

2, 5-Dimercapto-1, 3, 4-thiadiazole 에 의한 구리의 전위차 적정 정량

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Potentiometric Determination of Copper with 2, 5-Dimercapto-1, 3, 4-thiadiazole

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요 약. 은 전극을 지시전극으로 하고 표준칼로멜 전극을 기준전극으로 하여 전압플로워회로를 이용하여 수용액에서 2, 5-dimercapto-1, 3, 4-thiadiazole 에 의한 구리의 전위차 적정법을 연구하였다. 이 시약은 구리의 전위차 적정 정량에 뛰어나게 이용할 수 있었고 여러가지 가리움제를 사용하여 다른 이온들의 존재하에 대기중에서 미량의 구리를 직접 적정 정량할 수 있었다.

ABSTRACT. A potentiometric titration method has been developed for the titration of copper with 2, 5-dimercapto-1, 3, 4-thiadiazole in aqueous solution using a silver electrode as an indicator electrode *vs.* the standard calomel electrode as a reference electrode. The 2, 5-dimercapto-1, 3, 4-thiadiazole is very sensitive reagent for copper, which has been found to be highly selective for potentiometric determination of copper.

Direct titration of trace amount of copper (0.02~0.1 mg) is possible in the presence of a number of foreign ions in aqueous solution containing potassium hydrogen phthalate and sodium fluoride as masking agent under atmosphere.

INTRODUCTION

Numerous potentiometric titration procedures have been reported the determination of copper with mercaptans and its derivatives have been reported.²⁻⁶ Thus, Meloche and Kalbus² were titrated copper and silver potentiometrically with dithiooxamide, Miller and Hume³ have demonstrated that copper, gold(II), mercury(II), and

ferricyanide ions can be titrated with thioglycolate, Majumdar and Chakrabartty⁴ have examined the amperometric titration of palladium with 2, 5-dimercapto-1, 3, 4-thiadiazole. Stricks and Chakravarti⁵ show that the rotating dropping mercury electrode can be used as an indicator electrode for amperometric titration of copper with diethyldithiocarbamate, Liberti and Cervoni⁶ have reporting that copper can be titrated with

mercaptobenzothiazole. They used a rotating platinum electrode in the titration of 0.7~5mg copper in 25~50 ml of an acetate medium of pH 3.7~5.9.

Amperometric determination of silver with 2,5-dimercapto-1,3,4-thiadiazole have already been described; (I) in which an electrode system with rotating platinum electrode as an indicator electrode was shown to produce a high degree of precision and accuracy. This paper deals with the study of the potentiometry of copper with 2,5-dimercapto-1,3,4-thiadiazole. In an investigation of the properties of the 2,5-dimercapto-1,3,4-thiadiazole, it is found that this reagent quantitatively react with copper in aqueous solution without deaeration. During these investigations, an electrode system with silver metal as the indicating electrode was found to produce a high degree of precision and accuracy.

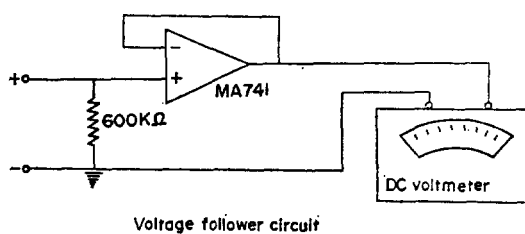
EXPERIMENTAL

Reagents. Analytical reagent grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaF, $\text{C}_3\text{H}_5\text{O}_4\text{K}$ and redistilled water were used throughout.

Standard Solution. Standard copper solution (0.1 mg/ml) was prepared by dissolving 0.2000 g of electrolytic copper foil in the least possible amount of concentrated nitric acid and dilute to 2 l with water. Fresh standard copper solution (0.02~0.1mg) was prepared daily. Standard solution of 0.001M 2,5-dimercapto-1,3,4-thiadiazole (E. Merk G. R. grade) was prepared by dissolving 0.1502 g of 2,5-dimercapto-1,3,4-thiadiazole in 15 ml of concentrated aqueous ammonia solution, diluting to 1 l with water. The reagent appears to be stable for one month at least: however, the strength was confirmed against the silver nitrate solution by amperometrically¹ before use.

Apparatus. A silver electrode served as the

indicator electrode and a standard calomel electrode was used as the reference electrode. Titrations were carried out using a DC voltmeter (0~0.3 V Yokogawa electric works LTD) with voltage follower circuit⁷ and magnetic stirrer with bar. Voltage follower circuit is as follows.



Titration. Transfer a suitable volume of solution containing 0.02~0.1mg of copper to the titration beaker(100 ml), add one gram of potassium hydrogen phthalate and 0.5 g of sodium fluoride. The contents of the beaker were diluted to 50 ml with water. A silver electrode and standard calomel electrode were immersed in the solution, and the potential developed by the electrode was measured with D.C. voltmeter (using voltage follower circuit). The contents of the beaker were stirred continuously with a magnetic stirrer and bar. 0.0001 M 2,5-dimercapto-1,3,4-thiadiazole solution was added slowly with micro buret. In the vicinity of the end point the 2,5-dimercapto-1,3,4-thiadiazole solution was added in 0.01 ml increments. The end point was taken as the number of milliliters where the greatest rate of change of electromotive force occurred. The potential jump was so sharp that the equivalence point could be estimated to the nearest 0.01 ml. After every titration the silver electrode was cleaned thoroughly by immersing it in 6 N nitric acid solution and rinsing with water. All titrations were carried out under the atmospheric air at room temperature.

RESULTS and DISCUSSION

The standard solution of copper ranging from 0.02 to 0.1mg were prepared by proper dilution of the standard copper solution and also standard solution of 0.0001 M 2,5-dimercapto-1,3,4-thiadiazole was prepared by dilution of the stock solution. Three titrations were carried out at each of four copper samples from 0.02 to 0.1 mg. The results are given in Table 1. Several

Table 1. Precision of determination for 0.02 ~0.1 mg of copper.

Cu added $\times 10^{-2}$ mg	Cu found $\times 10^{-2}$ mg	Dev.	Relative error %
2.00	1.96	-0.04	2.0
5.00	5.06	+0.06	1.0
7.00	6.98	-0.02	0.3
10.0	10.0	0.00	0.0

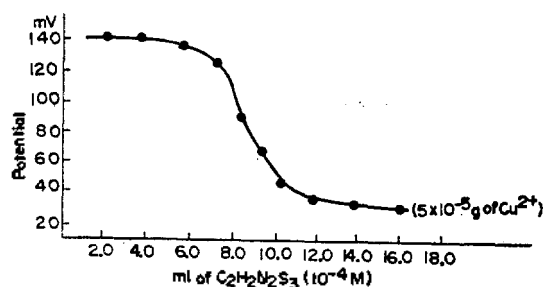


Fig. 1. Potentiometric titration curve.

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

Cu added $\times 10^{-2}$ mg	Foreign ions present $\times 10^{-2}$ mg	Cu found $\times 10^{-2}$ mg	Dev.	Relat. error %
2.00	50 Fe	2.02	+0.02	1.0
5.00	50 Fe	5.05	+0.05	1.0
5.00	100 Fe	5.06	+0.06	1.0
2.00	50 Co	2.01	+0.01	0.5
5.00	30 Co	5.04	+0.04	0.8
5.00	100 Co	5.05	+0.05	0.1
2.00	50 Ni	1.98	-0.02	1.0
5.00	50 Ni	4.69	-0.01	0.2
5.00	100 Ni	5.02	+0.02	0.4

representative curves, obtained at various copper concentrations by plotting the amount of 2,5-dimercapto-1,3,4-thiadiazole used vs. the potential reading in millivolts, are shown in Fig. 1. The change in electromotive force during a titration under these condition is about 150 mV.

From the results shown in the Table 1, it can be concluded that reproducible results were obtained in the determination of 0.02~0.1mg of copper. One mole of 2,5-dimercapto-1,3,4-thiadiazole was consumed by one mole of copper in the titration. Below about 0.01 mg of copper concentration the potential does not drop as quickly as it should do, and behaves erratically.

The effect of the presence of different concentration of Fe, Ni, and Co on the potentiometric determination of 0.02~0.1mg of copper with 2,5-dimercapto-1,3,4-thiadiazole was studied. The results are given in Table 2. From these results it can be concluded that it is possible to determine copper in the presence of large amounts of Fe, Ni, and Co. without any interference. Ag, Hg, Zn, and Au ions precipitate under these conditions.

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