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Design and Evaluation of a New Optode Based on Immobilization of indophenol on Triacetylcellulose Membrane for Determination of Nickel

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Abstract: An optode for nickel ion determination has been designed by immobilization of indophenol on triacetylcellose membrane. When the optode membrane is introduced into a real samples containing nickel, there is a color change from dark blue to purple, making it possible to use the change in absorbance at 645 nm as the analytical signal. The sensor could be used in the range of 0.05-3.5 µg ml^{-1} of Ni^{2+} ions with a limit of detection of 0.03 µg ml^{-1}. The response time of optode is within 8 min depending on the concentration of Ni^{2+}ions. It can be easily and completely regenerated by dilute ethylene diamine solution. The effect of different possible interfering species has been examined and was shown that the optode has a good selectivity. The results obtained for the determination of nickel ion in real samples using the proposed optode was gave satisfactory results.
Keywords: Optical sensor; Nickel; Indophenol.

1. Introduction

There is a huge variety of different chemical sensors, over the past two decades, the development and applications of optical chemical sensors have grown rapidly. An optode or (optrode) is an optical device that practically measured a specific substance by absorbance, chemical bonding or physical entrapment[1]. The sensing element consist of reagent dyes immobilized in organic or inorganic matrices. In most cases, a thin layer of polymer containing an immobilized indicator dye is the core element of such sensors[2]. Both the methods of immobilization and the class of matrix exert a significant effect on the performance of ion-selective layers[3].

Optochemical sensors based on organic polymeric thin or thick films have been investigated considerably in the last decade[4,5]. Organic indicator dyes and immobilization technique play important roles in the development and design of the optode. Normally, the immobilization of the indicator is achieved by absorption[6], chemical bonding[7] or physical entrapment[8] into the support materials. Reaction with the analyte changes the absorbance, fluorescence, reflectance and reflective index behavior of the sensitive layer[9-12].

The development of optical sensor in analytical chemistry is of great interest because of their possible application in biology, biotechnology, and ecology[13,14] and also because of their advantages such as small size, freedom from electrical interference, low cost, safety, the possibility of remote sensing, easy fabrication, good sensitivity and selectivity.

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 paper, we discuss the application of the indophenol immobilized on an optically transparent triacetylcellulose membrane for measuring the nickel ions in a real samples that were polluted with this ion that gave satisfactory results.

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. Phosphate buffer solutions were prepared from phosphoric acid/sodium hydroxide (0.1 M each). A stock solution of 1000 μg mL^{-1} Ni^{2+} ion was prepared by weighing 0.135 g of $Ni(NO_3)_2$ (Merck) and adjusting the volume to 100 mL. Working standard solutions of Ni (II) 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 μl) 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 7 for some minutes and the absorbance was measured at 645 nm. Then the nickel solution was injected into the cell and after mixing, the absorbance was measured at 645 nm after 8 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 indophenol (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 indophenol (2,6 dichloro phenolindo phenol sodium salt) which shown as DCPIS, was obtained after being equilibrated in buffer solution (pH 7) containing different concentrations of Ni (II) ions. To investigate the leaching of DCPIS from the membrane into test solution under the experimental conditions employed (i.e. in buffered solution of pH=7.0), the absorbance measurements at 645 nm of buffered solutions in the presence of the membrane was carried out with elapse of time. No measurable leaching was observed even at a period of 24 h.

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

The absorbance maxima of the immobilized DCPIS are located at 645 nm. The wavelength of 645 nm was selected for further studies because of higher selectivity and sensitivity at this wavelength. The complexation reaction of DCPIS with metal ions has been reported in the literature, and the results revealed the formation of complex with a 1:1 stoiechiometry.

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 2-10 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 645 nm. The absorbance measurements were made for 0.5 μg mL^{-1} silver ion at different pH values.

As it can be noticed in Fig.1, with increase in the pH of the solution, ΔA (difference between the absorbance of the immobilized DCPIS alone and the absorbance of the Ni- DCPIS complex) reaches a maximum value at pH 7, and then decreases. This phenomenon might be due to the fact that at lower pH values (pH<7), complexation is weak. At pH values higher than 7, Ni^{2+} forms different hydroxide species which make it unable to form complex with DCPIS. Thus, pH 7 was selected for further studies.

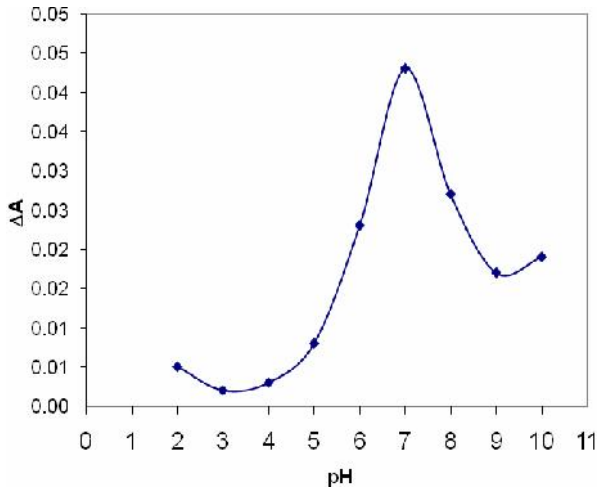

Figure 1. The effect of pH on the difference in absorbance in the presence of 0.5 mg mL^{-1} of Ni^{2+}

3.3. Response time

An important analytical feature of any optode film is its response time. In this work, the optode film was found to reach 95% of the final signal at 7-8 min depending on the concentration of Ni^{2+}. The response time of the present optode film is controlled by the time required for the analyte to diffuse form the bulk of the solution to the membrane interface and to associate with the indicator. Fig. 2 shows the time course for the absorption intensity of the membrane at 645 nm. In general, the response time is lower in concentrated solutions than dilute solution.

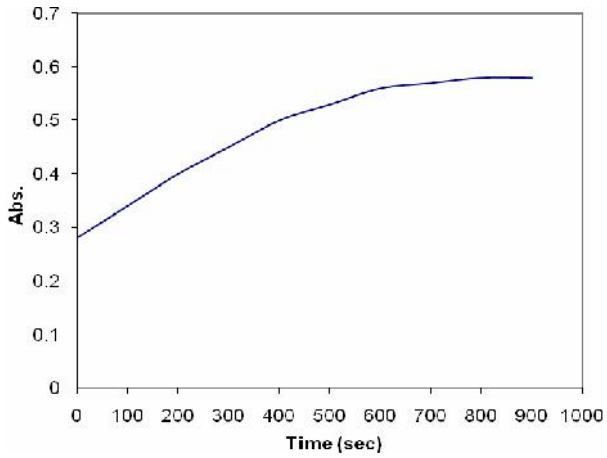

Figure 2. The response time

3.4. Dynamic range

The plot of the difference in absorbance against Ni^{2+} ion concentration can be used as a calibration plot for determination of nickel ions.

The calibration graph exhibited a linear range from 0.05 to 3.5 μg mL^{-1} which described by the equation:

$\Delta A = 0.0177 C_{Ni}^{2+} + 0.068$

ΔA is the absorbance difference (difference between the absorbance of immobilized DCPIS alone and the absorbance of the Ni- DCPIS complex) and C_{Ni}^{2+} is concentration of Ni^{2+} ion (μg mL^{-1}), with a correlation coefficient of 0.994.

In this case, 4.5 μg mL^{-1} was found as the concentration of Ni^{2+} 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 0.03 μg mL^{-1}.

3.5. Life time and stability

The lifetime of membrane was determined by adding a buffer solution (pH=7.0) in a cuvette including the film. The signal was recorded at wavelength of 645 nm over a period of about 24 h. No significant loss of the indicator occurs during this time. When the membrane was exposed to light, no drift in signal occurred and the membrane 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 five weeks under ambient conditions, which indicated that the film was stable over this period.

3.6. Regeneration of the optode

For a membrane to perform suitably, the color change must be reversible. Anions such as SCN^-, NO_3^-, SO_4^{2-}, Cl^- and EDTA were studied as regenerating reagents.

It was found that none of them was not useful for this study. The best result was obtained by applying ethylene diamine, which gave short membrane regeneration times (3-5 sec). After regeneration and for the next nickel concentration measurement, the optode should be placed in buffer (pH 7) for 10 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 *Cd(II) , Pb(II) , Ag(I) , Cu(II) , Zn(II) , Co(II) , Co(II), Mg(II)* and *Fe(III)* to solutions containing 0.05 μg mL^{-1} of nickel (II) 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.

3.8. Determination of Ni^{2+} in real samples

To show the applicability of the method, the method was applied to determine of cadmium in apple and planet samples under optimal experimental conditions. The results are given in Table 1. The nickel content of the samples has determined by atomic absorption spectrometry (AAS). From the results of five replicate measurements given in Table 1, it is immediately obvious that there is satisfactory agreement between the results obtained by the Ni^{2+}-selective optode and by AAS.

Table 1. Determination of Ni^{2+} in real samples by perposed method.

Sample	Ni (II) found (μg ml^{-1})		Standard deviation	Relative standard deviation (%)
	Optode[a]	AAS		
Apple	1.56	1.51	0.15	0.61
Apple	1.44	1.47	0.13	0.73
Apple	1.73	1.70	0.13	0.72
Plant	1.38	1.45	0.45	1.11
Plant	0.35	0.35	0.64	1.35
Plant	0.37	0.42	0.33	1.22

4. Conclusion

The optode described is easily prepared and provides a simple and inexpensive means for the determination of Ni^{2+} ions. The membrane responds to nickel ion by decrease absorbance. The sensor can be regeneration readily with a solution of ethylene diamine and has a long lifetime. The response of the optode was reproducible and the optode presented a good selectivity for Ni^{2+}over other metal ions. Since the sensor does not require solvent extraction, it can compete with standard optical fibers. The sensor can be applied for the analysis of real samples.

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