Determination of Ag(I) Ion at a Modified Carbon Paste Electrode Containing N,N'-Diphenyl Oxamide

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New approach for the determination of Ag(I) ion was performed by using a carbon paste electrode (CPE) containing N,N'-Diphenyl oxamide (DPO) with anodic stripping voltammetry. The CMEs have been prepared by making carbon paste mixtures containing an appropriate amount of DPO salt coated onto graphite particles to analyze trace metal ions via complexation followed by stripping voltammetry. Various experimental parameters affecting the response, such as pH, deposition time, temperature, and electrode composition, were carefully optimized. Using differential pulse anodic stripping voltammetry, the logarithmic linear response range for the Ag(I) ion was $1.0 \times 10^{-7} - 5.0 \times 10^{-9}$ M at the deposition time of 10 min, with the detection limit was 7.0×10^{-10} M. The detection limit adopted from anodic stripping differential pulse voltammetry was 7.0×10^{-10} M for silver and the relative standard deviation was ± 3.2% at a 5.0×10^{-8} M of Ag(I) ion (n = 7). The proposed electrode shows a very good selectivity for Ag(I) in a standard solution containing several metals at optimized conditions.

Key Words : Ag(I) ion, Differential pulse anodic stripping voltammetry, N,N'-Diphenyl oxamide, CME

Introduction

Several review articles have introduced the techniques adopting CMEs,[1-8] which are based on the formation of mono- or multi-layers of molecules on the electrode surface and of modified layers attached through the covalent bonding between a molecule and electrode. CME with stripping voltammetry is most sensitive and selective method to analyze metal ions.[9]

The increasing use of silver compounds and silver-containing preparations in industry and medicine, has resulted in an increased silver content of environmental samples.[10,11] Low level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect water used for drinking.[12] On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, vitamin E and vitamin B_{12}, have focused attention on its potential toxicity.[12,13]

A carbon paste electrode with various modifiers containing amino groups,[14] chelating resin,[15] Spanish moss,[16] derivatives of 18-crown-6 and 14-crown-5 ether,[17] and tetrathiacyclotetradecene[18] have been utilized for the determination of trace amounts of Ag(I) ion in variety of complicated samples. We have studied previously the determination of Ag(I) ion with a CPE containing 2-imino-1-cyclopentene-1-dithio-carboxylic acid[19] and cinchonidine.[20] The electrochemical simultaneous determination of Ag(I) and Hg(II) ions using chemically modified electrode containing glyoxal bis(2-hydroxyanyl)[21] also reported in our lab. The preconcentration and determination of silver ions with conductive polymers having amine groups were also reported.[22,23]

The present study tested a new approach for the determination of Ag(I) ion with a CPE containing N,N'-Diphenyl oxamide (DPO), which has high formation constants with metal ions.[24,25] DPO was synthesized and used for the determination of Ag(I) ion. The CMEs have been prepared by making carbon paste mixtures containing an appropriate amount of DPO salt coated onto graphite particles to analyze trace metal ions via complexation followed by stripping voltammetry. The technique involves a process of complex formation of the metal ion with DPO on the modified electrode surface. Various experimental parameters affecting the response were carefully optimized, and the CME performance was examined.

Experimental Section

Reagents and Synthesis. N,N'-Diphenyl oxamide (DPO) salt was prepared by the following procedure: 0.02 M of aniline solution was added dropwise to 50 mL of in a benzene solution containing 0.01 M oxalyl chloride with stirring. The stirring was continued for 3 h. The white precipitate was collected by filtration and washed with cold benzene followed by drying in a vacuum at room temperature for 1 day. The obtained DPO was recrystallized twice in chloroform.

Elemental analysis, GC/MS spectrometry and IR spectroscopy carried out for the characterization of a synthesized DPO salt. The result of elemental analysis − Anal. Calcd. For DPO salt: C; 60.95%, H; 4.75%, N; 10.14%. Found: C; 61.84%, H; 5.72%, N; 10.98%. IR characteristic frequencies: 3060 cm^{-1} (s, N-H), 1668 cm^{-1} (C=O), 1597 cm^{-1} (aromatic C-C), 1400, 1285 cm^{-1} (C-N), 750 cm^{-1} (aromatic C-H). GC/MS: m/z 277 ([M+H]$^{+}$, calculated 277). Metal ion solutions were prepared from either analytical grade nitrate or chloride salts from Aldrich Co. All the experiments were

performed in a 0.1 M citrate buffer solution. Reagent grade of graphite powder (Fluka Co.) rinsed with 96% ethanol four times and dried. All the other chemicals used in this experiment were reagent grade or better. Aqueous solution were prepared with doubly deionized water (18 MΩ·cm).

Standard reference material for trace elements on water, SRM 1634d, purchased from NIST (USA) and was shaken before use.

Fabrication of Modified Electrodes. Unmodified carbon paste was prepared by hand mixing of 5 g of reagent-grade graphite powder and 3 mL of Nujol oil (Sigma Co.) with a mortar and pestle. A modified paste was prepared in a similar fashion, except that the graphite powder was coated with a desired weight of DPO salt. Both unmodified and modified pastes were packed into 10 mL polyethylene syringes (5 mm diameter), the tip of which had been cut off. Electrical contact to the paste was established via inserting a thin copper wire thorough flank.

The surfaces of fresh CMEs were preconditioned by exposure to a 1.0×10^{-3} M Ag(I) ion solution for 3 min. Then, the electrode was rinsed with deionized water and placed in 0.1 M KNO$_3$ solution for 5 min with stirring. This conditioning cycle was repeated three times for each new CME surfaces. A fresh electrode surface was obtained by squeezing more out. The surplus of paste was cut out with a glass rod and the exposed-end polished on a paper until the surface showed shiny appearance.

Apparatus. Two 25-mL Pyrex cells housing with three-electrodes were used for the voltammetric measurements. One contained the electrolytic blank solution and the other contained the sample solution. The reference electrode was a SCE and an auxiliary electrode was a platinum wire. A vessel for a preconcentration was placed on a magnetic stirrer (600 rpm) with 1 cm stirring bar and thermostated at 25 ± 0.1 °C. The voltammetric measurements were carried out using a CV-104, Kosentech (S. Korea) and M273 potentiostat/galvanostat (Prinston Applied Research, USA). The potential scan rate was 100 mV/s for cyclic voltammetry. A continuous stream of nitrogen gas was passed through the solution during measurements were done. IR spectra were obtained with a Polaris FT-IR spectrometer (Mattson Co.). GC/MS data obtained with Kratos profile HV-3 GC/Mass spectrometer. Vario EL elemental analyzer performed an elemental analysis.

Analytical Procedure. Chemical accumulation of Ag(I) ion was carried out in a buffered preconcentration solution containing Ag(I) ion. A CME deposited with Ag(I) ion *via* complex formation was transferred from the preconcentration solution to a separate measuring cell, and washed with distilled water thoroughly. A stripping voltammograms were obtained after the CME was transferred into a cell containing only 0.1 M KNO$_3$ solution from −0.6 V to +0.6 V *vs.* SCE. Differential voltammograms were recorded from −0.2 V to +0.5 V *vs.* SCE. Measurement conditions for DPV were pH: 6.0, scan rate: 5 mV/s, pulse height: 0.025 V, pulse width: 0.05 s, condition voltage: −0.5 V, condition time: 1 min, and condition temp.: 25 °C.
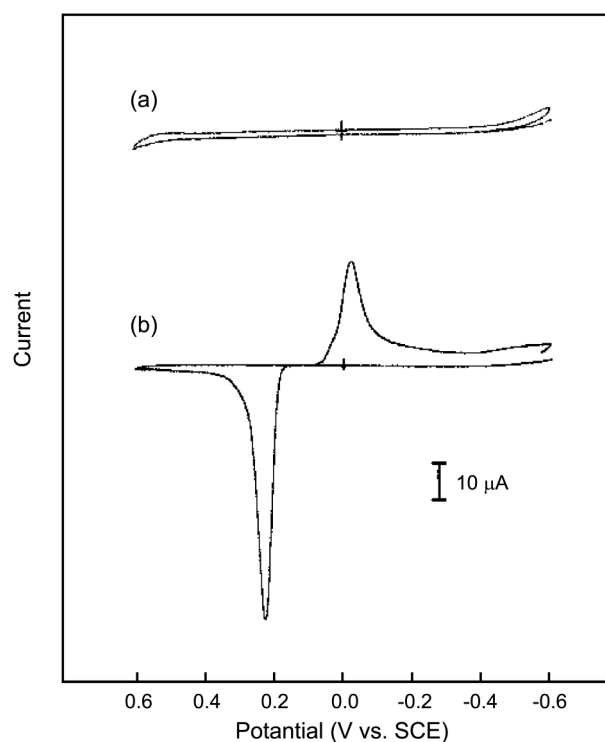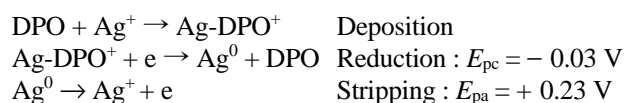

Figure 1. Cyclic voltammograms for the DPO-modified carbon paste electrode obtained (a) only in 0.1 M KNO$_3$ blank solution, (b) after dipping CPE in 1.0×10^{-5} M Ag (I) solution for 10 min (deposition temp.: 25 °C, scan rate: 100 mV/s).

Results and Discussion

Electrochemical Behavior of CPEs and the Deposition of Ag(I) Ion. Figure 1 shows CVs recorded for DPO salt modified CPEs (DPO-CPE) (a) in a 0.1 M KNO$_3$ blank solution and (b) after dipping a modified electrode into a pH 6 buffer solution having 1.0×10^{-5} M Ag(I) ion solution for 10 min and rinsed thoroughly with deionized water then transferred to a 0.1 M KNO$_3$ solution. There was no redox peak in the CV(a) over the potential of +0.6 V to −0.6 V *vs.* SCE. However, CV recorded for DPO-CPE in a blank solution after deposit of 1×10^{-5} M Ag(I) ion exhibits well-defined redox peak (Figure 1(b)). A CV recorded with the modified electrode deposited with Ag(I) ion shows anodic peak at +0.23 V and cathodic peak at −0.03 V *vs.* SCE. The height of this peak increases as the concentration of Ag(I) ion and the time of complexation increases.

The following equation summarizes the electrode surface reaction of the deposition and stripping steps with DPO modified electrode.

$$DPO + Ag^+ \rightarrow Ag\text{-}DPO^+ \qquad \text{Deposition}$$
$$Ag\text{-}DPO^+ + e \rightarrow Ag^0 + DPO \quad \text{Reduction}: E_{pc} = -0.03 \text{ V}$$
$$Ag^0 \rightarrow Ag^+ + e \qquad \text{Stripping}: E_{pa} = +0.23 \text{ V}$$

The CPE was regenerated for its next use by potential cycling in the blank solution until no peaks appeared after spiking a CPE into a 0.1 M nitric acid for few seconds. Several cycles of deposition and an oxidative removal of the test metal ions on the electrode show that fresh CPE's
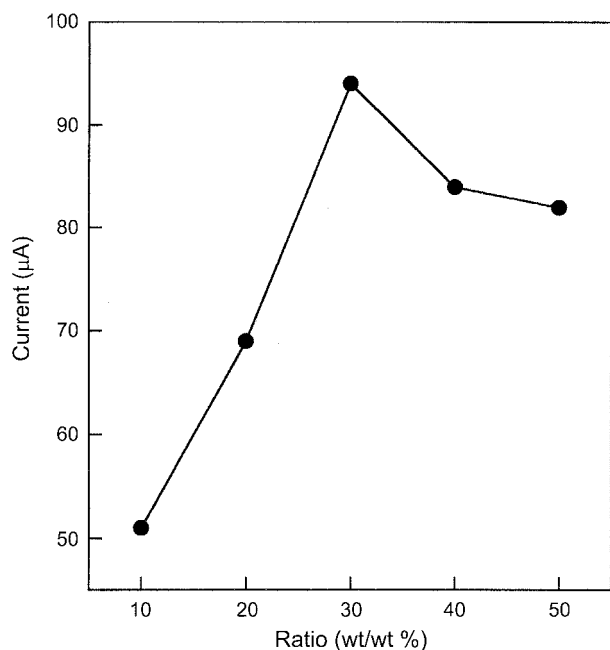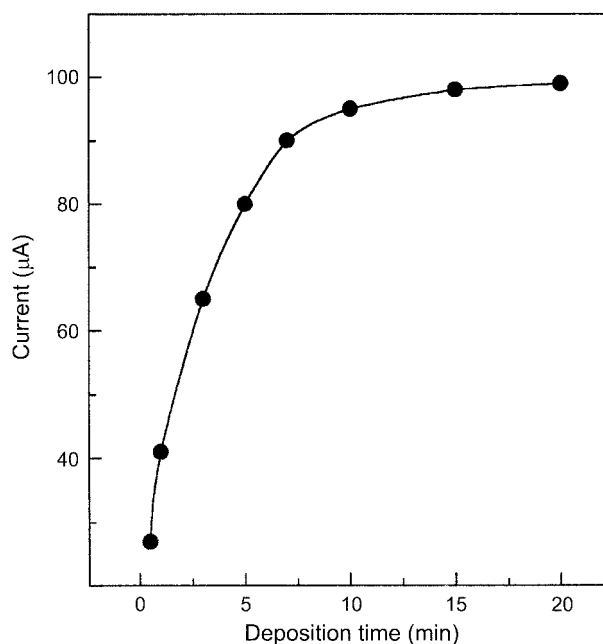
Figure 2. The effect of electrode composition (DPO/graphite, w/w %) on the peak current of the DPO-modified electrode. The concentration of Ag(I) ion was 1.0×10^{-5} M (deposition time: 10 min, deposition temp.: 25 °C, pH: 6.0, scan rate: 100 mV/s).

Figure 3. The effect of deposition time on the peak current of 30% DPO-modified electorde. The concentration of Ag(I) ion was 1.0×10^{-5} M (deposition time: 10 min, deposition temp.: 25 °C, pH: 6.0, scan rate: 100 mV/s).

Figure 4. The effect of solution temperature on the peak height of 30% DPO-modified electrode. The concentration of Ag(I) ion was 1.0×10^{-5} M (deposition time: 10 min, deposition temp.: 25 °C, pH: 6.0, scan rate: 100 mV/s).

surfaces are less efficient for up taking than ones pretreated with a Ag(I) ion solution.
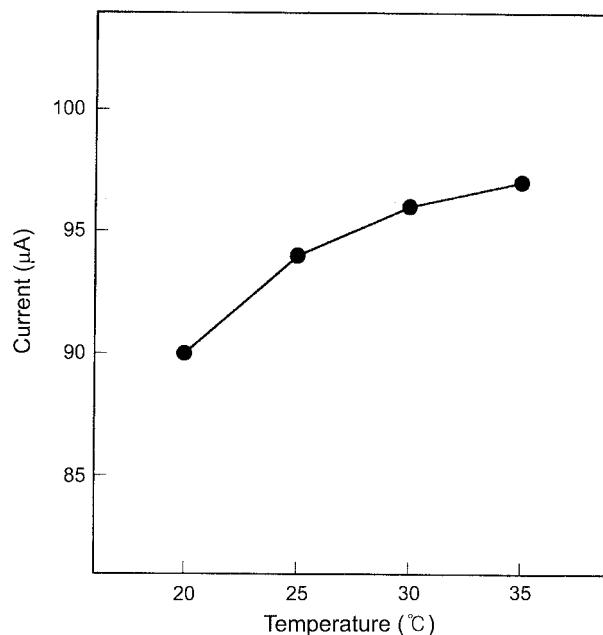
The first deposition of Ag(I) ion on a new CPE surface always resulted in somewhat smaller oxidation peak for the analyte. However, after three to five deposition/stripping cycles gave a good CME surface that CVs and DPVs of Ag(I) ion became highly reproducible and sensitive. For 7 to 8 runs, the relative standard deviation of the current for each scanning was $4.2 \pm 0.3\%$. The surface of CPEs was rather stable unless it was exposed to extreme potentials or extreme pH conditions.

Analytical Conditions. The analytical conditions for Ag(I) ion were optimized by anodic stripping voltammetry. Figure 2 shows the peak current variation according to the composition of CPEs. The CPEs composed of various ratios of DPO to graphite powder (10 to 50 w/w %) were simply immersed for 10 minutes in 1.0×10^{-3} M Ag(I) ion solution at room temperature. After this step, the CPE was rinsed thoroughly with distilled water, and the stripping voltammograms were recorded in 0.1 M KNO$_3$ blank solution. At all the compositions of DPO to graphite powder, Ag(I) ions responded to DPO modified CPEs. However, the peak heights of voltammograms were low and not reproducible for the 50% DPO-contained electrode. This might be presumably due to the resistance of CPEs being higher as the ratio of DPO to graphite becomes larger. All other electrodes except 50% CPE, exhibited well-defined peaks but the S/N ratio of the CPEs decreased as the content of DPO increases, and a maximum peak current obtained at an optimal content ratio of DPO and graphite was 30%.

The anodic peak height as a function of the accumulation time for 1.0×10^{-5} M Ag(I) ion in pH 6.0 buffer solutions is

shown in Figure 3. The peak current increased rapidly with the deposition time up to 10 min and became constant at a deposition time longer than 10 min. A sample volume of 25 mL and accumulation time of 10 min were used in subsequent experiments, considering the assay time and volume of sample needed for analysis.

Figure 4 shows the effect of the deposition temperature on
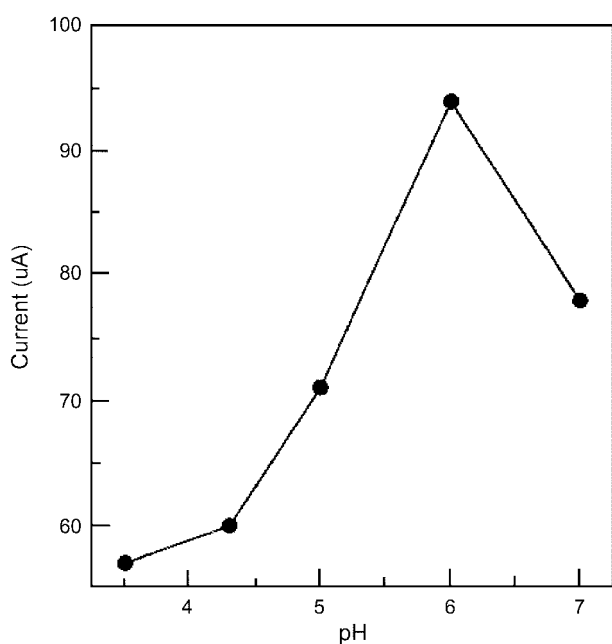
Figure 5. The pH effect of deposition solution on the peak height of 30% DPO-modified electrode. The concentration of Ag(I) ion was 1.0×10^{-5} M (deposition time: 10 min, deposition temp.: 25 $^{\circ}$C, pH: 6.0, scan rate: 100 mV/s).

Table 1. The optimized conditions for Ag(I) ion determination

Terms	Optimized conditions
Working electrode	CPE containing DPO salt
Electrode composition	30% (DPO salt/graphite w/w %)
Deposition time	10 min
Deposition temperature	25 $^{\circ}$C $\pm$ 0.1 $^{\circ}$C
Deposition pH	pH 6.0 buffer (citric acid/sodium citrate)
Interference effects of some metal ions	No effect
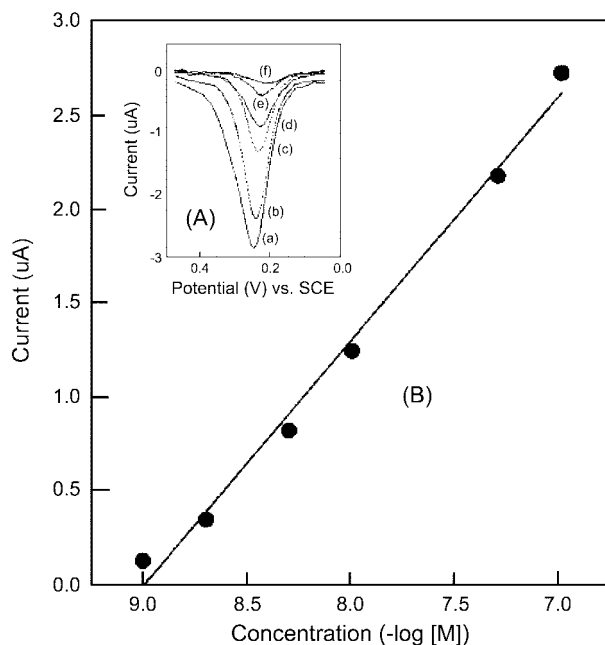
Figure 6. Differential pulse voltammograms (A) and a calibration plot (B) for Ag(I) with 30% DPO-modified electrode following 30 min stirring in Ag(I) solution : (a) 1.0×10^{-7} M, (b) 5.0×10^{-8} M, (c) 1.0×10^{-8} M, (d) 5.0×10^{-9} M, (e) 2.0×10^{-9} M, and (f) 1.0×10^{-9} M (pH 6.0, scan rate: 5 mV/s, pulse height: 0.025 V, pulse width: 0.05 s, condition voltage: -0.5 V, condition time: 1 min, condition temp.: 25 $^{\circ}$C).

the magnitude of the stripping peak current. When a 30% DPO -contained CPE was immersed for 10 min in distilled water spiked with 1.0×10^{-5} M of Ag(I) ion at each temperature. The current responses increased as the temperature increases from 25 to 35 $^{\circ}$C. However, at a temperature above 40 $^{\circ}$C, the peak height became lower. This was due to the roughness of the CPEs surface with slow dissolution of the complex into the bulk solution at higher temperature. The maximum anodic current was obtained at the temperature of 35 $^{\circ}$C, but it did not show good reproducible data. Hence, the deposition temperature of 25 $^{\circ}$C was employed for all subsequent experiments.

The effect of the pH of accumulation medium on the current response of DPO modified CPEs was investigated between 3.5 and 7.0. Figure 5 shows a plot of peak current of Ag(I) against pH of the 1.0×10^{-5} M of Ag(I) ion containing pH 6.0 buffer solution at 10 min deposition time. The stripping peak current increased as the pH of the solution increased and the maximum current was appeared at the pH of 6.0. Over the range of pH < 3.5 and pH > 7.0, the oxidation peak became smaller than those of range between 3.5 and 7.0, due to increasing of signal-to-noise.

The cottrell equation examined the effect of variation of scan rate on the anodic peak height of Ag(I). The anodic stripping peak current was linearly proportional to the root mean square of the scan rate, indicating the peak current corresponding to the stripping of Ag(I) ion diffused from the electrode surface.

No interference effect was seen for Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Mg(II), Mn(II), V(V), Hg(II) and Fe(II) in the same concentration on the oxidation signal of Ag(I) at the optimum conditions. Table 1 shows the optimum conditions

for Ag(I) determination with DPO -modified electrode.

The differential pulse anodic stripping voltammograms at different concentrations of Ag(I) under optimum conditions (up to 5.0×10^{-9} M) are shown in Figure 6. The peak current increased linearly with increasing concentration up to 1.0×10^{-7} M. A linear calibration graph was obtained in the concentration range 5, 0×10^{-9} M-1.0×10^{-7} M Ag(I). Least squares of these data yielded the slope of 0.132 (μA/ppb) for Ag(I) and the correlation coefficient was 0.992 with the relative standard deviation of $\pm$ 2.7%.

On the basis of the signal to background characteristics of the response, the detection limit of Ag(I) ion was 7.0×10^{-10} M $\pm$ 3.6% (N = 5, S/N = 3) for 10 min of deposition time using standard solution. Using longer preconcentration periods might attain better detectability.

Analytical Applications. In order to evaluate the performance of DPO modified carbon paste electrode in practical analytical applications, an experiment for the concentration

Table 2. Data for the calibration plot derived from the Standard Reference Material 1643d (n = 7)

Sample	Concentration		Standard Deviation
	Certified	Observed	
SRM 1643d	1.21 ppm	1.27 ppm	± 2.9%
Dilution to 10 fold	121 ppb	125 ppb	± 3.6%

dependence and a precision test was performed with a SRM 1643d sample (NIST, USA) that contains several heavy metal ions. The certified Ag(I) ion contents in this material was 1.27 (± 2.9%) ppm. Other components present in the range 1 to 500 ppm included Al, Ba, Be, Cd, Co, Cu, Fe, Pb, Li, Ni, Mn, Th, Se and Zn. A sample was diluted with DI water. The pH of solution was adjusted to 6.0 with citrate buffer. The results as shown in Table 2 were attained with a calibration curve method.

Conclusions

A new chemically modified carbon paste electrode has been developed using N,N'-Diphenyl Oxamide (DPO) for the determination of Ag(I) at trace levels by cyclic voltammetry and differential pulse anodic stripping voltammetry. The electrode offers a simplicity of electrode preparation, high stability and highly selective to determine the silver ion, which might to be resulted from the electron affinity of Ag(I) with DPO salt. The silver ion was chemically deposited with DPO salt. The oxidation peak potential of the silver ion was +0.23 V and the analytical conditions were investigated for the determination of silver ion using cyclic voltammetry.

The optimized parameters for the determination of silver ion are as following; pH of the deposition media 6.0, composition of CMCPE 30 (w/w %), deposition time 10 min, and deposition temperature 25 $^{\circ}$C. The detection limit adopted from anodic stripping differential pulse voltammetry was 7.0×10^{-10} M for silver and the relative standard deviation was ± 3.2% at a 5.0×10^{-8} M of Ag(I) ion for 7 runs.

The oxidation signal of Ag(I) was not influenced by the presence of other metal ions such as Na(I), K(I), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), MG(II), Mn(II), V(V), Hg(II), Pb(II) and Fe(II) at optimized conditions.

Conclusively, DPO is a good modifier for the silver determination in a sample containing several metal ions.

References

1. Murry, R. W. *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, pp 191-368.
2. Abruna, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135.
3. Widrig, C. A.; Porter, M. D.; Ryan, M. D.; Strein, T. G.; Ewing, A. G. *Anal. Chem.* **1990**, *62*, 1R.
4. Ryan, M. D.; Chambers, J. Q. *Anal. Chem.* **1992**, *64*, 79R.
5. Murray, R. W.; Ewing, A. G.; Durst, R. A. *Anal. Chem.* **1987**, *59*, 379A.
6. Imisides, M. D.; Jhon, R.; Riley, P. J.; Wallace, G. G. *Electroanalysis* **1991**, *3*, 879.
7. Won, M. S.; Bae, Y. J.; Lee, S. S.; Shim, Y. B. *Electroanalysis* **2001**, *12*, 13.
8. Kong, Y. T.; Choi, G. H.; Won, M. S.; Shim, Y. B. *Chemistry Letters* **2002**, *1*, 54.
9. Wang, J. *Stripping Analysis: Instumentation and Application*; Verlag Chemie: Deerfield Beach, FL, 1985.
10. *Treatise on Analytical Chemistry*; Kolthoff, M. H., Eiving, P. J., Eds.; Interscience: New York, 1966; Part II, Vol. 5.
11. Renner, H. *Ulmanns Encyclopedia of Industrial Chemistry,* 5th ed.; VCH: New York, 1993; vol. A24.
12. *Ambient Water Quality Criteria for Silver*; EPA 4405-80-071, Office of Water Regulation, Washington, DC, 1980.
13. *Metals and Their Compounds in the Environment*; Meian, E., Ed.; VCH: New York, 1991.
14. Cheek, G. T.; Nelson, R. F. *Anal. Lett.* **1978**, *A11*, 393.
15. Gao, Z.; Xu, Y.; Wang, G.; Zhao, Z. *Anal. Chim. Acta* **1990**, *229*, 213.
16. Wang, J.; Naser, N.; Darnall, D.; Garder-Toresdey, J. *Electroanalysis* **1992**, *4*, 71.
17. Turyan, I.; Mandler, D. *Electroanalysis* **1994**, *6*, 838.
18. Tanaka, S.; Yoshifa, H. *Talanta* **1989**, *36*, 1044.
19. Yeom, J. S.; Won, M. S.; Choi, S. N.; Shim, Y. B. *Bull. Korean Chem. Soc.* **1990**, *11*, 200.
20. Kim, S. H.; Won, M. S.; Shim, Y. B. *Bull. Korean Chem. Soc.* **1994**, *38*, 734.
21. Won, M. S.; Moon, D. H.; Shim, Y. B. *Electroanalysis* **1995**, *7*, 3421.
22. Lee, J. W.; Park, D. S.; Shim, Y. B.; Park, S. M. *J. Electrochem. Soc.* **1992**, *139*, 3507.
23. Park, D. S.; Shim, Y. B.; Park, S. M. *Electroanalysis* **1996**, *8*, 44.
24. Takeshima, T.; Yokoyama, M.; Iamaoto, T.; Akano, M.; Asaka, H. *J. Org. Chem.* **1996**, *34*, 730.
25. Prabhu, S. V.; Baldwin, R. P. *Anal. Chem.* **1987**, *59*, 1074.