

# Development of a Highly Sensitive and Selective Optical Chemical Sensor for the Determination of Zinc Based on Fluorescence Quenching of a Novel Schiff Base Ligand

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A sensitive new optical sensor for  $Zn^{2+}$  is described. This optode is based on a novel Schiff base ligand, 2-(2-hydroxy-5-chloro)benzaldehyde-[4-(3-methyl-3-mesitylcyclobutyl)-1,3-thiazol-2yl]hydrazone, in plasticized polyvinyl chloride membrane. This sensing membrane is capable of determining  $Zn^{2+}$  with a high sensitivity and selectivity over a wide dynamic range between  $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> at pH 6.0 with a lower detection limit of  $2.2 \times 10^{-7}$  mol L<sup>-1</sup> (14.4  $\mu$ g L<sup>-1</sup>). The sensor can readily be regenerated with 1.0 mol L<sup>-1</sup> EDTA solution. In addition to high stability, the sensor shows a unique selectivity toward  $Zn^{2+}$  with respect to common metal cations. The sensor was successfully applied for the determination of zinc real samples. The results obtained for the determination of zinc ions in hair samples using the proposed method was found to be comparable with the well-established flame atomic absorption method.

**Keywords:** Schiff Base, PVC Matrix, Fluorescence Spectroscopy, Optical Sensor, Zinc.

## 1. INTRODUCTION

Zinc is the most abundant transition metal in human bodies and is especially rich in the brain.<sup>1,2</sup> Zinc deficiency in human organisms occurs in cases of inadequate zinc absorption, increased zinc losses from the body or increased requirements for zinc. This deficiency leads to several disorders such as growth retardation, diarrhea, the decrease of the immunological defense, eye and skin lesions, malfunctioning of wound healing and other skin diseases.<sup>3</sup> Moreover, metabolic disorders of zinc have now been closely associated with a number of neurological diseases, such as Alzheimer's disease, Parkinson's diseases, epilepsy and hypoxia-ischemia.<sup>4</sup>

Zinc compounds are used in dermatology as antiseptic and disinfectant agents and in the preparation of ophthalmic solutions, insulin, mouthwashes and mineral-vitamin preparations.<sup>5</sup> Zinc occurs in hair at relatively high levels of about 100–300 mg kg<sup>-1</sup> and its determination can be useful for clinical and forensic purposes.<sup>6</sup> Because of the importance of zinc, simple and sensitive analytical methods for the determination of trace levels

of zinc are required. The commonly used analytical methods for the quantitative determination of zinc are flame atomic absorption spectrometry,<sup>7</sup> graphite furnace atomic absorption spectrometry,<sup>8</sup> inductively coupled plasma emission spectrometry,<sup>9</sup> inductively coupled plasma-mass spectrometry,<sup>10</sup> spectrophotometry<sup>11</sup> and voltammetry.<sup>12</sup> In spite of their exact and fast measurement capabilities, recent analytical interest has focused on developing optical sensors. They have the advantages of size, cost-effectiveness, simplicity, no necessity of the reference solution, and fieldwork applicability.<sup>13–15</sup>

Many works on the development of the optical sensors for zinc ion sensing have been reported recently.<sup>16–20</sup> Jeronimo et al.<sup>21</sup> reported the development of a sol-gel optical sensor for zinc analysis of based on incorporated 4-(2-pyridylazo)resorcinol (PAR). An optical sensor membrane for the detection of  $Zn^{2+}$  was offered by Rastergarzadeh and Rezaei.<sup>22</sup> The sensing membrane was made by immobilizing Zincon as an ion pair with methyltriethylammonium ion on triacetylcellulose membrane. Li et al.<sup>23</sup> have designed a new porphyrin derivative containing 2-(oxymethyl)pyridine units, which shows ratio-metric change of fluorescence intensity in the presence

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**Table I.** Some reported optical sensors for the determination of Zn<sup>2+</sup>.

Reagent	Working range (mol L <sup>-1</sup> )	Limit of detection (mol L <sup>-1</sup> )	Reference
PAR	$7.6 \times 10^{-8}$ to $3.8 \times 10^{-7}$	$3.1 \times 10^{-8}$	[21]
Zincon	$7.6 \times 10^{-7}$ to $3.1 \times 10^{-5}$	$1.6 \times 10^{-7}$	[22]
Porphyrin derivative	$3.2 \times 10^{-7}$ to $1.8 \times 10^{-4}$	$5.5 \times 10^{-8}$	[23]
Benzoxazole derivative	$8.0 \times 10^{-5}$ to $4.0 \times 10^{-3}$	$4.0 \times 10^{-5}$	[24]
Bis(pyrrol-2-yl-methyleneamine)	NR <sup>b</sup> to $9.6 \times 10^{-6}$	NR <sup>b</sup>	[25]
HQ3	$7.5 \times 10^{-8}$ to $2.5 \times 10^{-5}$	$1.5 \times 10^{-8}$	[26]
HCB <sup>a</sup>	$5.0 \times 10^{-7}$ to $1.0 \times 10^{-4}$	$2.2 \times 10^{-7}$	—

<sup>a</sup>Proposed sensor. <sup>b</sup>NR: not reported.

of Zn<sup>2+</sup>. Ma et al.<sup>24</sup> also developed a ratiometric fluorescent sensor for zinc ion based on covalently immobilized derivative of benzoxazole. A fluorescent sensor for zinc ion based on bis(pyrrol-2-yl-methyleneamine) ligands was offered by Wu et al.<sup>25</sup> Jiang and co-workers recently reported a high sensitive fluorescent sensor of zinc by using 8-pyridylmethoxy-2-methyl-quinoline (HQ3).<sup>26</sup> The reagents, working ranges and/or limits of detection (LOD) of zinc sensors have been summarized in Table I.

Various polymeric membranes have been used as supporting matrices for the preparation of optical chemical sensors in literature. The polymer materials act as a rigid support for the active chemical reagent, providing protective covering for the transduction materials, and can provide a certain degree of selectivity of analyte attributed to their structural features, particularly surface topography. Polyvinyl chloride (PVC) is optically transparent, and has good mechanical properties, homogeneity and preparation simplicity. PVC has a very high molecular weight (>100000 g mol<sup>-1</sup>) and forms a cage-like structure for holding reagent within it.<sup>27</sup> Up to now, there are several reports on application of PVC membrane as a sensing material. Our group has recently been involved in the study of optical sensor based on Schiff base ligands embedded in PVC.<sup>28–29</sup>

In this study, a simple method for detecting trace level of Zn<sup>2+</sup> has been developed. A novel Schiff base ligand embedded in PVC film has been utilized in construction of optical sensor for Zn<sup>2+</sup>. The method developed requires no pretreatment such as concentrating and extraction process. The fluorescent 2-(2-hydroxy-5-chloro)benzaldehyde-[4-(3-methyl-3-mesitylcyclobutyl)-1,3-thiazol-2yl]hydrazone (HCB) dye has been used for the first time as sensing agent in optical sensor design. The sensor has been successfully employed for the determination of zinc in hair samples.

## 2. EXPERIMENTAL DETAILS

### 2.1. Reagents

The polymer membrane components, polyvinylchloride (PVC) (product no. 81387, high molecular weight) and

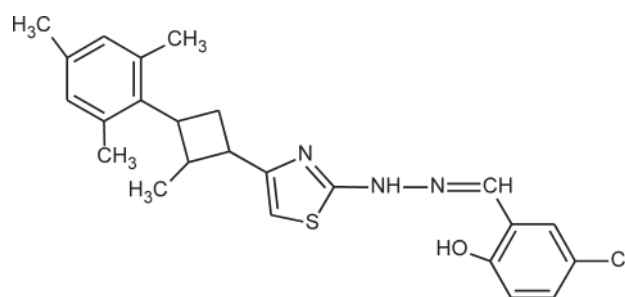
the plasticizers, bis-(2-ethylhexyl) phthalate (DOP), bis(2-ethylhexyl)sebecate (DOS), bis-(2-ethylhexyl)adipate (DAO) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. The lipophilic anionic additive reagent potassium tetrakis-(4-chlorophenyl) borate (PTCPB) was supplied by Aldrich. Absolute ethanol (EtOH), tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), acetone, nitric acid, hydrochloric acid, hydrogen peroxide and metallic zinc were purchased from Merck. Sheets of Mylar-type polyester (Dupont, Switzerland) were used as support. All solutions were prepared with glass-distilled water.

A stock standard solution containing  $1.50 \times 10^{-2}$  mol L<sup>-1</sup> Zn<sup>2+</sup> was prepared by dissolving 100.0 mg of metallic zinc in 2.0 mL concentrated hydrochloric acid and then diluting to 100.0 mL with distilled water.

The pH values of the solutions were checked using a digital pH meter (WTW) calibrated with standard buffer solutions of Merck. Buffer components and metal salts were of analytical grade (Merck and Fluka). Quinine sulphate (Sigma) was used as reference ( $\Phi_{st} = 0.54$ ) for fluorescence quantum yield calculations of the HCB dye. The synthesis of HCB dye has been performed in our laboratories.<sup>30</sup> The structure of the employed dye molecule is shown in Figure 1.

### 2.2. Apparatus

UV-Vis absorption spectra were recorded using Varian Cary 100 bio UV-Visible spectrophotometer. All fluorescence measurements were carried out on a Shimadzu RF-5301 PC spectrofluorimeter with a Xenon short arc lamp



**Fig. 1.** Chemical structure of 2-(2-hydroxy-5-chloro)benzaldehyde-[4-(3-methyl-3-mesitylcyclobutyl)-1,3-thiazol-2yl]hydrazone (HCB) dye.

as the light source. GBC 904 PBT atomic absorption spectrophotometer with an air-acetylene flame (FAAS), zinc hollow cathode lamp and deuterium background correction was also used for zinc measurements. The film thicknesses of the sensing slides were measured with Ambios Technology XP-1 HGH Resolution surface profiler. An abbe refractometer (Atago No. 15448) was used for the determination of refractive index.

### 2.3. Preparation of Polymer Film

The membrane cocktail was prepared by dissolving a mixture of 120 mg of PVC, 240 mg of plasticizer (DOP), 2.0 mg of PTCPB and 2.0 mg of HCB dye in 1.5 mL of dried THF. The cocktail was mixed for 1 h using a magnetic stirrer at room temperature about 25 °C. The prepared mixtures contained 33% PVC and 66% plasticizer by weight which is in accordance with the literature.<sup>31, 32</sup> The resulting cocktails were spread onto a polyester support (Mylar TM type) by knife coating located in a THF-saturated desiccator. The polymer support is optically fully transparent, ion impermeable and exhibits good adhesion to PVC. The films were kept in a desiccator in the dark. This way the photostability of the membrane was ensured and the damage from the ambient air of the laboratory was avoided. Each sensor film was cut to a size of 13 × 50 mm. The film thicknesses of the sensing slides were measured with the high resolution surface profiler and found to be  $4.84 \pm 0.052 \mu\text{m}$  for PVC matrices ( $n = 8$ ).

Absorption and fluorescence emission spectra of PVC membranes were recorded in quartz cells which were filled with sample solution. The polymer films were placed in diagonal position in the quartz cell. The advantage of this kind of placement was to improve the reproducibility of the measurements. All of the experiments were operated at room temperature,  $25 \pm 1$  °C. The membranes were not conditioned before use.

### 2.4. Preparation of Hair Samples

Approximately 0.5 g of hair sample was cut with stainless steel scissors from the nape of the neck in the scalp region. Hair washing prior to analysis is required to provide an accurate assessment of endogenous metal content. The washing procedure carried out in this work was the proposed one by the International Atomic Energy Agency,<sup>33</sup> using ultrapure water and acetone as washing solvents. The hair samples were decomposed using classic acid digestion method. To carry out the digestion of the samples, 0.3 g of washed hair samples were accurately weighed into a 100 mL beakers. Then 5 mL of concentrated  $\text{HNO}_3$  and 2.5 mL of 30% (v/v)  $\text{H}_2\text{O}_2$  were added and the mixture was heated on a hot plate for 1 h at 150 °C for complete digestion of the sample. The digests were brought to near

dryness, the residue was dissolved in water and made up to 25 mL.

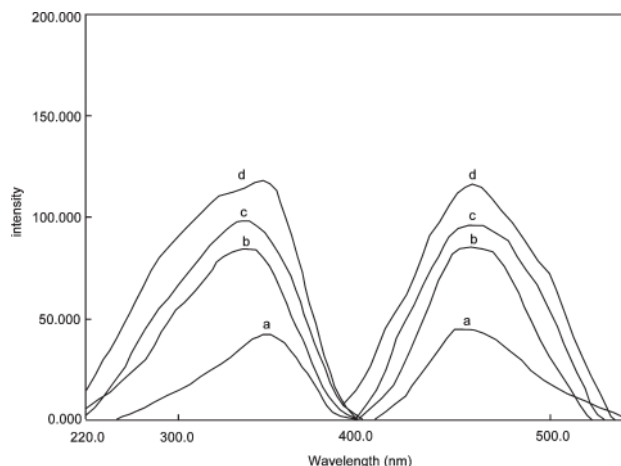
## 3. RESULTS AND DISCUSSION

### 3.1. Spectral Characterization Studies

The emission and related excitation spectra of thiazolyl hydrazone derivative dye, HCB, in the solvents of different polarities and PVC matrix, are presented in Figure 2. In all the employed solvents and PVC the Stokes shift values,  $\Delta\lambda_{\text{ST}}$  (the difference between excitation and emission maximum), calculated from the spectral data were quite high and was found to spread in the wavelength range of 107–125 nm (Table II). The HCB dye exhibited higher fluorescence intensity in PVC matrix compared to that in the solvents. The immobilization of dye molecules in solid matrix may reduce intramolecular motions and rearrangements, thus leading to enhanced fluorescence.

### 3.2. Fluorescence Quantum Yield Calculations

Fluorescence quantum yield values ( $\Phi_F$ ) of the HCB compound were calculated employing the comparative William's method which involves the use of well-characterized standards with known ( $\Phi_F$ ) values.<sup>34</sup> For this purpose, the UV-vis absorption and emission spectra of six different concentrations of reference standard (quinine sulphate in 0.1 M  $\text{H}_2\text{SO}_4$ ) and HCB were recorded. The integrated fluorescence intensities were plotted versus absorbance for the reference standard and the dye. The gradients of the plots are proportional to the quantity of the quantum yield of the studied molecules. The equations of the plots are  $y = 1723680 x$ ;  $R^2 = 0.9991$  for reference standard,  $y = 67375 x$ ;  $R^2 = 0.9919$  for HCB dye in PVC, and  $y = 30619 x$ ;  $R^2 = 0.9731$  for HCB dye in EtOH. The



**Fig. 2.** Excitation and emission spectra of HCB dye in different solvents and PVC. (a) THF ( $\lambda_{\text{ex}} = 348$  nm,  $\lambda_{\text{em}} = 455$  nm), (b) EtOH ( $\lambda_{\text{ex}} = 335$  nm,  $\lambda_{\text{em}} = 460$  nm), (c)  $\text{CHCl}_3$  ( $\lambda_{\text{ex}} = 337$  nm,  $\lambda_{\text{em}} = 462$  nm), (d) PVC ( $\lambda_{\text{ex}} = 340$  nm,  $\lambda_{\text{em}} = 464$  nm).

**Table II.** Emission and excitation spectra related data of HCB.

Solvent	Excitation wavelength $\lambda_{ex}$ (nm)	Emission wavelength $\lambda_{em}$ (nm)	Stokes shift $\Delta\lambda_{ST}$ (nm)	Refractive index $n$	Quantum yield $\Phi_F$
EtOH	335	460	125	1.3614	0.0099
CHCl <sub>3</sub>	337	462	125	1.4446	
THF	348	455	107	1.4070	
PVC	340	464	124	1.5247	0.0275

data obtained and quantum yield ( $\Phi_F$ ) values calculated according to Eq. (1) are shown in Table II.

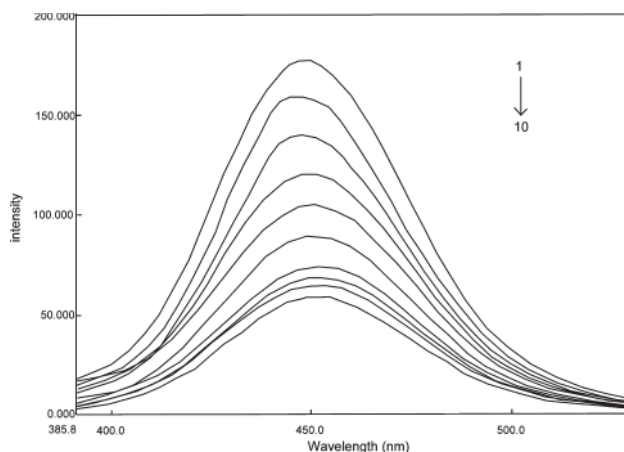
$$\theta_x = \theta_{ST} \left( \frac{\text{Grad}_x}{\text{Grad}_{ST}} \right) \left( \frac{n_x^2}{n_{ST}^2} \right) \quad (1)$$

Where ST and  $x$  denote standard and sample, respectively, Grad is the gradient from the plot and  $n$  is the refractive index of the solvent or polymer matrix material. According to the data obtained, the HCB dye exhibited quite high quantum yield in plasticized PVC.

### 3.3. Fluorescence Quenching of Sensor Membrane by Zn<sup>2+</sup>

Zn<sup>2+</sup> form a complex with HCB corresponding to the L<sub>2</sub>Zn. Zn<sup>2+</sup> bonding takes place with nitrogen of imine groups and by proton exchange with hydroxide groups.<sup>30</sup>

Figure 3 shows the fluorescence spectra of the HCB optode membrane exposed to a solution containing different concentrations of Zn<sup>2+</sup>, which are recorded at  $\lambda_{ex} = 336$  nm. As shown in Figure 3, one can see that the fluorescence intensities of the optode membrane decrease with increasing concentration of Zn<sup>2+</sup>, which constitutes the basis for the determination of Zn<sup>2+</sup> with the fluorescent sensor proposed in this paper.



**Fig. 3.** The fluorescence emission spectra of the sensing membrane exposed to the solution containing different concentrations of Zn<sup>2+</sup> at pH 6.0: (1) blank solution; (2)  $5.0 \times 10^{-7}$ , (3)  $1.0 \times 10^{-6}$ , (4)  $2.0 \times 10^{-6}$ , (5)  $4.0 \times 10^{-6}$ , (6)  $6.0 \times 10^{-6}$ , (7)  $1.2 \times 10^{-5}$ , (8)  $2.4 \times 10^{-5}$ , (9)  $4.8 \times 10^{-5}$ , (10)  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> Zn<sup>2+</sup> ( $\lambda_{ex} = 336$  nm).

**Table III.** Effect of different type of plasticizer on the response of the sensor for determination of Zn<sup>2+</sup>.

Plasticizer	Working concentration range (mol L <sup>-1</sup> )	Response time (min) ( $2.0 \times 10^{-6}$ mol L <sup>-1</sup> Zn <sup>2+</sup> )
DOS	$5.0 \times 10^{-7}$ to $9.6 \times 10^{-5}$	4
DOP	$5.0 \times 10^{-7}$ to $1.2 \times 10^{-4}$	3
DOA	$2.7 \times 10^{-6}$ to $3.4 \times 10^{-5}$	4
NPOE	$1.2 \times 10^{-6}$ to $1.0 \times 10^{-5}$	5

A linear calibration graph was obtained in the range of  $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> Zn<sup>2+</sup> by plotting  $I_0 - I/I_0$  versus  $-\log \text{Zn}^{2+}$ , where  $I_0$  is fluorescence intensity of the membrane in pH 6.0 buffer solution and  $I$  is the fluorescence intensity of the membrane in the Zn<sup>2+</sup> containing solutions. A straight line obtained from this plot can be described by the equation  $y = -0.2611x + 1.7886$  and the calculated correlation coefficient,  $r$ , was found to be 0.9841.

### 3.4. Effect of Membrane Composition

Because the nature of the plasticizer used affects the membrane characteristics such as dielectric constant, mobility and state of ionophores, it was also expected to play a key role in determining the ion selectivity of the membrane.<sup>35-36</sup> Four different plasticizers were investigated and the results are shown in Table III. Since DOP containing membrane revealed the best physical properties with maximum sensitivity and longer linear dynamic range for Zn<sup>2+</sup> ions, it was selected as the plasticizer.

Lipophilic borate salts, which are widely used additives in cation selective chemical sensors, were studied in terms of their chemical stability inside the plasticized PVC membranes.<sup>37</sup> The optical response characteristics of the optode membranes, and especially their selectivity, depend on the lipophilic ionic additive concentration. Amount of anionic sites in the membranes affects on linear range of optodes.<sup>35</sup> From Table IV one can see that the response concentration range of the optode membrane becomes wider and response time shorter as the amount of PTCPB in the optode membrane increases from 1% to 2%, which might be caused by the increasing hydrophilicity owing to the addition of PTCPB. However, the response concentration range of the optode membrane becomes narrower when the content of PTCPB is larger than 2%. Therefore, 2% PTCPB provided the best response for Zn<sup>2+</sup> and was chosen for further studies.

**Table IV.** Effect of PTCPB on the response behavior of the optodes.

Content of PTCPB(%)	Working concentration range (mol L <sup>-1</sup> )	Response time (min) ( $2.0 \times 10^{-6}$ mol L <sup>-1</sup> Zn <sup>2+</sup> )
1	$5.0 \times 10^{-6}$ to $8.6 \times 10^{-4}$	4
2	$5.0 \times 10^{-7}$ to $1.2 \times 10^{-4}$	3
3	$6.0 \times 10^{-7}$ to $1.0 \times 10^{-5}$	3

### 3.5. Effect of pH

The influence of pH of test solution on the fluorescence response of the proposed optical sensor was studied in the pH range of 4.0–9.0. The fluorescence intensity measurements were made in the presence  $2.0 \times 10^{-6}$  mol L<sup>-1</sup> Zn<sup>2+</sup> solution of different pH values. In a wide range of pH from 5.0 to 8.0, pH change does not affect significantly the response of the optode membrane, which provides convenient conditions for applications of the proposed sensor in determination of Zn<sup>2+</sup> in real samples. Below pH 5.0 and above pH 8.00 the sensor response decreased slightly. In subsequent experiments, Zn<sup>2+</sup> measurements were made in 0.1 mol L<sup>-1</sup> CH<sub>3</sub>COOH/NaCH<sub>3</sub>COO<sup>-</sup> buffer of pH 6.0.

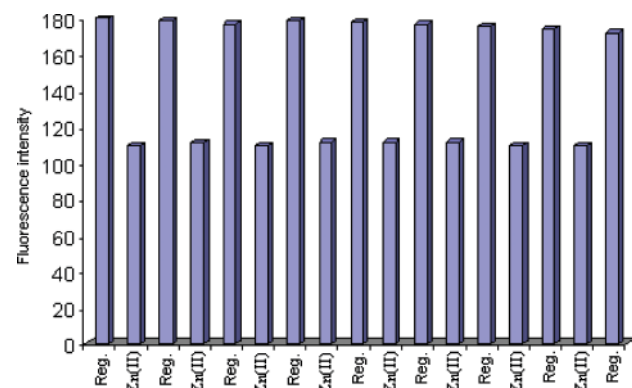
### 3.6. Reversibility and Reproducibility

The sensor was fully reversible within the dynamic working range and the approximate response time  $\tau_{90}$  was 3 min. The optical sensor was regenerated with 0.1 mol L<sup>-1</sup> EDTA solution (Fig. 4). The Zn<sup>2+</sup> complexed with HCB could be eluted out of the sensing membrane quickly and completely, which demonstrated the excellent reproducibility and reversibility of the sensor. Between the first and eighth cycles, the level of reproducibility of the upper signal level achieved was quite good with a low standard deviation,  $175.8 \pm 2.14$ . One sensor film could be used for about 20 repetitive cycles and when kept in a THF saturated desiccator in dark the same sensor film was found to be stable for at least four months.

The limit of detection (LOD) defined here as the concentration equivalent to a signal of blank plus three times the standard deviation of the blank<sup>38</sup> was calculated to be  $2.2 \times 10^{-7}$  mol L<sup>-1</sup> ( $14.4 \mu\text{g L}^{-1}$ ).

### 3.7. Selectivity

Some common ions including alkali, alkaline earth and heavy metal ions were chosen for the study on the



**Fig. 4.** Variation of the fluorescence of the membrane for repeatedly exposing into  $2.0 \times 10^{-6}$  mol L<sup>-1</sup> Zn<sup>2+</sup> solution and 1.0 mol L<sup>-1</sup> EDTA solution (Reg = Regeneration).

**Table V.** Interference of different metal ions to the fluorescence determination of Zn<sup>2+</sup> with the proposed sensor at pH 6.0.

Interferent	Concentration (mol L <sup>-1</sup> ) <sup>a</sup>	Relative error % ( $\Delta F^b/F_0^c \times 100$ )
Na <sup>+</sup>	$1.0 \times 10^{-2}$	2.9
K <sup>+</sup>	$1.0 \times 10^{-2}$	1.4
Ca <sup>2+</sup>	$1.0 \times 10^{-2}$	3.3
Mg <sup>2+</sup>	$1.0 \times 10^{-2}$	3.7
Ag <sup>+</sup>	$1.0 \times 10^{-2}$	1.6
Al <sup>3+</sup>	$1.0 \times 10^{-2}$	2.1
Co <sup>2+</sup>	$1.0 \times 10^{-2}$	4.6
Ni <sup>2+</sup>	$1.0 \times 10^{-2}$	6.3
Ni <sup>2+</sup>	$1.0 \times 10^{-3}$	1.9
Cu <sup>2+</sup>	$1.0 \times 10^{-2}$	6.8
Cu <sup>2+</sup>	$1.0 \times 10^{-3}$	2.8
Cd <sup>2+</sup>	$1.0 \times 10^{-2}$	2.3
Pb <sup>2+</sup>	$1.0 \times 10^{-2}$	1.4
Fe <sup>3+</sup>	$1.0 \times 10^{-2}$	2.1
Cr <sup>3+</sup>	$1.0 \times 10^{-2}$	3.2
Hg <sup>2+</sup>	$1.0 \times 10^{-2}$	2.4
SO <sub>4</sub> <sup>2-</sup>	$1.0 \times 10^{-2}$	1.9
NO <sub>3</sub> <sup>-</sup>	$1.0 \times 10^{-2}$	2.3
CO <sub>3</sub> <sup>2-</sup>	$1.0 \times 10^{-2}$	3.1
I <sup>-</sup>	$1.0 \times 10^{-2}$	2.2

<sup>a</sup>The concentration of Zn<sup>2+</sup> is fixed at  $2.0 \times 10^{-6}$  mol L<sup>-1</sup>. <sup>b</sup> $\Delta F$  is the difference of fluorescence intensities before and after exposure to interferent ions. <sup>c</sup> $F_0$  is the fluorescence intensity in the absence of interferent ions.

selectivity of the Zn<sup>2+</sup> sensor. A foreign species was considered not to interfere with measurement if a relative error caused by it was less than 5% in the determination of  $2.0 \times 10^{-6}$  mol L<sup>-1</sup> Zn<sup>2+</sup>. The results presented in Table V revealed that most of the species at  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> concentrations caused no interference. Ni<sup>2+</sup> and Cu<sup>2+</sup> interfered significantly, but  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> concentration of these cations could be tolerated without showing appreciable interfering effect on the Zn<sup>2+</sup> assay.

### 3.8. Analytical Application

In order to assess the usefulness of the proposed method for the determination of Zn<sup>2+</sup>, it was applied to actual samples of hair. For evaluating the accuracy of the method, a comparison between results obtained by the proposed method and FAAS was performed. From the results of three replicate measurements given in Table VI, it is immediately obvious that there is satisfactory agreement between the results obtained by the Zn<sup>2+</sup>-selective optode and by FAAS.

**Table VI.** Determination of zinc concentration in hair samples ( $n = 3$ ).

Hair sample	Amount of zinc ( $\mu\text{g kg}^{-1}$ )		Relative error(%)
	Optode	FAAS	
1	$172.6 \pm 0.7$	$170.5 \pm 0.8$	1.23
2	$121.9 \pm 1.2$	$118.4 \pm 1.5$	2.96
3	$128.2 \pm 0.9$	$132.4 \pm 1.2$	-3.17
4	$102.4 \pm 1.2$	$100.7 \pm 1.7$	1.68

#### 4. CONCLUSION

In the present work, a simple, sensitive, selective and inexpensive method was developed for the determination of zinc. The determination of  $Zn^{2+}$  was accomplished by making the use of a novel schiff base ligand embedded in PVC films. An excellent linear relationship was established between fluorescence intensity and  $Zn^{2+}$  concentration from  $5.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> with the detection limit of  $2.2 \times 10^{-7}$  mol L<sup>-1</sup> ( $14.4 \mu\text{g L}^{-1}$ ). It has also been shown that the response of this sensor does not vary significantly in the pH range 5.0–8.0. The sensor was applied successfully to the determination of zinc in scalp hair samples.

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