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A highly sensitive and selective bulk optode based on benzimidazol derivative as an ionophore and ETH5294 for the determination of ultra trace amount of silver ions

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ABSTRACT

A novel optical chemical sensor (optode) was fabricated for the determination of silver ions. The optical sensor was prepared by incorporating recently synthesized ionophore, 7-(1H-benzimidazol-1-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatriaza cyclopentadecine-3,11(4H,12H)-dione, sodium tetraphenyl borate (NaTPB) as an anionic additive, 3-octadecanoylimino-7-(diethylamino)-1,2-benzo-phenoxazine (ETH5294) as a chromoionophore, and dioctyl phthalate (DOP) as a plasticizer in a poly(vinyl chloride) membrane. The effect of several parameters in determining Ag^+ was studied and optimized. The spectrophotometric method (λ_{max} of 660 nm) was used for the determination of Ag^+. Under the optimum conditions, the optical sensor has a wide dynamic range of 1.02×10^{-11} to 8.94×10^{-5} mol L^{-1} Ag^+ with the detection limit as low as 2.8×10^{-12} mol L^{-1}. The response time of the sensor was ~150 s, with a RSD% of 0.4% (for 1.0×10^{-6} mol L^{-1}, $n=7$). The optode could be regenerated by 0.2 mol L^{-1} HCl solution. The interferences of potential interfering ions were studied. It was shown that the new optode was very selective to silver ions and had no significant response to common ions such as Mn^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+}, and Co^{2+}. It can be claimed that the sensor can specifically detect silver ions. The sensor was successfully applied for the determination of silver ions in different real samples.

1. Introduction

Optical sensors have received considerable attention in recent decades because of their advantages in comparison to ion-selective electrodes. Among such advantages, one can refer to ease of production, cheapness, good selectivity and sensitivity, high dynamic concentration range and also, low detection limit. In addition, for optodes, unlike ion-selective electrodes, there is no interference of electrical noises and they need no external reference [1–4].

Bulk optodes are one kind of such sensors with the analyte being extracted into their bulk membrane (and not merely on their surface). In bulk sensors, in addition to selective ionophore there are lipophilic sites that have charges opposite to analyte plus a secondary ionophore, called chromoionophore [5] or fluoroionophore [6]. Chromoionophore is usually an acid–base indicator. The color depends on the amount of protons of the solution being considered. By extracting analyte into the bulk of a membrane, the chromoionophore releases its proton to keep charge balance and change its color. The changes on absorption bands are measured by a spectrophotometer [3]. Until now, few optodes have been designed for the detection of several metal ions, among which mercury [7–11], selenium [12], nickel [13,14], zinc [15], copper [16], lead [17], and thallium [18] can be enumerated, although few optodes have been reported for silver [19–21].

Silver ions, as a heavy metal ion, likewise cadmium, chromium, copper, and mercury, is located in one of the most poisonous categories of toxic ions [22]. Due to the growing use of silver in medicine and industries, it could be found in the environment [23,24]. Various methods have been proposed for silver detection, including the application of ion-selective electrodes [25,26], flame absorption spectroscopy [27], inductively coupled plasma [28], and stripping voltametry [29]. Furthermore, because of the need to determine low concentration of silver in different samples, the sample preconcentration step has been widely required prior to its analysis [27–31].

In the present work, a recently synthesized ionophore [32], 7-(1H-benzimidazol-1-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1,

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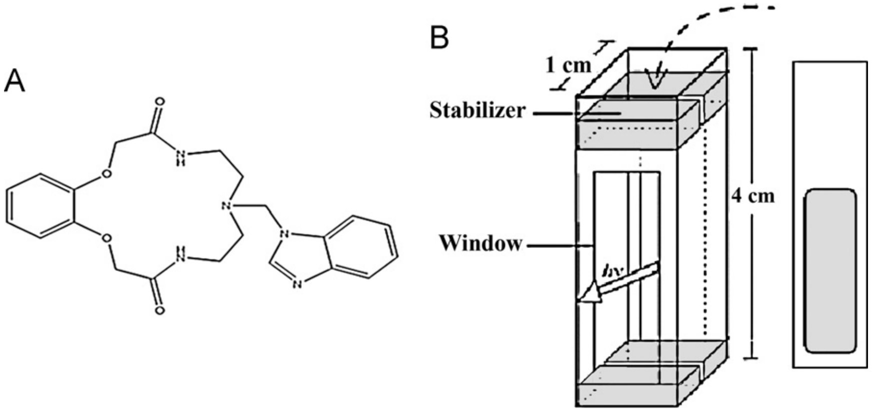

Fig. 1. (A) Structure of the ionophore. (B) A cell with the holder that used for the absorbance measurements.

13,4,7,10-benzodioxatriaza cyclopentadecine-3,11(4H,12H)-dione, (Fig. 1A) in PVC membrane containing a plasticizer and 3-octadecanoylimino-7-(diethylamino)-1,2-benzophenoxazine (ETH5294) was prepared. A highly selective optical chemical sensor is designed for detection of very low concentrations of silver ions without any pre-concentration steps. The detection limit and selectivity of this optode was comparable to those of all optical sensors mentioned above.

2. Experimental

2.1. Chemicals

7-(1H-benzimidazol-1-ylmethyl)-5,6,7,8,9,10-hexahydro-2H-1, 13,4,7,10-benzodioxa-triazacyclopentadecine3,11(4H,12H)-dione, $C_{22}H_{25}N_5O_4$ (MW: 423.465), is used as an ionophore which was prepared according to the method reported [32]. The ionophore is a white powder with m.p. of 180 °C. IR (KBr): 741(s), 818(m), 1049(s), 1126(s), 1215(m), 1261(s), 1450(m), 1504(s), 1535(s), 1597(w), 1678(υs), 2858(w), 3421(s) cm^{-1}. 1H–NMR (CDCl$_3$, 250 MHz): δ=2.84 (*t*, 4H, *J*=5.1 Hz), 3.61 (*t*, 4H, *J*=5.3 Hz),4.46 (s, 4H), 5.07 (s, 2H), 6.86–7.05 (m, 4H), 7.13–7.26 (m, 2H), 7.37 (s, 2H), 7.46 (d, 1H, *J*=7.9 Hz), 7.77 (d, 1H, *J*=7.7 Hz), 7.93 (s, 1H). 13C NMR (CDCl$_3$, 62.9 MHz): δ=35.2, 50.3, 60.3, 67.5, 109.6, 113.5, 120.5, 122.6, 123.6, 134.3, 143.3, 146.5, 167.6.

Analytical reagent grade chemicals (with the highest degree of purity available and free of silver ions) and tetrahydrofuran (THF), both from Merck, and deionized water were used throughout. ETH5294 and polyvinyl chloride (PVC) were obtained from Fluka. Dioctyl sebacate (DOS), dibutyl phthalate (DBP), dioctyl phthalate (DOP), and sodium tetraphenyl borate (NaTPB), all from Aldrich, were also used.

Buffer solution (0.1 mol L^{-1}) of pH 6.25 was prepared sodium citrate with addition of suitable amounts of nitric acid.

A stock solution of 0.010 mol L^{-1} Ag^{+} ions was prepared by dissolving an appropriate amount of AgNO$_3$ into a 100 mL standard flask and diluting it to the mark with deionized water. Lower concentrations were prepared by appropriate dilution of the stock solution with citrate buffer of pH 6.25.

2.2. Apparatus

A double beam UV–vis spectrophotometer (Cary 500 Scan, Varian, Palo Alto, CA, USA) with 1.0 cm quartz cells containing plastic holders (Fig. 1B) was used for the absorbance measurements.

pH measurements were taken by the pH/ion meter (Metrohm, Herisau, Switzerland), Model 827, which was equipped with a combined glass electrode.

Atomic absorption spectrometer, Shimadzu Model AA670 (Tokyo, Japan), furnished with an Ag-hollow cathode lamp was used. All of the parameters were adjusted according to the standard recommendation of the factory.

2.3. Membrane preparation

A typical membrane consisted of 31.0 mg PVC, 62.0 mg DOP, 2.0 mg NaTPB, 2.0 mg ionophore, and 2.0 mg ETH5294 dissolved in 1.0 mL of THF. The mixture was stirred with a magnetic stirrer for 15 min to achieve a homogeneous solution. A glass slide with 9 mm × 50 mm was selected and cleaned with 1.0 mol L^{-1} sulfuric acid and sodium hydroxide solutions, respectively. Then, it was washed with water and dried in an oven at 110 °C for 1 h. The membrane was cast by pipetting a 20 μL aliquot of the membrane solution onto the glass slide, and spreading it rapidly using a capillary glass tube. The membrane was allowed to stand in room temperature to dry for 4 h.

2.4. Measurement procedure

The sensor was placed in a 1.0 cm quartz cell (Fig. 1B) containing $\sim$3 mL of the citrate buffer solution (pH 6.25). After 150 s, its absorbance was measured at 660 nm. This procedure was repeated for a set of Ag^{+} standard solutions at different concentrations and the calibration curve was obtained by plotting their absorbance. In this way, the Ag^{+} concentration contained in the sample can be calculated from the calibration curve. The optode was regenerated in 0.2 mol L^{-1} HCl solution for $\sim$300 s and ready to use.

2.5. Sample preparation

Digestion of Silver Sulfadiazine (1.0% topical cream) was done by burning the cream in an oven and then dissolving its ash in the concentrated HNO$_3$. The resulting mixture was filtered and then diluted with deionized water. This solution was diluted with the citrate buffer of pH 6.25.

Polymetallic ore samples were prepared by acid digestion method according to the published procedure [33]. 0.300 g of the sample was transferred into a 15 mL polytetrafluoroethylene (PTFE) crucible in which a mixture of 3 mL of concentrated HCl, 3.0 mL of concentrated HF, 3.0 mL of concentrated HNO$_3$ and 0.5 mL of concentrated HClO$_4$ was added. Under gentle heating on a hot-plate at 120–150 °C, the sample was evaporated to almost complete dryness. After cooling to room temperature, the residue was dissolved in water on a hot plate. The final solution was made up to 20 mL. Then, 1.0 mL of the solution was diluted to 25 mL with the citrate buffer (pH 6.25) in a 25 mL standard flask.

Zayanderood river water was collected in polyethylene bottle and two drops of nitric acid was added. River water sample was filtered to remove any solid particles before analysis. Standard Ag^+ solution was spiked into 20 mL of the mineral water. The water samples were buffered and adjusted to pH 6.25. The absorbance measurement of the optode was performed under the optimum conditions. For all real samples the experiments were performed in six replicate measurements ($n=6$).

3. Results and discussion

3.1. Principle of the operation

The ionophore has –NH group and a suitable cavity that can interact with Ag^+ ions. It seems that the cavity size plays an important role in membrane selectivity. The organic membrane contains ionophore, chromoionophore (acid–base indicator), and anionic additive stabilized in polyvinyl chloride (which was plasticized by DOP). As previously mentioned, chromoionophore is an acid–base indicator, and its color depends on the amount of protons of the considering solution. By extraction of Ag^+ ion into the bulk of the membrane and complexation with the ionophore, the chromoionophore releases its proton to keep charge balance, and changes its color. This change could be measured by UV–vis spectrophotometer. When the membrane sensor is in contact with an aqueous solution containing silver ions, these ions interact with the membrane and form a complex with the ionophore; therefore, the charge balance is annihilated in the membrane. Renewing the charge balance makes it possible for cation exchange equilibrium to take place as can be seen below

$$Ag^+_{(aq)} + nL_{(org)} + HIn^+_{(org)} \leftrightarrow AgL^+_{n(org)} + In_{(org)} + H^+_{(aq)} \quad (1)$$

In this equation, 'n' is the stoichiometric coefficient of the ionophore in the complex formed, 'L' is the ionophore, In and HIn^+ are neutral and charged H^+–chromoionophore, respectively.

It can be seen that by the addition of silver ions into the aqueous solution, the chromoionophore is more deprotonated. The following equation gives the equilibrium constant of this ion-exchange reaction (3):

$$K_{exch} = (a_H[In]/[HIn^+])([AgL_n{}^+]/a_{Ag^+}[L]^n) = (K_a/K_{H^+})K_{Ag^+}\beta_{AgLn} \quad (2)$$

K_{exch} is a function of relative lipophilicity of silver ion and proton (K_{Ag} and K_H^+ respectively), stability of the complex formed (β^+_{AgLn}), and the acidity constant of the chromoionophore (K_a). The function of the sensors response to silver ion can be shown by [33]

$$a_{Ag+} = (K_{exch})^{-1} \times [(\alpha/1-\alpha)a_H{}^+] \times \{R_T-(1-\alpha)C_T\}/\{(L_T-R_T+(1-\alpha)C_T) \times n\} \quad (3)$$

Here, C_T, R_T, and L_T are analytical concentrations of the chromoionophore, anionic additive, and the ionophore, respectively; α is also the normalized absorption and a_H+ is the H+ activity.

All absorption measurements of chromoionophore have been performed at λ_{max} of its protonated form, which is 660 nm. The following equation gives the relative fraction of the deprotonated form of the chromoionophore [34]:

$$(1-\alpha) = \{[HIn^+]/([HIn^+]-[In]\} = 1-\{(A_p-A)/(A_P-A_D)\} \quad (4)$$

A_P and A_D are absorptions of the chromoionophore when completely protonated and deprotonated, respectively. Fig. 2 shows the changes in the spectrum of the membrane sensor as a function of silver ions concentration in aqueous solution at pH 6.25. The isobestic point on Fig. 2 confirms that the change in the absorbance of the optode is due to a simple chemical equilibrium between the two forms of the chromoionophore (HIn^+, In) in the membrane.

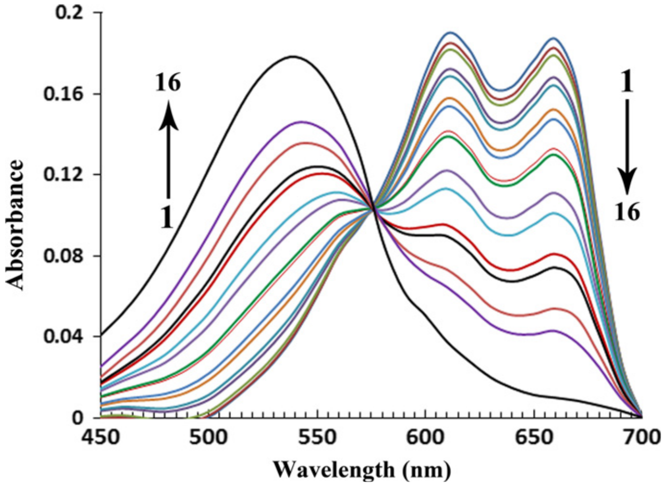

Fig. 2. Absorption spectra of optical sensor in citrate buffer solution (pH 6.25). Containing different concentration of Ag^+ (mol L^{-1}) as: (1) Blank solution (buffer); (2) 1.0×10^{-11}; (3) 5.0×10^{-11}; (4) 1.0×10^{-10}; (5) 5.0×10^{-10}; (6) 1.0×10^{-9}; (7) 5.0×10^{-9}; (8) 1.0×10^{-8}; (9) 5.0×10^{-8}; (10) 1.0×10^{-7}; (11) 5.0×10^{-7}; (12) 1.0×10^{-6}; (13) 5.0×10^{-6}; (14) 1.0×10^{-5}; (15) 5.0×10^{-5} and (16) 1.0×10^{-4} mol L^{-1}.

3.2. Optimizing the composition of the membrane components

Optodes response characters such as dynamic range and response time are related to the composition of the membrane components [3]. The single variable method was used to study the effect of the membrane compositions on the response of the optode. Thus, we prepared several membranes with different compositions as can be seen in Table 1. The response of each membrane was recorded in Ag^+ solutions with different concentrations. Based on the literature, the good ratio of plasticizer over PVC is 2:1 [7,18,20,35]. To select the best plasticizer, DOP, DOS, and DBP were tested (Table 1). The best membrane is one with more response range and better detection limits. The results showed that the compositions of the membranes specified by membranes 6, 9, and 12 are in agreement with the optimum compositions. Thus, 62.0 mg DOP, 2.0 mg NaTPB, 1.5 mg ETH5294, 31.0 mg PVC, and 2.0 mg of the ionophore (membrane no. 12, Table 1) were selected as the optimum membrane conditions.

3.3. Effect of sample solution pH

It is clear from Eq. (3) that apart from silver ions concentration, the optode response is also dependent on the solution pH. Therefore, the pH of the sample solution should be kept invariable using a suitable buffer. To find the optimum solution pH, different concentrations of silver(I) solutions were prepared in each pH, and the responses of the optical sensor in contact with those solutions were measured (Fig. 3). Fig. 3A shows the absorbance of the optode in solutions containing 1.0×10^{-7} mol L^{-1} Ag^+ at different pH, whereas Fig. 3B shows the calculated α *vs.* solution pH for the optode in solutions containing 1.0×10^{-7} mol L^{-1} Ag^+. Fig. 3C shows the response of the optode for different Ag^+ concentrations at different pH values. The results in Fig. 3 show that the best pH was 6.25. In higher pH values, hydroxyl ions could react with Ag^+ and therefore cause decreasing the

Table 1
Effect of composition of the membrane components (as mg) in the presence of 31 mg of PVC on the response of the optode.

No.	DOP	DOS	DBP	NaTPB	ETH5294	Ionophore	High and low detections limit (mol L−1)
1	62.0	–	–	2.0	1.5	1.5	9.6×10^{-11} to 1.3×10^{-4}
2	–	62.0	–	2.0	1.5	1.5	5.8×10^{-9} to 5.4×10^{-3}
3	–	–	62.0	2.0	1.5	1.5	9.8×10^{-10} to 1.8×10^{-3}
4	62.0	–	–	2.0	1.5	0.5	9.7×10^{-7} to 5.5×10^{-3}
5	62.0	–	–	2.0	1.5	1.5	7.5×10^{-9} to 1.0×10^{-2}
6	62.0	–	–	2.0	1.5	2.0	2.2×10^{-12} to 4.05×10^{-5}
7	62.0	–	–	2.0	1.5	2.5	1.1×10^{-11} to 2.9×10^{-4}
8	62.0	–	–	2.0	1.0	2.0	2.5×10^{-10} to 1.0×10^{-5}
9	62.0	–	–	2.0	1.5	2.0	2.2×10^{-12} to 4.05×10^{-5}
10	62.0	–	–	2.0	2.0	2.0	6.4×10^{-9} to 1.1×10^{-4}
11	62.0	–	–	1.0	1.5	2.0	1.3×10^{-9} to 4.7×10^{-4}
12	62.0	–	–	2.0	1.5	2.0	2.2×10^{-12} to 4.05×10^{-5}
13	62.0	–	–	3.0	1.5	2.0	1.8×10^{-12} to 4.2×10^{-5}
Optimum	62.0	–	–	2.0	1.5	2.0	2.2×10^{-12} to 4.05×10^{-5}

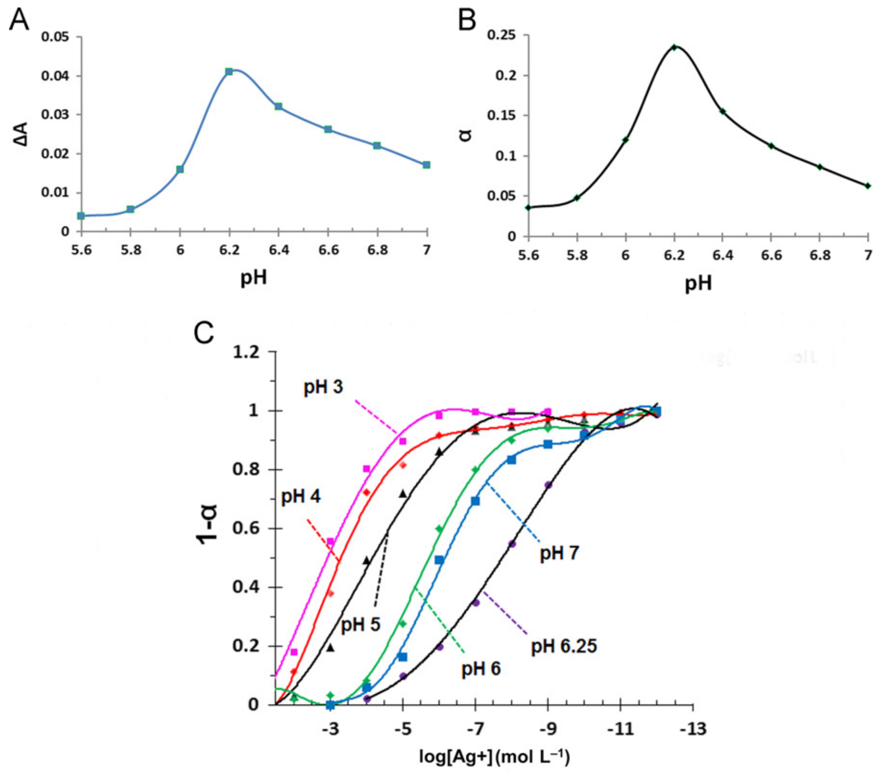

Fig. 3. (A) Absorbance of the optode in solutions containing 1.0×10^{-7} mol L^{-1} Ag^+ at different pH. (B) α *vs.* pH for the optode in solutions containing 1.0×10^{-7} mol L^{-1} Ag^+ at different pH values. (C) Response of the optode for different Ag^+ concentrations at different pH values.

concentration of Ag^+. In addition, decreasing in the response of the optode at lower pH is possibly due to the taking out of proton (H^+) from the aqueous solution into the membrane sensor and decreasing the exchange rate between Ag^+ (in solution) and H^+ (from the membrane). In addition, decreasing in the response of the optode at lower pH is possibly due to the competition between Ag^+ and H^+ for the active place in the membrane and therefore, increasing in H^+ from the solution, decreases the exchange rate between Ag^+ and H^+ from the membrane.

3.4. *Response time*

Response time of the optical sensor is the time it takes to obtain a constant value while it is located in a sample solution; in other words, it is the time necessary for the sensor layer to attain equilibrium with the sample solution. Except for very thin membranes, diffusion in organic phase is the time limiting step. Eq. (5) gives the period needed to attain 95% of steady state [3].

$$t_{95\%} = 1.13D^2/D_m \tag{5}$$

To obtain the response time, the optical sensor was put in a sample solution, and the changes in the absorption (or 1−α) of the membrane in λ_{max} was plotted *vs.* time. As can be seen in Fig. 4, the response time for Ag^+ concentrations of 1.0×10^{-4}, 1.0×10^{-8}, and 1.0×10^{-11} mol L^{-1} are 50, 100, and 150 s, respectively. Therefore, we selected 150 s as a suitable response time to cover all the analyte concentration.

3.5. *Reproducibility and short-term stability*

Reproducibility of the membrane and its repeatability were studied. To consider the membrane reproducibility, six sensors were prepared, and solutions of 1.0×10^{-10} and 1.0×10^{-6} mol L^{-1} of silver ions were measured seven times by the sensors. The RSD% was calculated as: 1.3 (for 1.0×10^{-6} mol L^{-1}) and 0.3 (for 1.0×10^{-10} mol L^{-1})

To consider the repeatability of the optode, silver ion solutions with concentrations of 1.0×10^{-10} and 1.0×10^{-6} mol L^{-1} were measured seven times by the optode. The results showed the RSD% of 0.4 (for 1.0×10^{-6} mol L^{-1}) and 0.1 (for 1.0×10^{-10} mol L^{-1}).

In order to evaluate the short-term stability of the optical sensor, the membrane was put in a sample solution containing 1.0×10^{-6} mol L^{-1} Ag^+, and the absorption was measured for 10 h (once each hour, and 5 times repeating each measurement). The RSD% was equal to 0.35. This experiment showed that the optode had a good stability and reproducibility.

3.6. *Regeneration of the optical sensor*

It is necessary that the sensor membrane be regenerated by a suitable solution so that it would get ready for the following measurements. It can be understood from Eq. (1) that the reaction is reversed if the aqueous solution is acidified, or a ligand is added that would form a complex with silver ions; so, the silver ions can be extracted from organic layer, and the membrane may be regenerated. The best selected regenerator is a solution in which the absorption of the sensor membrane after regeneration step is not significantly different from its absorption when it is newly prepared. To select the best regeneration solution, mineral acids such as HNO_3, H_2SO_4, HCl, H_3PO_4 and also solutions of EDTA and KCl (all 0.1 mol L^{-1} in concentration) were tested. To do this, the optode was put in 1.0×10^{-6} mol L^{-1} silver solution and after attaining the equilibrium, it was expelled and put in the regenerating solution until the absorption of the membrane got stabilized. As can be seen in the data given in Table 2, hydrochloric acid (0.10 mol L^{-1}) presented the highest percentage of regeneration of the membrane.

4. Analytical figures of merit

Fig. 2 shows that the absorption (at $\lambda_{660\ nm}$) of the sensor is decreased as the concentration of silver ions is increased. In the optimum condition and pH of 6.25, the optode response (1–α) at

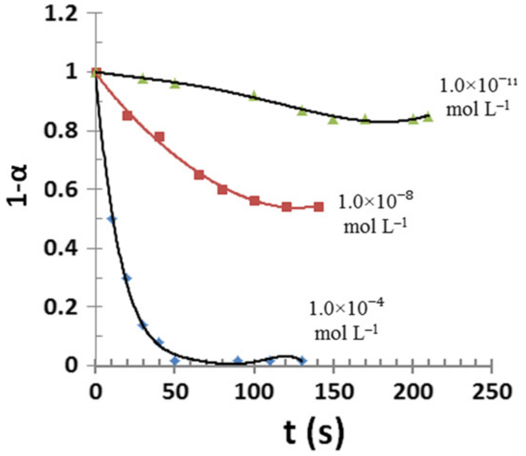

Fig. 4. Response time of the optode at pH 6.25.

Table 4
Interference study of potential interfering ions in the presence of 1.0×10^{-9} mol L^{-1} Ag^+.

Potentially interfering ions*	Relative error %
Mn^{2+}, Ti^{3+}, NH_4^+, MoO_4^{2-}, Pb^{2+}, Cr^{3+}, Al^{3+}, K^+, Cd^{2+} and Fe^{3+}	0.00
Ni^{2+}	3.95
Hg^{2+}	4.38
Co^{2+}, Mg^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+} and Cs^+	0.99
Li^+ and Ca^{2+}	1.98

* Tolerance limit for all potentially interfering ions was equal to 10,000.

Table 2
Regeneration of the optical sensor using 1.0×10^{-6} mol L^{-1} Ag^+.

Regenerations solution	Absorbance (fresh sensor)	Absorbance (after treatment)	Absorbance (regenerated sensor)	Regeneration (%)
HNO_3 (0.1 mol L^{-1})	0.1895	0.0315	0.1234	58.2
H_2SO_4 (0.1 mol L^{-1})	0.1869	0.0265	0.1371	68.9
H_3PO_4 (0.1 mol L^{-1})	0.1872	0.0321	0.0877	35.8
EDTA (0.1 mol L^{-1})	0.1889	0.0315	0.1102	50.0
KCl (0.1 mol L^{-1})	0.2015	0.0331	0.1265	55.5
HCl (0.1 mol L^{-1})	0.1918	0.0317	0.1841	95.2
HCl (0.2 mol L^{-1})	0.1892	0.0315	0.1875	98.9
HCl (0.5 mol L^{-1})	0.2129	0.0346	0.2080	97.2

Table 3
Comparison the analytical data of some method for the determination silver ions.

Method	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	RSD%	Reference
Optical chemical sensor	1.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-6}	–	19
Optical chemical sensor	5.0×10^{-9} to 5.0×10^{-5}	1.0×10^{-9}	0.67	20
Optical chemical sensor	up to 3.7×10^{-4}	9.3×10^{-8}	1.16	21
Ion selective electrode	1.0×10^{-6} to 0.1	2.0×10^{-7}	1.25	25
Ion selective electrode	1.0×10^{-6} to 1.0×10^{-1}	8.3×10^{-7}	–	26
Dispersive liquid–liquid microextraction, flame absorption spectroscopy	4.6×10^{-8} to 1.8×10^{-5}	1.1×10^{-8}	1.5	27
Inductively coupled plasma atomic emission spectrometry	9.27×10^{-7} to 9.27×10^{-5}	2.78×10^{-7}	1.79–8.30	28
Inductively coupled plasma mass spectrometry	1.85×10^{-9} to 4.63×10^{-6}	3.71×10^{-10}	2.26–4.79	28
Stripping voltammetry	6.5×10^{-7} to 9.3×10^{-6}	5.6×10^{-7}	1.5	29
Solid phase extraction, flame absorption spectroscopy	–	3.71×10^{-7}	4.44	30
Dispersive liquid–liquid extraction, flame absorption spectroscopy	9.27×10^{-10} to 9.27×10^{-8}	1.11×10^{-10}	3.5	31
Optical chemical sensor	1.02×10^{-11} to 8.94×10^{-5}	2.8×10^{-12}	0.41	This Work

Table 5
Determination of Ag+ in real samples.

Sample	Ag^+ added (mol L^{-1})	Ag^+ found*	GFAAS	$t_{cal.}$ ($t_{table(95\%,10)}$=2.23)
Mineral water	–	< Limit of detection	< Limit of detection	
	1.00×10^{-9}	$(0.99 \pm 0.21) \times 10^{-9}$	–	
	1.00×10^{-8}	$(9.82 \pm 0.23) \times 10^{-9}$	–	
	1.00×10^{-7}	$(9.87 \pm 0.20) \times 10^{-8}$	$(10.3 \pm 0.25) \times 10^{-7}$	2.22
	1.00×10^{-6}	$(9.86 \pm 0.12) \times 10^{-7}$	$(9.89 \pm 0.16) \times 10^{-7}$	2.10
Zayandehrood river water	–	$(6.23 \pm 0.18) \times 10^{-7}$	$(6.46 \pm 0.19) \times 10^{-7}$	1.53
Silver Sulfadiazine (1.0% topical cream)	–	(1.13 ± 0.02)%	(1.13 ± 0.02)%	0.25
Polymetallic ore (no. 1)	–	5.61 ± 0.31 μg g^{-1}	5.97 ± 0.13 μg g^{-1}	1.69
Polymetallic ore (no. 2)	–	6.67 ± 0.40 μg g^{-1}	6.54 ± 0.31 μg g^{-1}	0.41

* mol L^{-1} silver(I) found in the mineral water and Zayandehrood river water.

660 nm depends on the logarithm of the silver ions concentration in the range of 1.02×10^{-11} to 8.94×10^{-5} mol L^{-1} with a correlation equation of $(1-\alpha) = -0.1416 \log[Ag(I)]—0.5568$ ($r = 0.9971$, $n = 12$).

The detection limit (3 S/m, where *S* is the blank standard deviation ($n = 10$), and *m* is the slope of the calibration curve) was obtained as 2.8×10^{-12} mol L^{-1} Ag^+. Table 3 shows the figures of merit of the optode *vs.* previously reported methods for Ag^+ determination.

5. Selectivity

The effect of interfering ions on the selectivity of the optode was investigated. For this purpose, the response of the optical sensor was measured in a solution containing 1.0×10^{-8} mol L^{-1} Ag^+ under the optimum conditions. Then, the optical sensor response was measured in a solution containing the same concentration of silver ions and different concentrations of potentially interfering ions. These two responses were compared and the relative error was calculated. The results are shown in Table 4. Tolerance limit was defined as the concentration of added ions causing less than ±5% relative error [18]. Based on the results of the experiments conducted, the prepared optode is highly selective to Ag^+ to the extent that it has no significant response to common other ions. It can be claimed that the sensor can specifically detect silver ions.

6. Application

The sensor was used for the determination of Ag^+ in mineral water that is found to be free of silver. So the water samples were spiked with Ag^+ and the recoveries were calculated. The proposed optode was also used for the determination of Ag^+ ions in river water, Ag in polymetallic ore, and in Silver Sulfadiazine (1% topical cream). The accuracy of the results data were also checked with graphite furnace atomic absorption spectrometry (GFAAS). The results are given in Table 5.

7. Conclusion

We have successfully fabricated an optical chemical sensor for the determination of Ag^+. The proposed optical chemical sensor has such advantages as ease of production, low cost, good sensitivity and stability, regeneration ability, short response time, high dynamic concentration range and also low detection limit. In addition, the prepared optode is very selective to silver ion so that it has no significant response to other common ions such as Mn^{2+}, Ti^{3+}, Hg^{2+}, Fe^{3+}, MoO_4^{2-}, Pb^{2+}, Cr^{3+}, Al^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, and Zn^{2+}. The optical sensor can be claimed that the sensor can specifically detect silver ions. The sensor was also applied successfully for the determination of silver ions in real samples.

References

[1] W.R. Seitz, M.J. Sepaniak, CRC Crit. Rev. Anal. Chem. 19 (1988) 135–173.
[2] J. Janata, Anal. Chem. 64 (1992) 921A–927A.
[3] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083–3132.
[4] B. Valeur, I. Leray, Coord. Chem. Rev. 205 (2000) 3–40.
[5] J.P. Dix, F. Voglte, Chem. Ber. 114 (1981) 638–651.
[6] W.E. Morf, K. Seiler, B. Lehmann, C. Behringer, K. Hartman, W. Simon, Pure Appl. Chem. 61 (1989) 1613–1618.
[7] B. Khezri, M.K. Amini, A.R. Firooz, Anal. Bioanal. Chem. 390 (2008) 1943–1950.
[8] D. Compagnone, A. Ricci, M. Del Carlo, M. Chiarini, A. Pepe, C.Lo Sterzo, Microchim. Acta 170 (2010) 313–319.
[9] A. Yari, F. Papi, Sens, Actuators B 160 (2011) 698–704.
[10] A. Yari, H. Adelpour Abdoli, J. Hazard. Mater. 178 (2010) 713–717.
[11] A.A. Ensafi, M. Fouladgar, Sensors Actuators B 113 (2006) 88–93.
[12] L. dlC. Coo, I.S. Martinez, Talanta 64 (2004) 1317–1322.
[13] A. Yari, M.B. Gholivand, F. Rahhedayat, Measurement 44 (2011) 1691–1696.
[14] M.K. Amini, T. Momeni-Isfahani, J.H. Khorasani, M. Pourhossein, Talanta 63 (2004) 713–720.
[15] F. Abbasitabar, V. Shahabadi, M. Shamsipur, M. Akhond, Sensors Actuators B 156 (2011) 181–186.
[16] T.J. Sands, T.J. Cardwell, R.W. Cattrall, J.R. Farrell, P.J. Iles, S.D. Kolev, Sensors Actuators B 85 (2002) 33–41.
[17] A.A. Ensafi, Z. Nasr Isfahani, IEEE Sensors J. 7 (2007) 1112–1117.
[18] M. Fouladgar, A.A. Ensafi, Sensors Actuators B 143 (2010) 590–594.
[19] I. Murkovic, I. Oehme, G.J. Mohr, T. Ferber, O.S. Wolfbeis, Mikrochim. Acta 121 (1995) 249–258.
[20] M. Shamsipur, S. Rouhani, A. Mohajeri, M.R. Ganjali, Anal. Bioanal. Chem. 375 (2003) 692–697.
[21] M. Noroozifar, M. Khorasani-Motlagh, A. Taheri, R. Zare-Dorabei, Turk. J. Chem. 32 (2008) 249–257.
[22] H. Ratte, Environ. Toxicol. Chem. 18 (1999) 89–108.
[23] H. Rener, 4th Ed.,Ulmanns Encyklopadie der Technischen Chemie, vol. 21, Verlag Chemie, Weinheim, 1982.
[24] R. Soager, 1984. Metallic Raw Materials Dictionary, Bank Tobel, Zurich.
[25] M.E.M. Hassounaa, S.A.A. Elsuccarya, J.P. Grahamb, Sensors Actuators B 146 (2010) 79–90.
[26] C. Topcu, F. Coldur, M. Andac, I. Isildak, N Senyuz, H. Bati, Curr. Anal. Chem. 7 (2011) 136–145.
[27] S.Z. Mohammadi, D. Afzali, M.A. Taher, Y.M. Baghelani, Talanta 80 (2009) 875–879.
[28] Q.B. Lin, B. Li, H. Song, H.J. Wu, Food Add. Contam. 28 (2011) 1123–1128.
[29] H. Zejli, J.L. Hidalgo-Hidalgo de Cisneros, I.N. Rodriguez, K.R. Temsamani, Talanta 71 (2007) 1594–1598.
[30] H. Refiker, M. Merdivan, R.S. Aygun, Separ. Sci. Technol. 43 (2008) 179–191.
[31] P. Liang, L. Peng, Microchim. Acta 168 (2010) 45–50.
[32] H. Sharghi, R. Khalifeh, A.R. Salimi Beni, J. Iran. Chem. Soc. 7 (2010) 275–288.
[33] X. Cheng, K. Shao, S. Shen, S. Hu, H. Qiu, Geostand. Geoanal. Res. 35 (2011) 461–469.
[34] E. Bakker, W. Simon, Anal. Chem. 64 (1992) 1805–1812.
[35] C. Bualom, W. Ngeontae, S. Nitiyanontakit, P. Ngamukot, A. Imyim, T. Tuntulani, W. Aeungmaitrepirom, Talanta 82 (2010) 660–667.