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Utilization of a novel PVC- optical sensor for high sensitive and selective determination of zinc ion in real samples

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Graphical abstract
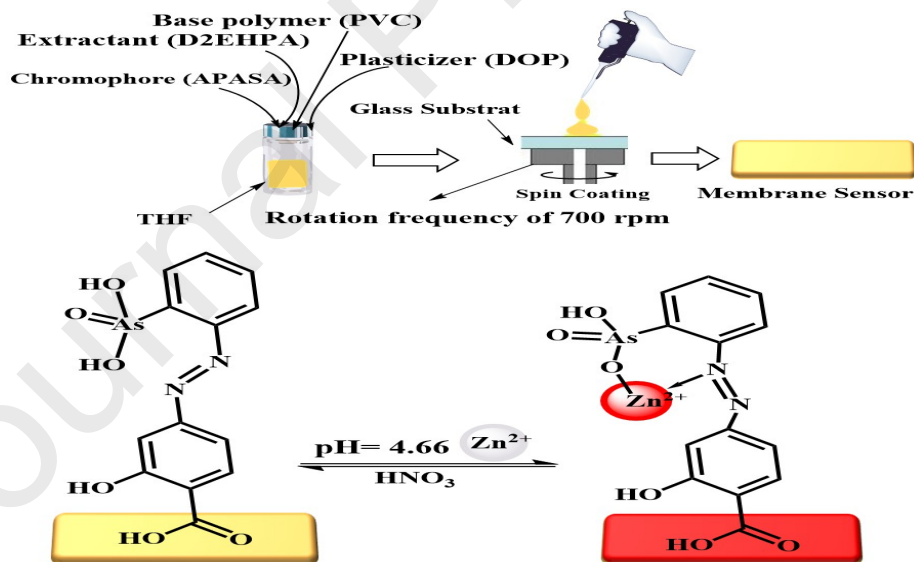
Representative diagram for the sensing Zn(II) optode

Highlights

1- Novel green optical sensor for Zn(III) determination is studied.

2- Effects of several experimental parameters are optimized.

3- Selectivity for Zn(II) over several cations and anions is investigated.

4- The method was applied to determine Zn(II) in environmental samples.

Abstract

A novel and highly specific bulk membrane optode was developed for the ultra-sensitive detection of zinc(II) in biological, pharmaceutical, and water samples. The polymer inclusion membrane (PIM) utilized in this study consists of 50% polyvinyl chloride (PVC) as a base polymer, 9.00% DOP (dioctylphthalate) as the plasticizer, and 40.0% D2EHPA (di(2-ethlyhexyl)phosphoric acid) as the carrier. To facilitate the spectrophotometric determination of zinc(II), a colorimetric reagent, namely 4-(2-arsonophenylazo) salicylic acid (APASA) {1.00%, m/v}, was employed. When Zn(II) was extracted into the PIM, it led to the creation of the zinc-D2EHPA complex. This complex then underwent a reaction with APASA, resulting in the formation of a red Zn−APASA complex with a maximum absorption wavelength (λ_{max}) of 558 nm. To optimize the response of the optode, a central composite design was employed, considering variables such as the amount of additive and reagent, response time, and pH. When operated under the specific optimal conditions, the sensor demonstrated a limit of quantification (LOQ) of 0.74 ng/mL (equivalent to 1.17×10^{-8} M) and a limit of detection (LOD) of 0.22 ng/mL (equivalent to 3.44×10^{-9} M). The optode membrane demonstrated excellent reproducibility, stability, and a relatively long lifespan, making it suitable for precise and accurate monitoring of Zn(II) ion content. Regeneration of the optode was achieved effectively using 0.25 nitric acid solution, and its response exhibited

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reversibility and reproducibility, showed a relative standard deviation of less than 1.33%. Moreover, the PIM-APASA optode exhibited a high level of effectiveness

in accurately determining the presence of Zn(II) ions in real environmental samples.

1. Introduction

Within the human body, zinc is considered the second most prevalent transition metal ion, surpassed only by iron in terms of abundance. Zinc assumes a vital role in numerous biochemical processes [1,2] and is considered an essential element for all animals, including humans. It can be found in a variety of foods such as cereals, rice, liver, meat, cheeses, oysters, nuts, and DNA-binding proteins. Zinc plays a crucial role as an essential component in various enzyme systems that are integral to fundamental processes in marine phytoplankton metabolism, including bicarbonate uptake [3] and phosphate uptake [4]. In human beings, zinc holds significant physiological importance in diverse processes such as mammalian reproduction, gene transcription, immune function, brain function, and pathology [5].

Elevated levels of Zn^{2+} have been linked to the onset of several diseases, including epilepsy, Alzheimer's disease, Parkinson's disease, ischemic stroke, breast cancer, and diabetes. Furthermore, Zn^{2+} possesses the capacity to directly impact numerous enzymatic and cellular functions [6,7]. For optimal health, it is recommended that women consume 12 mg of zinc daily, while men should aim for an intake of 15 mg per day. Furthermore, widespread exposure to zinc chloride can cause respiratory disorders [8,9]. However, it should be noted that zinc can become toxic when consumed in amounts exceeding physiological requirements [2]. It is used in mineral vitamin preparations, eye drops, mouthwashes, creams, ointments, and as a treatment against certain types of infections.

A wide range of analytical methods are frequently utilized for the quantitative assessment of zinc concentration, including molecular spectrophotometry [10–16], atomic absorption spectrometry (AAS) [17], flame atomic absorption spectrometry (FAAS) [18,19], graphite furnace atomic absorption spectrometry (GF-AAS) [20], inductively coupled plasma mass spectrometry (ICP-MS) [21], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [22], microprobe X-ray [23], chemiluminescence analysis [24], fluorescence analyses [25], and electro-analytical techniques [26–28]. While these techniques offer a minimal limit of detection, they can be time-intensive, financially burdensome, and susceptible to interference from the sample matrix [29]. In comparison, spectrochemical methods

are frequently preferred due to their relatively lower expenses, user-friendly nature, and widespread availability of instrumentation [30].

Several procedures, such as co-precipitation [31], liquid–liquid extraction (LLE) [32], solid phase extraction (SPE) [33,34], cloud-point extraction [35,36], and dispersive liquid–liquid micro-extraction [37], have been developed for the separation and preconcentration of zinc from different matrices. However, these methods often require large amounts of organic solvents, some of which are harmful and contaminate the environment due to their high vapor pressure.

Over the past two decades, there has been remarkable progress in the advancement and application of optical chemical sensors, commonly referred to as optodes. These sensors have found applications in the determination of diverse analytes, including cations [38,39], anions [40,41], neutral species [42,43], and gaseous compounds [44,45]. Optical sensors provide the benefits of straightforward instrumentation and are well-suited for creating multi-sensor arrays. Unlike ion-selective electrodes, they do not necessitate internal or external reference devices. Furthermore, optical sensors eliminate the requirement for prolonged preconditioning time and are resistant to interference from electrical noise [46].

The emergence of optical sensors, commonly referred to as optodes, as highly viable alternatives to conventional sensor technologies has generated significant interest [47–50]. Optodes have shown remarkable efficacy in the field of trace analysis of heavy metal ions, as well as in various applications including environmental monitoring, process control, and medical analysis [51–54].

A variety of optical sensors have been developed by incorporating lipophilic ligands as key components in membrane structures [55,56]. The selective interaction between the immobilized ligands and metal ions through color complexing reactions determines the sensor's selectivity and its suitability for a specific sample analysis. The performance of ion-sensitive layers is intricately shaped by the method of immobilization and the composition of the matrix, exerting a significant influence on their overall effectiveness [57]. Among the various optode designs, one noteworthy approach involves the use of a plasticized polymeric membrane embedded with a reactive compound that undergoes a striking color transformation upon encountering the target analyte. The fundamental principles and techniques of optical ion sensing have been extensively studied in the literature, providing knowledge about the complex operation of these sensors [58]. Moreover, the theoretical underpinnings of bulk optode membranes, which hinge on the reversible mass transfer of the analyte from the sample into the sensing layer, have been illuminated by the insightful research of Seiler and Simon [59]. Over the years, a plethora of ingenious optode configurations have emerged,

each tailored for the quantification of Zn^{2+} ions, showcasing the versatility and ingenuity within this field [60–66].

In the present investigation, a polymeric inclusion membrane (PIM) was utilized, comprising dioctylphthalate (DOP) as the plasticizer, polyvinyl chloride (PVC) as the base polymer, di(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant, and 4-(2-arsonophenylazo) salicylic acid (APASA) as the chromophore. APASA, known for its yellowish-orange color, was found in our study to form a red-colored complex with Zn^{2+} ions [67]. The primary aim of this study was to design and refine the PIM-APASA optode to enable precise and reliable quantification of Zn^{2+} ions in diverse real samples. The focus was on establishing optimal conditions to ensure accurate and robust measurements. To the best of our knowledge, no previous method utilizing optodes and involving the use of APASA has been reported for the determination of zinc.

2. Experimental

2.1. Reagents and solutions

The polymeric inclusion membranes (PIMs) were formulated using the following substances as received without any modifications: Dioctylphthalate (DOP) (99%, Sigma-Aldrich), high molecular weight PVC with a high molecular weight (Selectophore, Fluka), di-(2-ethylhexyl) phosphoric acid (D2EHPA) (97%, Sigma-Aldrich), and tetrahydrofuran (THF) (Analytical Grade, Lab-Scan Analytical Sciences). All solution preparations utilized deionized water obtained from the Barnstead Mega-Pure® System MP-12A.

To prepare a stock solution of zinc with a concentration of 1.20×10^{-3} M, 0.0785 g of $Zn(NO_3)_2 \cdot 6H_2O$ sourced from Merck (Darmstadt, Germany) was dissolved in precisely 200 mL of deionized water. The stock solution was then standardized using EDTA [68]. Subsequently, various diluted standard solutions were prepared by appropriately diluting the stock solution.

Borate, acetate, thiel, phosphate, and universal buffer solutions with pH values ranging from 2.00 to 12.0 were prepared using established procedures [69]. Stock solutions of interfering ions were prepared at a concentration of 15000 μg/mL by dissolving suitable salts sourced from Merck in double-distilled water.

The previously reported method [67] was used to make 4-(2-arsonophenylazo)salicylic acid (APASA) and figure out what it is. To create a 5.00 $\times 10^{-4}$ M APASA solution, the appropriate amount of pure reagent was dissolved

in a minimal volume of ethanol. Subsequently, the solution was diluted to the desired volume of 100 mL in a calibrated flask using the same solvent.

2.2. Apparatus

The experimental setup involved the use of a Shimadzu model 670 atomic absorption spectrometer with flame atomization. The operating parameters of the instrument were configured as per the manufacturer's guidelines. Atomic absorption measurements were conducted utilizing a nitrous oxide-acetylene flame. The pH values of the solutions were measured employing an Orion Research Model 601 A/digital ionalyzer pH meter. A UV-Vis spectrophotometer model V-670 from JASCO (Tokyo, Japan) was employed for spectral and absorbance measurements. To measure absorbance, the sensor membrane samples were placed inside a quartz cuvette. The absorbance readings were acquired by comparing the optical sensor samples to both air and a blank optode sample. The FT-IR spectrum was recorded in KBr pellets on a Shimadzu FT-IR 8101 PC infrared spectrometer in the range of 4000 to 500 cm^{-1}.The thickness of the PIM was determined using a Mitutoyo Digimatic Micrometer Series 293 MDC-MX Lite.

2.3. Stoichiometric detection

To determine the stoichiometry of the PIM-APASA complex, two methods were employed: the mole ratio method and the continuous-variation method (Job's method) [70,71]. These methods were carried out under pH 4.66 conditions using Zn(II) and APASA concentrations of 5.00×10^{-4} M.

2.4. Membrane formulation and optimization

PIMs were synthesized by dissolving a combined mass of 50 mg of PVC (the base polymer), 9.00 mg DOP (plasticizer), 40.0 mg D2EHPA (the extractant), and 1.00 mg APASA (the chromophore) in 10.0 mL of THF. The resulting solution was then carefully poured into a glass ring placed on a 10.0 cm-diameter glass plate. Maintaining a controlled temperature of 25.0 ± 2.00 °C, the solution was allowed to rest undisturbed overnight for natural evaporation of the THF solvent. Following the evaporation process, a precise volume of 100 µL of the solution was

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injected onto the glass plate. To ensure uniformity, the membrane underwent one minute of spinning at a rotation frequency of 700 rpm. Subsequently, the membrane was left to dry in ambient air for 10 minutes.

Following the described process, a homogeneous and mechanically strong membrane with a yellowish-orange color was obtained. The membrane exhibited flexibility, transparency, and a uniform thickness, which was determined to be 0.10 ± 0.001 mm using a digital micrometer. To facilitate further experimentation, the membrane was cut into square strips measuring approximately 0.75 cm^2. To optimize the composition of the membrane, triplicate trials were conducted at each concentration set. The concentration of dioctyl phthalate (DOP) varied between 6.00% and 12.0% (m/m), while that of polyvinyl chloride (PVC) was adjusted between 47.50% and 53.50% (m/m). The remaining component of the PIM, di(2-ethylhexyl)phosphoric acid (D2EHPA), maintained a constant concentration of 40.0%. After optimizing the main components of the PIM, the concentration of 4-(2-arsonophenylazo)salicylic acid (APASA) was also varied in the range of 0.50% to 1.50% (m/v). The extraction and quantitation experiments were subsequently carried out using the optimized membrane composition.

To optimize the pH conditions for the experiment, a spot test was performed. White spot test ceramic dishes were used to hold small strips of the optimized yellowish-orange-colored PIM-APASA. These strips were immersed in buffer solutions with different pH values. A drop of zinc solution was then added to each dish. The time taken for the color change indicating the formation of the PIM-APASA-Zn complex, as well as the intensity of the resulting red color, was carefully monitored within the pH range of 2.00–12.0. This allowed for the determination of the ideal pH range for the formation of the complex and the development of the desired color.

The membranes containing different amounts of APASA were placed on white, lint-free tissue inside a Petri dish and stored in a desiccator at a temperature of 25.0 ± 2.00 °C. The stability of the PIM is crucial for accurate quantification of Zn(II), and it is important to prevent leaching of APASA from the membrane. During storage, one factor that was closely monitored in the presence of APASA leachate. This was determined by inspecting the white lint-free tissue for any yellowish-orange discoloration. The appearance of a yellowish-orange color on the tissue paper indicated that some of the immobilized APASA had leached out from the PIM. This observation helped ensure the integrity and stability of the PIM for reliable Zn(II) determination.

2.5. Procedure

The optode membrane was positioned within the cell of the spectrophotometer, which 2.50 mL of pH 4.66 acetate buffer solution. A precise quantity of Zn^{2+} ion solution was introduced into the sample, and absorption spectra were recorded at

1.00 cm intervals across the wavelength range of 350–750 nm. By comparing the absorption spectra of the sample to a reference blank membrane, the optode's response to the presence of Zn^{2+} ions was analyzed.

2.6. Interference studies

To evaluate the selectivity and sensitivity of the newly developed optode, standard solutions were prepared. Each solution contained 150 ng/mL of Zn(II) and a 10,000-fold excess of one of the common base metal ions typically found in real samples: Mg(II), Ca(II), Fe(III), Al(III), Cd(II), Pb(II), Ni(II), Zn(II), and Co(II). These prepared solutions were then subjected to analysis using the aforementioned optode. The optode's response to each metal ion was carefully assessed, allowing for an evaluation of its selectivity and sensitivity in the presence of these potential interfering ions.

2.7. Procedure for zinc in pharmaceutical formulations

2.7.1. For Tablets

In order to determine the zinc content in VitaZinc capsules and Stresstabs/600, a single capsule was dissolved in aqua regia. The resulting solution was then subjected to evaporation to remove any excess solvent. The residue obtained from the previous step was treated with concentrated nitric acid (HNO_3) and subjected to multiple rounds of evaporation. This process was carried out to ensure the complete dissolution of the sample. This process was repeated four times to ensure accuracy. The final residue was then dissolved in deionized water to obtain a solution. From this solution, a measured portion was used to determine the zinc content using the previously developed and validated sensor technique. This approach provides a reliable and precise method for analyzing the zinc levels in the capsules, ensuring accuracy and quality control in the assessment of their zinc content.

2.7.2. Hamoderme (talc powder)

For the zinc analysis, a sample of 25.0 mg was mixed with 3.0 mL of concentrated nitric acid (HNO_3). The resulting solution was subsequently diluted and washed with deionized water to eliminate impurities. To remove any remaining solid residue, the solution was filtered. The filtrate, together with the

washings, was collected and brought to a final volume of 250 mL in a volumetric flask. This prepared solution was then subjected to zinc analysis using the previously described method. This rigorous sample preparation procedure ensures the removal of interfering substances and provides a clean sample for accurate determination of zinc content.

2.7.3. Prozoline zinc (solution)

To concentrate the solution, a 10-mL portion was subjected to evaporation until dryness, resulting in the formation of soluble salts. These salts were then dissolved in 2.00 mL of concentrated nitric acid (HNO_3). To remove any insoluble residue, the solution was filtered, and the residue was discarded. To further purify the filtered solution, it underwent three subsequent washes with deionized water. After the washing process, the resulting filtrate was adjusted to a final volume of 50.0 mL using a measuring flask. From this solution, an aliquot was taken and analyzed for zinc content using the previously described method, with the zinc concentration reported per 10.0 mL of the original solution. This concentration step and purification process enhance the accuracy and sensitivity of the zinc analysis, ensuring reliable results.

2.8. Vegetable Handling and Processing (Parsley, Basil)

Two varieties of vegetables, namely parsley and basil, were chosen for the analysis. These vegetables were purchased from a local supermarket. To prepare the samples, they were first air-dried and then subjected to further drying at a temperature of 105 °C for duration of 2.00 hours. Once dried, the vegetables were powdered. For the analysis, 0.30 g of parsley sample and 0.50 g of basil were separately placed in Teflon flasks. Then, 5.00 mL of 30% (v/v) HF and 5.00 mL of concentrated HNO_3 were added to each flask. After standing for 8.00 hours, the samples were digested in a microwave system at a temperature of 106 °C for 10 minutes. Following digestion, the resulting clear solutions were transferred to 400 mL beakers and diluted to a volume of 300 mL. The pH of the solutions was then adjusted to 5.00. An aliquot of the solution was subsequently analyzed using the method described earlier.

2.9. Analysis of zinc content in water samples

A comprehensive study was conducted on a specific set of water samples collected from the vicinity of Shobra-El-Khema and Benha cities. Each

environmental water sample was carefully filtered, and the resulting filtrate was subjected to a controlled evaporation process using a combination of 5.0 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3. After the evaporation step, the residue was allowed to cool down to a temperature of 25.0 ± 2.00 °C, following which it was treated with 10 mL of deionized water to dissolve any remaining salts. The resulting solution was then cooled and neutralized using dilute NH_4OH. The neutralized solution was subsequently filtered, and a precisely measured volume of the filtrate was transferred into a 25.0 mL calibrated flask, which was then filled to the mark with deionized water. A specified aliquot of this prepared sample solution was carefully selected, and the zinc content was determined using the established procedure mentioned earlier.

2.10. Investigation of zinc levels in the serum of individuals diagnosed with diabetes

The serum samples utilized in this research were obtained from a reputable medical diagnostic laboratory (MDL). To ensure accurate zinc measurements, the serum samples underwent a deprotenization process. This involved combining 4.00 mL of serum with a mixture of 2.00 mL containing 10.0% trichloroacetic acid and 0.10 M HCl. Following a 15.0-minute heating period and subsequent cooling for 10.0 minutes, the mixture underwent centrifugation. The sample was processed to remove proteins, resulting in a supernatant liquid. The concentration of zinc in this protein-free supernatant was then determined using the previously described method.

2.11. Powdered milk sample preparation

A precise amount of the powdered milk sample (2.00 g) was subjected to a treatment involving NaOH (1.00 g) dissolved in a small volume of deionized water. The mixture was carefully evaporated to dryness using a platinum dish. Subsequently, the resulting residue underwent a controlled heating process in a furnace at 500 °C for 20.0 minutes. Following the cooling step, the residue was dissolved by adding a solution composed of 2.00 mL of concentrated HNO_3 and 15.0 mL of deionized water [72]. The pH of the resultant solution was precisely fine-tuned to approximately 5.00 using NaOH, followed by meticulous dilution of the solution to a final volume of 50.0 mL with water in a measuring flask.

2.12. Hair sample preparation

To eliminate surface contaminants, the hair sample underwent a thorough washing procedure using a mixture of acetone and water. Subsequently, a precisely weighed quantity of clean hair weighing 1.00 g was subjected to dry-ashing in a furnace at 450 °C. Upon complete combustion, the resulting residue was dissolved in HNO_3. The pH of the resulting solution was then meticulously adjusted to around 5.00 using NaOH. Finally, the solution was diluted to a final volume of 50.0 mL with water in a measuring flask [73].

2.13. Preparation of red meat

The samples of red meat were carefully transported in sealed plastic bags to ensure their integrity. Upon arrival at the laboratory, the samples underwent a meticulous cleaning process, followed by a thorough rinsing with deionized water, in order to remove any surface impurities. Subsequently, the meat was skillfully cut into uniform pieces using a high-quality stainless-steel knife. To prepare the samples for analysis, they were subjected to a controlled drying process in an oven set at 65.0 °C for 48 hours, ensuring that the meat achieved a constant weight. Once dried, the samples were finely powdered, employing precise techniques to maintain accuracy. For digestion, an exact weight of 1.00 g of the powdered meat was meticulously measured and transferred to specially designed polyethylene vials. A carefully composed mixture of concentrated H_2SO_4 and HNO_3 in a ratio of 1:3 v/v, was added to facilitate the digestion process. To eliminate any interference from nitrogen dioxide, a small volume of 30.0% H_2O_2 was judiciously introduced. The digestion procedure continued until the solution attained a visually transparent appearance, indicating the completion of the process. Following digestion, the samples were transferred to a 250-mL beaker and expertly diluted with deionized water to reach a final volume of 200 mL, ensuring an optimal concentration for subsequent analysis.

3. Results and discussion

3.1. Stoichiometry of Zn(II)-APASA complex

Figure 1 shows the absorption spectra of APASA and the Zn-APASA complex. This gives us important information about the wavelengths at which they absorb the most light. Notably, the peak absorption of APASA is at 397 nm, while the Zn-APASA complex has a very clear absorption band at 558 nm. To ascertain the stoichiometry of the Zn-APASA complex, two methods, namely the molar ratio and Job's methods, were employed.

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The molar ratio method showed that the best absorption happened at a ratio of 1.00:0.90 (Zn:APASA), which shows that the two parts go together well. Similarly, Job's method yielded a mole ratio of 0.5, further substantiating the formation of a 1:1 stoichiometric ratio in the Zn-APASA complex. These findings, combined with the infrared (IR) spectra of APASA and the Zn-APASA complex, provided the basis for proposing the structural representation of the complex as depicted in Scheme 1.
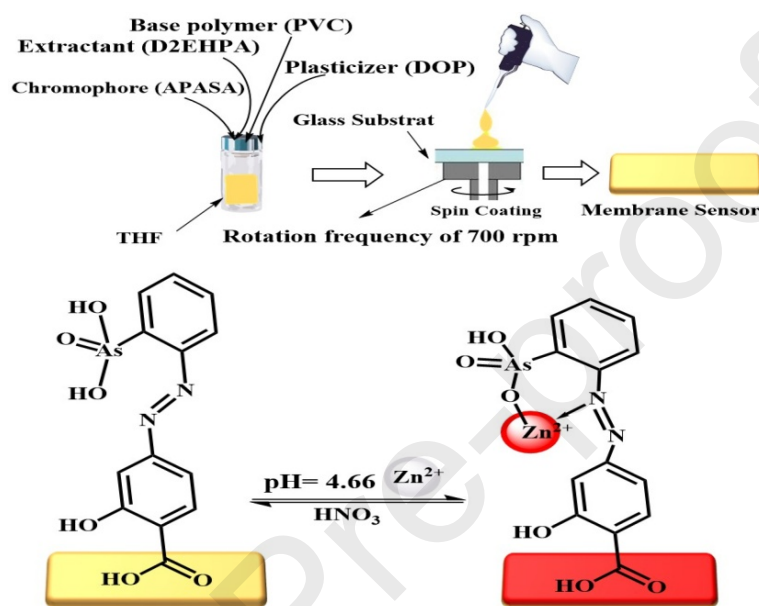
Scheme 1. Representative diagram for the sensing Zn(II) optodesensor

3.2. PIM optimization

In order to get Zn(II) out of aqueous solutions efficiently, you need a polymer inclusion membrane (PIM) with certain qualities: homogeneity, flexibility, and mechanical strength. Moreover, The PIM should be precisely thin to facilitate rapid regeneration, specifically the stripping of Zn(II) after sample measurement. At the same time, it should maintain its mechanical robustness to ensure durability and longevity. These essential characteristics served as the foundation for meticulously optimizing the composition of the optode membrane.

In a previous study that investigated a Zn(II)-based sensor, the optode membrane was carefully formulated with precise quantities of different components: 63.0 mg of NPOE, 3.00 mg of NaTPB, 31.5 mg of PVC, and 1.50 mg of ETH 5294, all expertly dissolved in 2.5 mL of THF saturated with DMPAHPD [74]. To further enhance the sensitivity, selectivity, and stability of the optode membrane, these concentrations were systematically adjusted. The critical

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elements in PIMs, crucial for achieving both strength and flexibility, are the plasticizer and the base polymer. Consequently, the concentrations of these components were intentionally adjusted at three specific levels while keeping the concentrations of D2EHPA and APASA constant at 40.0% and 0.50%, respectively, in all three experimental setups.

Among the various PIM formulations examined, those containing (53.5% PVC and 6.00% DOP) and (52.0% PVC and 7.50% DOP) demonstrated minimal chromophore leakage. However, the tightly packed PVC strands in these membranes led to rigidity. Conversely, the membrane with 12.0% DOP exhibited desirable flexibility but suffered from excessive oiliness due to an oversupply of plasticizer, resulting in chromophore leaching. The most optimal stability and flexibility were achieved with PIMs containing 50.5% PVC and 9.00% DOP. A comprehensive overview of the DOP and PVC ratios and their corresponding characteristics in the resulting PIMs is presented in Table 1. Following the meticulous optimization of the base polymer and plasticizer concentrations, the APASA concentration was systematically varied from 0.50 wt% to 1.50 wt%. Although increasing the amount of immobilized APASA beyond 1.00 wt% expedited its reaction with Zn(II), it led to a darker starting membrane color, significantly compromising sensitivity. Consequently, an APASA concentration of 1.00 wt% was judiciously selected as the optimal value, prompting adjustments to the PVC concentration, which was set at 50.0%. The resulting PIM-APASA formulation, characterized by PVC (50%), DOP (9.00%), D2EHPA (40.0%), and APASA (1.00%), demonstrated exceptional stability and flexibility without any observed leaching phenomena.

3.3. Acidity of the source phase

In this study, an acidic carrier, D2EHPA, was utilized for the transport and extraction of metal ions. The process involves the exchange of metal ions with protons in the carrier, which requires an acidic environment. Adjusting the solution to a lower pH enhances the selectivity [75]. Spot tests were conducted to examine the impact of pH before using the membrane. The results indicated that complex formation occurred faster between pH 4.35 and 5.05 compared to higher pH values. At higher pH levels (pH 8.00-10.0), Zn(II) ions precipitated as hydroxides. Further investigation revealed that at pH 4.66, the color development was rapid and easily observable with the naked eye. To optimize the pH, a range of 2.56 to 5.65 was tested (Fig. 2). After multiple runs, it was determined that the highest absorbance value was obtained at pH 4.66 compared to the range of pH 4.35 to 5.05. Subsequent experiments were therefore conducted at pH 4.66.

3.4. The membrane stability

The membrane optode developed in this study demonstrated a significantly prolonged lifespan, with storage inside a desiccator at 25.0 ± 2.00 °C allowing for up to three weeks of usability. The optode maintained its performance without any signs of deterioration for 10 repeated determinations. The optimized parameters are summarized in Table 2. Regarding the stop time, it was determined that a reasonable duration for the complex formation and detection by the optode is 3.0 minutes, which was identified as the optimum stop time. Experimental results using the optimized PIM-APASA demonstrated that when a water sample containing Zn(II) passed through the yellowish orange colored PIM-APASA, the color changed to red, indicating the formation of the APASA-Zn complex. The intensity of the red color increased with a higher number of Zn(II) ions being complexed with APASA, resulting in an increased absorbance. This trend continued until all the extracted Zn(II) had formed complexes with APASA, reaching a maximum at the optimum high concentration.

3.5. Regeneration and life time of the proposed optode

Regeneration is a crucial aspect of an optode membrane as it enables multiple uses of the sensor and minimizes reagent consumption. The regenerative process involves the utilization of an appropriate stripping reagent, as the sensor itself does not exhibit complete reversibility. The regeneration time refers to the period needed for the sensor to attain a stable baseline after being loaded with the regenerating solution. Several compounds, such as HCl, H_2SO_4, HNO_3, KI, KSCN, and KBr, were examined as potential stripping reagents. Although complete regeneration was accomplished using H_2SO_4 and HCl solutions, the process was relatively time-consuming, with the membranes recovering only 80% of their initial absorbance after 10.0 minutes. On the other hand, all other tested reagents proved to be efficient in regenerating the optode membranes, with the shortest regeneration time observed with HNO_3 solution. The concentration of the stripping reagent also had an impact on the regeneration process. Optimal results were obtained when utilizing a 0.25 M HNO_3 solution, although lower concentrations as low as 0.10 M could be used, but with longer regeneration times. When a 0.25 M HNO_3 stripping reagent was employed, the regeneration times for the sensor membranes after exposure to 100, 200, and 300 ng/mL Zn(II) solutions were 20.0, 35.0, and 50.0 seconds, respectively. It is important to note that the regeneration step is not necessary when transitioning from a lower to a higher zinc ion concentration.

3.6. Interference

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The comparative response of an optode membrane to the primary ion when compared to the presence of other ions in the solution is an essential characteristic that requires significant consideration [76]. These interfering cations and anions can have an impact on the ionophore within the optode or even react with Zn(II) ions, leading to reduced efficiency in diffusion and migration. To establish a tolerance limit, the concentration at which an error of more than ± 5.00% in absorbance occurs for a fixed Zn(II) ion concentration was determined [77,78]. In this context, the absorbance of the optode was carefully measured before and after introducing a fixed quantity of interference ions into a solution containing 150 ng/mL of Zn(II) ions, and the results are conveniently presented in Table 3. Encouragingly, the obtained results confirm the outstanding selectivity of the optode towards Zn(II) ions at λ_{max} = 558 nm, with minimal interference from other coexisting ions, except for Cd^{2+} ions, which exhibited no significant interference even at concentrations exceeding 150-fold mass ratios. This remarkable selectivity can be attributed to the strong binding affinity and reactivity of the azo group's nitrogen atoms towards Zn(II) ions, making them the most dominant and reactive species. Furthermore, the ionophores structural characteristics, including their resonance contribution, greatly enhance their ability to bind metal ions effectively. Consequently, the utilization of this optode for practical determination of Zn(II) ions holds great promise.

3.7. Response time

The response time is a vital analytical parameter for any optode, representing the minimum duration needed to achieve a stable absorbance close to 95.0% of the final equilibrium response. In this study, the optimized optode film demonstrated a rapid response time of 3.00 minutes, dependent on the concentration of Zn(II) ions. The response time is mostly determined by how long it takes for the analyte to move through the optode film from the bulk of the solution to the interface, where it reacts with the reagent. Notably, the response time exhibited an inverse relationship with the initial concentration of Zn(II) ions. Raising the concentration from 50.0 to 300 ng/mL resulted in a substantial increase in response time, ranging from 2.00 minutes to 5.00 minutes. Fig. 3 graphically represents the time-dependent changes in absorption intensity at 558 nm. Overall, the response time is shorter in concentrated solutions compared to dilute solutions, indicating the efficient performance of the optode film.

3.8. Dynamic range

The absorption spectrum of the optimized optode film, utilizing the established variables, was examined across a range of Zn(II) ion concentrations. The resulting

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calibration curve displayed a linear relationship extending from from 0.75 to 325 ng/mL (Table 4). Through the utilization of a widely accepted equation, the slope of the calibration curve, and the standard deviation of blank optodes and solution, the method's detection and quantification limits were determined to be 0.22 and 0.74 ng/mL, respectively [79]. The remarkable results highlight the method's capability to precisely and reliably detect and measure even the most tiny quantities of Zn(II) ions. These impressive figures underscore the method's ability to accurately and precisely detect and estimate even the most minute quantities of Zn(II) ions. Notably, this analysis can be conducted using an easily accessible and cost-effective instrument like a UV-vis spectrophotometer in conjunction with the optode membrane. Thus, this approach offers a practical and efficient means of determining low Zn(II) ion concentrations with exceptional accuracy and precision.

The response characteristics of the developed optode procedure were compared with recently reported sensor methods for zinc determination utilizing a variety of detection systems [30,61–66,74,80–91]. The summarized results are presented in Table 5. The comparison demonstrates several noteworthy advantages of the proposed method, including its simplicity, cost-effectiveness, rapid analysis time, low toxicity, and relatively high selectivity. While the primary focus of the optode was on Zn(II) detection, it is important to highlight its potential applicability for the determination of zinc in real samples, as it offers minimal interference from other metal ions.

The reproducibility of the optode membrane was assessed through multiple experiments using a single sensor. The results showed that the optode response for Zn(II) concentrations of 150 and 250 ng/mL exhibited low variability, with relative standard deviations (RSDs) of 1.22% and 1.85% respectively. To further evaluate the consistency of the membrane preparation method, six optodes were prepared from the same coating solution, and their responses to 150 and 250 ng/mL Zn(II) solutions were measured. The RSDs of the responses among the different membranes were found to be 1.47% and 2.05% respectively, indicating a satisfactory level of reproducibility. These findings demonstrate the reliability and robustness of the optode membrane for accurate and consistent Zn(II) determination.

3.9. Real samples analysis

The analytical performance of the proposed optode was evaluated by determining the concentration of Zn(II) in various water and pharmaceutical samples. The reliability of the method was confirmed by conducting six replicate measurements using the same optode, and the results obtained were found to be satisfactory, as summarized in Tables 6 and 7. In order to validate the procedure,

spiked real samples were analyzed to assess its performance in real-world scenarios. The accuracy and precision of the proposed method were evaluated by comparing the F-test (for precision) and t-value (for accuracy) with the FAAS method. The mean values obtained from the proposed method were within the acceptable range of the Student's t-test and F-test at a 95% confidence level, considering five degrees of freedom [91]. The calculated values presented in Tables 6 and 7 did not exceed the theoretical values, indicating good agreement between the results obtained by the proposed method and the FAAS method. The proposed procedure offers several advantages, including a wider range of determination, higher accuracy, improved stability, and reduced analysis time compared to other methods. These findings demonstrate the utility and reliability of the proposed optode for the determination of Zn(II) in various samples.

The developed optical sensor was successfully employed for the quantification of Zn(II) in hair and powdered milk samples using the optimized experimental parameters. To assess the accuracy of the method, a comparison was made between the results obtained by the proposed optode and FAAS. The data presented in Table 8 demonstrate good agreement between the results obtained from both methods. Additionally, the sensor was applied for the direct determination of zinc in various biological samples, yielding excellent results. This successful application further validates the feasibility and suitability of the proposed optode for practical analysis in different sample matrices.

The method's accuracy was thoroughly evaluated by quantifying the Zn(II) ion concentration in a diverse range of human serum samples, as outlined in Section 2.13. The comprehensive results, as presented in Table 9, were subjected to a rigorous statistical analysis by comparing them to the outcomes obtained through FAAS using the renowned Student's t-test. To assess any potential statistical differences, a one-sample t-test was conducted at a confidence level of 95%. Intriguingly, the study revealed no discernible correlation between serum Zn(II) concentrations and serum glucose in diabetic patients. However, it is noteworthy that a gradual decline in serum Zn(II) levels was observed among patients with higher glucose levels, as intriguingly illustrated in Table 9.

The statistical analysis yielded a calculated value (t_{calc}) that was found to be lower than the critical value (t_{tab}), indicating no significant differences between the results obtained from the proposed optode and FAAS. This significant finding emphasizes the accuracy and reliability of the developed sensor in quantifying serum Zn(II) concentrations, thereby establishing it as a viable alternative to conventional analytical methods.

To assess the accuracy of the procedure, a comparison was made between the results obtained using the proposed optode and the reference technique FAAS for various vegetable samples (parsley, basil) and red meat samples. The comparative results are presented in Table 10. It is evident that the results obtained by the

proposed optode show good agreement with those obtained by FAAS, indicating the accuracy and reliability of the developed optode for the determination of Zn(II) in these samples. This agreement between the two methods reinforces the suitability of the optode as an alternative and efficient analytical tool for Zn(II) analysis in food samples.

4. Conclusions

The developed optode is a very accurate, sensitive, highly selective, reasonably priced instrument for detecting zinc without any pretreatment or extraction. After optimization of the experimental circumstances, the attained results established that the optode response was dependent on the presence of film thickness, stirring effect, amounts of D2EHPA, APASA, DOP, and pH of the aqueous solution. In the measuring range from 0.75 to 325 ng/mL of Zn(II) at pH 4.66, the absorbance response demonstrates a respectable correlation, with detection and quantification limits of 0.22 and 0.74 ng/mL, respectively. In comparison to other published methods, the suggested technique provides a wider range of monitoring, more accuracy, more stability, and less time consuming. The proposed PIM optode is highly selective due to its lack of interference from most cations, anions, drugs, and pharmaceutical additives and excipients. Lastly, the fabricated optode can be effectively applied for routine zinc monitoring in water, pharmaceutical formulations, biological samples, and vegetable samples, and the results showed no significant difference compared to the FAAS procedure.

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Ethical statement

All biological studies were carried out in strict accordance with the animal welfare guidelines of the World Organization for Animal Health. All biological experiments were performed using protocols approved by the Laboratory Animal Ethics Committee of Egypt, which was approved by Commission on the Ethics of Scientific Research, Faculty of Medicine, Benha University. In all cases, informed written consent was obtained from each participant.

Author contributions

Reem Alshehri and **Hesham El-Feky**: conceptualization, data curation, investigation, methodology, visualization, validation, writing–original draft, writing–review & editing. **Alaa Amin** and **Abdelrazik M. Askar**: conceptualization, methodology, data curation, investigation, supervision, validation, writing–original draft, writing–review & editing. **Mai Aish**:

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to impugn the work reported.

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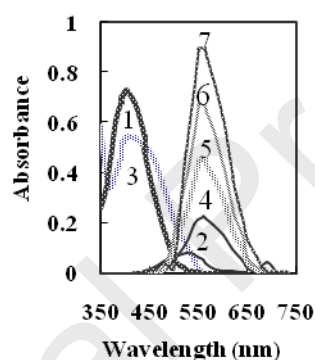
Fig. 1. Absorption spectra of 1- APASA in solution; 2- APASA-Zn in solution and 3- APASA optode 4 - 7 APASA -Zn optiode at 50, 100, 150 and 200 ng/mL at pH 4.66.

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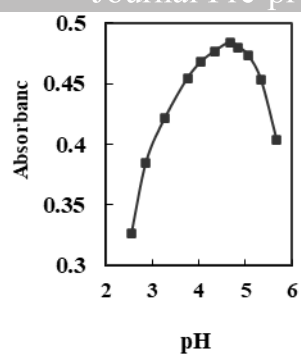
Fig. 2. Absorbance of the optode
in solutions containing 150 ng/mL
Zn(II) at different pH values..
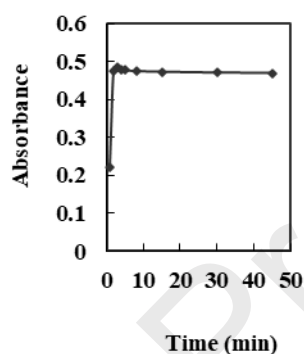
Fig. 3. Effect of response time on the
absorbance of the proposed optode; conditions:
[Zn(II)] = 150 ng/mL; T=25 °C; pH= 3.88.

Table 1. Quality of PIM as a function of DOP and PVC composition.

Conditions	PIM Characteristic
6.00% DOP, 53.5% PVC	- No leakage observed - Rigid membran
7.50% DOP, 52.0% PVC	- No leakage observed - Rigid membran
9.00% DOP, 50.5 % PVC	- Stable, no leaching observed - Flexibl

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12.0% DOP, 47.5% PVC   - Leaching observed - Oily membrane

Table 2. Optimization of the PIM for Zn-APASA optode.

Parameter	Optimal value	Range
PIM components:		
APASA (%, w/w)	40.0	–
DOP (%, w/w)	9.00	6.00–12.0
PVC (%, w/w)	50.0	47.5–53.5
ACPAP (%, w/w)	1.00	0.50−1.5.0
Other parameters:		
pH of the source phase	4.66	1.00−12.0
[HNO$_3$] (M)	0.25	0.04−0.20
Response time (min)	3.00	2.00−15.0

Table 3. Tolerance ratio (TR = ion/Zn(II) mass ratio) for various interfering ions in the determination of 150 ng/mL of Zn(II).

Ion	TR	Ion	TR
Na+, K+, Li$^+$, Cl$^-$	10000	Al^{3+}, Fe^{3+}, CO$_3$$^{2-}$	3200
Ca^{2+}, Mg^{2+}, Acetate	8500	Fe^{2+}, NH$_2$OH	2750
Ag+, Cu^{2+}, NO$_3$$^-$	7750	Ni^{2+}, SO$_4$$^{2-}$	2500
Sr^{2+}, Ba^{2+}, S$_2$O$_3$$^{2-}$	7000	Hg^{2+}, Co^{2+}, Oxalate	2250
Ge^{4+}, Ti^{4+}, Citrate	6000	Cu^{2+}, Sn^{2+}, HCO$_3$$^{2-}$	2000
Bi^{2+}, Sn^{2+}, Mn^{2+}	5500	Pb^{2+}, Pd^{2+}, SCN$^-$	1750
Zr^{4+}, Cr^{6+}, Succinate	4750	Au^{3+}, La^{3+}, Cr^{3+}	1500
Mo^{6+}, W^{6+}, Br$^-$	4250	Se^{4+}, Te^{4+}, NH$_4$$^+$	1200
Th^{4+}, UO$_2$$^{2+}$, B$_4O_7$$^{2-}$	3500	Cd^{2+}	150

Table 4. Analytical characteristics of the offered optical sensor

Parameters	optoc	Parameters	op
pH	4.66	Quantification limit (ng/0.7	
λ_{max}(nm)	558	Reproducibility (RSD%1.3	

Beer's range (ng/mL)	0.75–ʼ	Regression equation	
Ringbom range (ng/mL)	2.50-	Slope (ng/mL)	14
Molar absorptivity (L/mol	5. 85	Intercept	– (
Detection limit (ng/mL)	0.22	Correlation coefficient (0.9	

[a] For six replicate determination of 150 ng/mL Zn(II).

Table 5. Comparison between the proposed sensor with the recent literatures for zinc determination.

Method	Membrane cocktail composition	Dynamic range; (	LOD (	RT (n	R
Fluoresc	1-Methyl-1-phenyl-3-[1-hydroxyimino-2-(succinimido)et cyclobutane	8.0×10^{-8} to 1.6×1	$2.5 \times 1($	10.0	[:
Fluoresc	Bis(pyrrol-2-yl-methyleneamine)	NR–9.6×10^{-6}	NR		[:
Fluoresc	Schiff base, 2-(aminomethyl)benzimidazole	8.0×10^{-4} to 1.5×1	2.6×1	15.0	[:
Fluoresc	N,N`-bis-(1-hydroxyphenylimine)2,2`-pyridil	1.0×10^{-10} to $1.0 \times$	$6.3 \times 1($	5.00	[:
Fluoresc	PVC, spiropyran, potassium tetrakis-(4-chlorophenyl) bo dicapryl phthalate, THF	4.9×10^{-7} to $4.2 \times$		2.00–	[:
Fluoresc	Parared	1.0×10^{-6}–5.0×10	$8.0 \times$	1.0 m	[:
Reflectai	PAN	2.4×10^{-6}–5.0×10	$1.5 \times$		[(
Reflectai	Br-PADAP	NR[a]	4.7×1		[:
Reflectai	Br-PADAP	NR[a]	4.7×1		[:

Reflectan	PVC, NPOE, THF, 1-(2-pyridylazo)-2-naphthol	2.5×10^{-6} to 5.0×1	–	[
Absorbar	5-Br Salophen, DOS, NaTPB, PVC	4.9×10^{-5} to 4.5×1 $3.9\times$	5.00	[
Absorbar	N-Methyltetraphenylporphine	1.5×1	<5.00	[
Absorbar	2-Acetylpyridine benzoylhydrazone	100 to 1000 ng m 30 ng/	30.0	[
Absorbar	HDPC	4.59×10^{-7}–$1.83\times$ 2.4×1		[
Absorbar	Triacetylcellulose, zincon, Methyltrioctyl ammonium chlc	7.6×10^{-7} to 3.1×1	10.0–	[
Absorbar	PVC, dithizone, diethyl sebacate, THF	2.5×10^{-8} to 5.8×1 1.6×1	4.00	[
Absorbar	Bis-(trimethylolaminomethane)-4-tertbutyl-disalicylicimi	1.0 µg 1.00 n		[
Absorbar	Thiazole	10 µM NAa		[
Absorbar	N,N-phenylenebis(salicylideaminato)	1.5×1 NAa		[
Absorbar	5-(2`,4`-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dic	5.0×10^{-9} to 2.5×1 1.6×1	5.00 n	[
Absorbar	4-(2-arsonophenylazo) salicylic acid (APASA)	1.2×10^{-8} to 5.1×1 3.4×1	3.00 n	T

ᵃ NR: not reported. RT: Response time   TW: This work

Table 6. Determination of Zn(II) in spiked different water samples.

Sample	Zn added ng/mL	Proposed method		FAAS method		t-test[b]	F-test[c]
		Found[a] ng/mL	Recovery	Found[a] ng/mL	Recovery		
Tap water	0.00	51.5	---	52.2	---		
	75.0	128.2 ± 0.71	101.34	125.6 ± 1.89	98.74	1.64	3.22
	150	203.4 ± 0.55	100.94	205.7±1.72	101.73	1.72	3.02
	225	274.5 ± 0.48	99.28	281.2±1.58	101.44	1.54	2.77
Well water	0.00	49.5	---	48.8	---		
	50.0	102.5 ± 0.73	103.02	97.8 ± 1.46	98.99	1.45	2.56
	100	147.1 ± 0.51	98.39	150.2 ± 1.28	100.94	1.96	3.17
	150	195.6 ± 0.68	98.05	204.7±1.54	102.97	1.76	3.11
Spring water	0.00	15.0	---	14.5	---		
	100	113.5 ± 0.75	98.70	115.2 ± 1.26	100.61	1.93	3.26
	200	217.9 ± 0.52	101.34	212.5 ± 1.45	99.07	1.37	2.93
	300	308.7 ± 0.64	98.00	305.8 ± 1.13	97.23	2.02	3.57
River water	0.00	65.1	--	65.5	---		
	80.0	143.1 ± 0.72	98.62	147.7 ± 1.66	101.51	1.82	3.06

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	160	230.4 ± 0.45	102.35	221.5 ± 0.97	98.23	1.98	3.55
	240	313.0 ± 0.61	102.59	300.3±1.52	98.30	1.84	3.14
Sea water	0.00	85.3	---	85.0	---		
	40.0	127.5 ± 0.63	101.76	123.6 ±1.54	98.88	1.85	3.25
	80.0	162.3 ± 0.45	98.19	168.4±1.76	102.06	1.81	3.20
	120	208.7 ± 0.67	101.66	200.7±1.92	98.90	1.94	3.42
waste Water	0.0	98.5	---	98.0	---		
	60.0	161.1±0.67	101.64	155.9±1.47	98.67	1.42	2.87
	120	220.4 ± 0.31	100.87	214.3±1.67	98.30	1.75	3.31
	180	277.8 ± 0.65	99.75	282.3±1.45	101.55	1.57	2.96

[a]Mean ± Relative Standard Deviation (n = 5);

[b]Tabulated t-value for five degrees of freedom at P (0.95) is 2.57

[c]Tabulated F-value at P (0.95) is 5.05.

Table 7. Analysis of pharmaceutical formulations.

Sample	Certified value	Zinc found[a]	
		Proposed	FAAS
Stresstabs⁄ 600[b]	9.67 mg/capsule	9.70 ± 0.08 (1.47 & 2.98)	9.80 ± 0.43
Hamoderme (talc powder)[c]	243 mg/g	245.0 ± 0.09 (1.32 & 2.67)	240.2 ± 0.56
VitaZinc (capsule	25.0 mg/capsule	25.3 ± 0.06 (1.66 & 3.17)	24.0 ± 0.72
Prozoline zinc (solution)[e]	10.1 mg/10 mL	10.0 ± 0.11 (1.58 & 3.05)	10.35 ± 0.92

[a] Means ± standard deviations (t tests and F values are in parentheses in ''proposed method'' column).

[b] Manufactured by Egyptian International Pharmaceutical Industrial (EIPICO), Egypt (composed of 175 mg zinc gluconate, 50,000 IU vitamin A, and 100 mg vitamin E).

[c] Manufactured by Medical Union Pharmaceutical, Abuo-Sultan, Egypt (composed of 23.9 mg zinc sulfate, 20 mg thiamine monohydrate,

10 mg riboflavin, 100 mg nicotinamide, 10 mg pyridoxine HCl, 25 mg cyanocobalamine, 25 mg calcium pentothenate, and 3.0 mg cupric oxide).

[d] Manufactured by Nile Company for Pharmaceutical and Chemical Industry, Cairo, Egypt (each 100 g contains 0.5 g zinc sulfate, 1.0 g copper sulfate, 2.0 g camphor, 30 g zinc oxide, and 66.5 g talc purified).

[e] Manufactured by Kahira Pharmaceutical and Chemical Industrial (each 100 mL contains 250 mg zinc sulfate, 50 mg naphazoline HCl, 50 mg

maleate, and 2.0 mg cetrimide).

Table 8. Determination of zinc in hair and powdered milk samples

Sample	Found[a](µg/g) (%)		t- test[b]	F- value[c]
	PM	FAAS		
Hair (male)	161.4 ± 0.06	162.9± 1.31	1.43	3.05
Hair (female)	126.0 ± 0.07	123.2 ± 0.54	1.87	3.77`
Orange juice	83.5 ± 0.05	84.2 ± 1.43	1.56	3.19
Powdered milk 1	30.8 ± 0.04	31.4± 0.60	1.53	3.14
Powdered milk 2	42.4 ± 0.08	43.1 ± 1.03	1.67	3.33
Kidney	25.8 ± 0.10	25.4 ± 1.31	1.28	2.85
Saliva[d]	50.0 ± 0.07	49.1 ± 1.64	1.87	3.41
Feces	4900 ± 0.05	4915 ± 3.20	1.52	3.27
Urine[a]	48.5 ± 0.13	47.9 ± 1.80	1.77	3.54
Femur	185.0 ± 0.14	183.8 ± 2.20	1.63	3.37

[a]: Mean ± SD (n = 6).

[b]: Tabulated t-value for five degrees of freedom at P (0.95) is 2.57;

[c]: Tabulated F-value at P (0.95) is 5.05;

[d]: µg Zn(II) per L

Table 9. Assay of zinc in some human serum samples after application of proposed and FAAS procedures (n = 5).

Sample	Added (µg/mL)	Found[a] (µg/mL)		t -test	F value
		PM	FAAS		
Human serum 1	–	2.80 ± 0.60	2.80 ± 1.00		
	0.20	3.05 ± 0.50	2.90 ± 1.10	1.22	2.65
	0.40	3.13 ± 0.40	3.30 ± 0.80	1.54	2. 96
Human serum 2	–	1.40 ± 0.70	1.45 ± 1.30		
	0.30	1.75 ± 0.50	1.85 ± 1.60	1.84	3.32
	0.60	2.10 ± 0.80	1.95 ± 1.40	1.47	2.88
Human serum 3	–	2.55 ± 0.50	2.50 ± 1.50		
	0.40	3.05 ± 0.30	3.00 ± 1.30	1.52	3.22
	0.80	3.45 ± 0.60	3.20 ± 1.50	1.13	2.63
Human serum 4	–	1.60 ± 0.40	1.60 ± 1.20		
	0.90	2.60 ± 0.70	2.40 ± 1.40	1.39	2.77
	1.80	3.30 ± 0.50	3.55 ± 0.80	1.48	2.89

Note: PM, proposed method.

[a] Averages ± standard deviations of six determinations

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Table 10. Determination of zinc ion in vegetables (Parsley, Basil), andred meat.

Sample	Zn(II) added (μg/kg)	Zn(II) found[a] (μg/kg)		Recovery (%)	
		Proposed	FAAS	Proposed	FAAS
Parsley	0.00	n.d[b]	n.d[b]	---	
	1.50	1.47 ± 0.33	1.60 ± 0.60	98.00	106.66
	3.00	3.05 ± 0.25	3.10 ± 0.45	101.67	103.33
	4.50	4.50 ± 0.40	4.35 ± 0.70	100.00	96.67
Basil	0.00	---			
	1.00	1.02 ± 0.15	0.96 ± 0.80	102.00	96.00

	2.00	2.06 ± 0.45	1.90 ± 0.65	103.00	95.00
	3.00	3.10 ± 0.27	3.15 ± 0.77	103.33	105.00
Red meat	0.00	---			
	2.00	1.95 ± 0.43	1.90 ± 0.66	97.5	95.00
	4.00	4.05 ± 0.19	3.90 ± 0.70	101.25	97.50
	6.00	5.85 ± 0.33	6.15 ± 0.85	97.50	102.50

[a]: Mean $\pm$ SD ($n = 6$).[b]: Not detected.

Declaration of Interest Statement

The offered optode is a precise, sensitive, and highly selective device, in addition to low cost, for iron assessment without any pretreatment and extraction. After optimization of the experimental circumstances, the attained results established that the optode response was dependent on the presence of film thickness, stirring effect, amounts of D2EHPA, APASA, DOP, and pH of the aqueous solution. In the measuring range from 0.75 to 325 ng/mL of Zn(II) at pH 4.66, the absorbance response demonstrates a respectable correlation with detection and quantification limits of 0.22 and 0.74 ng/mL, were achieved, respectively. The proposed technique has a larger range of assessment, greater accuracy, more stability, and is less time consuming than other published methods. The proposed PIM optode is highly selective due to no interference from most cations, anions, drugs and pharmaceutical additives and excipients. Lastly, the fabricated optode can be effectively applied for routine zinc monitoring in water, pharmaceutical formulations, biological, and vegetables samples and the results showed no significant difference compared to FAAS procedure.

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