IAU-ARAK

J. Iran. Chem. Res. 4 (2011) 105-111

Journal of the Iranian Chemical Research

www.iau-jicr.com

Design novel optical sensor for determination of bismuth based on immobilization of 4-(4-nitrophenyl)-1-naphthol on a triacetylcellulose membrane

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Received 28 February 2011; received in revised form 26 May 2011; accepted 27 May 2011

Abstract

A novel optical sensor has been proposed for sensitive determination of bismuth ion based on immobilization of 4-(4-nitrophenylazo)-1-naphthol on a triacetylcellulose membrane. Chemical binding of bismuth ions in solution with a 4-(4-nitrophenylazo)-1-naphthol immobilized on the triacetylcelluse surface could be monitored spectrophotometrically. The optode shows excellent response over wide concentration range 0.4-3.6 μg mL^{-1} bismuth with a limit of detection of 0.14 μg mL^{-1} bismuth. The influence of factors responsible for the improved sensitivity of the sensor were studied and identified. The response time of the optode was 30 sec for a stirrer solution. The influence of potential interfering ions on the determination of 0.4 μg mL^{-1} bismuth was studied. The proposed optode was applied to the determination of bismuth in pharmaceutical formulation samples.

Keywords: Optode; Sensor; Bismuth; Determination; Spectrophotometric; Water samples.

1. Introduction

Optical chemical sensors or optode have become an important area of research since their introduction two decades ago. Optical sensors are compact and ideally suited to miniaturization while at the same time they are resisting to electrical interference and utilize the simplicity of photometric measurement. Recent decades have been an increase in the development of optical sensors for metals, because of easy fabrication, low cost, good selectivity and sensitivity [1-4]. Most optical sensor for determination of metal ions is based on either conventional indicator dyes, neural ionophores or on biological recognition components [5]. From the above compounds, organic indicator dyes and the immobilization technique play important roles in the development and design of the optode [6-9]. A common weakness of all of these membranes is the leakage of the reagent into aqueous solutions in contact with them. The ideal immobilization technique to produce a highly stable assembly of molecules that remain strictly to dissolve the reagent is covalent attachment to a functionalized support, by direct immobilization of ligand on the surface of membrane or increasing the lipophilicity of the corresponding reagent [10].

According to our knowledge, there is not any report for measuring of bismuth in real sample by using optical sensor that is covalently attachment of a molecule. In the present work, the

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fabrication of an optode for determination of low levels of bismuth is described in which the sensing reagent is 4-(4-nitrophenylazo)-1-naphthol immobilized on triacetylcellulose membrane. Also a simple method is presented for immobilizing reagent on membrane. The optode responds to bismuth ion by changing color reversibility from orange-red to yellow.

2. Experimental

2.1. Reagents

All reagents used in this work were of analytical grade. The indicator 4-(4-nitrophenylazo)-1-naphthol was obtained from Merck. Ethylene diamine was supplied from Merck. Universal buffer solutions were prepared from boric acid, citric acid and phosphoric acid (0.04 M) [11]. The final pH was adjusted by the addition of 0.2 M sodium hydroxide. A stock solution of 1000 μg mL^{-1} of Bi(III) ion was prepared from its commercial salt (nitrate). Standards of working solution were made by appropriate dilution daily as required.

2.2. Apparatus and measurement procedures

A Hewlett-Packard 8453 diode array spectrophotometer controlled by a Hewlett-Packard computer was used for recording the visible spectra and absorbance measurements. The sensing membrane was placed and fixed in a disposable cuvette and all measurements were performed in a batch mode. A Horiba M-12 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 3.0 and 9.0. The optode membrane response to different metal ions was investigated in universal buffer at different pH. The membrane was first exposed to the buffer solution and the absorbance was measured at 478 nm. Then the sample solution was added and the absorbance at 478 nm was again measured after 30 s.

2.3. Preparation of the sensor membrane

The immobilized indicator on triacetylcellulose was prepared according to the following procedure [12]. The transparent triacetylcellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hydrochloric for several seconds in order to remove colored gelatinous layers. The films were treated with a clear solution of 4-(4-nitrophenylazo)-1-naphthol (3 mg) in 10 mL ethylene diamine for 5 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

4-(4-nitrophenylazo)-1-naphthol (Fig. 1), is a photometric reagent for bismuth ions at a suitable pH.

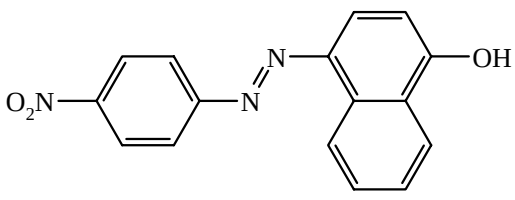

Fig. 1. Chemical structure of 4-(4-nitrophenylazo)-1-naphthol.

Its selectivity to certain metal ions may be achieved or improved by applying appropriate separation or using masking agents. The absorption spectra of the immobilized triacetylcellulose membrane obtained after being equilibrated in universal buffer solution (pH 10.0) containing different concentrations of bismuth ion shown in Fig. 2. These figure show that the formation of the complex on the surface of optode causes to appear as a new peak at 478 nm. According to the structure of 4-(4-nitrophenylazo)-1-naphthol, and the fact that only reagents with amino groups could be linked chemically with triacetylcellulose [13], we used ethylene diamine as a bridge between 4-(4-nitrophenylazo)-1-naphthol and triacetylcelluse film. The wavelength 478 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength.

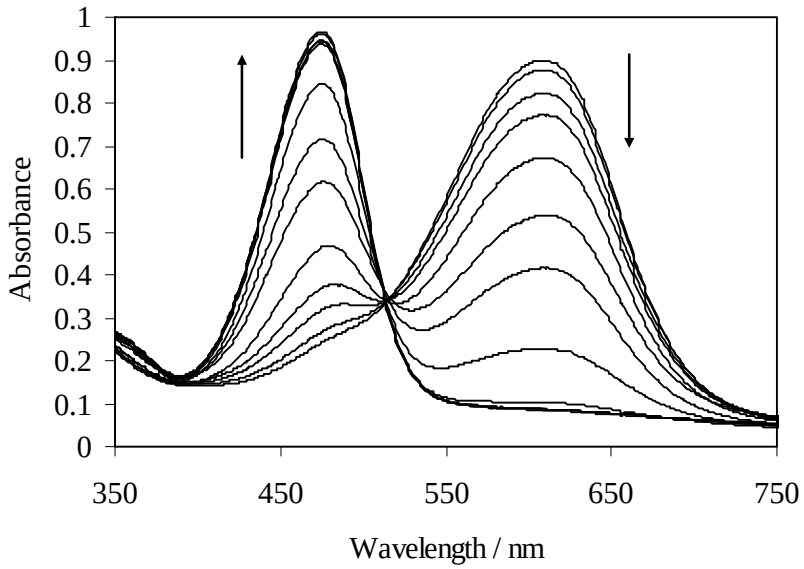

Fig. 2. Absorption spectra of optode film in the presence of 0.1-5.6 µg mL^{-1} of bismuth at pH 10.0

3.2. Effect of pH

The equilibrium of the complexation reaction of 4-(4-nitrophenylazo)-1-naphthol with bismuth ion is affected by the solution pH. The effect of pH on the complex was studied in the range of 1-11 by changing the universal buffer. The absorbance measurements were made for 2.4 µg mL^{-1} bismuth ion at different pH values at 478 nm. As can be seen in Fig. 3, a maximum value in the sensor response was obtained at pH 10.0. This pH was selected for further studied.

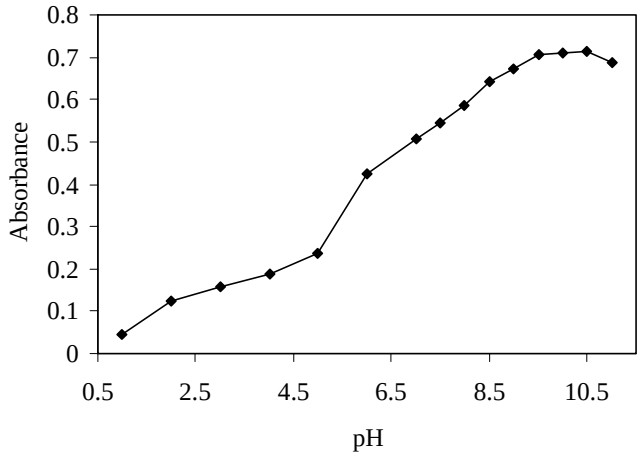

Fig. 3. Effect of pH on the optode film response.

3.3. Effect of the amount of 4-(4-nitrophenylazo)-1-naphthol

In addition to the optimization of the pH, it is also necessary to optimize the amount of ligand. The absorbance measurements were made for 2.4 μg mL^{-1} bismuth ion for membranes with different amounts of 4-(4-nitrophenylazo)-1-naphthol at 478 nm. Based on the results of the above mentioned studies, the optode obtained from a mixture of 3 mg of 4-(4-nitrophenylazo)-1-naphthol in 10 mL ethylene diamine was used for further studied.

3.4. Effect of the time of immobilization and response time

The influence of time of immobilization in optical properties of the sensor is important, because of its influence on the response time and dynamic range of sensor [14]. Therefore, the optimization of this parameter was evaluated by preparing 3 mg of 4-(4-nitrophenylazo)-1-naphthol in 10 mL ethylene diamine. Then the membrane was inserted into solutions for different times (1-11 min). The result optode was washed with water. Then the optode was inserted into 2.4 μg mL^{-1} bismuth solutions in pH 10.0 and the absorbance of the optodes was measured at 478 nm. The best signal was achieved 5 min immobilization as a suitable time.

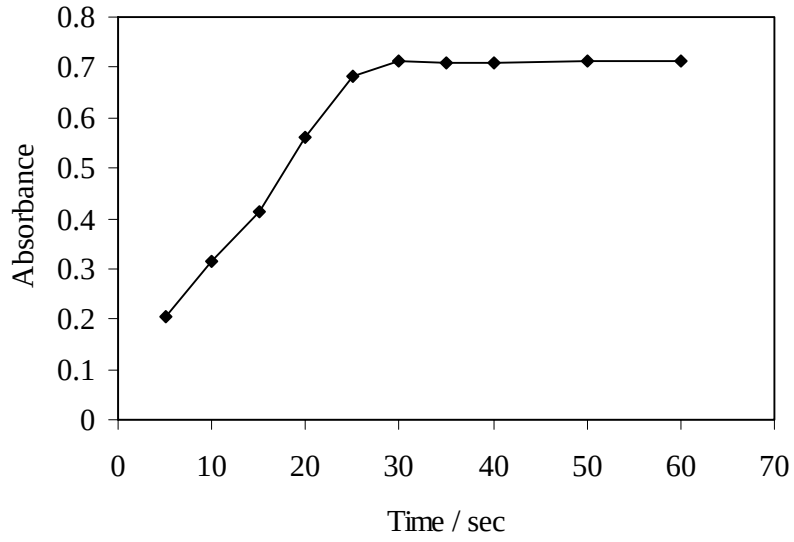

Fig. 4. Absorption as a function of time for the solution containing 2.4 μg mL^{-1} of bismuth at pH 10.0.

A further important feature of an optode is its response time. The response time is defined as the time required for 95% of the total signal change. The response time of the optode was measured as 30 s at 478 nm. Typical response curve of the sensor as a function of time at pH 10.0 is shown in Fig. 4. It should be noted that the signal leveled off after 30 s and no drift response was observed under the experimental condition employed.

3.5. Regeneration of the optode

Anions such as SCN^-, Br^-, I^- and EDTA were studied as regenerating reagents. It was found that SCN^-, Br^- and I^- were not useful for this study and the best result was obtained by applying EDTA, which gave short optode regeneration time (10 min). To study the influence of EDTA concentration on the optode response to bismuth ions, solutions of EDTA of different concentrations were studied in the range of 0.5 to 0.1 mol L^{-1}. A 0.4 mol L^{-1} EDTA concentration was thus selected as an optimum.

3.6. Dynamic range and reproducibility

Fig. 5 shows the absorption signals of the optode film to the various concentrations of bismuth ions in the range 0.1-5.6 μg mL^{-1}. In this case, 3.6 μg mL^{-1} was found as the concentration of bismuth ion that saturated the film. There is a linear correlation between absorbance of the optode and concentration of bismuth for the interval range 0.4-3.6 μg mL^{-1} bismuth, with a slope of 0.2830, intercept of 0.0012 and a correlation coefficient of 0.9971 (n=9) as shown in Fig. 6. The detection limit, defined as the average blank signal plus three times of its standard deviations (n=5), it equals to 0.14 μg mL^{-1} bismuth.

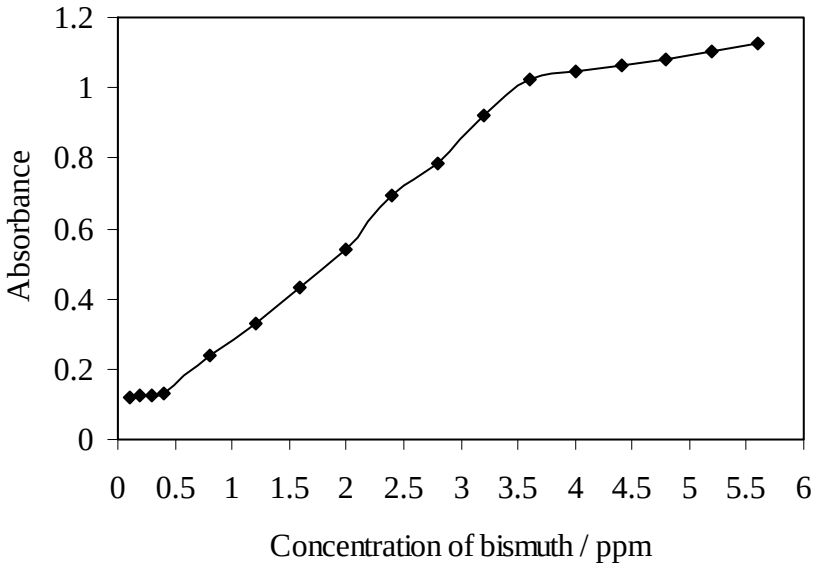

Fig. 5. The optode film response versus bismuth ion concentration in the range 0.1-5.6 μg mL^{-1} at pH 10.0.

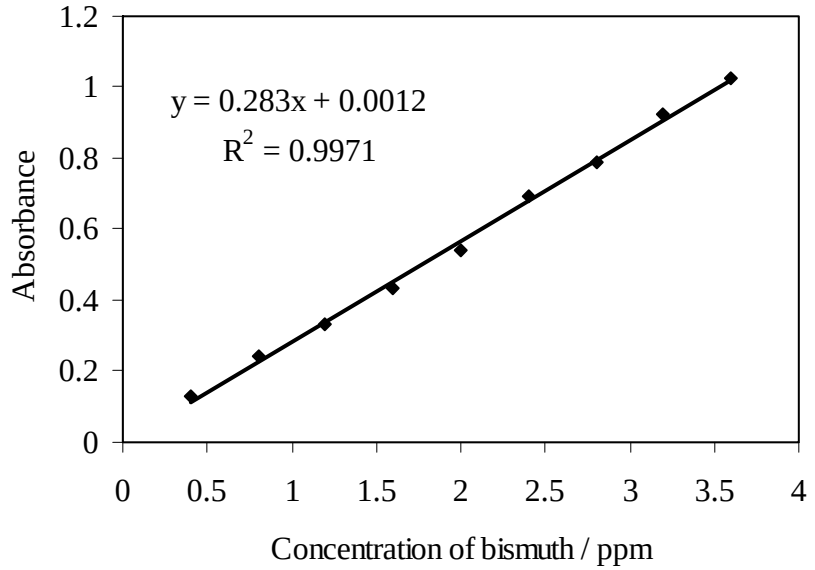

Fig. 6. Calibration curve for determination of bismuth using the optode.

The repeatability of the optode preparation was also checked for five separate optodes by measuring the absorbance of 4-(4-nitrophenylazo)-1-naphthol (612 nm). The results showed that the reproducibility of the optode preparation and dye leaching is at least 97.2%. In addition, the reproducibility for the determinations of bismuth was tested by performing six replicate

measurements of the absorbance for the optode using 0.5 and 2.0 μg mL^{-1} bismuth solutions. The relative standard deviations (R.S.D.) for these determinations were 1.42 and 1.08%, respectively.

3.7. Effect of foreign ions

To determine the selectivity of the optode, the optode was tested for the determination of 0.4 μg mL^{-1} of bismuth ions in the presence of different metal ions. The tolerance limit was taken as the concentration causing an error more than ± 5% in the analytical signal for determination of bismuth. The results indicated that cations such as Cd(II), Zn(II), Ba(II), Ca(II), Mg(II), La(III), Ce(IV), Sb(III), Al(III), Se(IV), Te(IV), Cr(VI), Pd(II) and Th(IV) (tolerance limit 500 μg mL^{-1}), Cu(II), Co(II), Fe(II), Ni(II), Hg(II), Fe(III) and Ga(III) (tolerance limit 100 μg mL^{-1}) did not show significant interferences in the determination of bismuth with optode.

3.8. Analytical application

The accuracy and precision of the proposed optode sensor as applied to the determination of the bismuth in the real matrix samples were checked via a recovery study, the standard addition method was used and sample spiking with different amount of bismuth were analyzed. As can be seen from Table 1, the results obtained in the determination of bismuth in water samples (river, waste and tap water) were quit good. Therefore, the present optode is able to predict the concentration of bismuth in the real matrix samples.

Table 1
Determination of bismuth in water samples

Sample	Bismuth added (μg mL^{-1})	Bismuth found (μg mL^{-1})*	Recovery (%)
Tap	-	No detected	-
Tap	2.0	1.86	93.0
River	-	No detected	-
River	2.0	2.14	107.0
Waste	-	0.53	-
Waste	2.0	2.71	109.0

* For three replicate measurements.

4. Conclusion

A novel optical sensor for bismuth was constructed by immobilization of 4-(4-nitrophenylazo)-1-naphthol on triacetylcellulose membrane. Although a number of sensors have been developed for bismuth determination, this is the first reported optical sensor for bismuth according to the immobilization of reagent in triacetylcelluse membrane. The present optical membrane is prepared using simple and fast approach, which is very safe and economical because of consuming inexpensive, nontoxic and available reagents. The results of this study show the optode can be successfully applied to the determination of bismuth in real samples.

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