An optical redox chemical sensor for determination of iodide
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**ABSTRACT**

A novel optical sensor based on a redox reaction for the determination of iodide has been developed. The optode membrane is constructed by immobilization of methyltrioctylammonium chloride on triacetylcellulose polymer. The exchange of chloride as counter ion with iodate in the membrane changes the color to yellow, when it is placed in acidic solution of iodide. The sensor can readily be regenerated by 0.1 mol L\(^{-1}\) NaOH in less than 15 s. The optode has a linear range of \(3.94 \times 10^{-6}\) to \(5.51 \times 10^{-5}\) mol L\(^{-1}\) of iodide ions with a limit of detection \(7.44 \times 10^{-7}\) mol L\(^{-1}\). The relative standard deviation for eight replicate measurements of \(3.94 \times 10^{-6}\) and \(1.57 \times 10^{-5}\) mol L\(^{-1}\) of iodide was 2.83 and 1.38%, respectively. The sensor was successfully applied to the determination of iodide in tablet, powdered milk and urine samples.

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1. Introduction

In recent years, the optical chemical sensors (optodes or optrodes) have become a rapidly expanding area of analytical chemistry. These sensors have opened up a new perspective in the search for simple, safe, rapid and remote systems for monitoring some important substances. Recent development in this field have also been driven by such factors as the availability of low-cost, miniature optoelectronic light source and detectors, the need for multianalyte array-based sensors particularly in the area of biosensing, advances in microfluidics and imaging technology. Optical chemical sensors employ optical transduction techniques to yield analyte information. The most widely used techniques applied in optical chemical sensors are optical absorption and luminescence, but sensors based on other spectroscopies as well as on optical parameters, such as refractive index and reflectivity have also been developed [1].

In most optical sensors, a reagent is immobilized in a solid matrix usually in the form of a monolith or a thin film. The reagents immobilized into the sensor are responsible for the extraction of the analyte into the sensing material and generating an optical signal proportional to the change in the concentration of the analyte [2]. Many of the existing optodes utilize color complexion reactions between immobilized ligands and analyte [3,4].

The utilization of color redox reactions has largely been ignored despite the fact that numerous substances of analytical interest are electroactive.

Optodes for a variety of analytes such as cations, anions and gaseous species have been reported [5–8]. In comparison with cation optodes, which are predominant, anion optodes are few in number.

Iodine is an essential micronutrient in human growth and metabolism [9]. Inadequate iodine during prenatal and early development periods, can lead to several diseases, including spontaneous abortion, increased infant mortality, hypothyroidism and cretinism [10]. World Health Organization (WHO) estimates that iodine deficiency disorders are a significant public health problem in many countries. Iodine plays as important role in influencing the proper function of thyroid gland, which is an essential part of thyroid hormones triiodothyronine (T3) and thyroxin (T4) [11]. Too low or excess ingestion of iodine may lead to hyperthyropathy or hypothyropathy and hyperthyroidism [12]. Therefore, there has been an increase in the analytical control of iodine in food, pharmaceutical products and biological samples such as urine. Iodine contents in urine have been widely used as a marker for status assessment of iodine deficiency disorder [13].

In order to determine low concentration levels of iodine and/or iodide, many methods based on different principles have been proposed. These include gas chromatography with mass spectrometry detection [14], electrostatic ion chromatography [15], capillary electrophoresis [16], chemiluminescence [17], pulse stripping analysis [18], inductively coupled plasma-mass spectrometry [19], indirect atomic absorption spectrometry [20].
These approaches, although sensitive, suffer from the need for expensive instrumentation. Therefore the development of analytical techniques that do not need expensive or complicated equipment for the determination of iodide becomes increasingly important. As it is known the optodes have gained considerably in practical reliability, and can be considered as inexpensive alternative to certain conventional analytical methods.

Several optical sensors have been reported for determination of iodide using different reagents. Urbano et al. described optical sensor for halides and pseudohalides using acridinium quinolinium indicators, which were immobilized onto a glass surface [21]. The sensors are able to indicate the concentration of halides in solution by virtue of the decrease in fluorescence intensity due to the quenching process. Liu et al. proposed a flow-through optosensor for determination of iodide based on a chelate room-temperature phosphorescence (RTP). The sensing phase in this sensor was prepared by immobilization of chelate of aluminum with quinolin-8-ol-5-sulphonic acid on an anion exchange resin [22]. In another research, a series of thin film optical sensors based on halide-sensitive fluorophores have been developed and characterized by Geddes et al. [23]. The sensor films use rhodamine, 6-methoxyquinoline, and harman dyes which have been functionalized and bound to a hydrophilic copolymer. Geddes also presented optical thin film polymeric sensors for determination of iodide based on two acridinium fluorophores that have been synthesized and immobilized in a hydrophilic copolymer [24]. Thin films of the copolymers swell in aqueous media allowing dye fluorescence to be dynamically quenched by the diffusion of halide ions.

In this paper, we describe a novel approach to optical chemical sensing which makes use of the redox properties for determination of iodide. This optode is prepared by immobilizing methyltrioctylammonium chloride on triacetylcellulose membrane according to a simple method.

2. Experimental

2.1. Apparatus

A GBC UV–vis spectrophotometer model Cintra 101 was used for recording the spectra, and the absorbance measurements were made using a PerkinElmer UV–vis spectrophotometer model 550S. The sensing membrane was placed in a glass cell and all measurements were performed in a batch mode.

Measurement of pH was performed using a Metrohm 632 pH-meter with a combined glass electrode.

2.2. Reagents and solutions

All reagents used were of analytical grade and double distilled water was used throughout.

A 7.87 × 10⁻³ mol L⁻¹ of iodide stock solution was prepared by dissolving 0.1307 g of potassium iodide (Merck) in water and diluting to 100 mL in a volumetric flask. Standard solutions were prepared by adequate dilution of the stock solution.

An iodine solution (0.2 mol L⁻¹) was prepared by dissolving 8.5600 g of potassium iodate (Merck) in water and diluting to 200 mL in a volumetric flask. The sulfuric acid solution 1.0 mol L⁻¹ was prepared by diluting 5.44 mL of concentrated H₂SO₄ (Merck) to 100 mL in volumetric flask.

2.3. Preparation of optical sensor

The following procedure for the preparation of sensor was performed in order to immobilize methyltrioctylammonium chloride on triacetylcellulose membrane [25]. For this purpose, the transparent triacetylcellulose membranes were produced from waste photographic films that had been previously treated with commercial sodium hypochlorite in order to remove colored gelatinous layers. The membranes were treated with a solution of 0.20 g methyltrioctylammonium chloride in 10 mL of ethylenediamine for 15 min at ambient temperature. Then, they were washed with water for removing the additional reagent. The optode membrane was stored under water when not in use.

2.4. Analytical procedure

The prepared membrane was placed in a solution of potassium iodate (0.20 mol L⁻¹) for 2 min, then it was washed and mounted into a spectrophotometer cell. A few mL of a solution containing iodide and sulfuric acid was transferred to cell, and the absorbance was measured at 370 nm after 8 min.

2.5. Preparation of powdered milk sample

14 g of milk sample was placed in a porcelain crucible, and 5 g of Na₂CO₃, 5 mL of a 6 mol L⁻¹ NaOH solution and 20 mL of MeOH were added. This mixture was allowed to dry slowly in a heater at 110 °C. Then it was placed in a cold muffle furnace, the temperature of which was slowly increased to 500 °C, to prevent analyte losses. Approximately 3 h later, when incineration was complete (white ash), the crucible was cooled down in a desiccator to room temperature. Then the ash was redissolved in hot water. The dissolve residue was filtered and the appropriate amount of H₂SO₄ added, diluted to 25 mL with water and the analytical procedure was applied [20].

2.6. Preparation of tablet sample

The procedure described in Section 2.5 was performed for preparation of Levothyroxine Na tablet sample. In this procedure 2 g of Na₂CO₃, 3 mL of NaOH and 10 mL of MeOH were added to one tablet (1.8910 g).

3. Results and discussion

3.1. Principle of operation and spectral characteristics

The adsorption of methyltrioctylammonium chloride (MTA⁺Cl⁻) on triacetylcellulose makes the membrane to be used as an anionic exchange membrane. The preliminary experiments showed that by placing this film in iodate solution the counter ion in membrane is exchanged with iodate and it can be used as an optical redox sensor. By placing the membrane containing iodate in acidic solution of iodide, the colorless membrane changed to yellow. This color changing is due to oxidation of iodide to I₃⁻ in membrane interface and then its immediate adsorption by anionic exchange phenomena, as described by following scheme:

\[ \text{MTA}^{+} \text{Cl}^{-} (\text{mem}) + \text{IO}_3^{-} (\text{aq}) \rightarrow \text{MTA}^{+} \text{IO}_3^{-} (\text{mem}) + \text{Cl}^{-} (\text{aq}) \]  \hspace{1cm} (1)

\[ \text{MTA}^{+} \text{IO}_3^{-} (\text{mem}) + I^- (\text{aq}) \rightarrow \text{MTA}^{+} I_3^- (\text{mem}) \]  \hspace{1cm} (2)

The absorption spectra of the proposed sensor in the absence and presence of iodide in different concentrations are shown in Fig. 1. As seen, upon addition of iodide the absorbance in maximum wavelength, 370 nm, increased therefore this wavelength was selected for measuring the absorbance of the optode.
Fig. 1. Absorption spectra of optode (a) in the absence and (b–e) in the presence of 3.94 \times 10^{-6}, 7.87 \times 10^{-6}, 1.57 \times 10^{-5} and 2.36 \times 10^{-5} mol L^{-1} of iodide, respectively.

3.2. The effect of variables on sensor response

The stability and sensitivity of the sensor depends significantly on the membrane composition. Therefore, the effects of solvent types, amount of methyltrioctylammonium chloride and preparation time on the response behavior were studied. The obtained results indicated that the membrane responded to iodide ions when it was prepared using ethylenediamine as solvent. The hydrolyzed cellulose film in ethylenediamine shaped the porous structure in the polymer, which minimizes barriers of mass transport between the analyte and immobilized reagent [26,27].

The amount of methyltrioctylammonium chloride had significant effect on the membrane response. At low amounts the response is low and higher values caused the membrane to be opaque. The highest response was obtained using 0.20 g of methyltrioctylammonium chloride. In another experiment, the presence time of membrane in methyltrioctylammonium chloride/ethylenediamine solution was investigated. The results indicated that the response increased with time, but over 15 min the membrane begins to dissolve and to deform. Thus, the optode was prepared by treating transparent triacetylcellulose membrane with a solution of 0.20 g methyltrioctylammonium chloride in 10 mL ethylenediamine for 15 min.

The reaction between iodate and iodide occurs when the solution is acidified with a strong acid [28]. Therefore, the influence of sulfuric acid concentration over the range of 0.02–0.10 mol L^{-1} on the response of optical sensor was studied. The obtained results denoted that this parameter had no effect on the response of optical sensor up to 0.1 mol L^{-1} of potassium nitrate.

3.3. Response time and regeneration

The absorbance response of the optode versus time in selected experimental conditions for 7.87 \times 10^{-6} and 3.94 \times 10^{-5} mol L^{-1} of iodide was studied. Fig. 4 shows that the proposed sensor reaches the output signal of 98% of steady-state response after 8 min. This result is the same for both concentration of iodide.

A good sensor should fully regenerate at a short time. The proposed optode was regenerated completely in 0.1 mol L^{-1} of NaOH in less than 15 s. The membrane could be regenerated about 50 times and used without any loss of sensitivity.

Fig. 2. Effect of sulfuric acid concentration on the optode response for solution containing 3.94 \times 10^{-5} mol L^{-1} of iodide.

Fig. 3. Effect of iodate concentration on the optode response for the solution containing 3.94 \times 10^{-3} mol L^{-1} of iodide and 0.04 mol L^{-1} of sulfuric acid.

Fig. 4. Absorbance as a function of time when the concentration of iodide was (a) 7.87 \times 10^{-6} and (b) 3.94 \times 10^{-5} mol L^{-1}.
3.4. Analytical figure of merit

The corresponding calibration graph (Fig. 5) based on absorbance of the optode versus iodide ion concentration was linear in the range of $3.94 \times 10^{-6}$ to $5.51 \times 10^{-5}$ mol L$^{-1}$ (0.5–7 µg mL$^{-1}$). The regression equation for the line was $A=7.57 \times 10^{2} C+7.27 \times 10^{-3}$ with correlation coefficient ($r$) of 0.9995, where $C$ is concentration of iodide in mol L$^{-1}$ and $A$ is absorbance of optode at 370 nm. The detection limit of the sensor based on three times the standard deviation of blank was $7.44 \times 10^{-7}$ mol L$^{-1}$.

3.5. Reproducibility and lifetime of the optode

The reproducibility of the membrane preparation was checked for five separate membranes by measuring the absorbance under optimum conditions for $7.87 \times 10^{-6}$ mol L$^{-1}$ of iodide. The results showed that the R.S.D. for the membrane preparation was less than 3.5%.

The precision using a single membrane was tested by performing eight replicate measurements for $3.94 \times 10^{-6}$ and $1.57 \times 10^{-5}$ mol L$^{-1}$ of iodide solutions. The relative standard deviation (R.S.D.) for these determinations was 2.83 and 1.38%, respectively.

In determination of the lifetime of the sensor, the change in the absorbance after keeping the membrane in water for 1 month was measured. The absorbance values of optode membrane at 370 nm only decreased about 2% over a period of 1 month. This result indicates that the optode is very stable, so it could be stored for more than 1 month without losing its characteristics.

3.6. Effect of foreign ions

In the presence of other ions, the selectivity of the optode was studied for $1.57 \times 10^{-5}$ mol L$^{-1}$ of iodide ion solution using the proposed method. The tolerance limit was defined as the maximum concentration of foreign ion causing ±5% error in the determination of iodide. The results are summarized in Table 1. As it is observed the optode is more selective to iodide than other anions under optimum conditions.

The interference of chloride and oxalate anions on the determination of iodide was eliminated using $8.9 \times 10^{-4}$ mol L$^{-1}$ of Cd(II) ion for chloride and $1.7 \times 10^{-3}$ mol L$^{-1}$ of Co(II) ion for oxalate because Cd(II) and Co(II) ions form complexes with chloride and oxalate anions, respectively.

3.7. Analytical application

3.7.1. Determination of iodide in tablet

The presented iodide optical sensor was applied to the determination of Levothyroxine Na (C$_{15}$H$_{10}$I$_{4}$NNaO$_{4}$) in two tablet samples (Iran Hormone). According to the obtained amount of iodide (Table 2) the average of Levothyroxine Na amount is 0.094 mg which is in good agreements with the reported values.

3.7.2. Determination of iodide in powdered milk and urine

The proposed optical sensor was also employed for the determination of iodide in powdered milk and urine samples. The possibility of applying the present optical sensor for analysis of samples was tested by determining the recovery of known amounts of iodide ion added to the samples. The given results in Table 3 show good agreement between added and detected concentration of the iodide in real samples.

4. Conclusion

This paper described a novel optical redox chemical sensor for determination of iodide. The sensing membrane was easily prepared and operated. The proposed optode can be regenerated quickly and the response of the optode is very reproducible. In comparison with other methods [21–24], the proposed sensor is more sensitive and it was prepared easily by using low-cost materials in a short time. In addition, the method is based on measuring the optode absorption by UV–vis spectrophotometry, which has the advantage of determinations by an inexpensive instrument in a rel-

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Table 1

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance ratio ([M]/[I$^-_{}$])</th>
</tr>
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<tbody>
<tr>
<td>CO$_3^{2-}$, NO$_3^-$, Cr$^{3+}$, Na$^+$</td>
<td>500</td>
</tr>
<tr>
<td>Ca$^{2+}$, Mg$^{2+}$</td>
<td>200</td>
</tr>
<tr>
<td>Co$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Cl$^-$</td>
<td>100</td>
</tr>
<tr>
<td>Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$</td>
<td>50</td>
</tr>
<tr>
<td>F$^-$</td>
<td>30</td>
</tr>
<tr>
<td>Ni$^{2+}$, C$_2$O$_4^{2-}$</td>
<td>10</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>2</td>
</tr>
</tbody>
</table>

a Masked by Cd$^{2+}$.

b Masked by Co$^{2+}$.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iodide found$^a$ (mol L$^{-1}$)</th>
<th>Levothyroxine Na found (mg)</th>
<th>Reported value (mg)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.89(\pm 0.03) \times 10^{-5}$</td>
<td>0.095</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>$1.87(\pm 0.03) \times 10^{-5}$</td>
<td>0.093</td>
<td>0.1</td>
</tr>
</tbody>
</table>

$^a$ Mean ± S.D. ($n=4$).

Table 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Amount of iodide (mol L$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Found$^a$</td>
</tr>
<tr>
<td></td>
<td>$7.87 \times 10^{-6}$</td>
<td>$1.69(\pm 0.05) \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$3.94 \times 10^{-6}$</td>
<td>$1.89(\pm 0.03) \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$7.87 \times 10^{-6}$</td>
<td>$2.31(\pm 0.04) \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ Mean ± S.D. ($n=4$).
atively short time. The proposed method could be widely applied to the determination of iodide in real samples with different compositions.

Acknowledgement

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References