	Pb(II)	10	110.0
Co(II)	20	108.3	$EDTA^{2-}$	10	107.3
Ni(II)	20	103.3	BO_2^-	100	108.8
Cu(II)	1	106.3	$B_4O_7^{2-}$	100	110.0
	10	109.9	CNO^-	10	108.6
Zn(II)	20	102.8	ClO_3^-	100	111.7
As(III)	10	105.3	ClO_4^-	10	109.5
Sr(II)	10	106.5	Citrate	100	106.7

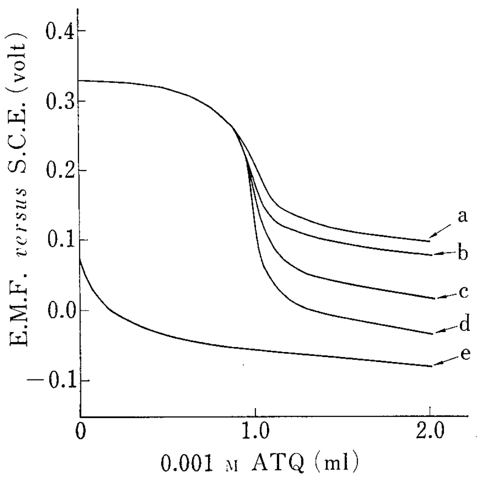

Fig. 4. Effect of pH on the Results of Potentiometric Titration of Silver Ions with 0.001 M ATQ

a: at pH 2.60, b: at 4.80, c: 6.63, d: at 7.31, e: alkaline solution.

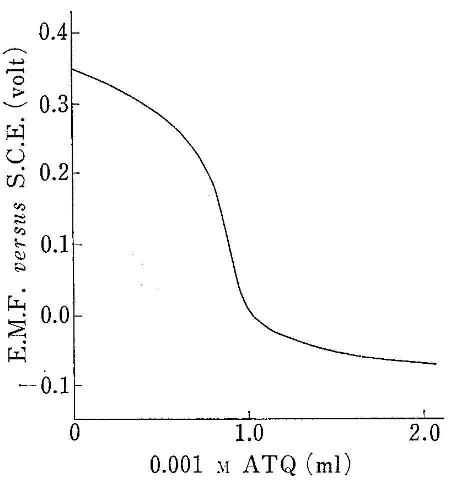

Fig. 5. Potentiometric Titration of Silver Protein with 0.001 M ATQ in Ethanolic Solution

Interference——The effect of foreign ions on the potentiometric determination of 107.4 μg (10^{-6} mol) of silver was examined. Anions such as nitrate and sulfate showed no interference. However, cyanide, thiosulfate, bisulfate, chloride, bromide, and iodide ions did interfere with the determination. Cations such as palladium, and mercurous and mercuric ions caused interference, but cupric ions did not interfere in 10-fold molar excess. Bismuth did not interfere in equimolar amounts. The results for the other ions examined are shown in Table VI.

Thus, XIX was found to be an excellent titrant for silver ions. Consequently, a potentiometric titration method was developed; the detection limit for silver was 0.0001 M (about 10 ppm). The coefficient of variation was 1.8 % (n=10) for 107.4 μg of silver.

TABLE VII. Determination of Silver in Silver Protein by Potentiometric Titration

No.	Sample[a] (g)	0.001 M XIX (ml)	Silver content (%)
1	1.368^4	0.930^1	7.94
2	1.368^6	0.924^8	7.90
3	1.369^7	0.938^0	8.00
4	1.371^3	0.979^8	8.21
5	1.370^3	0.958^8	8.18
Mean			8.05
s. d.			0.14
c. v.			1.8
J.P. IX method			7.92

a) Dissolved in 1000 ml of H_2O.

Potentiometric Titration of Silver Protein——The microdetermination of silver in silver protein was carried out potentiometrically with a 0.001 M ethanolic solution of XIX. The method is as follows; a 0.001 M aqueous solution of silver was prepared by dissolving an appropriate amount of silver protein. A mixture of 1.0 ml of the aqueous solution and 1 ml of ethanol was directly titrated with 0.001 M XIX according to the recommended procedure. A typical potentiometric curve is shown in Fig. 5. Silver protein was determined 5 times by the above method, and the results are shown in Table VII.

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