Introduction of a new nitrite-selective optical sensor for food analysis using a copper(II) schiff base complex

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Abstract

A copper(II) Schiff base complex, [Cu(cd4OMeSalMeen)], methyl-2-{[1-methyl-2-(4-methoxy-phenolate)mehylidynenitrilo]ethyl}amino-1-cyclopentene dithiocarboxylate copper(II), was incorporated into triacetylcellulose membrane and applied as ionophore in order to develop an anion-selective optical sensor for the analysis of nitrite by absorption spectrophotometry. At optimum pH 3.0, a linear calibration curve was observed for nitrite in the range of 0.50 to 7.00 mgL^{-1} with a detection limit of 0.04 mgL^{-1}. The response time of the optode ($t_{95\%}$) was found to be 8–10 min, depending on the nitrite ion concentration. The proposed sensor was fully recovered in nitric acid solution (0.1 M) and had acceptable reproducibility (RSD=1.9%). The optode exhibited good selectivity toward nitrite ion according to hard-soft acid base (HSAB) principle and the formation constant was calculated. The application of the sensor for determination of nitrite content in meat products was quiet successful.

Keywords: Optical sensor; copper(II) Schiff base; nitrite; spectrophotometry; formation constant.

Introduction

Nitrite has an important role in food industry. Various applications have been introduced for nitrite in the industry [1] , but its efficient role as a food additive is of great interest, especially in meat products. The preservative use of nitrite is due to its ability to prevent microbial growth, gives taste and color to the meat and inhibits lipid oxidation that leads to rancidity. Despite the above mentioned advantages, it can be toxic in high concentrations, causing environmental pollution and serious health problems for human [2]. The major concern is the formation of carcinogenic nitrosamines in meat products from the reaction of the amines with nitrite and subsequently their conversion to diazonium ions under acidic conditions (such as what occurs in the human stomach). Some of these nitrosamines can lead to the cancer because they form carbocations which can react with biological nucleophiles (such as DNA or an enzyme) in the cells and disrupt their normal function [3-5]. Obviously, it is a great deal to find a simple, fast and low-cost method for determination of nitrite in food.

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Different approaches have been developed for the analysis of nitrite [6], including kinetic [7,8], chromatography [9,10], spectrophotometric [11-15], spectroflurimetric [16-19], capillary electrophoresis [20-22], atomic absorption spectroscopy [1], pulse polarography [23] and electroanalytical methods [24-26]. However, some of these methods are expensive and time-consuming [27], and some of them suffer from poor sensitivity [17].

Among these techniques, optical sensors appeared to be more suited as they offer good selectivity, sensitivity, low detection limit and less complication [28-30]. Recently, sensors based on optical signal measurements and fabricated with Schiff bases as ionophores have been applied to determine specific ions. The selection of these bulk optodes is mainly because of their stability under different conditions and the possibility of tuning their electronic and steric features [31]. This method have been used successfully to analyze some metal cations such as Cr(III) [32], Ce(III) [33], Co(II) [34], Fe(III) [35,36], Pb(II) [37] and Ag(I) [38]. Nevertheless, only few articles have been reported the use of Schiff base ionophores for monitoring the anions [25,39].
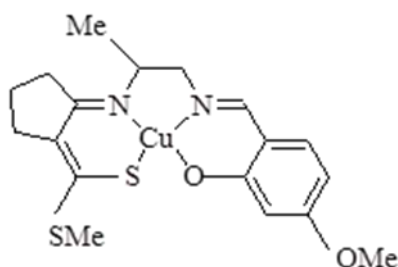
Figure 1. Schematic structure of the ionophore [Cu(cd4OMeSalMeen**)]** Schiff base complex.

Our research has been focused on applying [Cu(cd4OMesalMeen)] Schiff base complex (Figure 1) as a new sensor for quantitative determination of nitrite

and development of this optode for analyzing nitrite in real samples.

Experimental
Reagents and solutions
All chemicals were of the best available analytical grade and employed without any prior purification. Doubly distilled water was used throughout. Ethylenediamine was obtained from Merck. A stock solution of nitrite, 100 mgL^{-1}, was prepared by dissolving sodium nitrite (Merck) in water. Sample solutions were obtained daily by appropriate dilution. Buffer solutions, containing boric acid, acetic acid and phosphoric acid (0.04 M each) were prepared and different pHs were adjusted by addition of sodium hydroxide (0.2 M). [Cu(cd4OMesalMeen)] stock solution, 1.0×10^{-4} M, was prepared daily by dissolving 0.0042 g of the Schiff base and diluting with 100 mL ethylenediamine.

Apparatus
The absorbance measurements were carried out on a Shimadzu 1601 PC UV-Visible spectrophotometer. A pH-meter, Jenway model 3510, containing a combined glass electrode was used for monitoring pH adjustments.

Synthesis of the ionophore
The ionophore used throughout this research, [Cu(cd4OMeSalMeen)] Schiff base, was obtained as follows: At first, Methyl-2-(1-methyl-2'-aminoethane) amino-1 cyclopentenedithiocarboxylate (HcdMeen) was prepared applying published methods. Then, the ligand was formed by adding the equimolar amount of appropriate salicylaldehyde derivative and other diketon to a solution of HcdMeen in methanol. The yellow precipitate was recrystallized from 1:1 solution of methanol/chloroform. The preparation of the Schiff base was performed at the next step. A solution of copper(II) acetate (0.1 mmol) in 10 mL

of methanol was added to a solution of the resulting ligand (0.1 mmol) in 10 mL of chloroform/methanol (2:1). The mixture was stirred for 15 min and then allowed to stand at room temperature for 24 h. The product was filtered off and recrystallized from acetonitrile/methanol (1:1) to give [Cu(cd4OMeSalMeen)] as a reddish brown solid [40].

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 3–4 min in order to remove colored gelatinous layers and increase porosity of the membranes. Afterwards, the films were treated with a clear solution of [Cu(cd4OMeSalMeen)] in ethylenediamine for 4 min at room temperature. The membranes were finally washed with detergent solutions and rinsed with water. Prepared membranes were stable over several days of storage under pure water.

Measurement procedure
The prepared membrane was first placed in a 1.0 cm quartz cell containing 3 mL of the buffer solution at pH 3 for almost 15 min. After reaching equilibrium, the membrane sensor was mounted vertically inside the cell and the absorbance was measured at the fixed wavelength of 395 nm. Then, the sample cell was titrated with a known amount of nitrite solution, using Hamilton microliter syringe. The absorbance values were measured spectrophotometrically by monitoring the change in the absorbance of the sensor at 395 nm with the time intervals of 10 min.

Thermodynamic studies
The formation constant, K_{eq}, for the reaction of [Cu(cd4OMesalMeen)] and nitrite ion, was determined by spectrophotometric titration.

A solution from copper complex (10^{-4} M) with a constant ionic strength (*I*) of 0.1 M sodium perchlorate was prepared. Of each solution, 2.5 mL was transferred into the thermostated cell compartment of the UV- Vis instrument, which was kept at constant temperature 10, 20, 30, and 40 (±1˚C) by circulating water. Each solution was titrated by adding aliquots of the nitrite ion using a Hamilton microliter syringe. Concentrations of nitrite ion were varied in the range of 1 to 10 fold in excess. The absorption measurements were monitored at various wavelengths in 300-500 nm regions where the difference in absorption between the substrate and the product was the largest after the equilibrium attained.

Sample preparation
Meat products (six different brands of sausage: A, B, C, D, E, F) were collected from local markets in Shiraz, Iran. Extraction of nitrite from the meat products was made using the AOAC sample preparation procedure [41,42]. 5 g of each sample was transferred to the mixer and homogenized carefully. 50 mL of hot water (80 ℃) and a pellet of sodium hydroxide (to prevent the liberation of nitrous acid) were added and the mixture was shaken about 15 min for the complete extraction of nitrite.

The filtrate was then taken into a 500 mL beaker and the diluted solution was analyzed using the fabricated Schiff base sensor.

Results and discussion
Working principles and spectral characteristics of the optode
According to the experiments, the proposed Schiff base membrane revealed remarkable tendency toward NO_2^- ion over a wide variety of tested SCN^-, CN^-, I^-, OH^-, CH_3COO^-, PO_4^{3-}, SO_3^{2-} ions. The response mechanism of the optode is completely according to the hard-soft

acid base principle (HSAB) and is believed to be based on the complexation of nitrite ion (as borderline base) to the central copper(II) atom of the Schiff base (as borderline acid). The absorption spectra of the immobilized Schiff base and the resulting complex were recorded at the buffered solution (pH 3). As illustrated in Figure 2, the spectrum of the Schiff base includes two intense bands.
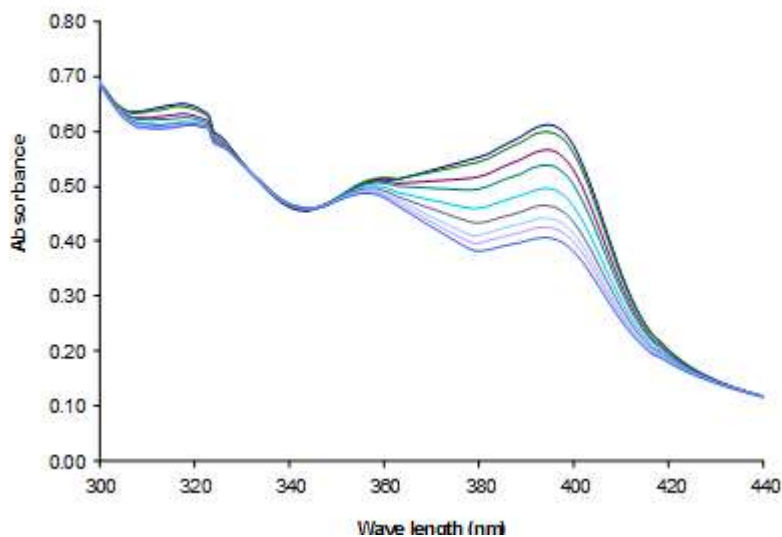

Figure 2. Absorption spectra of the optical sensor in the presence of (0.0– 8.0 mgL^{-1}) nitrite ion by addition of 1.0 mgL^{-1} in each interval at pH=3.

The absorption band at 395 nm is attributed to a metal to ligand charge transfer (MLCT) and the other band at 310 nm is assigned to a $\pi \rightarrow \pi^*$ transition [43]. All absorption measurements have been performed conveniently by monitoring the decay of the MLCT band at the corresponding λ_{max} (395 nm). The variation of the electronic spectra for [Cu(cd4OMesalMeen)] titrated with nitrite ion in ethylenediamine at T = 283 °K (Figure 2) is shown in which the absorption of adduct was different from the copper complex and nitrite ion. The position of the maxima is slightly changed upon the addition of nitrite which is most likely due to the subsequent interaction of nitrite with the

ionophore. As the nitrite concentration is increased, the absorption bands at 395 nm and 310 nm are decreased. The isosbestic points for this system show that there are only two species in equilibrium.

Effect of pH on the optode response
In order to investigate the impact of pH on the response of the optode, the absorbance data were recorded at different pHs ranging from 1–11. As can be seen from Figure 3, the maximum value of ΔA (defined as the difference in absorbance value between immobilized Schiff base and the complex) was occurred at pH 3. Therefore, this pH was chosen for further experiments.
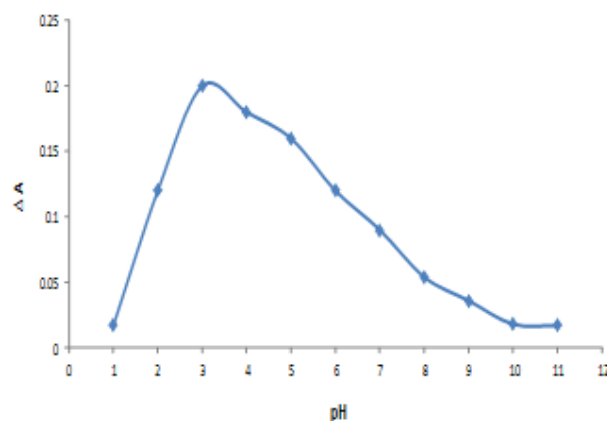
Figure 3. Effect of pH on the response of the nitrite-optical membrane sensor.

Response time

The rate determining step in this type of reactions is considered as the diffusion of the analyte to the optical membrane and association with the ionophore. The time required to reach 95% of this action is called "response time". The time-dependent response feature of the present bulk optode was studied by recording the absorbance change from a buffer solution at pH 3 to a buffered nitrite solution of 7.50 mgL^{-1}. The results are plotted in Figure 4. The response time of the membrane was found to be 8–10 min depending on the concentration of nitrite.
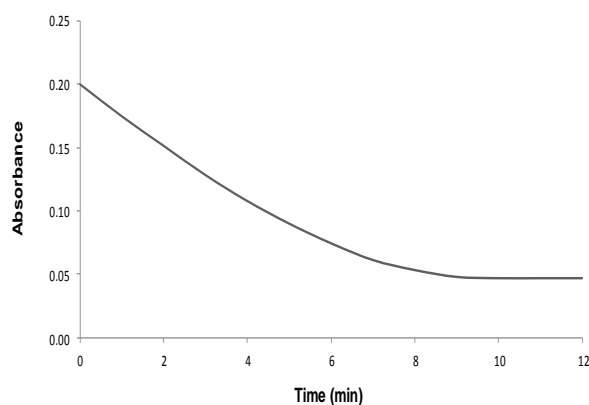
Figure 4. Typical response curve of the optode at 395 nm as a function of time when the membrane is exposed to 7.5 mgL^{-1} nitrite ion

$y = 0.0299x - 0.0106$
$R^2 = 0.9987$
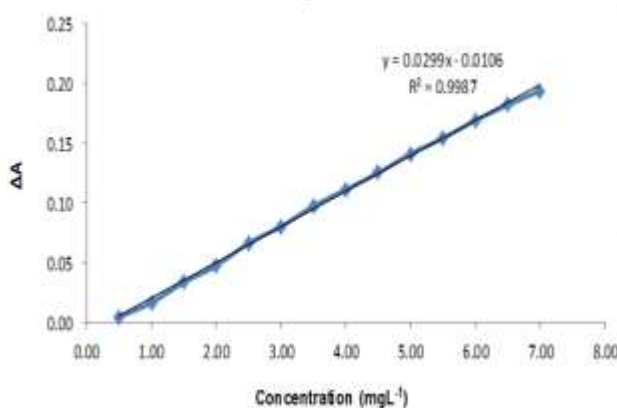
Figure 5. Callibration curve for the determination of nitrite ion using the optode

Dynamic range

The absorbance data of the optode membrane sensor were obtained upon changing the concentration of nitrite from 0.50 to 8.50 mgL^{-1}. As depicted in Figure 5 graph of ΔA, absorbance difference, against different concentrations of nitrite gives good straight-line between 0.50 to 7.00 mgL^{-1} fitted to the correlation equation ΔA= 0.0299 C − 0.0106 with a regression coefficient of 0.9987, where C is the nitrite ion concentration expressed in mgL^{-1}. The detection limit, defined as 3s$_b$/m, where s$_b$ is the standard deviation of the blank signal (n=14) and *m* is the slope of the calibration curve, was estimated to be 0.04 mgL^{-1}.

Regeneration of the optical sensor

Since the regeneration of the optode is an important feature, different reagents such as HCl, HNO$_3$, H$_2$SO$_4$, NaOH, EDTA and KSCN were tested to find which one is capable of recovering the membrane.

According to the results, the sensor showed efficient reversibility upon treatment with 0.1 M HNO$_3$ solution. After this regeneration step, the membrane should be placed in blank buffer solution (pH 3) for 10–15 min, and get ready for the next measurement.

Repeatability and reproducibility

The repeatability of the prepared membrane was evaluated by using a single membrane and performing seven replicate measurements for 4.0 mgL^{-1} nitrite buffered solution followed by recovering the membrane with 0.1 M HNO$_3$ solution. The resulting standard deviation was found to be 2.2%.

Determination of the reproducibility of the sensor was achieved by preparing 5 different membranes from the same mixture, exposing them into 4.0 mgL^{-1} nitrite solution and measuring the absorbance at 395 nm. The calculated standard deviation was 1.9%.

Effect of foreign ions

To study the selectivity of the fabricated membrane, the absorbance signals of the optode for nitrite ion were recorded in the presence of foreign species. The analysis was carried out in the buffered solution of pH 3, containing constant amount of nitrite ion, 1.0 mgL^{-1}, plus different concentrations of interfering ions (up to 1000 times of the analyte ion). The tolerance limit, defined as the concentration of added species causing less than ±5 relative error, was detected for each ion. As can be deduced from Table 1, no interference was observed and the sensor was completely selective to nitrite over the other studied foreign ions.

Table1. Effect of forign ions on the determination of 1.0 mgL^{-1} nitrite ion

Foreign ions	Tolerated molar ratio [interference]/[nitrit]
I$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Br$^-$	300
SCN$^-$, ClO$_3^-$, CH$_3$COO$^-$, HCO$_3^-$, CN$^-$, S$_2$O$_3^{2-}$, F$^-$, Oxalate, tartrate	300
K$^+$, Mn^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+}	1000
NH$_4^+$, Fe^{2+}, Sr^{2+}, Cr^{3+}, La^{3+}, Cu^{2+}, Pb^{2+}, Mg^{2+}, Ag$^+$	500
Fe^{3+}	100

Determination of nitrite in meat products
The application of the new Schiff base sensor was investigated by the analysis of nitrite in real samples. Six different samples of meat products, containing nitrite as food additive, were treated according to the routine AOAC sample preparation procedure and determination of nitrite content was achieved easily by applying the proposed optode. The results have been summarized in Table 2.

Table 2. Results of nitrite ion determination in meat samples

Sausage sample	Nitrite added (mgL^{-1})	Nitrite found (mgL^{-1})	Recovery (%)
	0.0	0	–
Sample A	1.0	1.1	110
	2.0	2.1	105
	0.0	1.5	–
Sample B	1.0	2.6	106
	2.0	3.4	93
	0.0	0.0	–
Sample C	1.0	1.1	110
	2.0	1.9	95
	0.0	0.0	–
Sample D	1.0	1.0	100
	2.0	2.1	105
	0.0	2.5	–
Sample E	1.0	3.6	104
	2.0	4.6	104
	0.0	0.0	–
Sample F	1.0	1.1	110
	2.0	1.9	95

Formation constant and thermodynamic free energy calculations for copper(II) Schiff base complex with nitrite ion in ethylenediamine solvent
The formation constant of the copper(II) Schiff base complex were calculated by using Ketelaar's equation (1).[44]

$$P = \frac{1}{(\varepsilon_C - \varepsilon_A - \varepsilon_D)} \cdot \left[\frac{1}{K} + (C_A^\circ + C_D^\circ) \right] \qquad (1)$$

where $P = C_A^\circ \times C_D^\circ / (A - A_A^\circ - A_D^\circ)$, C_A° and C_D° are the initial concentrations (mol. dm^{-3}) of the acceptor and the donor, respectively. A is the optical density of the solution including the acceptor and the donor, A_A° and A_D° are the optical densities of the pure acceptor and the pure donor in the solution of concentration C_A° and C_D°.

ε_C, ε_A and ε_D are the molar extinction coefficients (dm^3. mol^{-1}. cm^{-1}) of the complex, the acceptor and the donor, respectively. K_{eq} is the equilibrium constant of the formed adduct and the cell optical path length is 1 cm. The linear plots of P against $(C_A^\circ + C_D^\circ)$ for [Cu(cd4OMesalMeen)] titrated with nitrite ion at various temperatures in ethylenediamine are shown in Figure 6. It signifies that only a 1:1 adduct is formed, since the mixture of 1:1 and 1:2 or only 1:2 complex in a system would lead to a curve. The formation constant of the studied complex was calculated from the ratio of the slope to the intercept by least-square method. The K measurements were repeated at least twice and were reproducible.

The thermodynamic parameters were calculated by using the well-known van't Hoff equation (2).

$$\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (2)$$

where *K* is the equilibrium constant, R is the gas constant and T is the temperature in Kelvin. Thermodynamic parameters of the studied adduct were obtained from the linear plots of lnK_{eq} against 1/T. The

values of ΔH° and ΔS° were obtained from the slope and the intercept, respectively. The formation constant and the thermodynamic parameters data are collected in Table 3.

The linear plots of ln*K* against 1/T for the interaction of [Cu(cd4OMesalMeen)] with nitrite ion at various temperatures in ethylenediamine is shown in Figure 7.
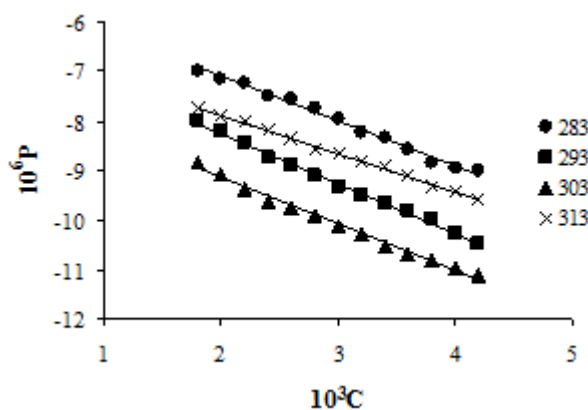
Figure 6. Plots *P* against *C* for [Cu(cd4OMesalMeen)] with nitrite ion in ethylenediamine, where $P = C_A^\circ \times C_D^\circ / (A - A_A^\circ - A_D^\circ)$ and $C = (C_A^\circ + C_D^\circ)$ at 293 K

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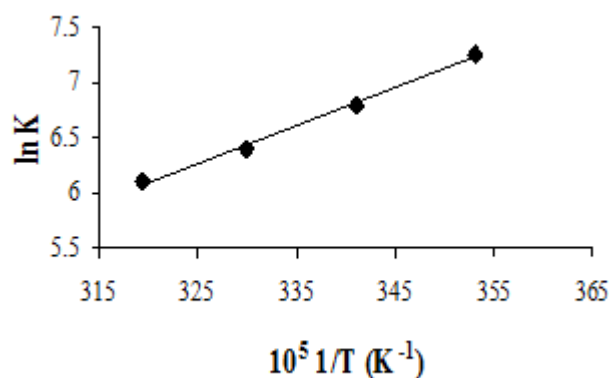
Figure 7. Plot of ln*K* against 1/T for [Cu(cd4OMesalMeen)] with nitrite ion, in ethylenediamine

Table 3. The formation constant and the thermodynamic parameter values ΔH°, ΔS° and ΔG° for the interaction between copper(II) Schiff base complex and nitrite ion in ethylenediamine at different temperatures (°K)

Keq × 10^{-2} (K)/(dm³. mol^{-1})	ΔH°/(kJ mol^{-1})	ΔS°/(J K^{-1}mol^{-1})	ΔG°/(kJ mol^{-1})^a
14.19±1.31 (T=273)			
8.98±0.37 (T=283)			
5.55±0.08 (T=293)			
4.50±0.09 (T=303)	-16.16±3.91	-42.47±9.20	-29.03±2.73

^{a} ΔG° values are calculated from ΔG° = ΔH° - *T*ΔS° at T = 303°K

Conclusion

A copper(II) Schiff base complex, [Cu(cd4OMeSalMeen)], was successfully immobilized on triacetylcellulose membrane and a new optical sensor was resulted for the analysis of nitrite ion. The proposed optode has provided a useful means for the determination of nitrite content in meat products as it possesses the advantages of simple preparation and handling, fast and easy regeneration, and low cost and good selectivity. The formation constant and thermodynamic parameters were calculated for the interaction of the Schiff base with nitrite ion and showed that the reaction was exothermic.

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