

*Full Paper*

## **A Solid-state Silver Ion Selective Electrode Based on Polyaniline/Eosin Y Nanocomposite Film**

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**Abstract-** Potentiometric sensor based on commercial pencil graphite electrodes coated with polyaniline (PAni) composite with Eosin Y (EY) termed as PGE/PAni-EY have been developed for potentiometric determination of silver ion. The electrode exhibited linear response with Nernstian slope of  $57.6 \pm 0.8$  mV per decade within the range of  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M with limit of detection  $6.5 \times 10^{-7}$  M silver ion. Fast and stable response time of the electrode (15 s) was obtained over the concentration range of  $1.0 \times 10^{-1}$  M to  $1.0 \times 10^{-4}$  M. This electrode was also used as indicator electrode in potentiometric titration of halide ions successfully. This study shows that the introduced electrode (PGE/PAni-EY) is highly selective toward silver ion and can be used to determine silver ions in solutions with high accuracy and precision.

**Keywords-** Silver electrode, Potentiometry, Polyaniline, Eosin Y, Nanocomposite

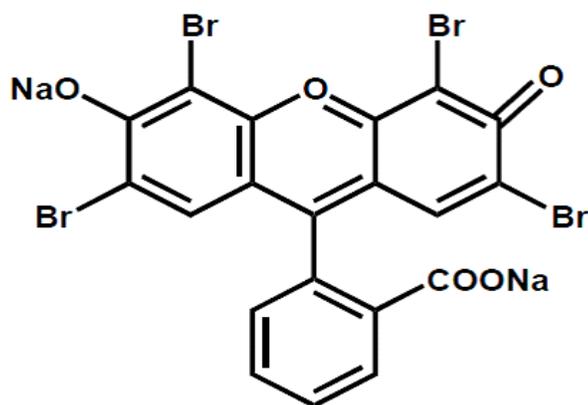
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### **1. INTRODUCTION**

There has been a growing interest in the development and application of potentiometric sensors for monitoring concentration of various species in biological, environmental and industrial fields. Miniaturized micro sensor electrodes have potentially significant future applications in the area of medicine, food and chemical processing, industrial and military applications, aerospace and robotic markets. Some of the main inherent advantages of micro sensors include improved performances, automation feasibility, high speed, small sample

volume and low costs [1-3]. All-solid-state ion-selective polymeric film electrodes (ASSE) are of especial interest in the field of potentiometric sensors because they are free from some limitations resulting from the presence of the inner reference solution, including the need to work in a vertical position, evaporation of the inner solution, and maintenance requirement. In recent years, there has been an increasing interest in the field of ISEs based on all solid state contact free of inner reference solution [4, 5].

Intrinsically conducting polymers (ICPs) are widely applied in the solid state ion selective electrodes [6-11]. Among the available ICPs, polyaniline is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties and better stability compared to other ICPs [12-14]. Due to mixed ionic and electronic conductivity; these materials generate electric response to the changes in the content of the potential determining species. Among conducting polymers, PANi has attracted a great deal of attention because of its unique electrical and electrochemical properties. PANi in contrast to many other conducting polymers can be easily prepared by either chemical or electrochemical methods from both aqueous and nonaqueous solvents and posses processability for commercial use [12,15,16]. PANi is stable and insoluble in most organic solvents has relatively high conductivity. The electro-active nature or the switching properties of PANi have been utilized as the basis of most proposed applications such as sensors, separation devices, rechargeable batteries and controlled drug release [17-23]. There are many studies showing that dye molecules such as photochromic dyes, ICP/dye composite and textile reactive dye can be incorporated into ICPs during synthesis [24-26]. When using polyelectrolyte anions, a fixed anionic environment for PANi is present whatever the redox state and ionic exchanges accompanying redox changes are of cationic nature [27, 28].



**Scheme 1.** Chemical structure of Eosin Y (EY)

In the current study, Eosin Y (Scheme I) a water soluble acid dye was employed as dopant of chemically prepared PANi (emeraldine base). We have already shown that PANi has strong affinity for adsorption of EY from aqueous solutions [29]. Eosin Y (scheme I) has also high affinity to silver ion for complexation reaction, so it was used as both polymer dopant and ionophore for silver ion.

## **2. EXPERIMENTAL**

### **2.1. Reagents and samples**

All chemicals used were of analytical reagent grade and prepared in deionized water. Aniline, silver nitrate, potassium iodide, sodium chloride, potassium bromide and all other cations used were of the highest purity available and used without any further purification. Standard AgNO<sub>3</sub> solutions were obtained by gradual dilution of a 0.10 M AgNO<sub>3</sub> solution. The stock solution of silver stored in a dark dish in order to prevent of photodecomposition. Metal nitrates and sulfates used for selectivity investigation were dissolved in deionized water, and mercury nitrate in 0.1 M nitric acid.

### **2.2. Synthesis of polyaniline (PANi)**

Polyaniline was synthesized by chemical oxidation of aniline (aniline distilled) from acidic solution (0.20 M) in HCl (1 M) using ammonium persulfate (APS) as the oxidant (0.50 M). After the temperature of the aniline solution reached -5 °C, the APS solution was added drop wise to the aniline solution at a rate of about 5 mL/min. This reaction mixture was kept stirring for 4 h, and kept unstirred for another 4 h and then filtered. The dark blue salt form of polyaniline (emeraldine salt, EB/HCl) powder was collected and washed by distilled water until the washing solution was colorless. The powder was then stirred in 0.10 M ammonia solution for 18 h to de-dope the polymer and formation of emeraldine base (EB). The emeraldine base (EB) form of polyaniline powder obtained was again washed by distilled water until the filtrate again became colorless. EB powder was first dried at room temperature and then dried at 60 °C .

### **2.3. Preparation of silver electrode (PGE/PAni-EY)**

Commercial pencil graphite leads (0.5 mm diameter) used as working electrodes were rinsed with nitric acid and water and allowed to dry at room temperature before coating. A mixture of 50 mg EB and 25 mg EY was dissolved in about 5 mL of N-methyl-pyrrolidone (NMP), and the polymer solution (1%) was mixed well. The pencil graphite electrodes (PGE) were then coated with polyaniline and EY solution, by repeated dipping (5 times, a few min between each dip coating). The coated thin layer of polyaniline composite was allowed to dry at 50 °C for 3 h. The electrode was conditioned for 48 h in 10<sup>-2</sup> M silver nitrate solution before potentiometric measurements.

## 2.4. Apparatus and potential measurement

The response characteristics of the prepared silver electrode (PGE/PAni-EY) were determined by recording potential as a function of  $\text{Ag}^+$  ion concentration. All the potential measurements were carried out with a digital voltmeter (DT9208A). The potential build up was measured using the galvanic cell of the following type:  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$  (saturated) || salt bridge ( $\text{KNO}_3$ ) | test solution | PAni Film, graphite electrode. The performance of each electrode was investigated by measuring its potential in silver nitrate solutions prepared in the range of  $1 \times 10^{-7}$  M to  $1 \times 10^{-1}$  M by serial dilution of the 0.10 M stock solution at constant pH (pH=4.5). The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential vs. the pAg. The response time of the electrode were obtained by measuring the time required to achieve a steady state potential (within  $\pm 1$  mV) when the electrode was immersed in  $\text{Ag}^+$  solutions with various concentrations.

## 3. RESULTS AND DISCUSSION

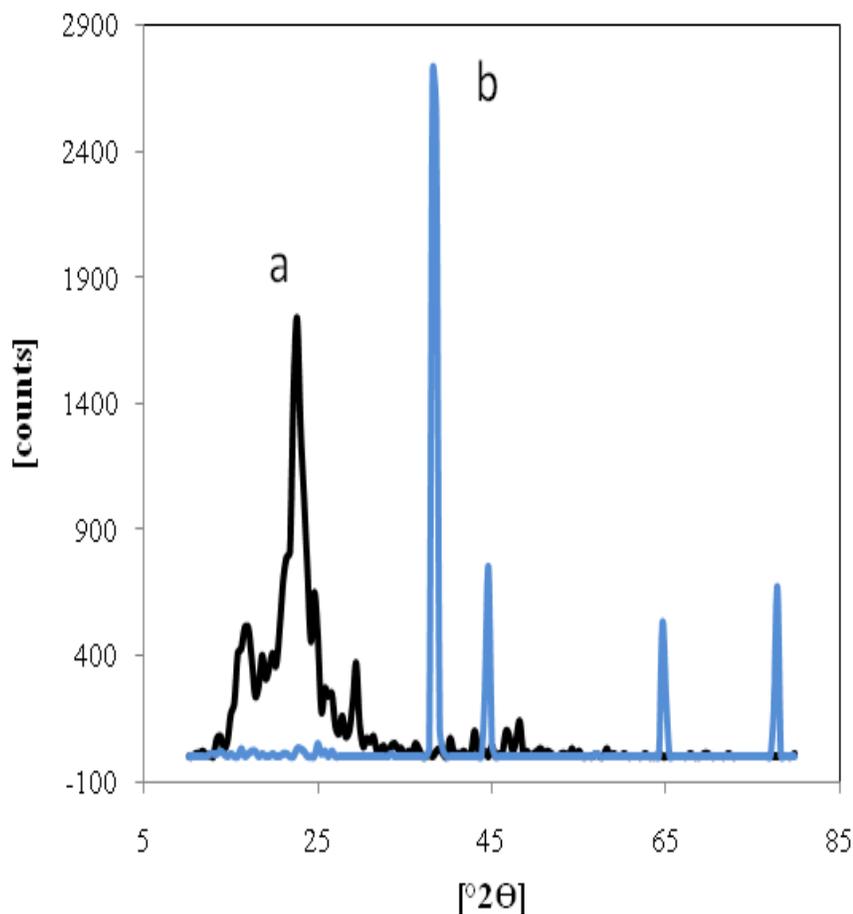
### 3.1. Characterisation of the prepared electrode

PGM/PAni-EY electrodes were prepared by dipping the graphite electrodes into the coating solution. Inspection of XRD patterns obtained from silver ion treated and untreated EB are shown in Fig. 1. As the result show, some silver nanoparticles deposition is formed on the surface of the polymer when it was exposed to silver ion solution. Based on the XRD patterns obtained, EB polymer showed an amorphous nature with a characteristic peak at  $2\Theta=22.6$  [Fig. 1(a)]. Silver-treated polymer didn't show this peak but show a new recognized sharp peak at  $2\Theta=38.2$  [Fig. 1(b)] corresponding to the presence of zero charge silver nano particles on the polymer surface [30]. The calculated intracrystalline d-spacing ( $d=2.356\text{\AA}$ ) using Bragg's Law confirms the presence of silver deposition during conditioning of the electrode coated by polymer with silver ion solution.

Formation of some silver nanoparticles ( $\text{Ag}^0$ ) on the polymer surface can be due to the redox reaction between reducible part of PAni and silver ion which can be shown as the following equation (Eq.1):

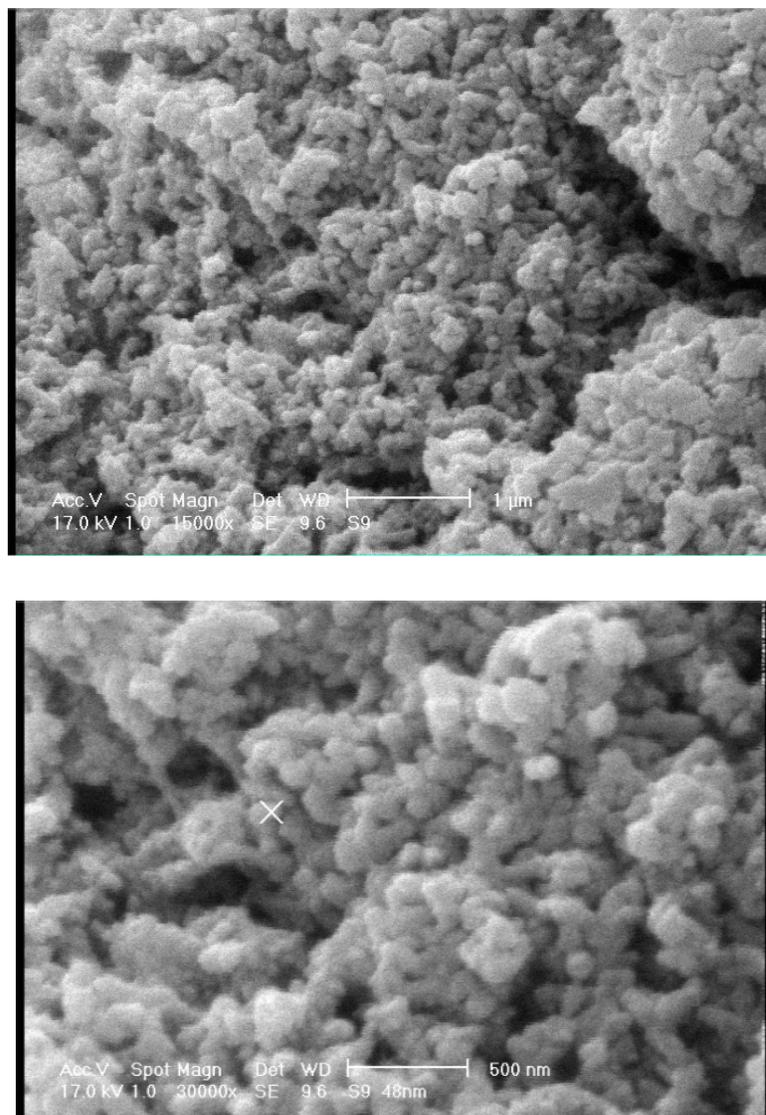


With increasing conditioning time or concentration of silver ion, more nanoparticles were observed which could be detected with visual inspection. However when the electrode was conditioned for 48 h at a solution of  $1.0 \times 10^{-2}$  M  $\text{Ag}^+$  ion, the formation of nano silver particles could be detected only by XRD and SEM analyses (Fig. 1 and Fig. 2).



**Fig. 1.** X-ray diffractograms patterns (XRD) obtained for: (a) untreated polymer, (b) treated polymer to silver ion solution ( $\lambda=1.5418$ )

In our preliminary investigation, it was found that using more concentrated silver solution for conditioning (e.g. 0.05M) or increasing conditioning time (>48 h), more silver particles are formed and the electrode was covered totally with silver nanoparticles and the electrode behaves the same as silver electrode which suffers from poor selectivity, lower dynamic range and high detection limit. So in all of further experiments, the optimized conditioning procedure was used. The surface morphology of the sensor electrode was further characterized using scanning electron microscopy (SEM). The samples used for SEM analysis (Fig. 2) were the same samples used for XRD analysis. As the SEM pictures clearly show, the silver nano particles is formed when the polymer coated electrode is conditioned with silver ion solution.



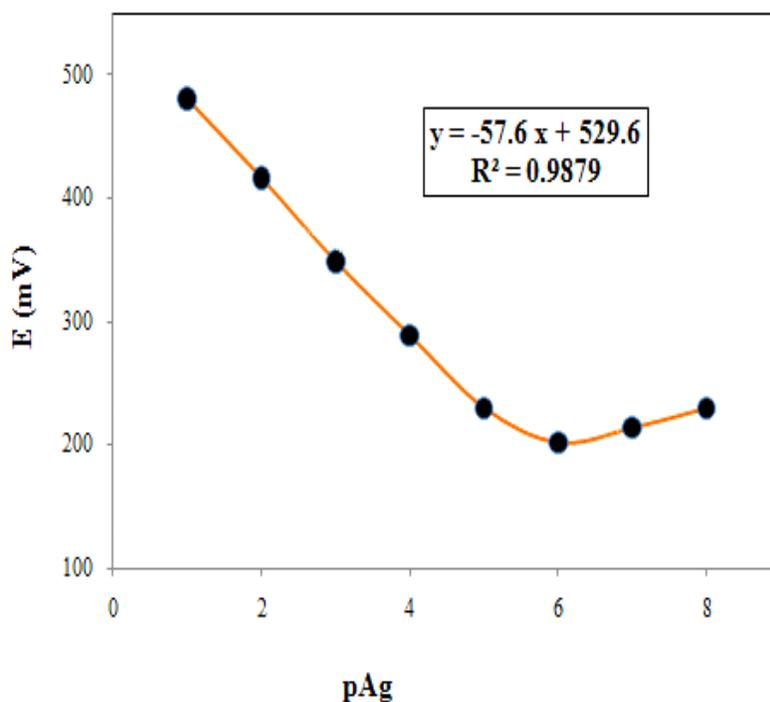
**Fig. 2.** SEM micrograph of PGE/PAni-EY after treatment with 0.01 M silver solution for 48 h with  $\times 150000$  and  $\times 30000$  magnifications

### 3.2. Potentiometric response

The potentiometric response of the prepared silver selective electrode was investigated against the silver ion concentration. For this purpose, appropriate aliquots of a stock solution of silver ion were introduced to the cell, and the corresponding potentials were determined. The potential readings were plotted against minus logarithmic values of the silver ion concentration. Over the concentration range from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M of silver ion in the calibration solution, the electrode potential response was linear with the concentration of silver ion (Eq. 2).

$$E = K + S \log [Ag^+] \quad (2)$$

Where  $E$  is the total potential (mV) developed between the sensing and reference electrodes.  $K$  (mV) is a constant which is characteristic of the particular ISE/reference pair electrodes and  $S$  is the electrode slope. The optimum conditioning time for of the fabricated silver sensor electrode after which it generated stable potentials was 48 h in the presence of  $1.0 \times 10^{-2}$  M  $\text{Ag}^+$  ion. The calibration curve, shown in Fig. 3, depicts linear range from  $1 \times 10^{-6}$  M to  $1 \times 10^{-1}$  M for PGE/PAni-EY with a Nernstian slope of  $-57.6$  mV/decade of  $\text{Ag}^+$  concentration. The practical limit of detection was found to be  $6.0 \times 10^{-7}$  M.



**Fig. 3.** Calibration curve obtained for potentiometric responses of PGE/PAni-EY to  $\text{Ag}^+$  ion

Polyaniline with  $\pi$ -electrons and nitrogen donor was successfully applied for the construction of silver ISEs. In the absence of EY, the electrode response (PGE/PAni) toward silver ion was also linear the same as that observed for PGME/PAni-EY, but the electrode was also suffered from poor reproducibility, selectivity and higher detection limit. It seems that partly formation of silver nanoparticles lowers detection limit and makes the potential development more feasible. Moreover, incorporation of EY with its  $\pi$ -electrons and  $\pi$ -coordinate groups has been found to improve the potentiometric response of the prepared electrode toward silver ion. The reproducibility and stability of the pencil graphite electrode was evaluated by repeated calibration with silver nitrate solution. Repeated monitoring and

calibration over several days, using this electrode, gave good slope reproducibility ( $\leq 0.8$  mV decade<sup>-1</sup>) as given in Table 1. The sensitivity of the electrode does not change when the potential are recorded from low to high and vice versa.

**Table 1.** Specifications of the PGE/PAni-EY

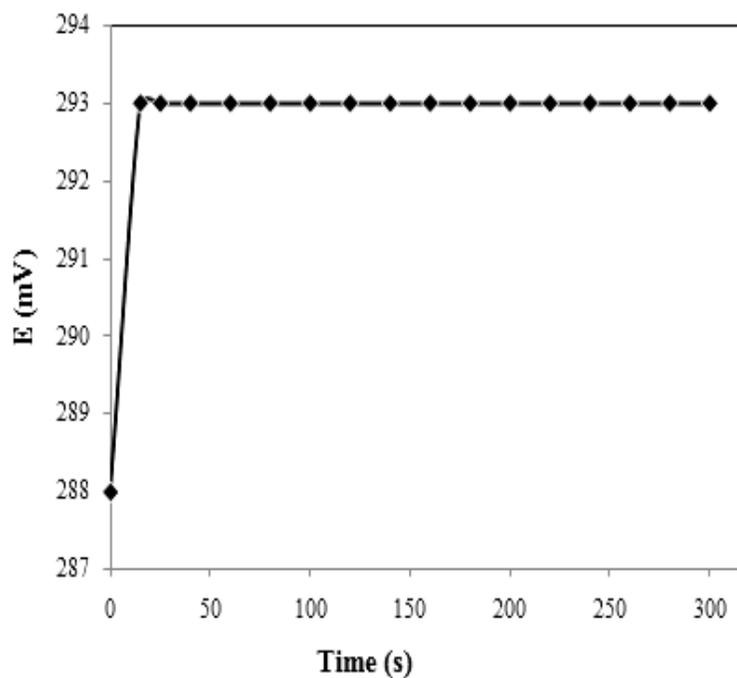
Properties	Values/range
Optimized film composition	PAni (67%), EY (33%),
Electrode type	Pencil graphite electrode (PGE)
pH range	4.0 -5.5
Conditioning time	At least 48 h in $10^{-2}$ M Ag <sup>+</sup>
Linear range (Ag <sup>+</sup> , M)	$1 \times 10^{-6}$ to $1 \times 10^{-1}$
Slope (mV decade <sup>-1</sup> )	57.6
Detection limit (M)	$\sim 6.4 \times 10^{-7}$
SD of slope (mV decade <sup>-1</sup> )	$\pm 0.8$
Response time (s)	$\sim 15$ s
Life time of the electrode	At least for 3 months

### 3.3. Static response time PGE/PAni-EY

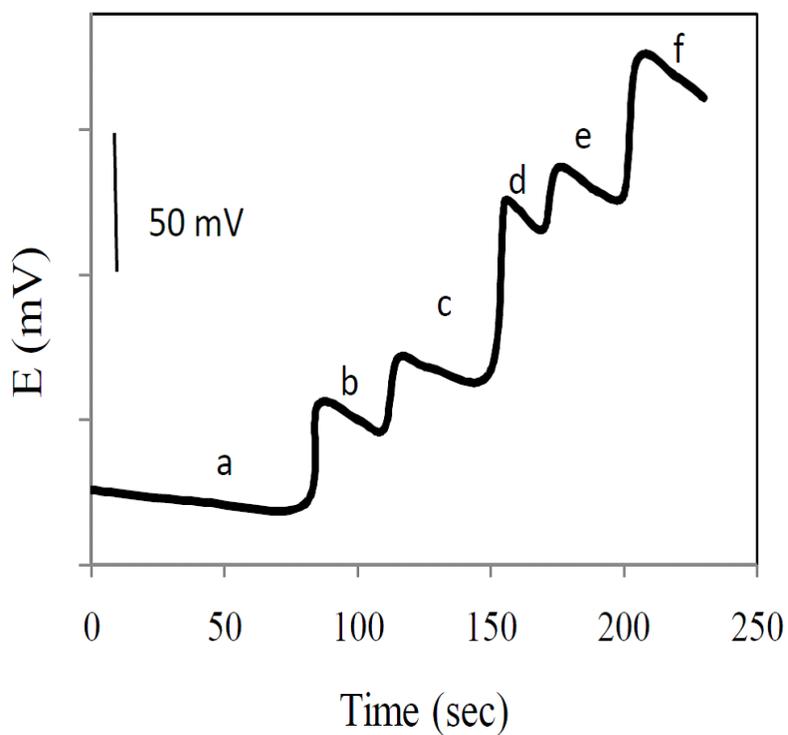
In order to test the stability of the potential reading of the electrode, it was put in a  $1.0 \times 10^{-4}$  M of silver ion. As the results interestingly show (Fig. 4) a very stable potential within 15 s was observed. Even after 5 minutes not any potential drift was observed (less than 1 mV).

### 3.4. Dynamic response time of the electrode

Dynamic response time, as an important factor for an ion selective electrode was also determined [29]. In this study, the practical response time was recorded by changing solution with different Ag<sup>+</sup> concentrations from  $10^{-5}$  to  $5.0 \times 10^{-3}$  M. The response time of the electrode was measured after successive immersion of the electrode in a series of Ag<sup>+</sup> solutions, in each of which the Ag<sup>+</sup> concentration increased tenfold from  $1.0 \times 10^{-5}$  to  $5.0 \times 10^{-3}$  M. The static response time thus obtained was 15 s for  $5.0 \times 10^{-2}$  M of silver ion solution. The actual potential vs. time trace is shown in Fig. 5.



**Fig. 4.** Static response time PGE/PAni-EY in a  $1.0 \times 10^{-4}$  M of silver ion

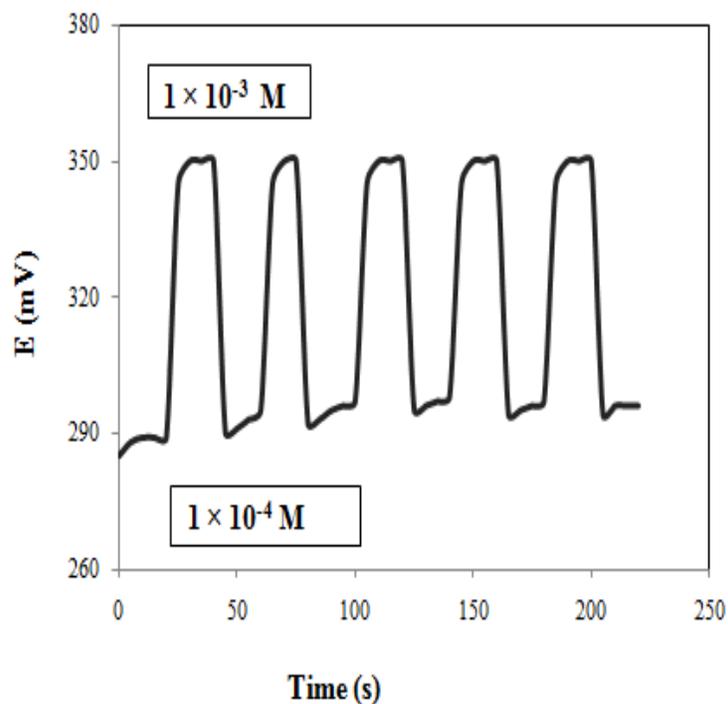


**Fig. 5.** Dynamic response time of the PGE/PAni-EY for step changes in concentration of  $Ag^+$  ion: (a)  $1.0 \times 10^{-5}$  (b)  $5.0 \times 10^{-5}$  (c)  $1.0 \times 10^{-4}$  (d)  $5.0 \times 10^{-4}$  (e)  $1.0 \times 10^{-3}$  (f)  $5.0 \times 10^{-3}$

As can be seen, the electrode reaches the equilibrium response in a time of about 15 s. The static response time thus obtained was 15 s for  $1.0 \times 10^{-4}$  M of  $\text{Ag}^+$  concentration. The electrode responses to silver ion are reversible and fast and they reached stable potentials in less than 15 s and remained constant for approximately 5 min, after which very slow changes within the resolution of the meter were recorded.

### 3. 5. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure with opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results are shown in Fig. 6. It shows that the potentiometric responses of the sensor was reversible and without any memory effect, although the time needed to reach equilibrium values were longer than that of low-to-high sample concentration. Noteworthy, it is well documented that, in the case of high-to-low concentration, the time needed to attain a stable potential is some 100 times larger than that required for the case of low-to-high concentrations (for a 10 times change in the cation concentration) [17].



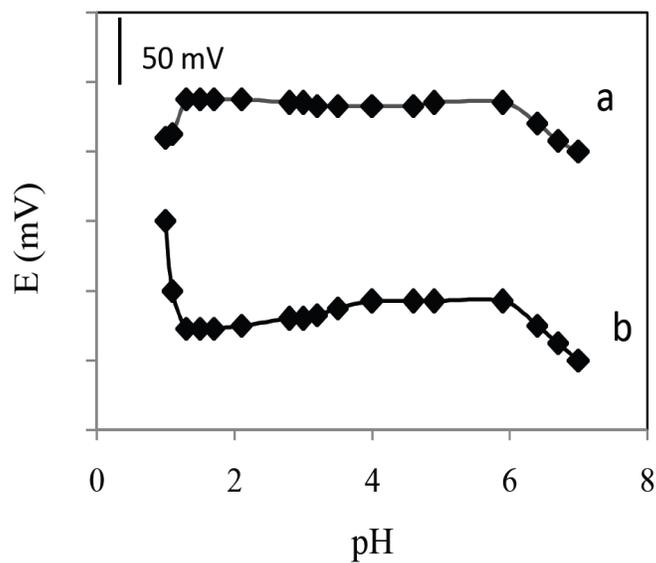
**Fig. 6.** Response characteristics of the PGE/PAni-EY for several high to-low sample cycles

Reproducibility of electrode was examined by using ten similar constructed electrodes under the optimum conditions. The results showed good reproducibility for the prepared electrode. For instance, the slopes observed were  $57.6 \pm 0.8$  mV/decade. The relative life time of the electrode was studied by periodically recalibrating in standard  $\text{Ag}^+$  solutions and calculating the response slope over the range of  $1.0 \times 10^{-6}$  M to  $1 \times 10^{-1}$  M  $\text{AgNO}_3$  solution. During this period, the electrode was in weekly use. Before each measurement, the electrode was conditioned for several hours in  $10^{-2}$  M  $\text{AgNO}_3$  solution. The fabricated silver ion solid state selective electrode was repeatedly calibrated 10 times over a period of 3 months, no significant change was observed in the linear range, slope of the calibration graphs (maximum deviation observed was  $\pm 2$  mV/decade). The response of the prepared electrodes has been studied in silver nitrate solutions in the range of  $1 \times 10^{-7}$  to  $1 \times 10^{-1}$  M at a fixed pH of 4.5. The amount of Eosin Y was changed while maintaining the same amount of EB in all of the films. The concentration of Eosin Y was varied from 33 to 50%. Optimum carrier amount for the electrodes based on Eosin Y were found to be 33%. Higher concentrations of Eosin Y resulted in lower sensitivity and decreased linear detection limit for silver ion.

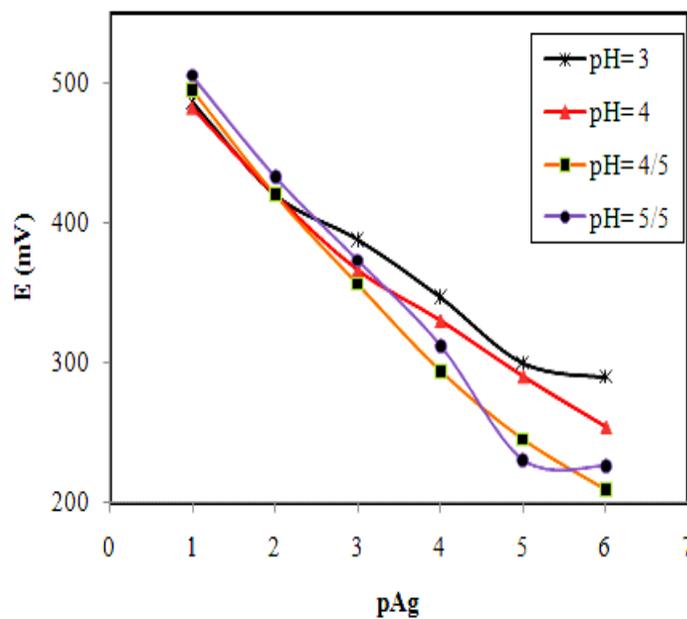
### 3.6. Effect of pH

The response of the PGE/PAni-EY toward solution pH was studied in the pH range from 1 to 7 using  $1 \times 10^{-3}$  M and  $1 \times 10^{-2}$  M  $\text{Ag}^+$  concentrations. The pH was adjusted by addition of dilute nitric acid or sodium hydroxide, as appropriate. It was observed that the potential responses were independent of pH over the range of approximately 1.5–6 for the electrode based on EY (Fig. 7). Variation of the potential at  $\text{pH} < 1.5$  could be related to protonation of PAni in the aqueous phase. At higher pH ( $>6$ ), the potential drop (negative slope) may be due to interference of hydroxide ions. Furthermore polyaniline is changed into a nonconducting material at  $\text{pH} > 4$ .

In order to investigate the effect of pH on the slope of the prepared electrode (PGE/PAni-EY), the electrode potential in different concentrations of silver ions was recorded at different pH values (3, 4, 4.5 and 5.5). The data recorded are shown in Fig. 8 and the slope and regression coefficients obtained have been summarized in Table 2. Based on linearity and Nerstian of the responses, pH of 4.5 and 5.5 were found the best pH values for potentiometric analysis using the fabricated silver electrode. All the further experiments were carried out at pH value of 4.5 which the response of electrode was very close to Nerstian with the highest value of  $R^2$ .



**Fig. 7.** Effect of pH on response of PGE/PAni-EY silver electrode at two different silver ion concentrations; (a) 10<sup>-2</sup> M, and (b) 10<sup>-3</sup> M



**Fig. 8.** Effect of pH on potentiometric response of PGE/PAni-EY electrode to silver ion

**Table 2.** Effect of pH on the slope and linearity of the response PGE/PAni-EY electrode to silver ion

pH	Concentration (M) range	Slope (mV/decade)	R <sup>2</sup>
3.0	10 <sup>-1</sup> – 10 <sup>-6</sup>	39.5	0.9700
4.0	" "	44.7	0.9868
4.5	" "	57.6	0.9879
5.5	" "	59.0	0.9733

### 3.7. Selectivity of the prepared electrode

Preliminary experiments revealed that PGE/PAni-EY was highly selective to Ag<sup>+</sup> ion with respect to several alkali, alkaline earth, transition and heavy metal ions (except for Hg<sup>2+</sup>). The selectivity is clearly one of the most important characteristics of a potentiometric sensor, which represents the preference of a sensor for the response to primary ion over other (interfering) ions that are present in the solution. Potentiometric selectivity coefficients ( $K_{Ag,B}^{pot}$ ) were evaluated according to IUPAC guidelines using separate solutions method (SSM) in which the potential of a cell comprising the sensor electrode and a reference electrode is measured with two separate solutions, one containing the silver ion A of the activity  $a_A$  (but no B) and the other containing the interfering ion B of the same activity  $a_A=a_B$  (but no A) [31,32]. Here the measured potential values are expressed by  $E_A$  and  $E_B$ , respectively. Different interfering anions of a concentration of 0.10 M (nitrate salts) were utilized and the results are obtained using the following equation (Eq.3):

$$\log K_{A,B}^{pot} = \frac{E_B - E_A}{S} + \left( \frac{1 - Z_A}{Z_B} \right) \log a_A \quad (3)$$

Where  $K_{A,B}^{pot}$  is the potentiometric selectivity coefficient, S the slope of the calibration plot,  $a_A$  the activity of silver, and  $Z_A$  and  $Z_B$  are the charges on Ag<sup>+</sup> and the interfering cation, respectively. The values of the selectivity coefficients obtained by this method are summarized in Table 3.

As it is evident from the data in Table 3, the  $\log K_{pot} Ag^+, X^-$  were less than -3 for mono and divalent cations (except for Hg<sup>2+</sup>) and the electrode can, therefore, be used for Ag<sup>+</sup> determination in the presence of several other cations without any important interference. It can be concluded that the present Ag<sup>+</sup> ion-selective electrode based on Eosin Y is highly selective towards silver ion and have fast response time, high selectivity, wide linear range and low detection limit.

**Table 3.** Selectivity coefficients of PGE/PAni-EY determined using Separate Solutions Method

Interfering ion	$\log K^{\text{pot}}_{\text{Ag}^+, \text{X}^-}$	Interfering ion	$\log K^{\text{pot}}_{\text{Ag}^+, \text{X}^-}$
Na <sup>+</sup>	-5.2	Pb <sup>2+</sup>	-4.84
K <sup>+</sup>	-4.34	Fe <sup>2+</sup>	-3.97
Hg <sup>2+</sup>	-1.1	Zn <sup>2+</sup>	-4.75
Cu <sup>2+</sup>	-2.93	Mg <sup>2+</sup>	-4.84
Co <sup>2+</sup>	-4.77	-	

### 3.8. Shelf lifetime of PGE/PAni-EY

In order to find out the useful shelf time of the prepared silver sensor electrode, the potentiometric responses of the electrode was measured at different time intervals and the slope of the electrode obtained from the calibration curve were then compared (Table 4).

**Table 4.** Environmental stability (shelf time) of PGE/PAni-EY electrode

Time (day)	Electrode Slope (mV/decade)	
1	57.6	
10	57.4	
17	56.8	
26	56.1	
35	54.6	$\bar{X} = 54.6$
45	54.2	
57	53.1	SD = $\pm 2.1$
66	53.4	
78	52.5	
85	52.4	
90	52.2	

### 3.9. Potentiometric titration of silver ion using PGE/PAni-EY electrode

PGE/PAni-EY with Hg/Hg<sub>2</sub>Cl<sub>2</sub> double junction reference electrode were used for monitoring the titration of silver ion solutions with standard solution of  $1 \times 10^{-2}$  M NaCl (as titrant). The silver indicator and calomel reference electrodes were immersed in a known Ag<sup>+</sup>

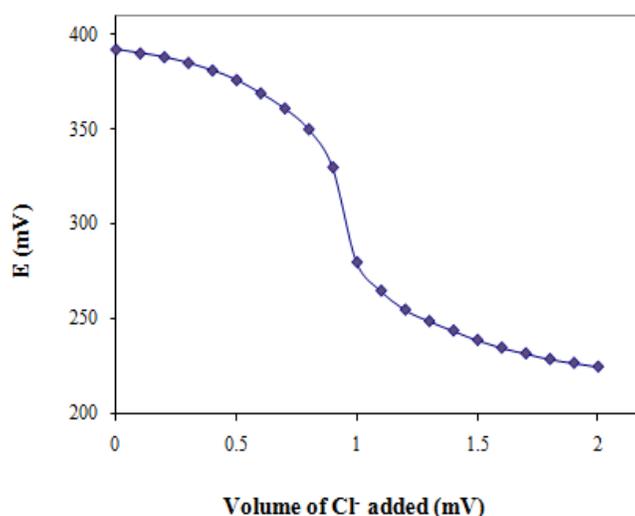
test solution (10.0 mL of  $1.0 \times 10^{-3}$  M) in a 50 mL beaker. The potential readings were recorded after each addition and the titration curve was plotted (Fig. 9). The equivalence point was calculated from the sharp inflection and well defined equivalence point.

As the potentiometric titration curve shows, the fabricated silver electrode can be used as indicator electrode for determination of silver ion via potentiometric titration successfully. The prepared silver electrode was also used for potentiometric titration of ternary mixture of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ), with a standard silver ion solution. The obtained titration curve is presented in Fig. 10. This suggests the possibility of sequential titration of three halide ions in the same solution without prior separation, as sequential binding of the halide ions with  $\text{Ag}^+$  ensures stepwise titration curves with sequential end point breaks.

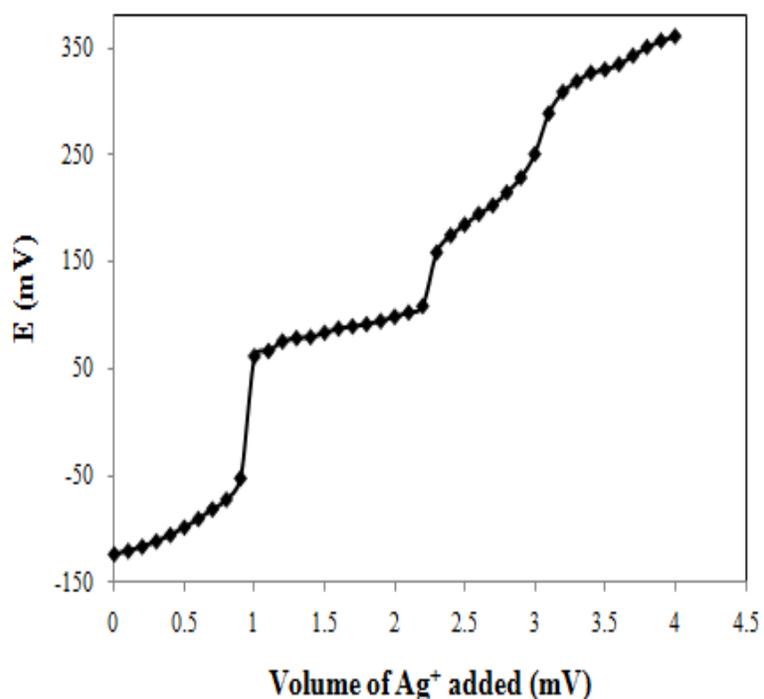
As the results show (Figs.9&10) the PGE/PAni-EY can be successfully applied as indicator electrode in potentiometric titration of silver ion with chloride and vice versa. Very good inflection points, showing perfect stoichiometry, were observed in all titrations.

### 3.10. Analysis of real samples

In order to examine the applicability of the fabricated electrode for determination of silver ions in real water solutions, a commercial grade mineral water (Nestle) containing various inorganic salts was selected. Determinations of silver in real samples were performed via spike or standard addition method [33]. The concentration of silver ion was changed from 0.050 to 0.0050 M by addition of a standard silver solution prepared from silver nitrate stock solution. The potentials were recorded using PGE/PAni-EY electrode as described before and the obtained concentrations from the calibration curve are shown in Table 5. As the results show, the introduced electrode can be used to measure silver ion in real samples with high precision.



**Fig. 9.** Potentiometric titration curve of  $1.0 \times 10^{-3}$  M silver ion with a standard solution of NaCl (0.01 M) using PGE/PAni-EY as indicator electrode



**Fig. 10.** Potentiometric titration plot of halides mixture ( $1.0 \times 10^{-3}$  M) with  $1.0 \times 10^{-2}$  M  $\text{Ag}^+$  using PGE/PAni-EY as indicator electrode

**Table 5.** Application of PGE/PAni-EY electrode for determination of silver ion in three commercial mineral drinking waters

Sample No.	Concentration (M)	Measured concentration	SD
1	$5.0 \times 10^{-3}$	$6.1 \times 10^{-3}$	$\pm 0.4 \times 10^{-3}$
2	$1.0 \times 10^{-2}$	$1.1 \times 10^{-2}$	$\pm 0.25 \times 10^{-2}$
3	$5.0 \times 10^{-2}$	$5.1 \times 10^{-2}$	$\pm 0.22 \times 10^{-2}$

In the last the performance of the introduced silver electrode was compared with some of silver ion selective electrodes which have previously been reported (Table 6).

**Table 6.** Comparison of some important characteristics of PGE/PAni-EY electrode with some of the previously reported silver electrodes

Shelf time (day)	Response time (s)	Slope (mV/decade)	Linear range (M)	Silver sensor electrode
30	10	61.4	$5.0 \times 10^{-8} - 1.0 \times 10^{-1}$	Ref. 34
8	20	60	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	Ref. 35
90	10	60.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	Ref. 36
60	10	59.0	$2.0 \times 10^{-8} - 1.0 \times 10^{-2}$	Ref. 37
90	15	57.6	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	<b>This study</b>

As it can be seen, the introduced electrode shows comparable or even superior characteristics over them in spite of its cost effective and simplicity of preparation.

#### 4. CONCLUSIONS

A potentiometric silver solid state sensor electrode based on EY shows fast, stable, reproducible, and selective characteristics toward silver ion. The sensor displays an almost Nernstian response ( $57.6 \text{ mVdecade}^{-1}$ ), offers a wide linear response range ( $1 \times 10^{-1}$  to  $1 \times 10^{-6}$  M), provides a lower limit of detection ( $6.4 \times 10^{-7}$  M), and exhibits much better selectivity than some previously reported  $\text{Ag}^+$  sensors. Synthesis of polymer/nanoparticles composite materials combine with the unique properties of silver nanoparticles possess new properties, which are not specific to the original components and make its perspectives attractive. The sensor has satisfactorily been used for determining of very small quantities of silver ions in real samples and for measurements of halides in aqueous solutions via potentiometric titration. Simplicity of the preparation as well as its high shelf lifetime makes this finding very important for both analytical and environmental monitoring applications.

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