

# Diphenylthiocarbazone Immobilized on the Triacetyl Cellulose Membrane as an Optical Silver Sensor

Meissam NOROOZIFAR<sup>1\*</sup>, Mozghan KHORASANI MOTLAGH<sup>2</sup>, Aboozer TAHERI<sup>1</sup>,  
Rohollah ZARE DORABEI<sup>1</sup>

<sup>1</sup>*Analytical Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan,  
Zahedan-IRAN*

*e-mail: mnoroozifar@chem.usb.ac.ir*

<sup>2</sup>*Inorganic Research Laboratory, Department of Chemistry, University of Sistan & Baluchestan,  
Zahedan-IRAN*

Received 27.06.2007

An optical sensor for the direct measurement of silver was developed. The basic element of this optode is the immobilization of diphenylthiocarbazone on a triacetyl cellulose membrane. This optode has a linear range of up to 40  $\mu\text{g mL}^{-1}$  of  $\text{Ag}^+$  ions, with a limit of detection of 0.01  $\mu\text{g mL}^{-1}$ . The response time of the optode was 4-7 min, depending on the concentration of  $\text{Ag}^+$  ions.

**Key Words:** Optical sensor,  $\text{Ag}^+$  ions, diphenylthiocarbazone.

## Introduction

Today, the silver content of environmental samples has increased with the increased use of silver and silver compounds for such industrial uses as photographic material, the structure of batteries and semiconductors, electroplating for both decorative and industrial applications, electronic devices, mirrors, cloud seeding, medicine, and jewelry.<sup>1-4</sup> Because of its marked antibacterial properties, its compounds and alloys have been widely used to disinfect water used for drinking and recreational purposes, in dental and pharmaceutical preparations, and in implanted prosthesis.<sup>5,6</sup> Silver can enter the environment via industrial water because it is often an impurity in copper, zinc, arsenic, and antimony industries,<sup>7</sup> and silver has been recognized as a toxic element in marine environments.<sup>8</sup> Bowen suggested that silver may pose a potential risk as a water pollutant because of the lack of recycling of mined silver.<sup>9</sup> Therefore, determination of trace amounts of silver is important for many areas of chemical analysis.

Recently, many methods have been reported in the literature for the determination of silver ions in different environmental, medicinal, and industrial samples, using solid phase extraction (SPE),<sup>10-13</sup> spectrophotometry,<sup>14</sup> cloud point extraction (CPE),<sup>15</sup> ion-pair extraction,<sup>16</sup> catalytic method,<sup>17</sup> ion-selective electrodes,<sup>18-24</sup> and bulk optodes.<sup>25-29</sup>

---

\*Corresponding author

Diphenylthiocarbazone (dithizone) has been used for the determination of silver ions as a reagent for cloud point extraction,<sup>15</sup> and has been immobilized on surfactant-coated alumina and silica gel as 2 new sorbents.<sup>12,13</sup> In this paper, we discuss the application of diphenylthiocarbazone immobilized on a triacetyl cellulose membrane for the detection of silver (I) ions. The membrane responds to silver (I) ions by changing color from green to red.

## Experimental

### Reagents

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise and were obtained from Merck Company. A silver standard stock solution ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving 0.1578 g of  $\text{AgNO}_3$  in 1 mL of nitric acid in a 100-mL volumetric flask, then diluting to mark with water. Working solutions were prepared daily from the stock solution by appropriate dilution with 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 0.2 M sodium hydroxide.

### Apparatus and measurement procedures

UV-Vis spectra and absorbance measurements were recorded on an Analytik Jena SPECORD S 100 spectrometer with a photodiode array detector. The sensing membrane was placed and fixed in a disposable plastic cuvette and all measurements were performed in a batch mode. A Metrohm 632 pH meter with a Metrohm double junction glass electrode was used for pH adjustment. The optode membrane response to different metal ions was investigated in universal buffer (0.04 M) at pH 2. The membrane was first exposed to the buffer solution and the absorbance was measured at 617.3 nm. Then, the sample solution was added and the absorbance at 617.3 nm was measured again after 8 min.

### Preparation of the sensor membrane

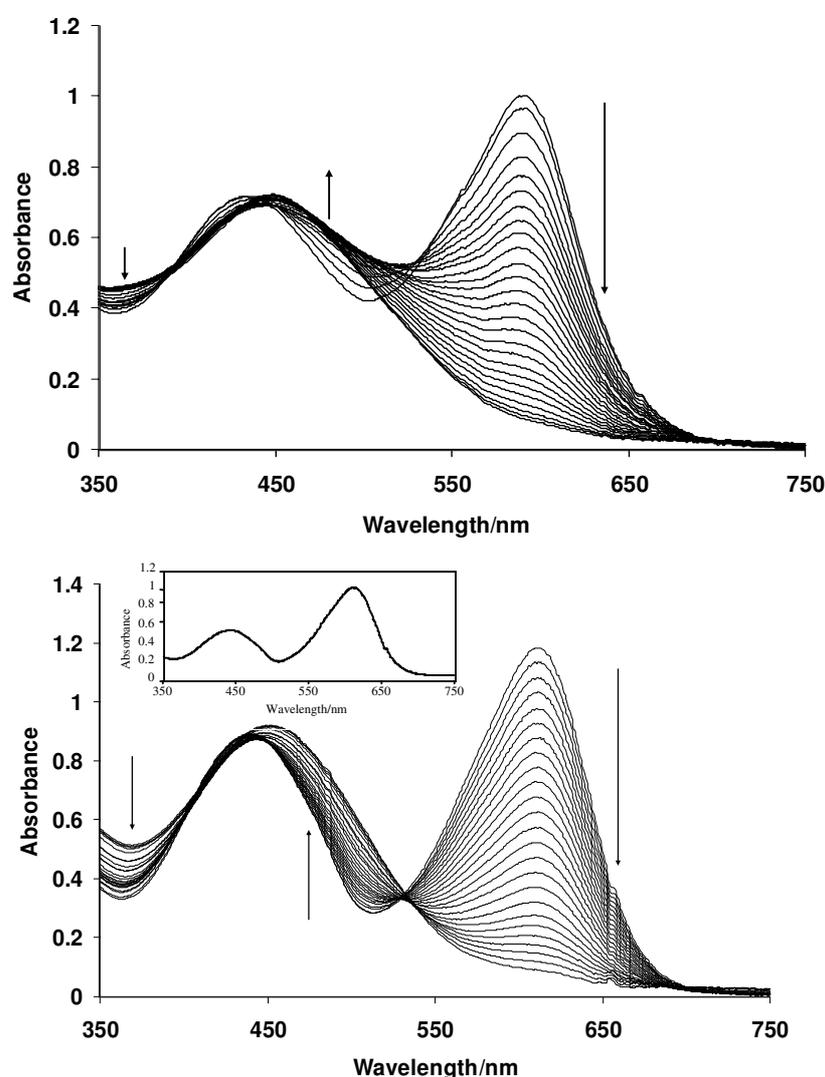
The transparent triacetyl cellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove colored gelatinous layers. The films ( $1 \text{ cm} \times 4 \text{ cm}$ ) were treated with a clear solution of diphenylthiocarbazone (0.004 g) in 10 mL of ethylene diamine ( $0.4 \text{ g L}^{-1}$ ) for 3 min at ambient temperature. The concentration of diphenylthiocarbazone decreased to  $0.387 \text{ g L}^{-1}$ , so the amount of trapped ligand in the membrane was  $1.3 \times 10^{-4} \text{ g}$ . Then, they were washed with water to remove ethylene diamine and loosely trapped indicator. The membranes were finally washed with detergent solutions and water. The prepared membranes were kept in water when not in use.

## Results and Discussion

### Spectral characteristics

The absorption spectra of diphenylthiocarbazone in solution of methanol/water and immobilized forms at pH 2 on hydrolyzed cellulose acetate are shown in Figure 1. The spectral change is a result of the addition

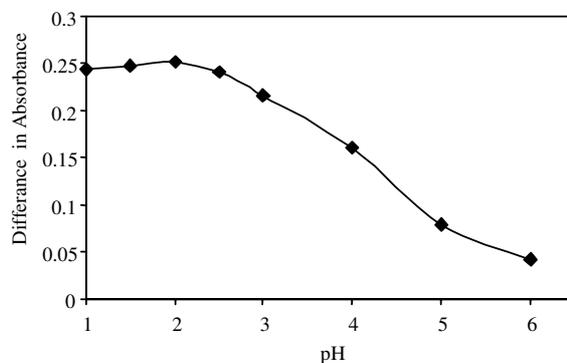
of  $\text{Ag}^+$  ions and complex formation in solution (Figure 1, up). The spectral characteristic of this solution showed 2 maxima at 593.7 and 437.6 nm (Figure 1, up). The absorption spectrum at 437.6 is shifted to 452 nm with increasing  $\text{Ag}^+$  concentration in solution. The spectral characteristic of this optical sensor showed 2 maxima at 614.1 and 441.7 nm (Figure 1, down and inset). The spectral change is a result of the addition of  $\text{Ag}^+$  ions and complex formation in the optode (Figure 1, down); there is a shift in these 2 maxima with increasing  $\text{Ag}^+$  concentration in the optode (617.1 instead of 614.1 nm and 450 instead of 441.7 nm). It is important to note that the absorption spectra of immobilized indicator are red shifted in comparison to those of their soluble form (617.1 instead of 593.7 nm and 450 instead of 437.6). This can suggest that the structured conformation of the immobilized indicators is more planar than that of its soluble analogue.<sup>31</sup> Additionally, the wavelength of 617.3 nm was selected for further study because of higher selectivity and sensitivity at this wavelength.



**Figure 1.** Absorption spectra for a  $1 \times 10^{-4}$  M diphenylthiocarbazone solution (up), absorption spectra of the optode film response to  $\text{Ag}^+$  in the range of 0-40  $\mu\text{g mL}^{-1}$  at pH 2 (inset), and absorption spectra of the diphenylthiocarbazone in the optode (down).

## Effect of pH

The effect of pH 1-8 on the complex was studied by changing the universal buffer. As can be seen in Figure 2, a maximum value in the sensor response was obtained at pH 2. This pH was selected for further study.



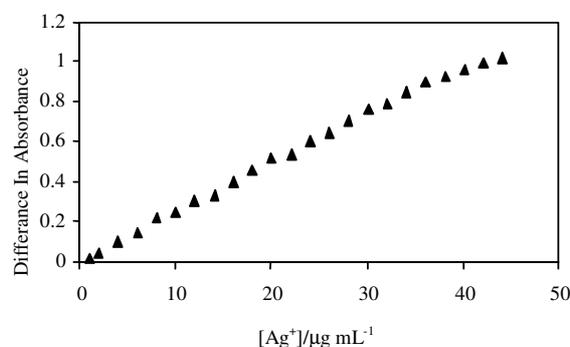
**Figure 2.** Effect of pH on the optode film response.

## Regeneration of the optode

Different compounds, such as EDTA, sulfosalicylic acid, glycine thioacetamide, HCl, HNO<sub>3</sub>, and thiourea were tested for regeneration of the Ag<sup>+</sup> optode. The best reagent was thiourea. There are several disadvantages of using other compounds, including a partial reversal effect and prolonged time for regeneration or washing for its removal. Regeneration time for thiourea was 5 min.

## Dynamic range

Figure 3 shows the absorption signals of the optode film in response to the various concentrations of Ag<sup>+</sup> ions in the range 0-44  $\mu\text{g mL}^{-1}$ . The calibration graph is linear up to 40  $\mu\text{g mL}^{-1}$  and is described by the equation,  $\Delta Abs = 0.0247[\text{Ag}^+] + 0.0051$  ( $R^2 = 0.9985$ ), where  $\Delta Abs$  is the absorbance difference (which is defined as the difference between the absorbance of immobilized diphenylthiocarbazone alone and the absorbance of the Ag-diphenylthiocarbazone complex),  $[\text{Ag}^+]$  is the silver ion concentration ( $\mu\text{g mL}^{-1}$ ),  $R^2$  is the R-squared value of the calibration curve.



**Figure 3.** The optode film response vs. Ag<sup>+</sup> ion concentrations in the range of 0-44  $\mu\text{g mL}^{-1}$  at pH 2.

Table 1. Comparison of some analytical performance data with the literature.

Reagent	Bead	Samples	Linear range	Detection limit	Coefficient of variation (%)	Ref
Tetradecyl-14-dithiacrown-4	Pellicular octadecylsilica beads coated with a lipophilic organic liquid	-	$10^{-6}$ - $10^{-2}$ M	-	-	25
Hexathia-18-crown-6 and benzo-3-octadecanoylimino-7-diethylaminophenoxazine	1,2-PVC	Drinking water sample	$5.0 \times 10^{-9}$ - $5.0 \times 10^{-5}$ M	$1.0 \times 10^{-9}$ M	-	28
Tetrakis( <i>p</i> -chlorophenyl)borate and 1-(dansylamidopropyl)-1-aza-4,7,10-trithiacyclododecane	PVC	Medical radiological film, photographic fixing solution and bleaching solution.	$5.0 \times 10^{-7}$ to $1.7 \times 10^{-2}$ M	$1.0 \times 10^{-7}$ M.	3.6	29
Diphenylthiocarbazone	Transparent triacetyl cellulose (produced from waste photographic film)	Synthetic samples, different kinds of photographic solutions and pharmaceutical	Up to $3.4 \times 10^{-4}$	0.01 $\mu$ g/mL ( $9.2 \times 10^{-8}$ M)	1.16	Presented work

The detection limit of the sensor film, which is defined as the concentration of the sample that yields a signal equal to the blank signal plus 3 times its standard deviation was  $0.01 \mu\text{g mL}^{-1}$ . The figure of merit of the proposed method and many publications in the literature for the determination of Ag with an optode system are summarized in Table 1. The linear range and detection limit of the proposed optode is acceptable when compared to the reported optodes; however, to date, the literature contains no such simple method for the preparation of the sensor membrane and chip reagent used for the determination of silver ions.

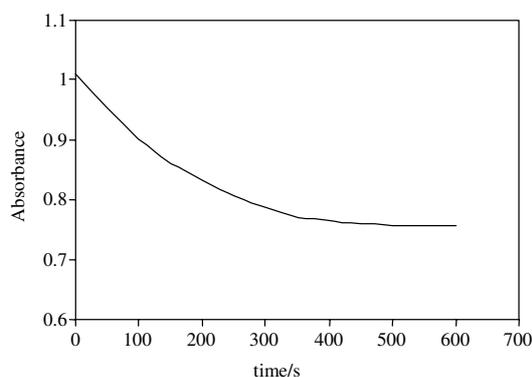
## Reproducibility

The repeatability and reproducibility of optical fiber sensors are 2 important characteristic features, both of which were studied in this work. To evaluate discrepancies in the response for successive runs using a single sensor, repeatability was evaluated by performing 10 determinations with the same standard solution of  $\text{Ag}^+$ . The coefficient of variation of sensor response for  $1.00 \mu\text{g mL}^{-1}$  of  $\text{Ag}^+$  was 1.16%.

The differences in the responses of individual sensors were evaluated by preparing 5 membranes from the same mixture and reproducibility was obtained by determining  $1.00 \mu\text{g mL}^{-1}$  of  $\text{Ag}^+$  (3 determinations). The coefficient of variation of response between membranes was 2.7%.

## Response time

In this work the optode film reached 95% of the final signal in 4-7 min, depending on the concentration of  $\text{Ag}^+$  (Figure 4). At high concentrations of  $\text{Ag}^+$  ions a rapid response was achieved, which resulted in a large change in response. At low concentrations of  $\text{Ag}^+$  ions a slower 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 3 processes: (1) diffusion in the film, (2) the rate of complex formation between the metal ion and ligand, and (3) the rate of complex dissociation.<sup>31</sup>



**Figure 4.** Typical response curve of the film optode at 617.3 nm as a function of time when the film was exposed to  $44 \mu\text{g mL}^{-1}$   $\text{Ag}^+$  at  $\text{pH} = 2$ .

## Lifetime and stability

The lifetime of the optode film was determined by adding buffer solution ( $\text{pH} 2$ ) to the cuvette that contained the film. The signal was recorded at a wavelength of 617.3 nm over a period of time (about 10 h). No significant loss of the indicator occurred during this time. When the film was exposed to light, no drift in

signal occurred and the optode was stable over the experiment, with no leaching of the indicator. However, prepared membranes were kept under water when not in use to prevent them from drying out.

Additionally, the stability of response of the film was investigated over 4 weeks under ambient conditions, which indicated that the film was stable during this period.

## Effect of foreign ions

To determine the selectivity of the optode film, the film was tested for the determination of  $0.5 \mu\text{g mL}^{-1}$  of  $\text{Ag}^+$  ions in the presence of other metal ions. The tolerance limit was taken as the concentration that caused an error of  $\pm 5\%$  in the determination of  $\text{Ag}^+$ . The results are shown in Table 2.

**Table 2.** Effect of foreign ions on the determination of  $0.5 \mu\text{g mL}^{-1}$  of  $\text{Ag}^+$ .

Interferent	Concentration of interferent ( $\mu\text{g mL}^{-1}$ )	Silver found ( $\mu\text{g mL}^{-1}$ )	Error (%)
$\text{Na}^+$	500	0.507	1.4
$\text{K}^+$	500	0.502	0.4
$\text{Ba}^{2+}$	500	0.504	0.8
$\text{Ca}^{2+}$	500	0.508	1.6
$\text{Mg}^{2+}$	500	0.511	2.2
$\text{Mn}^{2+}$	500	0.517	3.4
$\text{Fe}^{3+}$	500	0.486	-2.8
$\text{Co}^{3+}$	500	0.513	2.6
$\text{Ni}^{2+}$	500	0.493	-1.4
$\text{Pb}^{2+}$	500	0.476	- 3.8
$\text{Zn}^{2+}$	500	0.523	3.6
$\text{Cd}^{2+}$	500	0.516	3.2
$\text{Al}^{3+}$	500	0.508	1.6
$\text{Bi}^{3+}$	500	Precipitated	-
$\text{Cu}^{2+}, \text{Hg}^{2+}$	1	-	-

## Recovery tests

Recovery tests using the proposed method were performed using 4 different samples, and the test for each sample was carried out in triplicate. As shown in Table 3, the recovery of silver was between 99.5% and 101.2%.

**Table 3.** Results of the recovery test.

Samples	Concentration ( $\mu\text{g mL}^{-1}$ ) <sup>a</sup>	Added ( $\mu\text{g mL}^{-1}$ )	Found ( $\mu\text{g mL}^{-1}$ ) <sup>b</sup>	Recovery (%)
River Water	nd <sup>c</sup>	5.00	5.06	101.2
Photographic Solution	4.00	5.00	9.08	100.9
Silver Sulfadiazine Topical Cream	3.00	5.00	7.96	99.5
Drinking Water	nd <sup>c</sup>	5.00	4.98	99.6

<sup>a</sup>Determined by atomic absorption spectrometry.<sup>b</sup>Average of 3 determinations using the proposed method.<sup>c</sup>Not detected.

### Application to Synthetic sample and real samples

The proposed method was applied to the determination of silver ions in synthetic samples, different photographic solutions, and pharmaceuticals; the results are shown in Table 4.

**Table 4.** Determination of Ag(I) in real and synthetic samples.

Sample	Ag(I) found $\mu\text{g mL}^{-1}$ (by AAS)	Ag(I) found $\mu\text{g mL}^{-1}$ (by proposed method)	RSD (%) for proposed method (n = 7)	RE%
Synthetic sample 1	1.00	1.01	0.47	+1.00
Synthetic sample 2	10.00	9.91	0.82	-0.90
Synthetic sample 3	20.00	20.06	0.63	+0.30
Photographic Solution 1	470.40	473.80	0.86	+ 0.72
Photographic Solution 2	426.70	425.25	0.58	-0.34
Silver Sulfadiazine Topical Cream, 1%	147.50 (0.99% m/m)	148.74 (0.99% m/m)	1.16	+0.84

### Conclusion

The optode described in this work is easily prepared and provides a simple, fast, and inexpensive means for the determination of Ag<sup>+</sup> ions. The membrane responds to silver ions by changing color from green to red. The sensor can be regenerated readily with a solution of thiourea and has a long lifetime. The response of the optode was reproducible and the optode presented a good selectivity for Ag<sup>+</sup> ions over general metal ions.

### Acknowledgements

The authors gratefully thank the University of Sistan & Baluchestan (USB) for providing financial support.

### References

1. K. Chiba, I. Inamoto and M. Saeki, **J. Anal. At. Spectrom.** **7**, 115-119 (1992).
2. M. Grayson, **Kirk-Othmer Encyclopedia of Chemical Technology** **3<sup>rd</sup> ed.**, vol. 21, Wiley, New York, 1980.
3. H. Renner, **Ullmann's Encyklopädie der Technischen Chemie** **4<sup>th</sup> ed.**, vol. 21, Verlag Chemie, Weinheim, 1982.
4. N.N. Greenwood and A. Earnshaw, **Chemistry of the Elements**, Pergamon Press, New York, 1989.
5. I. Kojimia and A. Takayanagi, **J. Anal. At. Spectrom.** **11**, 607-610 (1996).
6. Silver Institute Letter, **Silver Purifies Water on Drilling Rigs**, Vol. 7 (1), 1997.
7. R. Soager, **Metallic Raw Materials Dictionary**, Bank Tober, Zürich, 1984.
8. P. Bermejo-Barrera, J. Moreda-Pineiro, A. Moreda-Pineiro and A. Bermejo-Barrera, **Talanta** **43**, 35-44 (1996).
9. H.J.M. Bowen, **Trace Element Biochemistry**, Academic Press, London, 1966.
10. S. Dadfarnia, A.M. Haji Shabani and M. Gohari, **Talanta** **64**, 682-687 (2004).
11. G. Yang, Q. Hu, J. Yang, Z. Huang and J. Yin, **Anal. Sci.** **19**, 299-302 (2003).
12. G. Absalan and A. Aghaei Goudi, **Separation and Purification Technology** **38** 209-214 (2004).
13. O. Zaporozhets, N. Petruniock and V. Sukhan, **Talanta** **50**, 865-873 (1999).
14. P. Nagaraja, M. S. H. Kumar, and H. S. Yathirajan, **Anal. Sci.** **18**, 815-817 (2002).
15. J. L. Manzoori and G. Karim-Nezhad, **Anal. Chim. Acta** **484**, 155-161 (2003).
16. I. Kojima, M. Kataoka, M. Yamada and m.Yamaguchi, **Anal. Sci.** **16**, 1045-1048 (2000).
17. A. Safavi, R. Mirzajani, **Anal. Sci.** **18**, 329-332 (2002).
18. M. H. Mashhadizadeh, M. Shamsipur, **Anal. Chim. Acta** **381**, 111-116 (1999).
19. D. Liu, J. Liu, D. Tian, W. Hong, X. Zhou and J.C. Yu, **Anal. Chim. Acta** **416**, 139-144 (2000).
20. K. Kimura, S. Yajima, K. Tatsumi, M. Yokohama and M. Oue, **Anal. Chem.** **72**, 5290-5294 (2000).
21. R.K. Mahjan, M. Kumar, V. Sharma and I. Kaur, **Analyst** **126**, 505-507 (2001).
22. M. Shamsipur, M. Javanbakht, V. Lippolis, A. Garau, G. De Filippo, M.R. Ganjali and A. Yari, **Anal. Chim. Acta** **462**, 225-234 (2002).
23. M. Shamsipur, M. Javanbakht, M.R. Ganjali, M.F. Mousavi, V. Lippolis and A. Garau, **Electroanalysis** **14**, 1691-1698 (2002).
24. M. M. Ardakani, H. Dehghan, M. Jalayer and H.R. Zare, **Anal. Sci.** **20**, 1667-1672 (2004).
25. H. Hisamoto, E. Nakagawa, K. Nagatsuka, Y. Abe, S. Sato, D. Siswanta and K. Suzuki, **Anal. Chem.** **67**, 1315-1321 (1995).
26. M. Lerchi, F. Orsini, Z. Cimerman and E. Pretsch, **Anal. Chem.** **68**, 3210-3214 (1996).
27. S.H. Kim, S.K. Han, S.H. Park, S.M. Lee, S.M. Lee, K.N. Koh and S.W. Kang, **Dyes and Pigments** **41**, 221-226 (1999).
28. M. Shamsipur, S. Rouhani, A. Mohajeri and M.R. Ganjali, **Anal. Bioanal. Chem.** **375**, 692-697 (2003).
29. M. Shamsipur, K. Alizadeh, M. Hosseini, C. Caltagirone and V. Lippolis, **Sensors and Actuators B** **113**, 892-899 (2006).
30. T.P. Jones and M.D. Porter, **Anal. Chem.** **60**, 404-406 (1988).
31. B. Kuswandi and R. Narayanaswamy, **J. Environ. Monit.** **1**, 109-114 (1999).