

Mercapto 화합물에 의한 은의 정량 (제 3 보).

2-Mercaptothiazoline 에 의한 은의 전류적정

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(1973. 10. 13 접수)

Determination of Silver with Mercaptans (III).

Amperometric Titration of Silver with

2-Mercaptothiazoline.

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(Received Oct. 13, 1973)

요 약. 은에 현하여 대단히 예민한 시약으로서 2-mercaptothiazoline를 알게 되었으며, 이 시약으로 은의 전류법 정량에 뛰어난게 이용할수 있다. 이 방법은 암모니아 수용액에서 2-mercaptothiazoline으로써 전류법적정에 의한 미량의 은을 정량하는데 EDTA를 막기제로 사용하여 많은 다른 이온들의 존재하에 대기중에서 미량의 은을 직접 적정할수가 있었으며 방해 이온들은 금과 백금 뿐이나, 미량의 은을 이 방법에 의하여 상대오차 $\pm 5\%$ 이내로 정량할 수 있다.

Abstract. 2-Mercaptothiazoline is very sensitive reagent for silver, which have been used for highly selective amperometric determination of silver. A method is described for the determination of micro-quantity of silver by amperometric titration with 2-mercaptothiazoline in ammonical solution.

Direct titration of milligram amount of silver (0.05~1.00mg) is possible in the presence of a number of foreign ions in ammonical solution containing ethylenediaminetetraacetic acid as masking agent under atmosphere. The interfering elements are gold and platinum. The milligram amounts of silver can be determined by the proposed method within an error $\pm 5\%$.

Introduction

Numerous amperometric titration procedures for the determination of silver with mercaptans and its derivatives have been reported.¹⁻⁵ Thus,

Kolthoff and Laitinen¹ titrate silver amperometrically with chloride, Saxena and Sharma³ recommended the use of alkali pyrovanadate in presence of 20% alcoholic solution that contains sodium nitrate as the base electrolyte, Dolezal, Hencel and Simon⁴ titrate silver amperometrically

with complexone, or with iodide in the presence of complexone as masking agent, Malinek and Rehak⁵ have reported that silver can be titrated with mercapto-phenylthio-thiazole and mercapto-benzo-thiazole in the presence of ethylenediamine tetraacetic acid (EDTA) as masking agent in a chloride-free medium which contains 0.01% gelatin and is adjusted with sodium hydroxide solution so that pH lies between 5 and 8 (bromocresol purple). Bera and Chakrabartty⁵ recommended the use of benzimidazole-2-yl methane thiol in acetate buffer medium (pH 4~5) under nitrogen atmosphere. However, none of the methods cited above is useful in the case of that the traces of silver are to be determined in the presence of excess of other ions and none of the methods is satisfactory without separation of the interfering substances under atmosphere. In the previous paper,^{6,7} the author et al, have reported that silver can be titrated with 2,5-dimercapto-1,3,4-thiadiazole and 2-mercapto-benzoxazole.

In an investigation of the properties of the 2-mercaptothiazoline (2-thiazoline-2-thiol), it is found that 2-mercaptothiazoline is precipitated quantitatively with silver in ammonical solution without deaeration. In the present paper, the reaction between Ag^+ and $\text{C}_3\text{H}_4\text{NS}_2^-$ ions has been investigated by means of amperometric titrations between silver nitrate and 2-mercaptothiazoline at the various concentrations of aqueous and of ammonical solution without deaeration. A sensitive and specific procedure for the quantitative determination of silver using 2-mercaptothiazoline in the presence of other cations and anions have been developed.

Experimental

Reagents. Analytical reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, HgCl_2 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$,

HAuCl_4 , PbO_2 , ZnCl_2 , NaBiO_3 , CaCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$, FeSO_4 , NH_4OH , $\text{Na}_2\text{-EDTA}$ and distilled water are used throughout.

Standard Solution. Standard silver solution (1mg Ag/ml) is prepared by dissolving 0.4249g of silver nitrate (Fisher Analytical Reagent A. C. S. Certified) in a 250ml volumetric flask containing 1ml of concentrated nitric acid and diluting to the mark with water; silver content is determined by the Mohr's method. Fresh silver (0.1mg Ag/ml) nitrate solution is prepared daily. Standard solution of 0.01M 2-mercaptothiazoline (Tokyo Kasei E. P. grade) is prepared by dissolving 0.1192g of 2-mercaptothiazoline in a 100 ml volumetric flask containing 15 ml of concentrated aqueous ammonia solution, diluting to the mark with water (1M ammonical solution). Standardized with silver standard solution.

Apparatus. A rotating platinum electrode served as the indicator electrode and a mercury-mercury(II) iodide half-cell⁸ is used as the reference electrode (potential-0.23 *v. s.* S. C. E.). Titrations are carried out using a galvanometer with the sensitivity of 0.05×10^{-6} ampere (G-M Laboratories Inc.). A synchronous motor is used in order to rotate the electrode (600 rpm) in the short time of titration.

Titration. Transfer a suitable volume of solution containing 0.05~1.00 mg of silver to the titration beaker, add 15ml of 2M ammonia solution and water to make the final volume 50 ml, titrate the solution with 0.001M 2-mercaptothiazoline ammonical solution, using rotating platinum electrode and mercury-mercury(II) iodide half-cell short-circuit through a microammeter. The intersection of the two straight line branches of the L-shaped titration curve is taken as the end point.

All titration are carried out under the atmospheric air at room temperature.

Sample Analysis

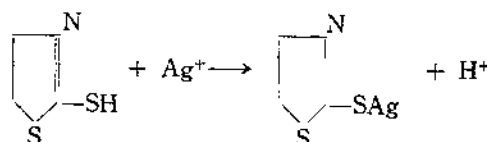
Procedure. Weigh out about 0.5g of silver alloy (silver ware) and dissolve it in a mixture of 10 ml of water and 10 ml of nitric acid, boil the solution to expel nitrogen oxide, cool to the room temperature and dilute accurately to 250 ml. Transfer to the beaker a suitable aliquot containing 0.1~1.0 mg of silver, neutralize it with ammonia solution and add 25 ml of 2 M ammonia solution in excess and add 10 ml of 10 % EDTA and water to make the final volume 50 ml. Titrate the silver as mentioned above. The results are shown in Table 3.

Results and Discussion

The results are shown in Table 1, 2, Fig. 1. The reaction between 2-mercaptothiazoline and silver may be due to the formation of a chelate. The addition of an ammonical solution of 2-mercaptothiazoline to a solution containing silver ions resulted in a precipitate. One mole of 2-mercaptothiazoline is consumed by one mole of silver nitrate in the titration.

The precipitate does not show the absorption band of C=S and S-H stretching vibration at 1563 cm^{-1} and $2550\sim 2600\text{ cm}^{-1}$, it is considered that the precipitate may have formula $\text{C}_3\text{H}_4\text{N}_2\text{S}_2\text{Ag}$.

The reaction is



The silver compound is insoluble in most organic solvents and decomposed in concentrated nitric acid. From the results shown in Table 1, it can be concluded that reproducible results are obtained in the determination 0.05~1.00 mg of silver when 1 M ammonical solution is used. The silver concentration over the range 10^{-5} to 10^{-7} M can be easily followed. Below about 10^{-8} M of silver concentration the current does not decrease as quickly as it should do.

From the results shown in Table 2, direct titration is possible in the presence of moderate amounts of Cu, Hg, Cd, Pb, Zn, Bi, Ca, Mg, Ni, Mn, and Fe.

Table 1. Effects of pH

	Ag added, mg	pH	Ag found, mg	dev.	relative error %
A*	0.050	2-7	0.049	-0.001	2.0
	0.100	2-7	0.099	-0.001	1.0
	0.500	2-7	0.498	-0.002	0.4
	1.000	2-7	1.002	+0.002	0.2
B*	0.100	9-12	0.097	-0.003	3.0
	0.500	9-12	0.500	0.000	0.0
	1.000	9-12	1.000	0.000	0.0
C*	0.300	10	0.300	0.000	0.0
	0.500	10	0.495	-0.005	1.0
	1.000	10	1.009	+0.009	0.9

*pH is adjusted with nitric acid in A, with ammonia in B, and with ammonia-ammonium chloride buffer in C, respectively.

Table 2. Determination of silver in presence of foreign ions.

Ag added, mg	Foreign ions present, mg	EDTA added, g	Ag found, mg	dev.
0.300			0.300	0.000
0.300		0.5	0.299	-0.001
0.500		0.5	0.500	0.000
1.000		1.0	1.000	0.000
0.100	5 Cd	1.0	0.105	+0.005
0.100	5 Cu	1.0	0.0989	-0.0011
0.100	5 Zn	1.0	0.103	+0.003
0.100	5 Pb	1.0	0.102	+0.002
0.100	5 Hg	1.0	0.0993	-0.0007
0.500	5 Bi	1.0	0.496	-0.004
0.500	5 Ca	1.0	0.500	0.000
0.500	5 Mg	1.0	0.499	-0.001
0.500	5 Mn	1.0	0.495	-0.005
0.500	5 Ni	1.0	0.507	+0.007
0.500	5 Fe	1.0	0.498	-0.002
1.000	10 Cu, 10 Zn, 10 Pb, 10 Cd	1.0	0.996	-0.004
1.000	10 Hg, 10 Ca, 10 Bi, 10 Fe	1.0	1.018	+0.018
1.000	10 Ni, 10 Mn, 10 Zn, 10 Cu	1.0	1.013	+0.013

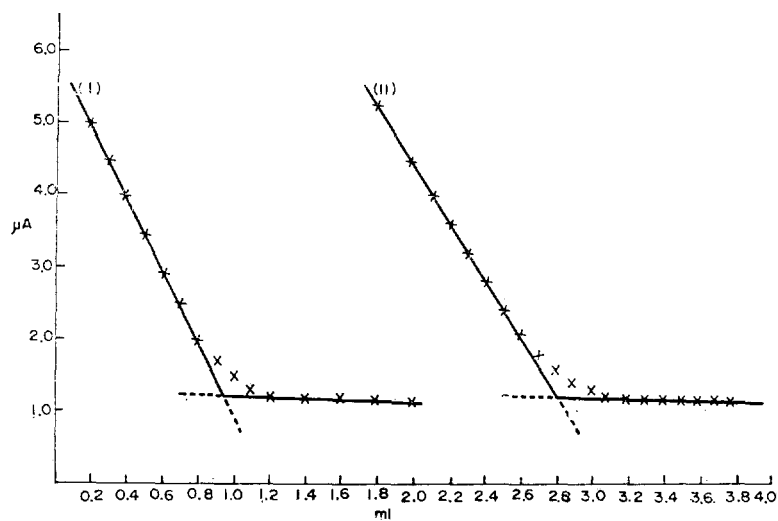


Fig. 1. The amperometric titration of silver. 0.1 mg Ag titrated with $10^{-3}M$ $C_2H_5NS_2$ (I): 0.3mg Ag titrated with $10^{-3}M$ $C_2H_5NS_2$ (II).

Table 3. Determination of silver in several silver alloys.

Sample	Present method Ag%	Mohr's method Ag%
Chopstick	67.5	67.5
Tea Spoon	71.4	71.4
Spoon	69.8	69.8

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