



Construction of Modified Carbon Paste Electrode by a New Pantazene Ligand for Ultra-Trace Determination of Ion Silver in Real Samples

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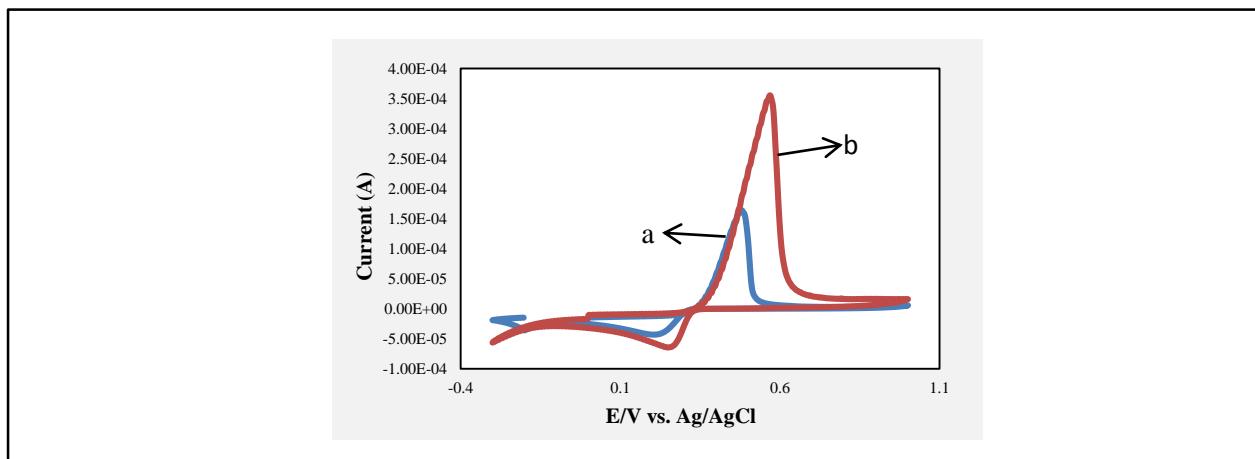
Carbon paste electrode

Silver

ABSTRACT

A new ligand, 1,5-bis(para methoxyphenyl)-3-ethyl-1,4-pantazadiene has been synthesized by reaction of the 4-methoxyaniline (*p*-anisidine) with ethylamine. The mixture was stirred in an ice bath for 30 min. The structure of the synthesized compound resulted from the IR and ¹HNMR and ¹³CNMR. Afterwards, a carbon paste electrode modified with this new ligand was developed for the silver determination at nano molar level concentration. The electrochemical properties of this modified electrode was investigated by employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods in an acetate buffer solution (pH=4.8). The effect of pH, scan rate, percentage of modifier and buffer as supporting electrolyte on the electrode process were investigated. The oxidation peak of Ag⁺ was observed at about 0.4-0.5 V. The resulting electrode demonstrated linear response across a 10⁻⁹ to 10⁻⁸ mol/L⁻¹ of silver concentration range with a detection limit value of 1.61×10⁻¹⁰ mol/L⁻¹, on the basis of a signal to noise ratio of 3. Relative Standard deviation (RSD%) of the electrode performance was 2.41%. This MCPE, showed high sensitivity and selectivity to Ag⁺ ions in aqueous samples.

GRAPHICAL ABSTRACT



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Introduction

In normal conditions, silver is found at low concentrations in environmental samples such as water, soil and foods, but due to human activities, significant amounts of this metallic ion is imported into the environment. The main sources of human infections, including mining, industrial waste, electronic and electrical industries, using of fertilizers containing heavy metals, and *etc*, are all causes of water and environment pollutions [1].

At present, shuttle missions and the International Space Station (ISS) employ iodine (up to 3 mg/L⁻¹) or silver (I) (up to 0.5 mg/L⁻¹) as bacterial growth inhibitors. Periodic monitoring of these compounds is therefore required to confirm that their concentrations are held at levels that are sufficient for effective biocidal action, but below those which may affect crew health. Long term exposure to high silver levels can cause argyria, whereas extended exposure to high iodine levels may induce thyroid dysfunction [2]. To these ends, the testing method must be simple, rapid, and operable in microgravity [3]. Maximum contaminant level for total silver in drinking water, the US Environmental Protection Agency (EPA) fixed it as 0.1 mg/L⁻¹. It is also reported that the concentration of silver in water higher than 0.17 µg/L⁻¹ is toxic to fish and microorganism [4,5]. The measurement and identification of ultra-trace levels in drinking water, water sources near factories and industries that released their waste into the rivers is very important [6].

The trace and ultra-trace determination of silver is usually carried out after preconcentration by solid phase extraction [7,8], ligand cloud point extraction [9], ligand-less cloud point extraction [10], cloud point extraction-flame atomic absorption [11], ligand modified magnetic nanocomposite [12], simple solvent bar micro-extraction [13],

three-phase solvent bar micro-extraction [14], and determination by flame or furnace atomic absorption spectrometry [15,16]. The rapid methods involving bulk optode based on an ionophore [17], high sensitive and selective optical sensor [18], optical recognition [19] have used too. But electrochemical method is one of the most desirable methods for determination of silver because of its low cost, high sensitivity and simple preparation [5,20]. Cyclic voltammetry (CV), is very frequently used because it offers a wealth of experimental information and insights into both the kinetic and thermodynamic details of many chemical systems [21]. The importance of DPV in chemical analysis is based on its superior elimination of the capacitive/background current this is achieved by sampling the current twice: once before pulse application and then at the end of the pulse [22]. Carbon paste electrodes (CPEs), belong to promising electrochemical sensors of wide applicability. They have various advantages including ease of preparation, speed of getting a new reproducible surface, low residual current, porous surface and low cost [23,24]. The ligand modifier at the electrode surface, significantly improved sensitivity and selectivity of electrochemical methods can also reduce the detection limit.

In this work, a selective and specific pantazene ligand (Figure 1) have synthesized and used as a modifier for silver selective carbon paste electrode and used for ultra-trace determination of silver (I) in aqueous media by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Different experimental conditions, including the percentage of modifier, the structure and pH of the electrolyte solution (buffer), scan rate, linear range and detection limit were investigated and optimized.

Experimental

Reagents and Materials

All commercially available chemicals were of reagent grade and used as purchased [25]. Graphite powder (spectrum grade, size <20 μm) and paraffin oil were obtained from Merck Chemical Company. The new ligand (L), were synthesized with high purity. Standard solutions of Ag^+ and other metal ions were prepared from nitrate salts (all from Merck) in buffer solutions. All chemicals were of analytical reagent grade and were used as received. Double distilled water (DDW) was used throughout [26].

Instruments

Electrochemical measurements were carried with three electrode system, Ag/AgCl (reference electrode), a platinum wire (counter electrode) and modified/unmodified carbon paste electrode (working electrode), that three electrodes were fixed into the quartz cells. All experiments were carried out at the room temperature. The pH of solutions was measured with a 713 pH-meter from Metrohm, with a glass electrode. All voltammetric measurements including cyclic voltammetry (CV) and differential pulse voltammetry (DPV), were performed using a Autolab B.V, potentiostat- galvanostat and evaluated with a computer (Pentium IV, 1200 MHz) equipped with Nova1.8 software. FT- IR spectra were performed on a JASCO 4200 spectrometer using KBr discs. NMR spectra were recorded on a Bruker (300 MHz) spectrometer. Chemical shifts (ppm) were referenced to the internal standard tetramethylsilane (TMS).

Preparation procedure of ligand (L)

The new pantazene ligand (L) was synthesized and purified based on the reaction between Anisidine in concentrated hydrochloric acid and ice-water mixture, sodium nitrate, ethyl amine. A yellow precipitate was obtained, washed with water and methanol and after fully dried, purified

with acetonitrile at 30 °C.

Spectroscopy data of Ligand (L)

M.p. 115-117 °C, IR (KBr, ν_{max}): wave number of start: 330 cm^{-1} , end: 6000 cm^{-1} : 1177 (C-H), 1244 (C-O:), 1343 (Ar-N), 1499 (Ar C-C), 1597 (N=N), 1642 (NH_2 in plane bend), 2957 (C-O), 3061 (Ar-H). ^1H NMR (300 MHz, DMSO-d_6) δ_{H} : 3.70 (s, 5H, C_2H_5), 3.80 (s, 6H, 2CH_3), 7.03 (d, $J = 8.45$ Hz, 4H, H-Ar), 7.60 (d, $J = 8.41$ Hz, 4H, H-Ar) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ_{C} : 28.3, 55.4 (CH_3), 114.5, 123.1, 141.8, 159.6 ppm.

Preparation of modified carbon paste electrode

The carbon paste was prepared by hand-mixing graphite powder (0.07 gr) and paraffin oil (0.03 gr) with a porcelain pestle and mortar. After the mixture homogenization, the paste was packed carefully into the tube tip (inner diameter: 3.4 mm) and a bare copper wire was inserted through the opposite end to produce electrical contact. For avoided possible air gaps, often enhancing the electrode resistance [27]. Finally, were polished the surface it (UMCPE: unmodified carbon paste electrode). For the preparation of modified carbon paste electrodes (MCPE), values of 2 to 10 percent modifier (0.002- 0.01 gr), was added to the carbon paste.

Preparation of real samples

In order to demonstrate the applicability and reliability of the method for real samples, several water samples and another samples were prepared and analyzed by the method. Water samples including avaj thermal spring (from near of Hamedan city) and waste water of dental (from dental of karaj city) were collected into the clean holder of sample. These samples without any procedures were used. 1 gram of other samples including Hair colors (Albura and Kalyon), sunscreen cream (Sun Safe), eyebrow color (Dani One) and fish ton were measured. Then they were heated

over heater at 120-150 °C. Dry ashing were made and solved with 10ml of concentrated HCl and were volumed in 100 mL. super phosphate fertilizer was placed in water and dilute nitric acid for 24 hours then straightened with filter paper.

Results and Discussion

Characterization of Ligand (L)

(Ligand L) has been synthesized by reaction of the 4-methoxyaniline (*p*-anisidine) with ethylamine (Figure 1).

The structure of Ligand L was characterized by the spectroscopic data. The IR spectrum of the ligands shows a broad band at 3438-stretch, which can be attributed to the N-H group. C-O stretch band is observed at 1244 and 2957 cm^{-1} in the Ligand L. The ^1H NMR spectra of synthesized compound are consistent with its structure. The ^1H NMR spectra of compound are simple and consist of

the aromatic proton signals and 2 singlet signals related to the resonance of the C-H proton, which appeared at 3.70 and 3.80 ppm, respectively. The aromatic protons resonate as a multiple signal at 7.03-7.60 ppm.

Electrochemical behavior of the modified electrode

The cyclic voltammograms for UMCPE and MCPE were compared and the highest peak current (i_p) of oxidation was observed for 6% modifier (Figure 2). The catalytic rule of the modifier caused the anodic over potential to be lowered and enhancement of the anodic peak current in the electrode process [28]. At first cyclic voltammetric measurements were carried out at $0.1 \text{ V}\cdot\text{s}^{-1}$ scan rate, and then scan rate was changed and optimized. The effect of scan rates has shown in (Figure 3 a, b). As seen in this Figure the best scan rate is $0.10 \text{ V}\cdot\text{s}^{-1}$ and used for all experiments [29-33].

Figure 1. Synthesis of pantazene ligand (L)

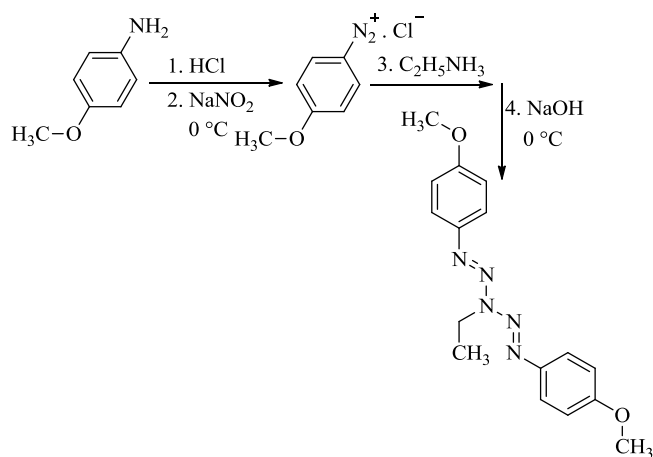
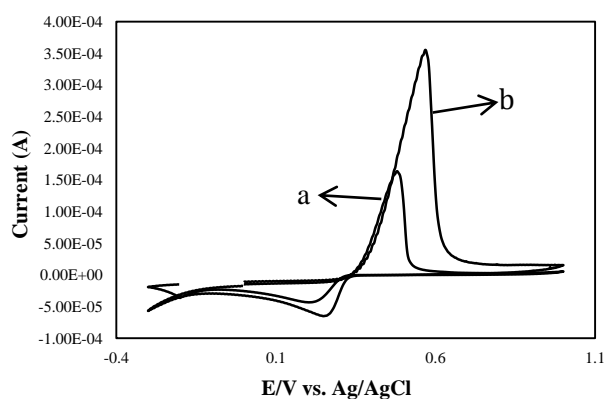


Figure 2. Cyclic voltammogram of Ag^+ ($5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$), scan rate ($0.1 \text{ V}\cdot\text{s}^{-1}$), supporting electrolyte (B-R = 5) as electrolyte solution, a) CPE, b) MCPE



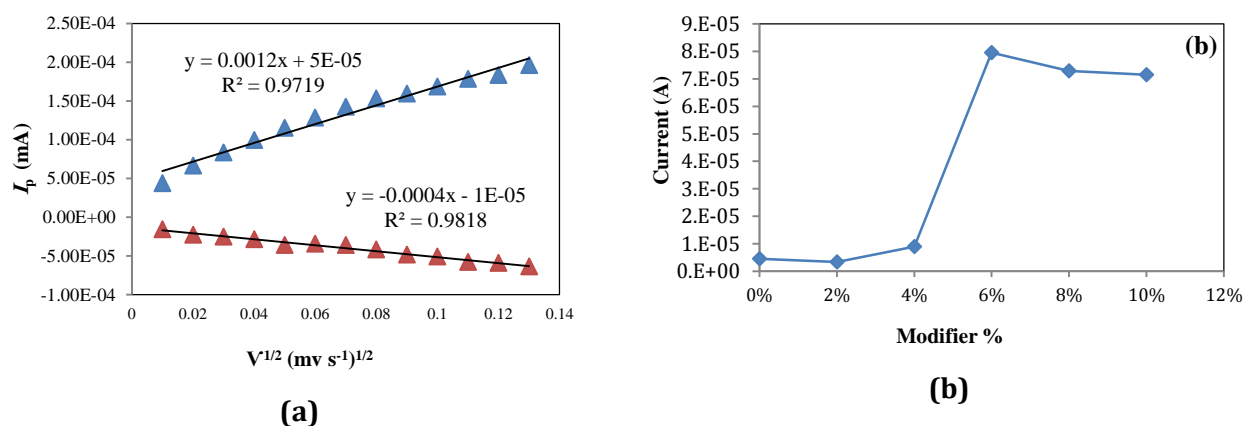


Figure 3. (a) Plot of scan rate vs current of LMCPE at different scan rates from 10 to 130 mVs⁻¹ (b) The effect of percentage of modifier on the peak current at LMCPE. (Ag^+ concentration = 5.0×10^{-5} mol.L⁻¹, Supporting electrolyte = 0.2 mol.L⁻¹ B-R buffer at pH = 5)

Device parameters for differential pulse voltammetry (DPV) including step potential: 0.005 V, modulation amplitude: 0.16 V, modulation time: 0.03 S and interval time: 0.5 S were studied and optimized.

Optimization of pH and supporting electrolyte

The effect of solution pH on peak current (I_p) have shown in Table 1. As shown from this data the acetate buffer at pH=4.8 was the optimal buffer, and used as optimum pH in all experiments.

Calibration curve

Detection limit of method was estimated under optimal conditions with DPV. At first, standard deviation of blank (0.2 M acetate buffer solution) was measured by replicate determinations of the blank signals. Then 10 μ L Ag^+ solution (10^{-6} mol/L⁻¹), was added to the 10 mL buffer that was already optimized.

Oxidation peak was climbed by adding each time a solution of silver (Figure 4 a, b). Slope of calibration curve was obtained, then the limit of detection calculated from $LOD = 3S_b/m$ equation, where LOD, S_b and m are the detection limit, standard deviation of the blank and the slope of the calibration curve respectively. The resulting electrode demonstrated a detection limit value of 1.610×10^{-10} mol/L⁻¹, on the basis of a signal to noise ratio of 3. Silver solution was prepared with a certain concentration. Then RSD% was obtained with 5 times measurement of prepared solution with DPV under optimize condition. The result of RSD% was characterizing 2.41% that shows the repeatability of MCPE for the estimation and determination of Ag^+ ions. It can be seen that the peak currents have a good linear relationship with the concentration of Ag (I) in the range from 10^{-9} to 10^{-8} mol/L⁻¹.

Table 1. The I_p amounts of 5×10^{-6} mol.L⁻¹ Ag^+ solution at different pH

Buffer (pH)	I_p (A)
B-R (2)	7.95×10^{-5}
B-R (3)	7.00×10^{-6}
B-R (4)	1.00×10^{-6}
B-R (5)	8.69×10^{-5}
B-R (6)	1.00×10^{-6}

B-R (7)	4.00×10^{-6}
B-R (8)	2.00×10^{-6}
B-R (9)	1.00×10^{-6}
B-R (10)	1.00×10^{-6}
Phosphate (4)	6.00×10^{-5}
Phosphate (5)	5.50×10^{-5}
Phosphate (6)	1.00×10^{-5}
Phosphate (7)	1.90×10^{-5}
Phosphate (8)	7.00×10^{-6}
Borate (9)	1.00×10^{-6}
Ammonium (10)	2.30×10^{-5}
Acetate (3)	3.00×10^{-6}
Acetate (4)	1.53×10^{-4}
Acetate (4.81)	3.43×10^{-4}

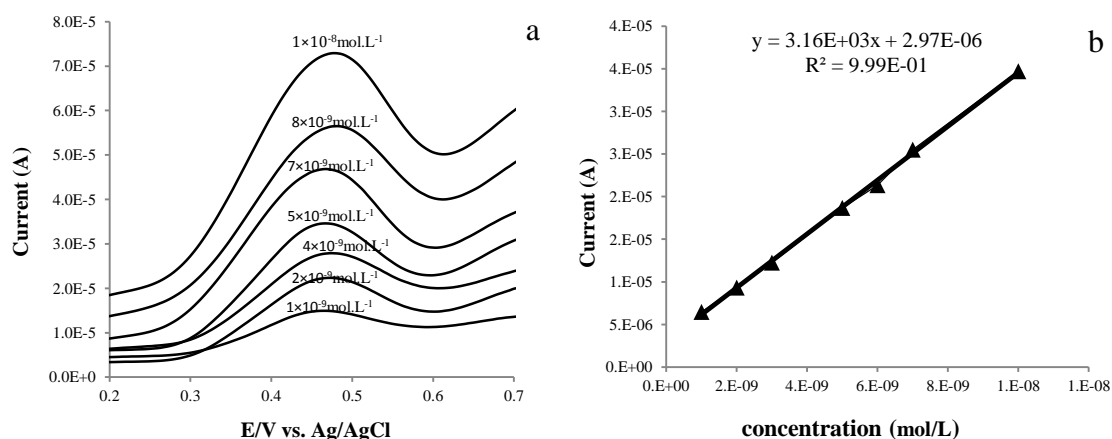


Figure 4. (a) Voltammograms for additions of solutions with different concentrations of Ag⁺. (b) The calibration curve for LMCPE. Other conditions were as in Figure 3

Interferences study

To evaluate the effect of interference, 20 $\mu\text{g/L}^{-1}$ of Ag⁺ ions was used. For this work, some solutions containing several of cations and anions were prepared in different concentration and were characterized effect of interferences on performance of the pantazene ligand. When the concentration of interference was arrived to a specified limit, oxidation peak was changed and current change was went up from 5%. This rang was showed effect of cation-anion interferences that can be accompany with increasing or decreasing the oxidation peak

or changes in the peak potential of oxidation.

At the coexisting ion concentration that affected the DPV peak current of Ag⁺ only a 5% change of peak current is allowed. For some ions such as Mg²⁺, Na⁺, were occurred both of these change. All of the results indicate in Table 2.

Real sample analysis

Some real samples were collected from various places, including thermal spring and waste water of dental medicine. For this purpose, 9.5 mL of acetate solution (supporting electrolyte) with 0.5 mL of real

sample were mixed and putted into the cell of Autolab instrument and the first current was characterized. Then, the aliquot amounts of Ag⁺ ion standard solution were added and increasing the current was

measured. This procedure was used 3 times for each sample and the RSD% was obtained. The results have listed in Table 3 and shown a good agreement.

Table 2. The effect of interferences on the peak current change, Ag⁺ ions concentration: 1×10^{-8}

Interfering ions	Concentration (10^{-8} mol.L ⁻¹)	Peak current change (%)
Cd ³⁺	0.5	- 3.0
Fe ²⁺	3	+ 4.6
Al ³⁺	5	- 5.7
Au ³⁺	11	-4.8
Ni ²⁺	13	- 3.9
Pb ²⁺	30	- 5.3
Co ²⁺	80	- 4.2
Cu ²⁺	140	- 8.0
Zn ²⁺	4000	+ 3.2
Mg ²⁺	4000	- 4.8
Na ⁺	30000	- 4.5
Ca ²⁺	30000	+ 5.2
Cl ⁻	2000	- 4.8
Br ⁻	3000	- 4.5
NO ₃ ⁻	4500	- 3.7

Table 3. Recovery of Ag⁺ ion from different samples by DPV with standard additions method (N = 3)

Samples	Concentration (10^{-8} mol/L ⁻¹)	Found±RSD% (10^{-8} mol/L ⁻¹)	Recovery%
Super phosphate fertilizer	0	2.363±0.0499	----
	20	24.061±0.0029	107.59
	30	32.213±1.9147	99.54
	40	42.110±1.8347	99.40
Hair Color (Albura)	0	49.200±0.7077	----
	20	68.770±1.0983	99.38
	30	86.980±1.9700	109.38
	40	89.850±0.1260	99.28
Hair Color (Kalyon)	0	12.760±0.0110	----
	20	34.402±1.1897	105.01
	30	42.675±1.5833	99.80
	40	53.444±0.2770	101.30
Sunblock Cream (Sunsafe)	0	14.008±0.2393	----
	20	35.823±1.2860	105.34
	30	43.878±1.5032	99.71
	40	49.604±1.3687	91.85

	0	20.380±0.1559	----
Ebro Color (Danione)	20	42.860±4.7281	106.14
	30	55.325±0.2360	109.82
	40	62.635±4.2964	103.74
	0	0.285±0.0743	----
Avaj thermal spring	20	19.822±0.3160	97.71
	30	29.069±0.1588	95.98
	40	42.521±1.8036	105.55
Waste water of Dental (Karaj)	0	1.6317±0.2683	----
	20	20.122±0.2160	93.02
	40	41.670±0.0495	100.09
Fish ton	0	7.042±0.0301	-----
	20	25.046±0.8932	92.63
	40	50.098±0.7906	108.39

Conclusion

In this work, a selective and specific pantazene ligand have synthesized and used as a modifier for silver selective carbon paste electrode and used for ultra-trace determination of silver(I) in aqueous media by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Different experimental conditions, including the percentage of modifier, the structure and pH of the electrolyte solution (buffer), scan rate, linear range and detection limit were investigated and optimized. The resulting electrode demonstrated linear response across a 10^{-9} to 10^{-8} mol.L⁻¹ of silver concentration range with a detection limit value of 1.61×10^{-10} mol/L⁻¹, on the basis of a signal to noise ratio of 3. Relative Standard deviation (RSD%) of the electrode performance was 2.41%. This MCPE, were showed high sensitivity and selectivity to Ag⁺ ions in aqueous samples.

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