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Iron-selective Poly(Vinyl Chloride) Membrane Electrode Based on Norfloxacin as a Neutral Carrier

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In the present study ion-selective PVC membrane sensor for iron ions based on (norfloxacin)1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid (NOR) as adequate ionophor has been prepared and studied. The electrode exhibit a good response for Fe^{3+} over a linear range from 1.0×10^{-5} to 1.0×10^{-1} mol l^{-1} with a slope of 19.58±0.2 and 19.27±0.2 mV per decade and a detection limit of $(5.0\pm1.0)\times10^{-6}$ mol l^{-1} for *o*-nitrophenyl octyl ether (o-NPOE) and dioctylphthalate (DOP) plasticized based membrane sensors, respectively. The investigated membrane electrode revealed good and fast response in a pH range of 3.0–8.0 for more than 4.0 months without any considerable difference in potentials. The proposed sensor shows comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions. It was utilized as an indicator electrode in potentiometric determination of iron ions in some real samples.

Keywords: PVC sensor; Environmental samples; Iron (III) determination; Norfloxacin.

1. INTRODUCTION

The mineral iron (Fe) is integral to biological life. It is an extremely adaptable substance and this can be seen in its incredible range of biological contributions. For example, iron provides the active part of proteins. It helps to make up oxygen and contributes to electron transfer in metalloenzymes like dehydratases and oxidases [1]. In fact, it is one of the most important micronutrient components for the health of all living animals, plants, and biotic enzymes [2]. When it comes to mammals, approximately 70% of active iron is picked up in the form of porphyrinic materials. They are found in cytochromes, myoglobin, and haemoglobin. The chemical characteristics of iron (solubility, valence, and level of intricacy) are what determine the nature of its biological and environmental influence [3, 5].

The permitted amount of iron in drinking water is advised by the World Health Organisation (WHO) and European legislation to be 2mg L^{-1} and 0.2 mg L^{-1}, respectively (WHO 2003 & European Community, 1998, http://www.who.int/water_sanitation_health/dwq/chemicals/iron.pdf). This is the rule adhered to by most of Europe, because health experts believe that it keeps people safe and provides them with an optimal volume of iron. Consequently, this study aims to identify effective techniques for quantitatively determining the amount of iron in various different matrices. It is clear that iron is an essential mineral, because the lack of it leads to substantial health problems in humans and animals. This is a condition known as anaemia. Yet, it should be noted that too much iron can cause health problems as well. They include coronary disease, arthritis, liver dysfunction, diabetes, and an elevated risk of cancer [6-8]. This is why being able to measure and regulate its use is very important for governments and health experts.

It is also possible to scrutinise and analyse iron complexes, as well as identify their species. Several methods are a viable choice for this. They include atomic absorption spectrophotometer (AAS) [9-12], inductively coupled plasma- optical emission spectrometry (ICP-OES) [5,13], inductively coupled plasma-mass spectrometry (ICP-MS) [14-16], cathodic or anodic stripping voltammetry [17,18], chromatography [19,20] and spectroscopic sensor [21]. The problem is that, while generally quite effective, not all of these methods are efficient, affordable, or easy to use. Some produce matrix interferences and demonstrate no linearity for calibration curves. Furthermore, various different complexing agents can be used to gather iron complexes at the top of substances like as salicylaldoxime [22], 1-(2-piridylazo)-2-naphthol [23], 1-nitroso-2-naphthol (NN) [24,25], IL-rGO/AuNDs/Nafion [26] and2, 3-dihydroxynaphtalene (DHN) [27,28], so that they can be easily collected. For many years, scientists have been fascinated by ion-selective electrodes (ISEs). Some are already very familiar to them. Precipitate based ion-selective electrodes, for example, are widely used as a way to identify different types of –cations and –anions [29-31]. Ultimately, scientists are interested in their potential applications because they are cheap to use, easy to work with, and reasonably predictable in their behaviour. They also happen to be non-destructive and generally deliver analytical results quite quickly [32]. In this work, we report a highly selective and sensitive iron membrane electrode for fast monitoring of trace level of Fe^{3+} ion based on (NOR). In this work, Iron membrane electrode with high selectivity and sensitivity for rapid detection of trace level of Fe^{3+} based on NOR is presented and demonstrated.

2. EXPERIMENTAL

2.1. Reagents and solutions

The chemicals involved in this work are of pure grade unless otherwise specified. Chemicals like o-nitrophenyloctyl ether (o-NPOE), Potassium tetrakis (p-chlorophenyl) borate (KTpClPB) and high molecular mass poly (vinyl chloride) (PVC) were purchased from Fluka (Buchs, Switzerland). Tetrahydrofuran (THF), pure iron salt and dioctylphthalate (DOP) were bought from Aldrich Chemical

Co. (Milwaukee, USA). Pure norfloxacin was provided by Egyptian Int. Pharmaceutical Industries Co. (E.I.P.I.Co) (Egypt). Double distilled water was used for the preparation of the solutions.

2.2. EMF measurements and apparatus

The electrochemical measurements were measured with a PTI-15 digital pH meter using Fe-NOR-PVC matrix membrane sensors in conjunction with a double-junction silver/silver chloride (Ag/AgCl) reference electrode (Orion Model 90-02) containing 10% (w/v) potassium nitrate in outer compartment at laboratory ambient temperature. The internal filling solution of ISE was a 0.01 mol l^{-1} Fe^{3+} solution. The pH measurements were carried out using a glass/Ag-AgCl combination electrode (consort, S 210 B BB5).

Every EMF calculation is conducted with the help of the following tools; Ag/AgCl reference electrode (Orion Model 90-02), PVC membrane/sample solution, and the Ag–AgCl/ internal solution (0.01 mol l^{-1}iron (III)).

2.3. Iron(III)-PVC Membrane sensor

To create the membrane, specific quantities of a powdered metal ion complex (Fe-NOR) (2.92mg), PVC (32 mg), KTpClPB (1.08 mg), and plasticiser (DOP and o-NPOE) (64 mg) are added to THF (6ml). Following which, the formula is moved over to a glass ring and plate system, with a diameter of 30mm. The THF is left to evaporate out of the formula over a period of two days. This process occurs at an ambient room temperature. Next, the ion-selective membranes were made by cutting a section (7mm) of clear PVC membrane (0.2mm thick) using Fluka punch. The last stage is to enable electrode conditioning. This happens over a period of two days, after the internal Ag/AgCl reference electrode (1.0mm diameter) is fully immersed in the 0.01 mol l^{-1} solution of Fe(III). To do this, the PVC membrane gets added to a lab produced electrode body. This is made up of a conical glass container. There is a polyethylene pipe at one end [33, 34]. The container is loaded with an internal reference solution (0.01 mol l^{-1} iron/salt).

2.4. Sensor calibration

For the purposes of this study, the original calibration graph was recycled and reused for subsequent Fe (III) calculations. There are two viable ways to calibrate the sensor. The first is to soak the sensor in 50 mL-beakers of a 1.0×10^{-6} - 1.0×10^{-2} mol l^{-1} iron salt standard solution (20mL aliquots). To start, the volume of salt is kept very low, but it gets steadily increased throughout the process. Alternatively, a continues spiking of 10^{-6}mol l^{-1} calibrant solution with akiquots of standard solution could reach a calibration. In the last stage, the EMF data was captured and converted it into graph form. This is to represent the function of the logarithm of the iron ion concentration.

2.5. Selectivity coefficient determination

The following equation (1) was used to calculate the The values of potentiometric selectivity coefficient $\left(k_{Iron.,B}^{pot}\right)$ were calculated by applying in equation 1, in accordance with the separate solution method [35].

$$log\ k_{Iron.,B}^{pot} = \frac{E_{B.} - E_{Iron}}{S} - \log a_{Iron} + \frac{Z_{Iron.}}{Z_B} \log a_B$$

Equation 1: mathematical formula showing the way to calculate the potentiometric selectivity coefficient

The response potentials of the sensor for iron ion and interferent B, both at 0.01 mol l^{-1}, are represented by $E_{Iron.}$ and E_B , respectively. S stands for the sensor slope. A_{Iron} is the primary ion activity whereas a_B is the activity of an interfering ion. Charges of the charge of the primary ion and interfering ion are represented by Z_{Iron} and Z_B, respectively.

2.6. Sample preparation

The sample was prepared by heated 200g of individual samples for 5 h in an electrical furnace at 750 ^{o}C for Fe(III) analysis in all treated samples. The residuals were separated and dissolved in nitric acid then complete to 25 mL mark with deionized water. The determination of Fe(III) in the two vitamin formulations (Ferose-f and Ferovit) was conducted through several steps. First of all, heating 0.2 mL of liquid samples until dryness then dissolved in 1 mL of aqua-regia. Then followed by heating them to dryness, again, in order to oxidize Fe(II) to Fe(III). After that, the samples were dissolved in few amount of methanol and placed in a 50 mL volumetric flask, which then completed with the same solution. One aliquot of the sample solution was individually extracted and the standard method was used to identify any iron ion. The Fe^{3+} ion was contained in various types of sample. For each one, a pH of 5.0 was achieved and maintained.

2.7. Complexometric EDTA titration

0.0001 mol l^{-1} of Fe (III) salt standard solution was prepared and certain volume was added to a 5.0 mL of 25% aqueous ammonia solution in presence of portion of metallochromic indicator. This is followed by adjusting pH value of the mixture to 5.0 and the solution diluted to 50 mL with water and followed by titration with 0.01 mol l^{-1} EDTA solution [36].

3. RESULTS AND DISCUSSION

The application and development of ion-selective electrodes (ISEs) continue to be of interest for heavy metals ions analysis because their advantages of simple design and operation, reasonable selectivity, fast response, high accuracy, wide concentration range applicability to turbid and colored solutions and low detection limit.

Dioctylphthalate and o-nitrophenyloctyl ether were used as suitable solvent mediators to prepare plasticised PVC matrix membrane sensors using ionophore (NOR) and electrochemically evaluated as iron (III) sensor under static mode of operation according to IUPAC recommendations[35]. The reason for using ionophore (NOR) is that it offers elevated lipophilicity, high exchange capacity and ability to form counter-ions with different inorganic cations, with varying degrees of selectivity and reliability [37].

3.1. Characterization of the sensor performance

Refer to Table One for data gathered over a period of twelve weeks. It relates to both membrane sensors and demonstrates their degree of efficacy in this proposed role/function. For both sensors, the table indicates an elevated level of reliability and accuracy.

Table 1. Response characteristics of Fe-NOR PVC membrane sensors.

Parameter	Fe-NOR	
	***o*-NPOE**	**DOP**
Slope, (mV decade^{-1})	19.58	19.27
Intercept, (mV)	483.4	446.5
Correlation coefficient, (r)	0.9915	0.9915
Lower limit of detection, (mol L^{-1})	5.0×10^{-6}	5.0×10^{-6}
Lower limit of linear range, (mol L^{-1})	1.0×10^{-5}	1.0×10^{-5}
Working pH range	3.0-8.0	3.0-8.0
Life span/week	11	12

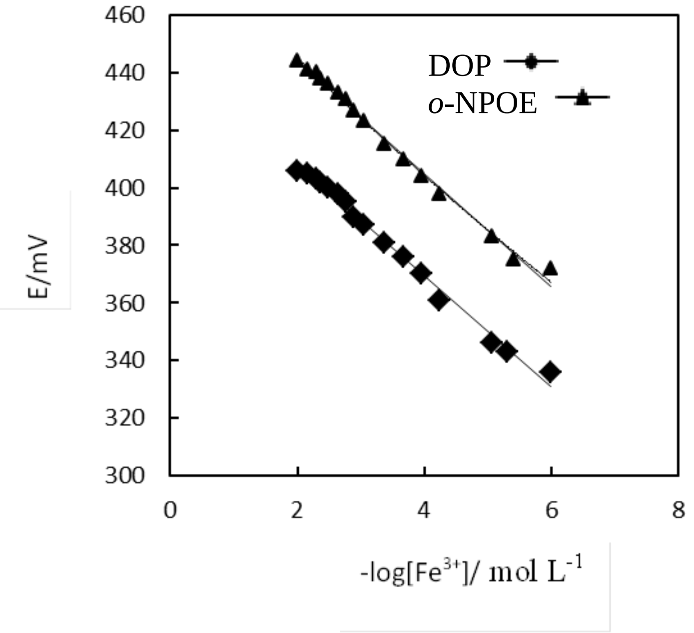

Figure 1. Calibration curve of the Fe(III) membrane sensors.

According to Figure 1, when iron-based membrane sensors are plasticised with either *o*-nitrophenyl-octyl ether or dioctylphthalate, they show similar characteristics. They produced clear Nernstian responses over a concentration range of 1.0×10^{-6} -1.0×10^{-2} mol l^{-1} iron ion with cationic slopes of 19.58 ± 0.2 and 19.27 ± 0.2 mV decade$^{-1,}$ as well as detection limits of 5.0×10^{-6} and 5.0×10^{-6} mol l^{-1} iron ion for *o*-NPOE and DOP based membrane sensors, respectively. Refer to data from the least squares analysis to observe these correlations.

It should be noted that the chosen plasticisers demonstrate a number of different dielectric constants. For this reason, each sensor was immersed in an iron (III) formula for a period of 48 hours. Only then could it be fully utilised as an iron sensor.

The least squares analysis indicates the following:

$E\ (mV) = (19.58 \pm 0.2) \log a_{Fe(III)} + (483.4 \pm 0.2)$ and

$E\ (mV) = (19.27 \pm 0.2) \log a_{Fe(III)} + (446.7 \pm 0.2)$

For the *o*-NPOE and DOP based membrane sensors, respectively.

It is very important to take rate of response into account when working with membrane sensors. They must be able to detect ion quickly and provide accurate determinations. The plasticised Fe(III) membrane sensor ended up providing extremely fast responses, across the entire concentration gradient. The response times obtained using both membrane sensors, for 0.001 mol l^{-1} Fe (III), were 10 s for each one of them. . Moreover, a series of different concentrations of Fe (III), from 0.00001 to 0.01 mol l^{-1}, were prepared and the sensor's response time was obtained, as shown in Figure 2.

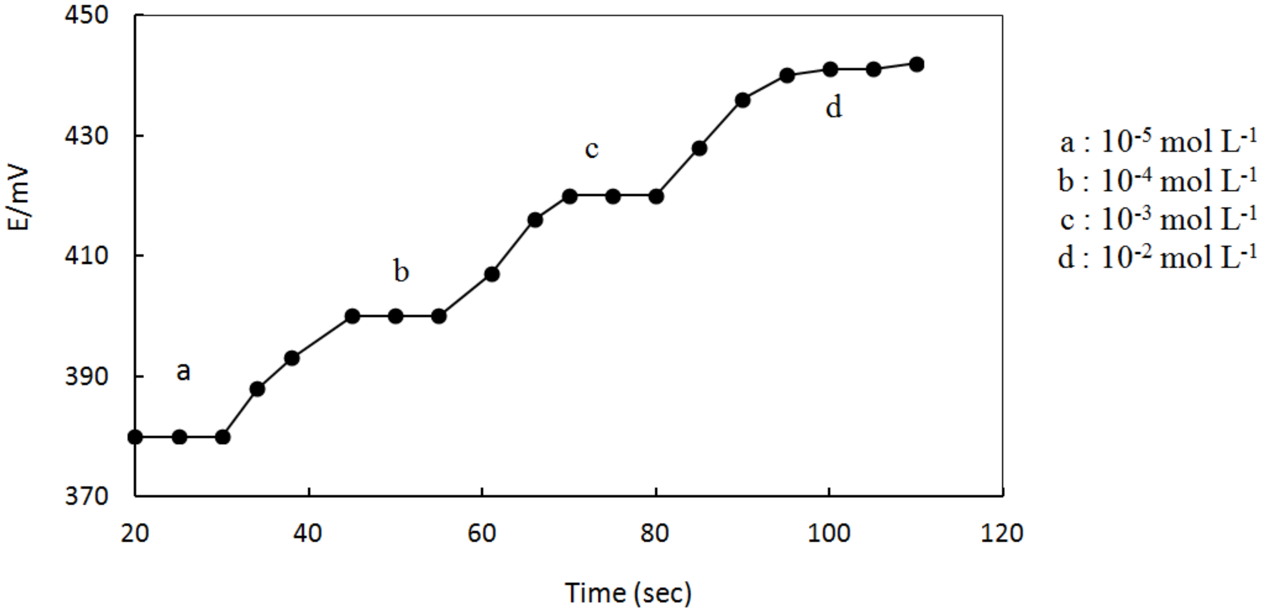

Figure 2. Dynamic response time of the electrode for step changes in the concentration of Fe(III).

It was noticed that the fluctuation of the slope did not exceed 0.9 mV per decade during the study period, three months, In fact, all calculations for the membrane sensors remained consistent and controlled (fluctuating within a range of ± 0.2 mV). The *o*-NPOE and DOP sensors produced valuable data for eleven and twelve weeks, respectively. Following which, the linear range and calibration slope used to determine response time began to rapidly decline. This was likely caused by the membranes drawing strength from the ion-pair. It is at this point that fresh membranes need to be created.

3.2 Effect of pH

The next step was to find out how altering the pH levels would affect the potentiometric responses of iron PVC matrix membrane sensors.

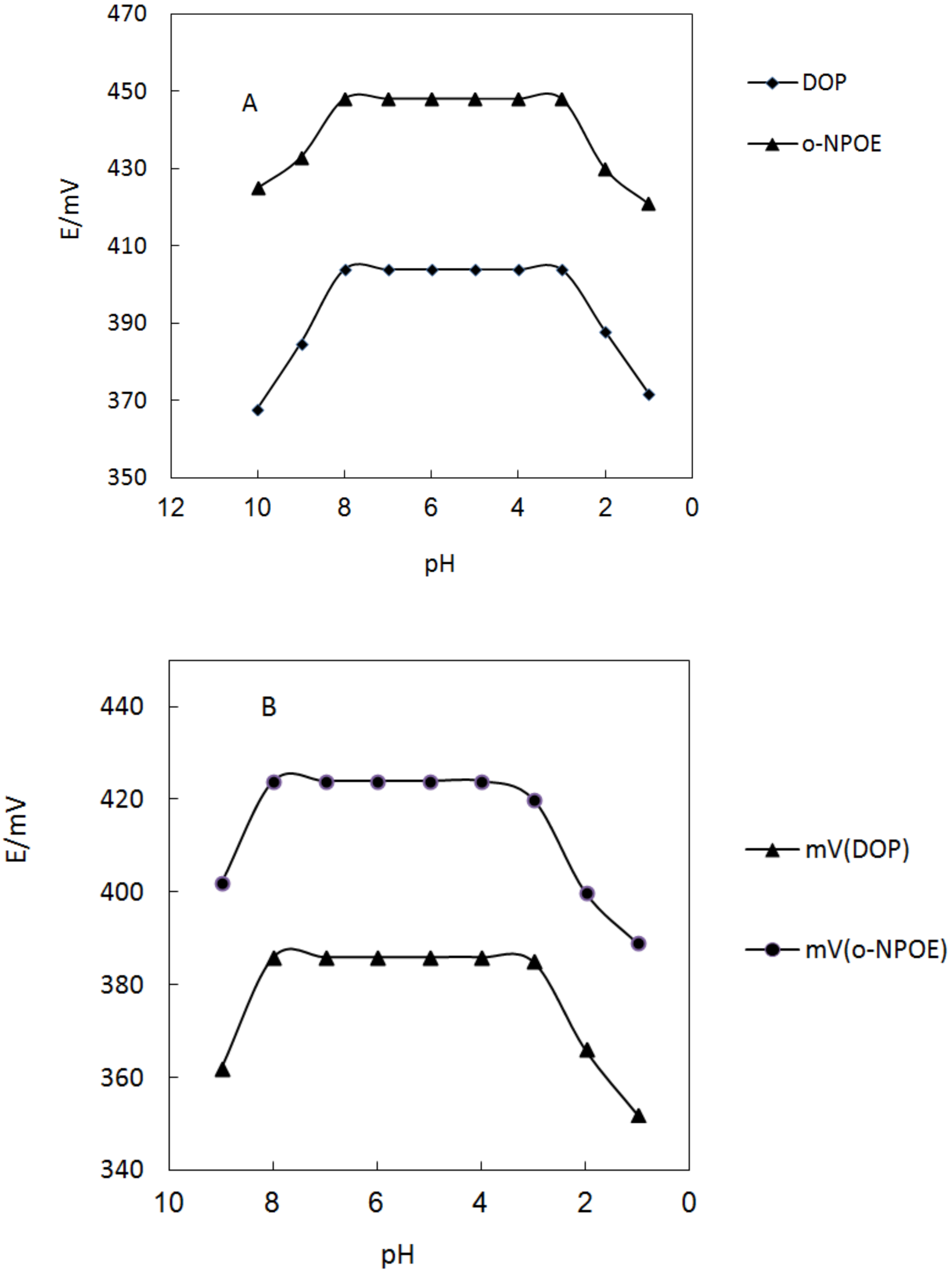

Figure 3. pH-potential Profile of Fe(III) membrane sensors at different concentrations. (A) 0.01 mol l^{-1} (B) 0.001 mol l^{-1}.

The pH potential profiles (refer to Figure 3) clearly show that the potential values for both sensors remain stable and consistent, across a pH range of ~ 3.0 - 8.0. The important thing to know is that, with a pH of this level, the iron becomes entirely ionized. It is identified as a trivalent ionic species, because it gets dissociated. When the pH is held at 3.0 or less and the iron solution at 0.001 mol l^{-1} iron (III), the plasticised membrane sensors produce lower values. This is a result of contributions from H^+ ions. At pH levels above 8, there was a small reduction in the potential values for both sensors. Finally, when the strength of the iron (III) solution is increased (≥0.01 mol l^{-1}), the potential values are actually smaller. This is caused by persistent precipitation of the ionophore in its acidic form. To calculate these values, two iron solutions (0.001 and 0.01 mol l^{-1} iron (III)) were utilized. Then the pH was altered by incorporating small amounts of diluted sodium hydroxide or hydrochloric acid. No borate buffer solution was added in this case.

3.3 Effect of Foreign Ions

The separate solution technique [35] was employed to calculate the level of interference and the associated potentiometric selectivity coefficients $\left(k_{Iron.,B}^{pot}\right)$. Crucially, the potentiometric response times for the iron sensors were evaluated while iron was still present. This was done because, in many cases, the substance influences the values of the iron (III) solutions. This degree of selectivity is equivalent to reported electrodes over multiple metal ions. Though, the difference is that improved selectivity is demonstrated for Pb^{2+}, Cu^{2+}, Mg^{2+} and Hg^{2+}. Consequently, it should be considered an effective and viable Fe^{3+} selective sensor. In most cases, the DOP plasticiser has lower selectivity when compared to the *o*-NPOE based membrane sensor.

Table 2. Potentiometric selectivity coefficients $K_{Fe(III),B}^{pot}$ of Fe-NOR PVC membrane sensors.

Interferent, B	$K_{Fe(III),B}^{pot}$	
	***o*-NPOE**	**DOP**
Hg^{2+}	6.0×10^{-3}	2.0×10^{-3}
Sr^{2+}	3.0×10^{-3}	1.0×10^{-3}
Ce^{3+}	7.0×10^{-4}	1.0×10^{-3}
La^{3+}	4.5×10^{-3}	8.0×10^{-4}
Ba^{2+}	1.8×10^{-3}	3.2×10^{-3}
Mg^{2+}	7.2×10^{-4}	8.0×10^{-4}
Na^+	1.0×10^{-4}	1.5×10^{-4}
NH_4^+	5.0×10^{-3}	2.0×10^{-3}
K^+	8.5×10^{-4}	7.3×10^{-4}
Ca^{2+}	2.5×10^{-4}	1.0×10^{-4}
Al^{3+}	5.0×10^{-3}	8.0×10^{-3}
Eu^{3+}	7.0×10^{-4}	1.0×10^{-4}
Yb^{3+}	2.0×10^{-4}	3.0×10^{-4}

According to Table 2, iron (III) is correctly identified in the presence of 60-fold molar excess cations and there is no interference recorded.

3.4. Comparison of the characteristics of iron(III) electrode

Limit of detection, linear range, pH range and slope of some of the iron (III) selective electrodes were tabulated for comparative purposes [38-40] against proposed membrane electrodes. The proposed electrodes represent accepted data in comparison to those published for other reported methods as shown in table 3.

Table 3. Comparison of iron (III) selective electrodes based on NOR with those previously reported in literature.

Ionophore	**pH range**	**Detection limit** (mol l^{-1})	**Linear range** (mol l^{-1})	**Slope**	**Ref.**
4-Amino-6-methyl-3-methylmercapto-1,2,4-triazin-5- one	2.2–4.8	6.8×10^{-7}	1.0×10^{-6}–1.0×10^{-1}	19.4	[38]
2-Phenyl-1,3-bis[3’-aza-4’ -(2‘ - hydroxyphenyl) prop-4-en-1’ -yl]-1,3-imidazolidine	3.5–5.5	5.0×10^{-6}	6.3×10^{-6}–1.0×10^{-1}	20.0	[39]
Bis-benzilthiocarbohydrazide	1.6–4.3	8.6×10^{-8}	1.0×10^{-7}–1.0×10^{-2}	19.6	[40]
1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid (NOR)	3.0-8.0	5.0×10^{-6}	1.0×10^{-5} - 1.0×10^{-1}	19.58 19.27	This work

3.5. Analytical applications

Table 4. The utilision Fe-NOR-PVC-based membrane sensors for the determination of Fe in real samples.

Sample	**Recovery[*], %**		
	ISE		**EDTA Method [32]**
	***o*-NPOE**	**DOP**	
Cinnamon	99 ± 0.32	98 ± 0.26	100.3 ± 0.2
Wheat bran	97 ± 0.28	96 ± 0.37	96 ± 0.2
Ferose-f	93 ± 0.25	98 ± 0.37	99 ± 0.2
Ferovit	96 ± 0.38	97 ± 0.51	97 ± 0.2

***** Average of 5 measurements ± S.D.

This indicates that no substantial discrepancy exists between the potential techniques and processes, certainly when it comes to accuracy and reliability. Nevertheless, the preferred sensor does provide a viable method of evaluating and testing for Fe^{3+} ion in different samples Table 4. Furthermore, the proposed sensor is a valuable solution, because it is easy to use and gives dependable outcomes.

Table 5. Precision and recovery for the determination of Fe(III) in binary mixtures. The iron concentration was kept constant at 0.0001 mol l^{-1} for every measurement.

Fe^{3+} (mol l^{-1})	**Added cation (0.01** mol l^{-1}**)**	**Recovery (%)***		**RSD (%)**	
		***o*-NPOE**	**DOP**	***o*-NPOE**	**DOP**
		Fe-NOR	**Fe-NOR**	**Fe-NOR**	**Fe-NOR**
(1 x 10^{-4})	La^{3+}	100.3	100.2	1.3	1.5
(1 x 10^{-4})	Ba^{2+}	97.2	97.8	1.2	0.6
(1 x 10^{-4})	Mg^{2+}	98.8	97.7	1.2	0.4
(1 x 10^{-4})	Na^{+}	96.2	97.2	1.1	0.5
(1 x 10^{-4})	NH^{4+}	96.4	97.4	1.1	0.8
(1 x 10^{-4})	K^{+}	97.2	98.5	0.9	1.1
(1 x 10^{-4})	Ca^{2+}	97.5	98.2	0.8	1.5
(1 x 10^{-4})	Al^{3+}	92.2	90.6	1.9	1.9
(1 x 10^{-4})	Eu^{3+}	97.2	97.5	1.8	1.9
(1 x 10^{-4})	Yb^{3+}	97.5	98.4	1.6	1.7

* Average of five measurements

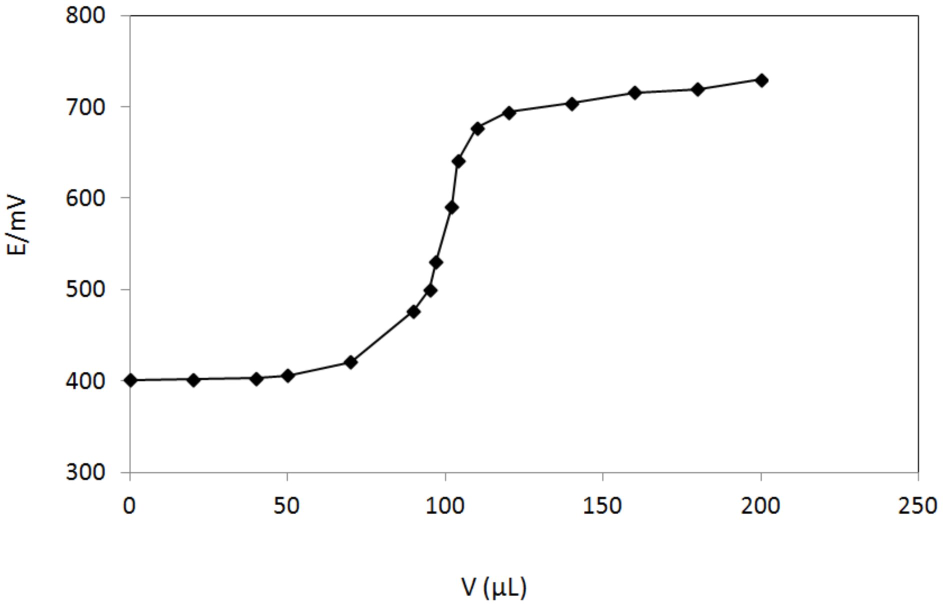

Figure 4. Potentiometric titration curve of 10.0 mL of a 0.0001 mol l^{-1} Fe(III) solution, with a 0.01 mol l^{-1} EDTA using the proposed membrane sensor as an indicator electrode.

It is also compatible with turbid and coloured samples. It can be used to test ionophore mixtures and the response times are always satisfying swift. Finally, the method is affordable, straightforward, and could potentially be used to enhance automated testing equipment. As the sensors ended up performing very well and demonstrating a sufficient degree of selectivity, they could also be useful when considering the regulation of Fe (III) ions’ strength in binary samples. For most binary formulas, the capture of Fe (III) ions is within the 90.6–100.3% range. The data relating to this part of the study can be found in Table 5.

To see the potential use of the proposed sensor, a titration of 0.0001 mol l^{-1} Fe (III) against 0.01 mol l^{-1} EDTA was performed, the sensor was employed as an indicator electrode, and the pH was around 5.0. The titration curve is shown in Figure 4, from which a sharp end point is noticed and the Fe (III) ions’ concentration would be calculated with good accuracy.

4. CONCLUSIONS

Norfloxacillin was used for developing iron(III) ion-selective electrode as a new sensing carrier. This is owing to its valuable properties, such as low cost, a long lifetime and good selectivity. The developed electrode was successfully demonstrated for the determination of iron(III) in two vitamin formulations as well as plant samples. The proposed sensor exhibited high selectivity, sensitivity, suitable stability, good reproducibility, wide linear range, low detection limit, and fast response time towards Fe^{3+} ion. Moreover, it can be successfully applied as an indicator electrode in potentiometric titration of Fe^{3+} ion with EDTA as well as in real samples.

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