



International Journal of ChemTech Research CODEN( USA): IJCRGG ISSN : 0974-4290 Vol.5, No.5, pp 2497-2502, July-Sept 2013

# Design and Evaluation of a Silver Optical Sensor Based on Immobilization of Rose Bengal on Triacetylcellulose Membrane

# Mohammad Reza Baezzat\*, Razie Abdollahi

Department of Chemistry, College of Sciences, Payame Noor University (PNU) Shiraz, 71955-1368, IRAN

**Abstract:** In present study characterization of an optical sensor membrane is described for the determination of  $Ag^+$  ions based on the immobilization of Rose bengal on a triacetylcellulose membrane. Under optimum conditions, the proposed membrane displayed a linear range of 0.05-1.0 µg mL<sup>-1</sup> with a limit of detection of 0.035 µg mL<sup>-1</sup> at a wavelength of 558 nm. The response time of the optode was about 8-10 min, depending on the concentration of silver ions. The sensor can readily be regenerated with the 0.5 M EDTA. The optode is fully reversible and the selectivity of optode to  $Ag^+$  ions in universal buffer (pH=5) is relatively good with  $Mn^{2+}$  ion as interferences. The proposed optode was successfully for the determination of silver in photographic film. **Keywords:** Optical sensor; Rose bengal; Triacetylcellulose.

# **1. Introduction**

The development of sensors with an optical transduction of the chemical recognition process (optical sensors, optodes) has become a highly relevant and rapidly expanding area in analytical chemistry<sup>1-4</sup>.

So recent decades have been an increase in the development of optodes as viable alternatives to other types of sensors that's because of its advantages of easy fabrication, good sensitivity and selectivity and low cost of such these optodes<sup>5-9</sup>.

These optical sensing devices are based on absorption, reflection, fluorescence or chemiluminescence's, and they commonly make use of chemical compounds that drastically change their optical properties as the result of the actual recognition process<sup>10</sup>.

Silver is important elements that have widespread applications<sup>11</sup>. Absorbed silver ion is widely distributed in the body because these ions are bound to protein and are also precipitated as silver chloride at the sites of application<sup>12</sup>. These toxic metal elements exist in many environmental samples such as soil, water and plants<sup>13</sup>. For these reason, establishing rapid and accurate methods for the determination of these cations for industrial process, quality and pollution control is important. Several analytical techniques such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace silver with sufficient sensitivity for most of applications<sup>14-16</sup>.

Although these methods have good sensitivity, but they require expensive instruments, well-controlled experimental conditions and profound sample-making. Optical sensors have attracted the attention of many researchers because of easy fabrication, freedom from electrical interference, low cost, safety, good selectivity

and sensitivity and the possibility of remote sensing. In optochemical sensors (so called optrodes) or optodes, the sensing element consists of reagent dyes immobilized in organic or inorganic matrices. The indicator dye undergoes a binding reaction with the ions.

In this work, a silver optical sensor based on immobilization of Rose Bengal reagent, on a triacetylcellulose membrane is introduced. The membrane responds to silver (I) which is spectroscopically detected in the absorbance mode. The proposed method offers a selective and sensitive method for Ag (I) analysis in real samples.

# 2. Experimental

#### 2.1. Reagents

All chemicals were prepared from analytical reagent grade and were supplied from Merck Company. All aqueous solutions were prepared with double distilled water. Universal buffer solutions were prepared from boric acid/citric acid/phosphoric acid (0.04 M each). The final pH was adjusted by the addition of 0.1 M sodium hydroxide. A stock solution of 1000  $\mu$ g mL<sup>-1</sup> Ag<sup>+</sup> ion was prepared by weighing 0.157 g of AgNO<sub>3</sub> (Merck) and adjusting the volume to 100 mL. Working standard solutions of Ag (I) were prepared from the stock solution by suitable dilution with water.

#### 2.2. Apparatus and measurement procedures

A Shimadzu UV-Vis spectrophotometer with a 1cm cell was used for recording the visible spectra and absorbance measurements. A Jenway 3510 pH-meter was used to check the pH of the solutions. A Hamilton syringe (10  $\mu$ l) was used to inject small volumes of reagent into the cell. The constructed membrane was placed vertically in a disposable plastic cuvette and all measurements were performed in a batch mode. The membrane was first exposed to the universal buffer solution at pH 5 for some minutes and the absorbance was measured at 558 nm. Then the silver solution was injected into the cell and after mixing, the absorbance was measured at 558 nm after 10 min.

#### 2.3. Preparation of the sensor membrane

The immobilized indicator on triacetylcellulose was prepared according to the following procedure. The transparent triacetylcellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove colored gelatinous layers. The films were treated with a clear solution of Rose bengal (0.02 g) in 20 ml ethylene diamine for 7 min at ambient temperature. Then they were washed with water for removing ethylene diamine and loosely trapped indicator. The membranes were finally washed with detergent solutions and water. Prepared membranes were kept under water when not in use.

# 3. Results and discussion

# **3.1. Spectral characteristics**

The absorption spectra of immobilized Rose bengal, which was obtained after being equilibrated in buffer solution (pH 5) containing different concentrations of Ag (I) ions.

The spectral change is result of increase of silver ions concentration in the membrane, which is due to the extraction of silver ion into the membrane and complex formation.

The absorbance maxima of the immobilized Rose bengal are located at 558 nm. The wavelength of 558 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength.

# **3.2.** The effect of buffer solution on the optode membrane response

The effect of the pH of the sample solution on the membrane response was studied in the pH range of 1-9 by changing the universal buffer pH. Fig.1 shows the effect of pH values on the absorbance intensity of the optode

membrane at the fixed wavelength of 558 nm. The absorbance measurements were made for 0.7  $\mu$ g mL<sup>-1</sup> silver ion at different pH values.

As it can be noticed in Fig.1, with increase in the pH of the solution, A (difference between the absorbance of the immobilized Rose bengal alone and the absorbance of the Ag- Rose bengal complex) reaches a maximum value at pH 5, and then decreases. This phenomenon might be due to the fact that at lower pH values (pH<5), complexation is weak. At pH values higher than 5,  $Ag^+$  forms different hydroxide species which make it unable to form complex with Rose bengal. Thus, pH 5 was selected for further studies.



Figure 1. The effect of pH on the difference in absorbance

#### 3.3. Dynamic range

The plot of the difference in absorbance against  $Ag^+$  ion concentration can be used as a calibration plot for determination of silver ions.

The calibration graph exhibited a linear range from 0.05 to  $1.0\mu g mL^{-1}$  which described by the equation:

 $A = 0.592 C_{Ag}^{+} + 0.039$ 

 $\Delta A$  is the absorbance difference(difference between the absorbance of immobilized Rose bengal alone and the absorbance of the Ag- Rose bengal complex) and  $C_{Ag}^+$  is concentration of  $Ag^+$  ion (µg mL<sup>-1</sup>), with a correlation coefficient of 0.997.

In this case, 0.95  $\mu$ g mL<sup>-1</sup> was found as the concentration of Ag<sup>+</sup> ion that saturates the film. Detection limit of the lead optode, defined as that concentration of the sample yielding a signal equal to the blank signal plus three times of its standard deviation, was found to be 0.035  $\mu$ g mL<sup>-1</sup>.

# **3.4. Response time**

The response time of the optode is controlled by the time required for the analyte to diffuse from the bulk of the solution to the membrane interface and to associate with the indicator.

The response time was tested by recording the absorbance change from a pure buffer (pH=5) to a buffered silver solution of 0.7  $\mu$ g mL<sup>-1</sup>.

The membrane was found to reach 95% of the final signal at 8-10 min depending on the concentration of  $Ag^+$  (Fig. 2).

At high Ag (I) concentrations, a rapid response was achieved, which resulted in a large change in response. At low Ag (I) concentrations, a longer response time was produced by the optode film.

This is due to the fact that the response time of the optode film is governed by three processes: (1) diffusion in the film (2) the rate of complex formation between metal ion and ligand, and (3) the rate of complex dissociation.



Figure 2. The curve of response time

# 3.5. Life time and stability

The lifetime of the optode membrane was determined by immersing the membrane into the cell containing the buffer solution (pH 5).

The absorbance signal was recorded at wavelength of 558 nm over a period of about 10 h. During this period, there was no evidence of leakage of reagent from the membrane and no drift in signal was observed and the sensing phase was stable over the experiment.

The prepared membranes were kept under water, while were not in use, to prevent them from being drying out. Additionally the stability of response of the film was investigated over six weeks under water, which indicated that the film was stable over this period.

# **3.6.** Regeneration of the optode

A good sensor should be regenerated at a short period of a time. The regeneration time was defined as the time taken for the sensor to reach the baseline signal (the signal observed in the buffer solution at pH 5).

Some reagent including EDTA (0.05M),HNO3(0.1M), ethylene diamine and HCl(0.1M) were studied as regenerating reagents.

Ethylene diamine tetraacetic acid was concluded to be the best reagent, which gave short membrane regeneration times (10-30 S). After this regeneration and for the next lead concentration measurements, the optode should be placed in buffer (pH 5) for 10-15 min.

# **3.7. Effect of foreign ions**

One of the most important characteristics of an optical membrane sensor is its relative response towards the primary ion over other ions present in the solution. For this purpose, a study of the effect of foreign ions was made by adding different amounts of other ions including Al(III), Mn(II), Sn(II), Ni(II), Cu(II), Zn(II), Co(II), Co(II), Cd(II), Mg(II) and Fe(II) to solutions containing 0.01 µg mL<sup>-1</sup> of silver (I) ion. The tolerance limit was taken as the concentration of the interfering species causing an error less than ±5%. The results showed at the

applied pH value the following ions did not interfere even a 100 fold excess of the above ions. The main interfering species in the determination of  $Ag^+$  was  $Mn^{2+}$ .

### **3.8.** Determination of Ag<sup>+</sup> in photographic film samples

In order to test the analytical validity of the proposed optode, this optode was applied to the determination of Ag(I) in photographic film samples. For this purpose a particle of photographic film was added to 3 mL of hypochloride sodium and set the pH as 5, then the solution was added to 50 mL volumetric flask and diluted to mark and determined the silver by the purposed method. The results are given in Table 1.

Samples No.	Concentration $Ag^+$ (µg mL <sup>-1</sup> )		Recoverv%	RSD%
	Added	Found	Recovery/0	<b>R.D</b> . <b>D</b> /0
	-	0.50	-	-
1	0.2	0.252	108.6	2.7
	0.3	0.351	107.8	2.3
	0.4	0.449	96.74	1.5
2	-	0.70	-	-
	0.05	0.751	111.15	2.7
	0.10	0.831	109.02	1.3
	0.15	0.912	104.45	1.5

Table1. Determination of silver ion in photographic film samples.

# 4. Conclusion

The new silver optode reported in this research is easily prepared and provides a simple, fast, and inexpensive means for determination of Ag(I) ions. The sensor can be regenerated readily with a solution of ethylene diamine tetraacetic acid and has a long life time. The response of the optode was reproducible. The optical sensor has a good selectivity toward Ag(I) versus other metal ions except for  $Mn^{2+}$ .

It has wide dynamic range and low cost. This optical sensor can be applied for the determination of  $Ag^+$  ions in some real samples.

# Acknowledgment

The authors gratefully acknowledge the support of this work by Shiraz Payame Noor University Research council (Grant No. 7/72096).

# **References:**

- 1. I. Oehme, O.S. Wolfbeis, Mikrochim. Acta 126(1997)177-192.
- 2. W.R. Seitz, Anal. Chem. 56(1984)16A-34A.
- 3. O.S. Wolfbeis, Fresenius Z. Anal. Chem. 325 (1986) 387-392.
- 4. W. Simon, Chimia 44 (1990) 395-396.
- 5. C. Sanchez Pedreño, J.A. Ortuño, M.I. Albero, M.S. Garcia, M.Valero, Anal. Chim. Acta 414(2000)195-203.
- 6. M.I. Albero, J.A. Ortuno, M.S. Garcýa, C. SanchezPedreno, R. Exposito, J. Pharm. Biomed. Anal. 29(2002)779-786.
- 7. J.E. Madden, T.J. Cardwell, R.W. Cattrol, L.W. Deady, Anal. Chim. Acta 319(1996)129-134.
- 8. W.H. Chan, R.H. Yang , T. Moa, K.M. Wang, Anal. Chim. Acta 460(2002)123–132.
- 9. C. SanchezPedreno, M.S. Garcia, J.A. Ortuno, M.I. Albero, E. Ballester, Fresenius. J. Anal. Chem. 369(2001)680–683.

- 10. W.E. Morf, K. Seiler, B. Rusterholz, W. Simon, Anal. Chem. 62(1990)738-742.
- 11. Smith, I. C.; Carson, B. L. Trace Metals in the Environment; Ann Arbor Science Publisher's Inc: Ann Arbor, MI, 1977; vol 2.
- 12. Berman, E. toxic metals and their Analyses; USA, Heyden & son Ltd, 1990, 65-177-195.
- 13. Vaisanen, A.; Suontamo, R.; Silvonen, J.; Rintala, J. Anal and bio Anal chem. 2002, 373 (1-2), 93-97.
- 14. Manzoori, J. L.; Abdolmohammad-Zadeh, H.; and Amjadi, M. J. Hazard. Mat. 2007, 144, 458–463.
- 15. Bavili Tabrizi, A. J. Hazard. Mat. B. 2007, 139, 260-264.
- 16. Dimitrovaa, B.; Benkheddab, K.; Ivanovaa, E.; and Adamsb, F. J. Analytical Sciences and Spectroscopy. 2004, 49, No. 6.

\*\*\*\*\*