

Podand로 변성된 Carbon Paste전극을 이용한 Ag(I)이온의 벗김 전압 - 전류법 정량

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Stripping Voltammetric Determination of Ag(I) with Carbon Paste Electrode Modified with Podand Compounds

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The enhancement of selectivity and sensitivity is a prime target to attain in analytical chemistry. One of the method to achieve the noble aim is to use CME(chemically modified electrode)¹, in which role of the modifier is very important because choice of relevant modifier can greatly enhance the selectivity and sensitivity in analysis due to selective preconcentration of the proposed chemical species at the electrode surface prior to voltammetric determination. Therefore analytical application of various kinds of modifier, such as chelate ligand,^{2,3} ion exchange,^{4,5} etc., has been explored.

Silver ion(I) is capable of forming complexes with ligands having oxygen, nitrogen, and sulfur as ligating atoms. Thus analyses of Ag(I) with CMEs, in which macrocyclic ligands having sulfur⁶ and other ligands having nitrogen and oxygen⁷ together as modifier were used, have been reported. But exploitation of podand as a modifier for carbon paste electrode to analyze Ag(I) has not been reported.

In this paper, we describe the effects of pH, anions, interfering metal ions in Ag(I) analysis using chemically modified electrode with acyclic ligand, podand compounds, having sulfur and oxygen as ligating atoms.

EXPERIMENTAL

Reagent. Podand compounds, 1,11-bis (thiophenoxy)-3,6,9-trioxaundecane ($\text{Ph}_2\text{O}_3\text{S}_2$) and 1,9-bis (thiophenoxy)-3,6-trioxaundecane ($\text{Ph}_2\text{O}_2\text{S}_2$) were synthesized according to procedures described in the literature⁸. All solutions were prepared from analytical-grade chemicals and doubly distilled water. Silver nitrate was purchased from Fluka Co.

Apparatus. Bioanalytical Systems Model CV-27 voltammograph, Uchida Model YR-41T X-Y recorder, and DMS Co. magnetic stirrer Model DS-201 M were used.

Chemically modified carbon paste electrodes were prepared by grinding 0.1 g podand compound with a mortar and pestle, then adding 0.2 g graphite powder; after additional grinding of the mixture, 0.14 ml paraffin oil was added and the whole was thoroughly mixed. The paste was packed into one end of 8 cm polyethylene tube with inner diameter of 0.5 cm, and a 10 cm copper bar with diameter of 0.5 cm was used for electrical connection. A Pt wire and Ag-AgCl(BAS Model MF 2020) were used as auxiliary and reference electrode, respectively. In order to prevent the formation of complexes and precipitation between Ag

(I) and chloride ion, a two compartments cell, that is, the auxiliary and working electrodes are contained in a compartment and the reference electrode in other compartment, was used with a salt bridge by filling a U-tube with 4 ml of 0.1 M NaClO₄ solution containing 0.4 g of agar.

Procedure. A fresh working electrode surface was used for each preconcentration/voltammetric cycle, and smoothed with the surfaces of watch glass. For the preconcentration step, the working electrode was immersed in 50 ml of 0.1 M NaClO₄ electrolyte solution containing Ag(I) for a given time, which was stirred by a magnetic bar at 500 rpm, during which it was held at +0.5 V vs. Ag/AgCl. After the preconcentration, the working electrode was rinsed with distilled water, and the accumulated Ag(I) ion at the electrode surface was reduced at -0.3 V for 2 min in pH 6 acetate buffer solution with ionic strength of 0.1 without stirring. Then the electrode was subject to potential scanning between -0.3 V and +0.7 V at a scan rate of 100 mV s⁻¹. The supporting electrolyte solution for reference electrode was always pH 6 acetate buffer with an ionic strength of 0.1.

RESULTS AND DISCUSSION

Reduction potential of Ag(I) deposited at the unmodified electrode was +0.05 V, while that at the modified electrode with podand compounds was -0.25 V. This indicates that the Ag(I) is deposited at the surface by formation of a complex with the podand compounds.

In the preconcentration step, Ag(I) was deposited in a 0.1 M NaClO₄ solution with ionic strength of 0.1, during which it was held at a given potential between +0.2 V and +0.8 V. A typical oxidation peak of cyclic voltammogram, obtained under the condition of an applied potential of +0.5 V for the deposition, is shown in Fig. 1(A), while Fig. 1(B) is a cyclic voltammogram obtained under the same experimental conditions with unmodified carbon paste electrode. If Ag(I) was deposited at open-circuit, and then cyclic voltammogram for silver measurement was obtained, a distorted or splitted oxidation peak is obtained in-

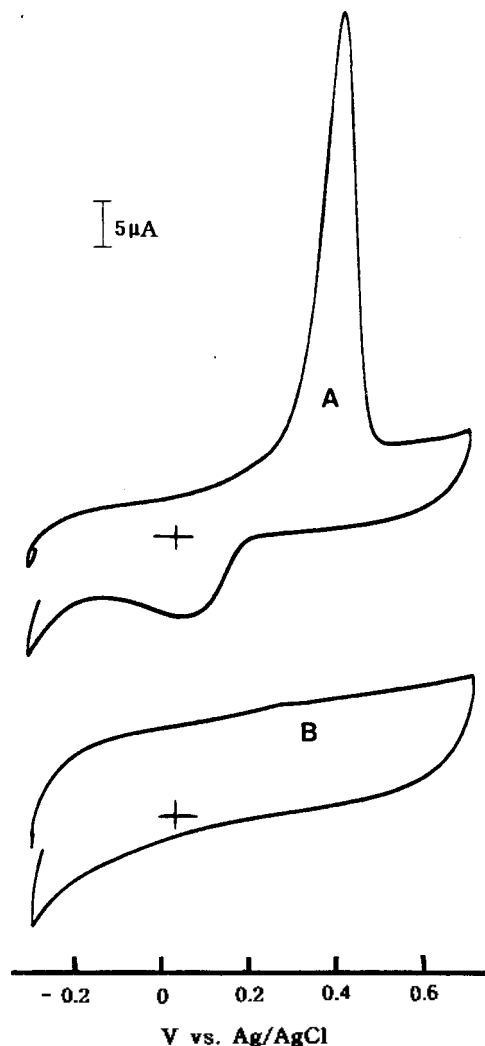


Fig. 1. Cyclic voltammograms for 1.5×10^{-5} M Ag(I) obtained with carbon paste electrode; A-modified electrode with Pb₂O₂S₂, B-unmodified electrode. Deposition time; 2 min at +0.5 V in 0.1 M NaClO₄ solution with stirring. Reduction time; 2 min at -0.3 V in pH 6 acetate buffer solution. Scan rate; 100 mV s⁻¹.

stead of the well-defined one as shown in Fig. 1(A), suggesting that, under the close-circuit, uniform deposition of Ag(I) at the electrode surface is possible.

Anion effects on the preconcentration/voltammetric response were investigated. The nitrate, phosphate, perchlorate, oxalate, hexafluorophosphate, and acetate were examined under the same ionic

Table 1. Anion effects on magnitudes of peak current

anions	hexafluoro-phosphate	perchlorate	nitrate	acetate	phosphate	oxalate
relative peak current*	117	100	7	5	8	5

*Relative to peak current (taken as 100) of silver deposited in 0.1 M NaClO₄ solution.

strength of 0.1 and the results are given in Table 1. As shown in Table 1, perchlorate and hexafluorophosphate, which not only have smaller hydration enthalpy than other anions but also are more hydrophobic, showed larger anodic stripping peak current by factors of about 15-20 times than other anions. From this results, it is supposed that Ag(I) are accumulated at the electrode surface via formation of ion-pair between Ag(I)-podand complex and the relatively hydrophobic anions. Also, it was observed that the preconcentration/voltammetric response is not dependent on the kind of cationic species, K⁺ and Na⁺, which is one component of supporting electrolyte used, indicating that the cations do not affect the complexation between Ag(I) and podand.

Voltammetric responses were observed to be dependent on the supporting electrolyte used for reduction of Ag(I). The pH 6 phosphate and acetate buffer solution, and 0.1 M NaClO₄ and KPF₆ solution with a constant ionic strength of 0.1 were examined for reduction of Ag(I) deposited at the electrode at a constant potential of +0.5 V. Among them, the NaClO₄ and KPF₆ solutions showed not only decrease of the peak current, indicating a decrease in the Ag(I) concentration at the electrode, but also larger residual current followed the appearance of stripping peak. These were proportional to the time of the electrode in the NaClO₄ and KPF₆ solutions prior to reduction of Ag(I) as well as the concentration of NaClO₄ and KPF₆ electrolyte in the solutions. Generally the stability constants of complexes, formed between Ag(I) and macrocyclic or acyclic ligand having sulfur and/or oxygen as ligating atoms, are not large even in organic solvent with low polarity⁹. Then the stability constants of Ag(I)-podand complexes in water will be much smaller. Therefore the release of de-

posited Ag(I) via the decomplexation become easy, especially in the presence of higher concentration of ClO₄⁻ and PF₆⁻, leading ion-pair formation with Ag(I) in the bulk solution.

Table 2 shows pH effects on the preconcentration/voltammetric response. The pH and ionic strength of the solution used for deposition of Ag(I) were adjusted by conc. HClO₄ and NaClO₄ together except pH 1 solution, for which conc. HClO₄ was used only. The magnitude of the peak current obtained in a pH 1 solution(0.1 M HClO₄) decreases by about 26% compared with that obtained in pH 6 as shown in Table 2, suggesting that the ligating atoms, sulfur and oxygen, of the ligand have better affinity for proton than Na⁺.

Ligand effects on the preconcentration/voltammetric response were investigated. The electrode modified with Ph₂O₂S₂ yielded a response similar to one modified with Ph₂O₃S₂. This may be attributed to similar stability constants of Ag(I)-podand complexes. Because the thermodynamic stability constants of Ag(I)-podand complexes in water are not available, a direct comparison would be impossible. But the fact that the stability constants of Ag(I)-Ph₂O₂S₂ and Ag(I)-Ph₂O₃S₂ are log 5.92 and log 5.50 in methanol⁸, respectively, could provides a good basis for interpretation of the experimental results.

Possible interferences from coexisting metal ions were evaluated and the results are shown in Table 3. The presence of 50 times as much Zn(II), Pb(II), Cu(II), Ni(II) and Cd(II) as silver did not show in-

Table 2. pH effects on magnitudes of peak current

pH	6	5	4	3	2	1
relative peak current*	100	100	98	82	79	74

*Relative to peak current (taken as 100) of silver deposited in 0.1 M NaClO₄ solution of pH 6.

Table 3. Interference effects of other metal ions

metal ions	Zn ²⁺		Ni ²⁺		Pb ²⁺		Cd ²⁺		Cu ²⁺		Hg ²⁺		Hg ⁺	
[metal ion]/[Ag ⁺]*	1	50	1	50	1	50	1	50	1	50	1	5	1	5
relative peak current**	100	99	100	101	101	99	99	101	100	99	99	10	98	15

*[Ag⁺]: 1.5×10^{-5} M, **Relative to peak current (taken as 100) of silver in the absence of other metal ions.

terference. But, in the stripping voltammetry with electrolysis at -0.3 V at an unmodified carbon paste electrode, copper(II) interfered because the stripping peak potentials for silver ($+0.40$ V) and copper ($+0.22$ V) partially overlap in determination of high level silver. Hg(I) and Hg(II) showed serious interference, that is, partial overlapping of the stripping peak potential of mercury ($+0.6$ V) with that of silver ($+0.4$ V), and a large decrease of stripping current by the addition of 5 times as much Hg(I) and Hg(II) as silver, which may be attributed to that Hg(I) and Hg(II) compete with silver(I) for complex formation.

As the results of other studies^{6,10} for the determination of silver with modified electrode, the increases of deposition time and amount of the ligands, here podands, in making the electrode enhance the peak current in a limited range.

Under the experimental conditions of that the Ag(I) was deposited in 0.1 M NaClO₄ for 2 min at $+0.5$ V, and reduced at in pH 6 acetate buffer solution with an ionic strength of 0.1 for 2 min at -0.3 V, the determinations of silver were carried out three times for each sample. The calibration curve was linear from 4.0×10^{-6} M to 9.0×10^{-5} M with a correlation coefficient of 0.983 . A de-

tection limit near 8.5×10^{-7} M is estimated, based on the signal corresponding to three times the blank signal. Further lowering of the detection limit may be achieved by using longer preconcentration times and increase of the amount of podand ligands in making the electrode.

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