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A Novel Iron Optical Sensor Based on 2-(2-Benzothiazolylazo)Phenol Polymer Inclusion Membrane

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Abstract
The use of a polymer inclusion membrane (PIM) as a sensing material is a novel approach to overcome the selectivity and stability of the optical chemical sensor (optode). In this work, non-plasticized PIM containing poly vinyl chloride (PVC) as a support base, 2-(2-benzothiazolylazo)phenol (BTAP) as a reagent and Aliquat 336 as a fixed carrier (ionophore) was prepared and its performance was tested for application in an optode to determine Fe^{3+} ions. The results showed that PIM properties are greatly affected by the membrane composition. The studies revealed that the optode response was dependent on film thickness, the presence of plasticizer, stirring effect, concentration of BTAP, concentration of Aliquat 336 and pH of the aqueous solution used. A linear calibration curve in the range from 5.0–210 ng mL^{-1} of Fe^{3+}, with a detection and quantification limits of 1.60 and 4.95 ng mL^{-1}, respectively were obtained. The maximum wavelength (λ_{max}) for the PIM based optical optode was 581 nm. The PIM developed in this investigation was found to be stable, has good mechanical strength, sensitive and reusable. Lastly, the PIM was successfully applied as an optical sensor to determine Fe^{3+} ions in natural water, food, biological and environmental samples, and the obtained result is comparable to atomic absorption spectrometry method.

Keywords
Iron(III) Determination; Optical Optode; Spectrophotometry; Thiazolylazo; Biological and Environmental Analysis.

1. INTRODUCTION

The interest in the separation, preconcentration and determination of trace metals in natural waters has increased in the last decades because of the environmental problems and public health studies. Iron is the most important transition element involved in living system, being vital to both plants and animals. It is at the active center of molecules responsible for oxygen transport, electron transport and is found in such diverse metallo-enzyme as nitrogenase, various oxidases, hydro-genases, reductases, dehydrogenases, deoxygenases and dehydrases. Iron deficiency caused anemia and may cause various health problems (heart disease, arthritis, cancer, diabetes and liver diseases) [1]. Iron was restricted to 2.0 mg L^{-1} by World Health Organization [2] and 200 µg L^{-1} by European Legislation [3]. Iron involved in enormous range of function and the whole gamut of life forms, from bacteria to man. Iron has two readily inter converted oxidation states [4,5]. Excess concentration of iron is potentially toxic to human due to its pro-oxidant activity. Determination of oxidation state of iron in aquatic system is very important for environmental and biological studies due to the influence of the chemical forms on the bioavailability of iron and physicochemical and toxicological properties of other trace elements and organic substrates [6–8]. Iron-containing proteins contain ferric ions, at least transiently. Well studied examples include iron–sulfur clusters, ferritin, oxyhemoglobin, and the cytochromes were done. Excess amounts of iron can be toxic. Oxidation ability of iron is a leading cause of poisoning in human body. Gulp of large amounts of iron salt causes vomiting and intestinal bleeding [9–15]. High iron concentration within water pipelines promotes undesirable bacterial growth (iron bacteria), resulting in the deposition of a slimy coating on the pipelines [16]. For these reasons, separation of iron ions is important and separation techniques have been developed in recent years.

Expensive analytical methods such as capillary electrophoresis (CE) [17], inductively coupled plasma optical emission spectrometry (ICP-OES) [18], and inductively coupled plasma mass spectrometry (ICP-MS) [19], have been employed to determine Fe(II) and Fe(III). Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of metal ions [20–22]. Common availability of the instrumentation, simplicity of the methods and the speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternate.

various procedures for spectrophotometric

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determination of Fe^{3+} have some disadvantages like low sensitivity, heating process, time consuming, and the use of large amounts of organic solvents, which could increase the environmental pollution like the following methods: N. Hirayama et al., (ε =0.43 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =560 nm, leave in water bath for 19 min at °C) [23], Lih-Fen (ε =1.2×10^4 L mol^{-1} cm^{-1}, λ_{max} =514 nm, shaking for 10 min in water bath 55°C) [24], Hemlata Mohabey et al., (ε =1.21 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =520 nm, benzene for extracting) [25], M.C.C. Areias et al., (ε =1.26 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =375 nm) [26], Astrid et al., (λ_{max} =473, 506 nm, chloroform for extracting, shaking for 20 min) [27]. J. Miura (ε =1.53 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =396 nm) [28], Prodromos B. et al., (ε =2.08 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =386 nm) [29], G.S.R. Krishnamurti (ε =2.15 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =595 nm) [30], Prodromos B. et al., (ε =2.30 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =471 nm, shaking for 30 min at 50°C) [31], M.V. Dawson et al. (ε =2.79× 10^4 L mol^{-1} cm^{-1}, λ_{max} =562 nm) [32], Yoshio shijo (ε=17.3 × 10^4 L mol^{-1} cm^{-1}, λ_{max} =613 nm, benzene and xylene for extracting, long procedure) [33]. The spectra of the mixed ligand complex formed were characterized by high intensity. However, these methods have important limitations, namely complex sample preparation, expensive and complicated instrumentation, are time consuming, difficult to operate and unsuitable for field monitoring. However, these drawbacks could be overcome by utilizing an optical chemical sensor (optode).

Optodes offer numerous improvements compared with the conventional procedures. Advantages such as simple and low cost of operation, easy sample preparation, reasonably fast response, high sensitivity and wide response range have been attracted many researchers to utilize the procedure and some optodes commercialized [34].

In recent years, analytical chemists found one of the most challenging tasks is constructing highly selective and sensitive optodes. Many approaches have been taken [35–44], one of which is the development of a sensitive optical sensing layer (e.g., membranes, beads or sol–gel). This is because optical transduction, which involves a chemical interaction between the reagent and the analyte phase to generate an optical chemical sensor, is fully dependent upon this sensing layer. In regard to optodes, immobilization techniques, the nature of organic reagents used, and sensing techniques are the main parameters affecting their performance. In general, the immobilization techniques used in preparing optical sensing layers can be categorized into adsorption, covalent binding and entrapment [45]. The adsorption technique is not preferred due to the limitation of the amount of immobilized reagent and is prone to leaching. Although the covalent binding technique is free from the leaching problem, the method is usually complex (i.e., it requires an appropriate reagent with a suitable functional group for immobilization). In contrast, the entrapment technique is straight forward. Solid matrices, such as polymers or sol–gel derived materials, are suitable for the immobilization process. Such matrices provide selectivity, flexibility, and chemical and mechanical stability to the constructed optode. During the application of optodes, polymers are mostly applied in the form of membranes or thin films. For the membrane type optical optode sensing layer, the membranes not only act as the support for the immobilized reagent, but also enable permeation of certain chemical species. However, in some cases the immobilized reagent is inaccessible to the target analyte. This has an adverse effect on the optode performance, such as reducing its sensitivity, response time, reproducibility and repeatability. To overcome this problem, several methodologies, as the introduction of novel reagents and schemes, the lipophilization of the dye molecules, the use of sol–gel and the apply of an ion-exchanger, have been proposed [46–50].

In this study, a novel approach for enhancing the selectivity and sensitivity of an optical optode has been developed. By using spectrophotometric technique, the constructed optode exhibited greater selectivity and sensitivity for the detection of the Fe^{3+} ion. In terms of dye reagent, this investigation focused on the application of newly synthesized 2-(2-benzothiazolylazo)phenol (BTAP). A non-plasticized PVC optode based on the polymer inclusion membrane (PIM) technique was prepared and characterized to estimate its potential application for Fe^{3+} ion sensing. A tremendous improvement of the reagent sensitivity was achieved after its immobilization into the membrane matrix, thus making this novel system ideal for Fe^{3+} sensing.

2. EXPERIMENTAL

2.1. Reagents and apparatus

Poly vinyl chloride (PVC) (MW 200,000), Aliquat 336, sodium chloride (NaCl) and sodium hydroxide (NaOH) were analytical grade reagents purchased from Sigma-Aldrich. Acetic acid (CH_3COOH), sulphuric acid (H_2SO_4), tetrahydofuran (THF), nitric acid (HNO_3) and dichloromethane (DCM) were obtained from BDH. Cellulose triacetate (CTA) and dioctyl phthalate (DOP) were products of Fluka. Other chemicals used were sodium acetate (Analar) and ethanol (Hamburg Chemicals). The standard solutions of Fe^{3+} were prepared by appropriate

dilution of a stock standard solution of Fe^{3+} with double distilled water (DDW) (AAS standard, 1000 µg mL^{-1}, Merck (Darmstadt Germany).
2-(2-Benzothiazolylazo)phenol (BTAP) used in this studies was prepared [51] according to the procedure described previously (Fig. 1). An appropriate weight was dissolved in 100 mL of absolute ethanol (4 x 10^{-4} mol L^{-1}). The solution was stable for more than one month. The solutions of different pH 2.75 – 10.63 of different buffer solutions were prepared as described early [52].

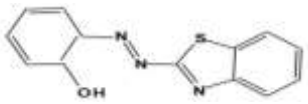

Fig. 1. 2-(2-Benzothiazolylazo)phenol structure.

Solution of PVC was prepared by dissolving 400 mg of PVC in 10 mL of THF. A separate solution containing 100 mg Aliquat 336 was prepared in 5.0 mL of THF. Then both solutions were mixed and stirred for 2.0 h to form a homogenous casting solution. After that, the casting solution was spread on a 9 cm diameter flat bottom Petri dish, which was then kept on a leveled surface for uniform PIM formation. The lid of the Petri dish was covered with filter paper to allow gradual evaporation of THF from the casting solution. After leaving the THF to evaporate from the casting solution for one days, the transparent PIM was peeled off from the Petri dish. The PIM was then washed with deionized water for three times. Then the PIM was immersed and stirred in 20 mL of BTAP (8.0×10^{-4} mol L^{-1}) for 3.0 h to form a uniform colour on it. The PIM was washed again with deionized water for three times to remove unbound reagent and soluble component and dried between folds of tissue paper. Later, the PIM was kept into a sealed airtight plastic bag prior to use. Finally, the PIM was cut to the area of 2.0 cm × 1.0 cm and this size was maintained throughout the experiment. In addition, the PIM thickness was measured by using digital microscope (Ray Vision Y 103) that was coupled with video camera (JVC TK-C 751EG). As for the preparation of the control optode which consists of PVC and dioctyl phthalate (DOP) (Fluka), the optode was prepared by dissolving 400 mg of PVC and 100 mg of DOP in 15 mL of THF. After being stirred for 2.0 h, the casting solution was spread on a 9.0 cm diameter flat bottom Petri dish and were left to evaporate for one day. Finally the transparent membrane was immersed and stirred in 20 mL of BTAP (8.0×10^{-4} mol L^{-1}) for 2.0 h to form a uniform colour on it.

Spectral analysis of the Fe^{3+} aqueous samples was carried out to determine the sensitivity of Fe^{3} - BTAP-Aliquat 336 complex. The absorbance of the complex acts as a function of Fe^{3+} concentration. Therefore, samples containing known amount of Fe^{3+} (volume 25 mL) were prepared for this purpose by using standard solutions of Fe^{3+} containing 5.0 – 210 ng mL^{-1}. The pH of these sample solutions were adjusted to pH 8.0. Buffer solutions used in this study was thiel buffer system. A microprocessor-based pH meter model Orion research model 601 A/digital ionalyzer was used for pH measurements. Initially, a PIM of 2.0 cm × 1.0 cm was immersed in Fe^{3+} solution, with the concentration ranges from 5.0 – 210 ng mL^{-1}. Then it was well stirred for 5.0 min. The PIM was washed again with deionized water and dried with folds of tissue paper. Next, the dried PIM was immersed into the cell and its absorption spectra was recorded.
This procedure was repeated for other Fe^{3+} samples. Freshly prepared PIM was used for every measurement. The absorbance measurements of these samples were carried out at 581 nm by using Perkin-Elmer λ_{12B} spectrophotometer with quartz 10 mm.

2.2. Real sample preparation

Liver, lentil, kidney bean, meat and egg as examples of foods that are rich sources of iron and various water samples (River, mineral and tap water) were selected as real samples. The food samples were purchased from a local hypermarket. The water samples were obtained from Benha city.

2.2.1. Determination of iron (III) in food grains samples

Grain samples such as mung (Phaseolusaureus) and gram (Cicerarietinum) were purchased from a local market (Benha, Egypt) and prepared for the analysis of iron(III) content [53]. Five gram samples of the grains were dried for 24 h in an oven at 70 °C before being digested with nitric and perchloric acids over a period of 10 h. The resulting residue was then heated at 45 °C for 7.0 h in 5.0 mL of concentrated hydrochloric acid and evaporated to dryness to give a residue which was dissolved in 0.1 mol L^{-1} hydrochloric acid before being filtered into a 25 mL flask.

2.2.2. Determination of iron (III) in biological and environmental samples

Human blood (1.0–2.0 mL) and urine (10–20 mL) samples were collected in pre-cleaned polyethylene bottles from volunteers. The procedure involved in the preparation of these

biological samples has been described in earlier studies [54,55].

2.2.3. Determination of Fe(III) in meat and liver

A 1.0 g of meat or Liver was weighted and taken into glass digester flask. Then, 10 mL of concentrated nitric acid was added to sample and the mixture was heated at 220 °C for 1.0 h. After cooling to room temperature, 5.0 mL hydrogen peroxide was added to the mixture and heated for 1.0 h and resulting mixture was diluted by deionized water [56,57], adjustment of the pH was performed by using of sodium hydroxide and hydrochloric acid.

2.2.4. Determination of Fe(III) in lentils and beans

A 1.0 g of cleaned and dried lentils or kidney bean was weighted and grinded by Electric Grain Mill. Then the powder heated in silica crucible for 3.0 h on a hot plate and placed in the furnace for 24 h at 650 °C. After cooling at room temperature, the residue was dissolved in 10 mL of concentrated nitric acid and heated. When the mixture dried, 5.0 Ml hydrogen peroxide added and heated again. The resulting material diluted with deionized water and the pH of solution adjusted to 8.0.

2.2.5. Determination of Fe(III) in water samples

Water samples were collected in pre-cleaned polyethylene bottles and stored in a refrigerator at 5 °C prior to being analyzed. The water samples were filtered by filter paper and centrifuged (5000 rpm for 10 min) and exposed UV irradiation (2.0 h). Then, pH was adjusted to 8.0.

2.2.6. Determination of Fe(III) in egg

In order to oxidize to organic matter, the sample was placed in the furnace for 5.0 h at 600 °C, then the obtained residue was digested by 10 mL of concentrated nitric acid and heated up to 200 °C for 1.0 h. After cooling at room temperature, 5.0 mL hydrogen peroxide added to the mixture and evaporated. Resulting residue was diluted with deionized water.

2.2.7. Determination of Fe(III) in milk sample

To 10 mL of human or cow's milk, few drops of concentrated nitric acid were added, and the sample was centrifuged for few minutes. Then the supernatant solution was taken, its pH was adjusted to 8.0, and the resulting solution was diluted to 100 mL in a volumetric flask. The solution was then analyzed according to the given procedure. For analysis of infant dry formula milk, 0.5 g of milk powder was dissolved in water. The protein was separated after addition of few drops of concentrated nitric acid. The pH of the supernatant was adjusted to 8.0 and the resulting solution was diluted to 250 mL. The sample was then treated according to the given procedure.

3. RESULT AND DISCUSSION

3.1. PIM characterization

Initially, PIM prepared in this study was found to be wrinkled, non-homogeneous and non-uniform. However, after several modifications of the preparation techniques of the PIM, a flexible, homogeneous, transparent and self-supporting membrane was produced. Major modifications, such as varying the membrane composition, setting the room temperature to 20 °C, controlling the humidity of the room and allowing the casting solution to evaporate for 24 h instead of 18 h were found to be essential to prepare a high-quality PIM. These observations prove that external factors such as temperature and humidity significantly affect the preparation steps of the PIM. It was also observed that the PIM produced did not change its physical appearance despite being kept in a sealed bag for three months.

The average thickness of PIM prepared in this study was found to be 25 ± 5 mm. This thickness of the PIM produced is suitable for ion mobility for the reaction of ligand-metal complex due to the membrane is not too thick (>100 mm) and not too thin (< 5.0 mm) and it is suitable to be applied as a transducer for an optical optode sensor based on the co-extraction principle [58].

3.2. Optimization of the PIM-based optode

The selection of a reagent to be applied in an optode is its molar absorptivity. High molar absorptivity of a reagent is preferred because it will increase the light absorption at a given wavelength, thereby increasing the sensitivity of the reagent when it reacts with the target analyte. In addition to the advantages of high lipophilicity and high molar absorptivity, BTAP is capable of preventing the metal ion from undergoing the ion hydrolysis effect. This advantage is due to the presence of azo group in one of its aromatic rings, which increases the ligand acidity value. The high acidity value of BTAP prohibits the Fe^{3+} ion from forming a metal hydroxide as $Fe(OH)_3$. The formation of this complex decreases the sensitivity for Fe^{3+} ions due to a reduction in the availability of Fe^{3+} ions. Results from the experiments showed that the use of BTAP overcame the major problems usually encountered when using other reagents in optical sensors, such as leaching of the reagent from the support matrix and low solubility in water. No indication of leaching was observed during the experiment. In addition, the immobilized BTAP in a PIM-based optode (red in colour)

transformed to a bright deep red colour due to its reaction with Fe^{3+} at a specific pH as a result of proton dissociation. Fig. 1 shows the absorption spectra of the control optode (consists of PVC:DOP: BTAP) and the PIM-based optode (consists of PVC: Aliquat 336: BTAP) upon contact with Fe^{3+}. The maximum absorption wavelengths (λ_{max}) for the control optode and PIM-based optode were 546 and 581 nm, respectively. The reaction between the PIM-based optode and Fe^{3+} is based on the ion-exchange principle. According to Oehme and Wolfbeis [59], the process generally happens when a lipophilic quaternary ammonium salt is used in the sensing membrane. In this case, the BTAP reagent is able to form a strong ionic bond with Aliquat 336 due to ion pairing between the negative charge of the hydroxyl group of BTAP and the positive charge of Aliquat 336. The extraction of Fe^{3+} ions into the membrane phase is coupled with the release of protons from the membrane into solution as described by the equation: (1) where (L) is Aliquat 336, (Ind) is BTAP and the subscripts (memb) and (aq) refer to the membrane phase and aqueous phase, respectively. As expected from the proposed cation exchange mechanism, the response of Fe^{3+} was highly pH dependent because the absorbance was related to the ratio of the activities of Fe^{3+} and protons.

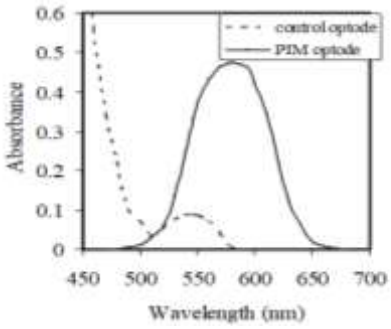

Fig. 2. Absorption spectra of a-control optode (PVC; DOP; BTAP) and PIM based optode (PVC; Aliqout 336; BTAP) upon comtact with 100 ng mL^{-1} Fe^{3+} [BTAP; 8×10^{-4} M] and pH 8.0.

Other than the quantity of reagent immobilized in the PIM, the sensitivity and selectivity of the optode for Fe^{3+} ion sensing also depends on the pH value. An optimum pH value of the reaction was examined in different types of buffer solutions (acetate, borate, phosphate, thiel and universal). The optimum buffer media is thiel buffer solution of pH 8.0. (Fig. 2). Moreover, the optimum volume used for 25 mL sample was 7.5 mL. The result obtained proved that the presence of Aliquat 336 within the PIM did not influence the optimum pH value for the formation of BTAP and Fe^{3+} complex. Complex formation between BTAP and Fe^{3+} still occurs within the optimum pH range of 7.5 – 8.5 for complexation of Fe^{3+} in aqueous solution. From this result, it can be affirmed that the interaction between BTAP and Aliquat 336 had no effect on the functional groups of the BTDP, which was used in the formation of complexes with Fe^{3+} ion. It was observed that the absorbance at lower and higher pH values were decreased. The former happened due to the formation of $Fe(OH)_3$, while the latter happened because of dissociation of the formed complex in a solid form, which could prevent Fe^{3+} from binding to the immobilized BTAP.

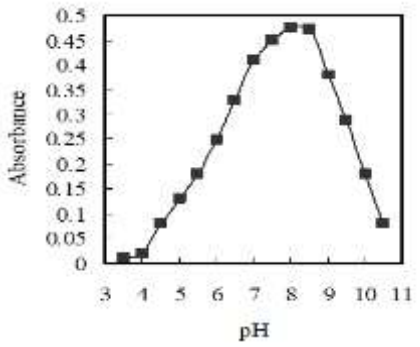

Fig. 3. Effect of pH on the optode response for 100 ng mL^{-1} of Fe^{3+} on using 5×10^{-4} M of BTAP at the optimum condition.

Besides the immobilization technique and pH value for the reaction to take place, the performance of an optode also depends on the type and quantity of the reagent immobilized [60]. The effect of BTAP concentration in the preparation of the optode with fixed concentration of Fe^{3+} ion 100 ng mL^{-1} and pH 8.0. As the initial concentration of BTAP increases, the optode response is also increased up to a concentration of 8.0×10^{-4} mol L^{-1}. This response was achieved because this concentration of BTAP was sufficient to react with Fe^{3+} ions in the presence of Aliquat 336.

Maximum absorbance of the PIM-based optode was achieved at pH 8.0, while the highest absorbance was observed at a BTAP concentration of 8.0×10^{-4} mol L^{-1}. This absorbance was achieved because the BTAP concentration had reached its complete equilibration with Fe^{3+}. Interestingly, there was a large bathochromic shift, from 546 to 581 nm, in the λ_{max} of the PIM-based optode relative to the control optode. This unique phenomenon occurred largely due to the presence of Aliquat 336 and BTAP in the PIM optode. In addition, it was clear that the sensitivity of the PIM-based optode was also higher than the sensitivity of the control optode (ten times). This was the other

significant result obtained from the present study. The absorbance from the PIM-based optode upon contact with Fe^{3+} increased about ten-fold compared to the control optode. Such consequences are due to the formation of higher order complexes (higher ligand : metal ratio) on the interfaces of Aliquat 336 and the extra extraction capability provided by Aliquat 336 [61,62].

$$[\mathrm{L} + \mathrm{Ind} -](\mathrm{memb}) + \mathrm{Fe3} + (\mathrm{aq}) \rightleftarrows [Fe^{3+} + L^{+}\,Ind^{-}]_{(memb)} + 3L^{+}{}_{(aq)} \quad (1)$$

The parameters affecting PIM composition, as mass composition and thickness, were also investigated. The PIM produced in this study was homogenous, transparent and self-supporting. The average thickness of the PIM was found to be 20 ± 5 µm; hence, the PIM was suitable to be utilized in a stirred aqueous solution environment and appeared to have good mechanical strength. Several combinations of the matrix-forming polymer (PVC), plasticizer (DOP), extractant (Aliquat 336) and the reagent (BTAP) were studied to optimize Fe^{3+} uptake in the PIM at a pH of 8.0. Table 1 lists the different PIM compositions and their absorbance at 581 nm. The proportion of the PIM was optimized to increase their absorbance, uniformity and mechanical strength. To determine the optimum composition, each PIM was prepared by fixing its mass to 500 mg and varying the mass composition of the different components (PVC, Aliquat 336 and DOP). The comparison of the absorbance of the different PIMs after loading them with fixed amounts of Fe^{3+} at pH 8.0 proved that PIM, with a composition of PVC = 75 wt.% (m/m), Aliquat 336 = 25 wt.% (m/m), produced the highest absorbance value at 581 nm. This appealing result proved that the most sensitive, homogeneous and transparent PIM can be prepared without the use of plasticizer. In this case, Aliquat 336 also acts as a plasticizer in addition to its major function as an extractant. This observation can be explained by the structure and features of Aliquat 336, which has a polar group that is able to reduce intermolecular attractive forces among chains in the polymer systems, which allow the entrapment of reagent and the formation of self-supporting membrane. Although there are other plasticizers that can be used in the preparation of the PIM [63], only one type of plasticizer was utilized in this study. Here, DOP was used as the plasticizer for the preparation of the PIM to compare the analytical performances between the plasticized PIM and the non-plasticized PIM. DOP was chosen because its characteristics such as high molecular weight, ability to dissolve within the substrate, low viscosity, low cost compared to other plasticizers, ready availability in the laboratory and, most importantly, its performance is equivalent to other expensive plasticizers. As for the type of base polymer used, PVC was chosen because of it provides permeation selectivity for certain species, acts as solid support, is highly suitable for plasticization, has a relatively low cost, and is readily available. Prior to this study, Aliquat 336 was never used as a plasticizer in the optical sensors field.

Stirring the Fe^{3+} ion solution has a large influence on the response of the optode. About ten fold enhancement of absorbance was achieved when the Fe^{3+} solution was stirred compared with the non-stirred Fe^{3+} ion solution. This observation can be explained by the movement of Fe^{3+} ions towards the immobilized BTAP. The stirring process has accelerated the diffusion of Fe^{3+} ions across the PIM to the BTAP and consequently expedited the reaction between Fe^{3+} ions and BTAP. As for the non-stirring process, the diffusion of Fe^{3+} ions across the PIM only depends on the concentration gradient [63].

The working range of the PIM-based optode was studied under the optimum experimental conditions, and the average of five absorbance readings at each concentration were plotted versus Fe^{3+} concentrations. Fig. 3 shows the dynamic range of the system after five min of reaction, which was determined to be linear from 5.0–210 ng mL^{-1} with a correlation coefficient (R^2) of 0.9967 (Table 1).

Table 1. Analytical features of the proposed method

Parameters	PIM optode	Parameters	PIM
pH	8.0	Regression equation	
Optimum [ATAP]	8.0×10^{-4}	Slope (µg mL^{-1})	6.21
Reaction time (min)	5.0	Intercept	- 0.05
Stirring time (min)	10	Correlation coefficient (*r*)	0.9988
Beer's range (ng $mL^{-1)}$	5.0 - 210	RSD [a] (%)	1.67
Ringbom range (ng $mL^{-1)}$	20 - 200	Detection limits (ng mL^{-1})	1.60
Molar absorptivity (L mol^{-1} cm^{-1})	1.22×10^6	Quantification limits (ng mL^{-1})	4.95
Sandell sensitivity (ng cm^{-2})	0.016	enhancement factor	500

In addition, the limit of detection and quantification [64] were evaluated using 3σ/s, and 10σ/s, respectively, where σ is the standard deviation of the blank and s is the slope of the linear calibration plot. The calculated values were 1.60 and 4.95 ng mL^{-1}, respectively.

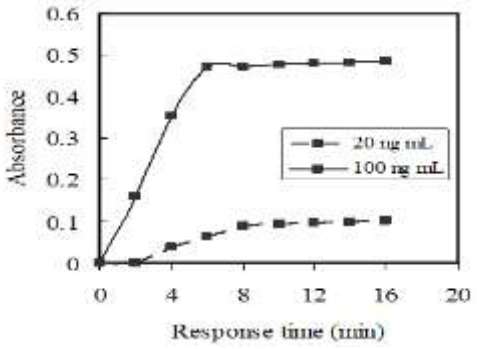

Fig. 3. Stady state response time of the optode towords different Fe^{3+} concentration ---- 20 ng mL^{-1} and - for 100 ng mL^{-1}.

The low detection limit obtained in this study, as compared to other preconcentration methods [65–74], proves that the presence of Aliquat 336 in the PIM increased the sensitivity of the constructed optode (Table 2). In this case, the BTAP –Aliquat 336 complex extracted more Fe^{3+} ions from the aqueous phase into the membrane, which resulted in the formation of more Fe^{3+}- BTAP –Aliquat 336 complexes. The formation of these complexes increased the absorbance values, thus enhancing the PIM-based optodes sensitivity. The rapidity, selectivity and sensitivity of the proposed method were compared with the other spectrophotometric methods which were used for the determination of Fe^{3+} in environmental sample. The present method is more convenient and cost beneficial than earlier reported methods.

Also, comparing with other spectrophotometric methods [23−33], it reveals that the proposed method was highly sensitive (ε =2.65 × 10^5 L mol^{-1} cm^{-1}) in addition to low deterction and quantification limits and a wider range of determination. Present method requires no solvent for the rapid determination of Fe^{3+}. The data obtained by various methods were found to be comparable (Table 2).

The reversibility of the PIM-based optode was investigated by repeating three cycles of the optode with 100 ng mL^{-1} Fe^{3+} aqueous solution and regenerating the optode with 0.5 mol L^{-1} F^- aqueous solution. The structure of BTAP is the reason that this optode is fully reversible. The existence of a azo group in the BTAP molecule is expected to eliminate the leaching problem. In addition, this azo group is also able to hinder Fe^{3+} ions from undergoing hydrolysis [65].

Most of the interferences ions used in this work (EDTA, F^-,PO_4^{-2}, Be^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Al^{3+}, Hg^{2+}, Mg^{2+}, Pb^{2+} and Zn^{2+}) have low interference or did not interfere at all with the measurement of the constructed optode. These results also proved that these ions formed complexes with BTAP, although they were less stable compared to the Fe^{3+}–BTAP complex. The notable selectivity displayed by the PIM-based optode likely resulted from the presence of Aliquat 336, which plays a part in enhancing the sorption of ions (especially metal cations) from the liquid phase into the membrane phase. The reproducibility of the optode was illustrated by measuring the response of the same optode to the Fe^{3+} aqueous solution 100 ng mL^{-1} eight times. The relative standard deviation (RSD) for repeatability and reproducibility of the optode were found to be 1.32% and 3.87 %, respectively.

Table 2. Comparison of different extraction methods with spectrophotometric detection.

Extraction method	LDR, ng mL^{-1}	DL, ng mL^{-1}	PF	Volume, mL	Ref
Solvent extraction	60–1800	5	50	250	[65]
Surfactant-mediated extraction	0.0–6000	–	12.5	125	[66]
Dispersive liquid-liquid microextraction	25–1000	7.5	7.14	5	[67]
SPE-silica gel-polyethylene glycol	1–60	0.75	125	250	[68]
Cloud point extraction	5–112	0.8	20	10	[69]
Dispersive liquid-liquid microextraction	5–400	1.5	10	5	[70]
DLLME-SFO[a]	95–1070	25	500	60	[71]
SPE[b] octadecylsilica membrane disks	10–700	0.08	60	600	[72]
SPE-halloysite nanotubes	5–500	1.3	50	50	[73]
SFODME[c]	0.83–27	0.11	12	10	[74]
PIM - NTDP	5.0 - 210	1.60	250	25	This work

Note. LDR is linear dynamic range, DT is detection limit, PF is preconcentration factor.
[a] Dispersive liquid–liquid microextraction based on solidification of floating organic drop.
[b] Solid-phase extraction.
[c] Solidified floating organic drop microextraction.

These results prove that the optode is operational because the RSD value for both parameters is below or within the acceptable limit (< 5.0 %) [62].

According to Narayanaswamy and Wolfbeis, studies on the repeatability and reproducibility abilities of the optode are very important in the development of chemical sensors [61]. These parameters are useful in evaluating the capability of the optode to be used repeatedly or able to provide precise and consistent results, albeit from different sets of constructed optode. The relative standard deviation (RSD) value for repeatability of the optode was found to be 1.32%, while reproducibility was found to be 2.56%. The reason for the dissimilarity is due to the variation in construction, such as concentration of the immobilized BTAP and thickness of the PIM [62].

To evaluate the reversibility performance of the constructed optode, 100 ng mL^{-1} Fe^{3+} was introduced to the optode, followed with 0.5 mol L^{-1} of F^{-}. The result showed that the optode is fully reversible and average time to regenerate the optode is about five min. The reproducibility of the optode after regeneration was also studied. The reproducibility was calculated based on three cycles of regeneration and the result was satisfactory, with RSD of 1.87%. The ability of this optode to regenerate is mainly due to the BTAP itself. The presence of a hydroxyl group in the BTAP molecule is expected to diminish the leaching problem. BTAP, which is a lipophilic molecule, is able to hinder itself from leaching out to the analyte aqueous solution. In addition, the presence of Aliquat 336, which also acts as a plasticizer, is able to contain BTAP within the PIM effectively. Thus, it reduces the possibility of BTAP being leached out from PIM even after a few regeneration cycles.

The stability of the optode was also tested for a period of time (14 days) in equilibrating solution of pH 8.0. The optode used was found to be stable and produced highest absorbance at pH 8.0 with calculated R.S.D value of 1.83%. The results showed that the absorbance of the optode continued to be constant even after exposure into equilibrating solution and to air atmosphere. This is due to the nature of the optode that contained Aliquat 336, which its function was to bind the components within the optode thus providing chemical and physical stability.

3.2. Applications to real samples

In order to confirm the applicability of the proposed procedure, it has been applied to the determination of nanogram amounts of Fe^{3+} in water and in real samples. The uptake experiment was done under specified experimental conditions such as pH 8.0 (with thiel buffer) and volume = 25 mL, using 0.5 mL of the effluent sample containing Fe^{3+} ions. The optode film (2 cm x 1 cm) was taken out for the absorbance measurements after exposure as described above. The mean absorbance values were then calculated. The calibration plot was constructed by adding known amount of Fe^{3+} in buffered solution as described above.

3.2.1. Water, food and biological analysis

Results for the analysis of three water samples (Mineral, tap and River) and five food and biological samples (meat, beans, lentils, eggs, and liver) are given in Table 3. Since a standard method for the determination of Fe^{3+} in water has been reported in literature, and AAS method as accepted independent method is available, the accuracy of the method was examined by recovery study of the spiked samples. The recovery of the spikes added to water samples is given in Table 3. The quantitative recovery of the Fe^{3+} spikes and relative standard deviation of 1.75% confirm the good precision and accuracy of the proposed optode method.

The performance of the proposed method was assessed by calculation of the t value (for accuracy) and F test (for precision) [75] compared with AAS method. The mean values were obtained in Student's t and F tests at 95% confidence limits for five degrees of freedom. The results showed that the calculated values (Table 3) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability, and being less time consuming show the advantage of the proposed method over other method.

To test the reliability of the proposed procedure, it was employed to determine the trace amounts of Fe^{3+} in different food and biological real samples [Table 4,5]. In order to verify the accuracy of the established procedure, recovery experiments were also carried out by spiking the samples with different amounts of Fe^{3+} before any pretreatment. Table 4 and 5 shows the obtained results. As can be seen, recoveries between 98.8% and 101.5% were obtained, which confirm the accuracy of the proposed procedure. Thus, these results indicated that the membrane optode method developed in the present work is accurate, simple, and low in cost for analyzing water, food and biological samples containing traces of Fe^{3+} ions.

Table 3. Determination of Fe^{3+} ions in real samples.

Sample	added	Amount found (ng L^{-1})		RSD	t-test	F-value
	(ng L^{-1})	Proposed	AAS	(%)		
Mineral	0.00	8.26 ± 0.20	8.30 ± 0.45	1.48		
water	5.00	13.09 ± 0.28	13.50 ± 0.67	1.61	1.23	
	10.0	18.44 ± 0.27	18.05 ±0.81	1.52		3.03
Benha	0.00	9.10 ± 0.17	9.25 ± 0.48	1.36	1.76	
City water	7.5	16.40 ± 0.00	17.00 ± 0.41	1 25		2.27
	15.0	24.35 ± 0.34	23.85 ± 0.75	1.75	1.45	
River water	0.00	11.70 ± 0.59	11.55 ± 1.16	1.14		2.70
	10.0	22.0 ± 0.28	21.40 ± 0.59	0.67	1.86	
	20.0	31.145 ± 0.27	32.10 ± 0.73	0.65		2.38
Meat	0.00	29.55 ± 0.47	29.75 ± 0.95	0.83	1.35	
	4.00	33.80 ± 0.00	33.45 ± 0.38	0 72		3.13
	8.00	37.15 ± 0.68	38,20 ± 1.56	1.47	1.92	
Beans	0.00	10.48 ± 0.48	10.60 ± 1.83	1.26		2.84
	8.00	18.10 ± 0.00	18.85 ± 0.88	0.64	1.58	
	16.0	26.75 ± 0.00	25.95 ± 0.64	0.45		3.41
Lentils	0.00	8.65 ± 0.67	8.50 ± 2.87	1.52	1.33	
	15.0	23.90 ± 0.68	23.30 ± 2.96	1.54		3.25
	30.00	38.25 ± 0.000	39.10 ± 0.78	0.79	1.19	
Eggs	0.00	6.44 ± 0.32	6.25 ± 1.27	0.76		2.85
	12.0	18.18 ± 0.35	18.00 ± 1.62	1.42	1.76	
	24.0	30.80 ± 0.28	30.00 ± 0.76	0.62		2.59
Liver	0.00	26.2 ± 0.18	26.40 ± 0.69	0.56	1.44	
	6.00	32.62 ± 1.20	32.85 ± 1.47	2.47		2.78
	12.0	37.90 ± 0.56	38.80 ± 2.11	1.12	1.73	

Table 4. Fe^{3+} ions in food samples.

Samples	Source[2]/amount	Iron(III) in ng mL^{-1}			
		Present method (n = 6)		AAS method (n = 6)	
		Found	%RSD	Found	%RSD
Milk	Cow/100 mL	47	1.37	48	2.21
	Buffalo/ 100 mL	58	1.29	59	2.28
Food grain	Mung (Phaseolus aureus)/2.0 g	625	1.52	622	3.11
	Chickpea (Cicer arietinum)/5.0 g	89	1.67	88	3.26

Note: Source[2]: Benha markets, Benha, Egypt

Table 5. Fe^{3+}ion present in biological samples.

Samples	NDS method (n = 6)		AAS Method (n = 6)		Source[1]
	Fe^{3+}, Found, ng L^{-1}	%RSD	Fe(III),Found, ng L^{-1}	%RSD	
Blood	1070	1.1	1040	1.1	Adult Normal
Urine	260	1.3	240	1.2	
Blood	510	1.5	530	1.4	Patient (Anemia)
Urine	160	1.7	150	1.8	

Note: Source[1]: Medical College, Benha city, Egypt

4. CONCLUSION

The developed PIM that has been successfully characterized and optimized for applying as a sensing material in Fe^{3+} optode. The prepared PIM based optode displayed an encouraging response over a range of 5..0 – 210 ng mL^{-1} of Fe^{3+} ions concentrations. The optode can be regenerated within min and shows good repeatability and reproducibility without significant decrease in sensitivity . Furthermore, the optode shows better selectivity for Fe^{3+} ion and has been applied to determine Fe^{3+} in natural water, food, biological and environmental samples and obtained result is comparable to atomic absorption spectrometry method.

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سنسور نوری جدید برای اندازه‌گیری آهن بر مبنای غشای پولیمری ۲-(۲-بنزوتیازولیل‌آزو) فنل

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چکیده

استفاده از غشای شامل پولیمر (PIM) بعنوان یک ماده حساس، روشی جدید برای دستیابی به انتخابگری و پایداری الکترودهای شیمیایی نوری می‌باشد. در این کار یک PIM بدون پلاستی سایزر و هادی پلی وینیل کلرید (PVC) بعنوان یک تکیه‌گاه، ۲-(۲-بنزوتیازولیل آزو) به عنوان واکنشگر و AliquaT336 به عنوان حامل (یونوفر) تهیه و کارایی آن برای تعیین یون‌های Fe^{3+} بررسی گردید. نتایج نشان داد که خواص PIM به مقدار زیادی بستگی به ترکیب غشا دارد. مطالعات نشان داد که پاسخ الکترود به ضخامت فیلم، حضور پلاستی سایزر، هم زدن، غلظت ۲-(۲-بنزوتیازولیل آزو)، غلظت Aliquat 336 و pH محلول مورد استفاده دارد. منحنی کالیبراسیون در محدوده ۲۱۰-۵,۰ نانوگرم بر میلی‌لیتر Fe^{3+} با حدود تشخیص و تعیین به ترتیب ۱,۶۰ و ۴,۹۵ نانوگرم بر میلی‌لیتر بدست آمد. طول موج ماکزیمم برای PIM برابر با ۵۸۱ نانومتر بود. PIM ارائه شده در این تحقیق پایدار، قدرت مکانیکی خوب، حساس و قابل استفاده مجدد بود. نهایتاً، PIM بطور موفقیت‌آمیزی بعنوان یک سنسور نوری جهت تعیین Fe^{3+} در آب‌های طبیعی، غذا و نمونه‌های محیطی و بیولوژیکی بکارگرفته شد و نتایج بدست آمده با روش طیف‌سنجی جذب اتمی مقایسه گردید.

واژه‌های کلیدی

تعیین Fe^{3+}؛ سنسور نوری؛ اسپکتروفتومتری؛ تیازولیل آزو؛ آنالیز نمونه‌های محیطی و بیولوژیکی.