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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 3.94×10^{-6} to 5.51×10^{-5} mol L^{-1} of iodide ions with a limit of detection 7.44×10^{-7} mol L^{-1}. The relative standard deviation for eight replicate measurements of 3.94×10^{-6} and 1.57×10^{-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.

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, hypothyrodism 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 hypertrophy or hypothyroidism 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].

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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 fluorophored 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 iodate 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 H_2SO_4 (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 Na_2CO_3, 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 H_2SO_4 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 Na_2CO_3, 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 I_3^- in membrane interface and then its immediate adsorption by anionic exchange phenomena, as described by following scheme:

$$MTA^+Cl^-_{(mem.)} + IO_3{}^-_{(aq.)} \rightarrow MTA^+IO_3{}^-_{(mem.)} + Cl^-_{(aq.)} \quad (1)$$

$$\underset{\text{(colorless)}}{MTA^+IO^-_{3(mem.)}} + I^-_{(aq.)} \xrightarrow{H^+} \underset{\text{(yellow)}}{MTA^+I^-_{3(mem.)}} \quad (2)$$

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.