

## A Novel Iron(III) Selective Potentiometric Sensor Based on 9-Ethylacenaphtho [1, 2-B]Quinoxaline

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9-ethylacenaphtho[1,2-b]quinoxaline (EANQ) was synthesized and used as an active component for fabrication of PVC-based polymeric membrane (PME) for sensing Fe<sup>3+</sup> ions. The electrodes display a Nernstian behavior (19.5±0.3mV decade<sup>-1</sup>) over wide Fe<sup>3+</sup> ion concentration ranges 2.3×10<sup>-7</sup>-5.0×10<sup>-2</sup> M with very low limits of detection (9.6×10<sup>-8</sup> M). The electrodes have a relatively fast response time (<25 s), a satisfactory reproducibility and relatively long life time. The proposed sensors show a fairly good selectivity toward Fe<sup>3+</sup> ion in comparison to other common cations. The potentiometric responses are independent of the pH of the test solutions in the pH range 2.9–7.1. The practical utility of the proposed electrodes have been demonstrated by their use in potentiometric titration of Fe<sup>3+</sup> with EDTA. It was also successfully applied in the determination of Ferric ions in aqueous samples and the results obtained agreed with those obtained with atomic absorption spectrometer (AAS).

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**Keywords:** Fe(III) ion-selective electrode; PVC membrane; 9-ethylacenaphtho[1,2-b]quinoxaline; Potentiometry; sensors

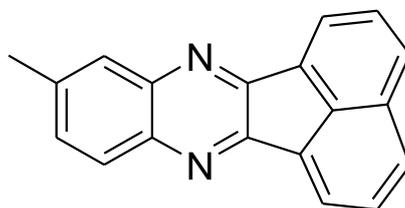
### 1. INTRODUCTION

Iron is a vital element in the human body and is taking effective role in oxygen transport, storage and also in electron transport [1,2]. The enzymes which are taking part in the synthesis of amino acids, hormones and neurotransmitters need Fe<sup>3+</sup>. There is around 10-15 mg of iron to be exhibited in the food daily intake, and studies report that the normal subjects assimilate around 10% of the amount of iron from the food [3]. Due to the deficiency of iron, the amount of red blood cells in the body reduces and can be a cause of anemia. In addition, the surplus amount of iron is stored in the heart, liver and other organs [4,5] and this extra iron cannot be spontaneously released from the body,

but it is stored as mentioned above and can put other organs at risk of impairment [6]. Moreover, excess or less iron pounds in the human body are also cancer causing factors [7]. It is therefore very important for clinical, environmental and industrial purposes to efficiently detect  $\text{Fe}^{3+}$  ion.

There are many methods for the detection of iron ions such as atomic absorption spectroscopy (AAS) [8], inductively coupled plasma (ICP) [9], etc. But these methods have many limitations such as high cost and instability if a large number of samples analysis is needed [10,11]. Moreover, the potentiometric based sensing method is simple, inexpensive, rapid and more reliable for the analysing for ions detection. In the literature, it is also reported that ion selective electrodes (ISEs) was used for the determination of cations as well as anions and also used for pharmaceutical compounds [12-22], with some research also reported on  $\text{Fe}^{3+}$  detection [23-30]. It is clear that it is necessary to improve the sensitivity of  $\text{Fe}^{3+}$  sensors and develop selective electrodes having relatively quick response for the determination of the  $\text{Fe}^{3+}$  concentration; especially when small volumes of the sample is available.

In the present work, we used 9- ethylacnaphtho [1, 2-b] quinoxaline (EANQ, Figure 1) as an excellent carrier in construction of a polymeric membrane (PME) for Iron ion. The influences of the membrane positions on the potential response of the  $\text{Fe}^{3+}$  sensors were investigated.



**Figure 1** Structure of ligand (EANQ)

The PME has limit of detection of  $9.6 \times 10^{-8}$  M. The potentiometric response of electrode is independent of pH in the pH range of 2.9-7.1.

## 2. EXPERIMENTAL

### 2.1. Reagents

Reagent grade nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), Benzylacetate (BA), tetrahydrofuron (THF) and high relative molecular weight PVC call from Merck were used as received. Nitrate slats of all cations used call from Merck were of the highest purity available and used without any further purification except for vacuum drying over  $\text{P}_2\text{O}_5$ . Triply distilled deionized water was used throughout.

### 2.2. Synthesis of ligand

A round-bottomed flask equipped with a magnet and condenser was charged with 4-methylbenzene-1, 2-diamine (1.0 mmol), acenaphthylene-1, 2-dione (1.0 mmol), water (5 mL) and

FeCl<sub>3</sub> catalyst (20 mmol%). The resulting mixture was stirred in an oil bath at reflux temperature (100 °C) for 80 min, and the course of the reaction was monitored using TLC on silica gel. Finally, the reaction mixture was cooled and the crude mixture was purified by column chromatography to give the desired products in 90% yield [31-33].

### 2.3. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 29 mg of powdered PVC, 60 mg of plasticizer NPOE, 4mg of additive NaTPB, and 7mg of ionophore EANQ in 4mL of fresh THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5mm o.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3mm thickness was formed. The tube was then pulled out from the mixture and kept at the room temperature for about 24 h. The tube was then filled with an internal filling solution ( $1.0 \times 10^{-3} \text{M}$  of Fe<sup>3+</sup>). The electrode was finally conditioned by soaking in a  $1.0 \times 10^{-2} \text{M}$  Fe<sup>3+</sup> solution for 24 h [34-37]. A silver/silver chloride wire was used as an internal reference electrode.

### 2.4. The emf measurements

The emf measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

Ag–AgCl|3M KCl| internal solution,  $1.0 \times 10^{-3} \text{M}$  Fe<sup>3+</sup>| PVC membrane |test solution | Hg – Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Hückel procedure [38].

## 3. RESULTS AND DISCUSSION

### 3.1. Preliminary study of EANQ complexation with some metal ions

To examine ligand selectivity against various metal ions including Fe(III), Ni(II), Cd(II), Co(II), Zn(II), La(III), Ag(I), etc, the interaction of EANQ with metal ions in an acetonitrile solution by conductometric method was investigated [39-45]. In all measurements, the cell should be thermostated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In typical experiments, 20 mL of an ion solution ( $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) is placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. Then, a known amount of an ionophore or a ligand ( $1.0 \times 10^{-2} \text{ mol L}^{-1}$ ) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved. The 1:1 binding of the

cations with the ionophore and the complex formation constant in terms of the molar conductance can be expressed as [39]:

$$(1) K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]}$$

Where:

$$(2) K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})}$$

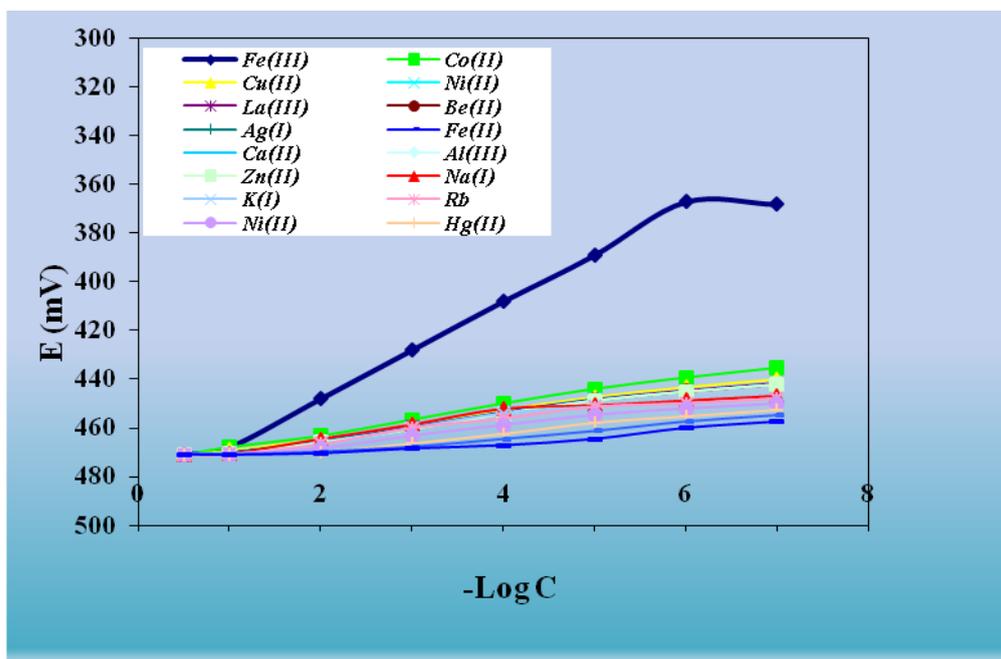
Where,  $\Lambda_M$  is the molar conductance of the cation before the addition of the ionophore;  $\Lambda_{ML}$  is the molar conductance of the complexes,  $\Lambda_{obs}$  the molar conductance of the solution during titration,  $C_L$  the analytical concentration of the added ionophore and  $C_M$  the analytical concentration of the cation salt. The complex formation constant ( $K_f$ ) and the molar conductance of the complex,  $\Lambda_{ML}$ , were obtained by computer fitting Eqs. (1) and (2) to the molar conductance–mole ratio data, using the nonlinear least-squares program KINFIT [46]. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values of the resulting 1:1 complexes in Table 1 showed that  $\log K_f$  is  $4.93 \pm 0.05$  for  $Fe^{3+}$  and  $3.33 \pm 0.07$  or less for other metal ions used. As can be seen from these results, EANQ can be used as a sensing material in a Fe (III) sensor.

**Table 1.** The formation constants of L - $M^{n+}$  complexes at  $25.0 \pm 0.1$  °C

Ion	Log $K_f$	Ion	Log $K_f$
Fe(III)	$4.93 \pm 0.05$	Al(III)	$2.76 \pm 0.05$
Co(II)	$3.33 \pm 0.07$	Zn(II)	$2.66 \pm 0.04$
Cu(II)	$3.25 \pm 0.02$	Na(I)	$2.55 \pm 0.02$
Ni(II)	$3.09 \pm 0.06$	K(I)	$2.39 \pm 0.03$
La(III)	$2.95 \pm 0.04$	Rb(I)	$2.22 \pm 0.04$
Be(II)	$2.83 \pm 0.04$	Hg(II)	<2.0
Ag(I)	$2.70 \pm 0.05$	Mg(II)	<2.0
Fe(II)	$2.68 \pm 0.03$	Pb(II)	<2.0
Ca(II)	$2.59 \pm 0.04$	Mn(II)	<2.0

### 3.2. Potential response

In order to check the suitability of EANQ as an ion carrier for Fe(III) and other metal ions, it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations including a number of metal ion such as Fe(III), Ni(II), Cd(II), Co(II), Zn(II), La(III), Ag(I), etc. At first experiment we used 30 mg PVC, 60 mg BA, 5 mg EANQ and 5 mg NaTPB for membrane fabrication. The potential responses different ion-selective electrodes based on EANQ are depicted in Fig. 2. With the exception of Fe(III) ions, all the tested cations showed relatively weak responses in the concentration range  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>, due to their weak interactions with the ionophore.



**Figure 2.** Potential response of various ion-selective electrodes based on EANQ

### 3.3. Optimization of potentiometric response of the PME

It is well-known that the sensitivity, sensitivity and the linearity of the ion-selective electrodes not only depend on the nature of ionophore used but also significantly on the membrane position and the properties of plasticizers and additives used [46-49]. Thus, the effects of membrane position and the nature and the amount of plasticizer and additive on the potential response of the Fe ion-selective electrode were investigated and the results are summarized in Table 2.

It is reported that the response characteristics of ion selective electrodes are largely affected by the nature and amount of plasticizer used [46-49]. This is due to the influence of plasticizer on dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [46, 47]. As it is seen from Table 2, among four different plasticizers used, NPOE with the highest polarity in the series resulted in the best response slope and linearity.

As it was expected, the amount of ionophore EANQ was also found to affect the PVC-membrane sensitivity (Nos. 2-4). As it is obvious from table 2 (Nos. 2-4), optimization of amount of ionophore in the membrane was performed in the absence of any additive. The calibration slope increased with ionophore content up to a value of 5 %. However, further increase in the amount of EANQ resulted in diminished calibration slope of the electrode (e.g. No. 4), presumably due to some inhomogeneities and possible saturation of the membrane [46]. The sensitivity of the PVC-membrane is quite low in the absence of a proper lipophilic additive (Nos. 2-7). However, the presence of some 10% OA, 4% KTpCIPB and especially 4% NaTPB resulted in increased sensitivity and a more or less Nernstian behavior of the membrane sensor (Table 2, Nos. 9, 12 and 15, respectively), as expected [46-49]. Obviously, the response of lipophilic anions in cations selective membrane electrodes not only diminished the ohmic resistance and enhances the response behavior and selectivity but also, in cases

where the extraction capability is poor, increases the sensitivity of the membrane electrode [47-49]. Moreover, additives may catalyze the exchange kinetic at the sample-membrane interface [46]. From the data presented in Table 2, it is seen that the addition of NaTPB will increase the sensitivity of the electrode response considerably.

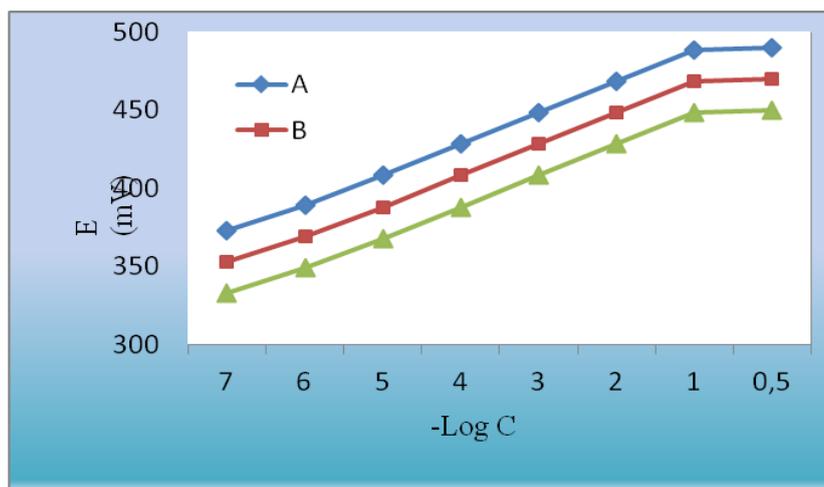
**Table 2.** Optimization of membrane ingredients during design of Fe(III) selective membrane sensor

No.	composition (%)				Slope mV/decade	Concentration range M	DL (M)
	PVC	Plasticizer	EANQ	Additive			
1	38	DBP,62	-	-	~0	-	-
2	35	DBP,62	3	-	7.5	$5.1 \times 10^{-5}$ - $4.0 \times 10^{-2}$	$3.1 \times 10^{-5}$
3	33	DBP,62	5	-	9.1	$2.3 \times 10^{-5}$ - $1.8 \times 10^{-2}$	$9.8 \times 10^{-6}$
4	31	DBP,62	7	-	8.4	$3.9 \times 10^{-5}$ - $7.7 \times 10^{-2}$	$1.0 \times 10^{-5}$
5	33	BA,62	5	-	7.5	$5.0 \times 10^{-5}$ - $3.5 \times 10^{-2}$	$2.4 \times 10^{-5}$
6	33	DOP,62	5	-	8.9	$3.6 \times 10^{-6}$ - $4.0 \times 10^{-1}$	$1.0 \times 10^{-6}$
7	33	NPOE,62	5	-	10.5	$9.5 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$4.8 \times 10^{-6}$
8	33	NPOE,57	5	OA,5	12.1	$4.5 \times 10^{-6}$ - $2.0 \times 10^{-2}$	$2.9 \times 10^{-6}$
9	33	NPOE,52	5	OA,10	14.8	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$8.9 \times 10^{-6}$
10	33	NPOE,47	5	OA,15	13.2	$3.0 \times 10^{-6}$ - $5.0 \times 10^{-1}$	$1.0 \times 10^{-6}$
11	33	NPOE,59	5	KTpCIPB,3	15.5	$1.0 \times 10^{-6}$ - $3.3 \times 10^{-3}$	$8.9 \times 10^{-7}$
12	33	NPOE,58	5	KTpCIPB,4	16.1	$8.9 \times 10^{-7}$ - $1.0 \times 10^{-3}$	$6.8 \times 10^{-7}$
13	33	NPOE,57	5	KTpCIPB,5	15.9	$7.6 \times 10^{-7}$ - $2.5 \times 10^{-3}$	$5.9 \times 10^{-7}$
14	33	NPOE,59	5	NaTPB,3	18.2	$5.4 \times 10^{-7}$ - $4.9 \times 10^{-2}$	$2.2 \times 10^{-7}$
15	33	NPOE,58	5	NaTPB,4	19.5	$2.3 \times 10^{-7}$ - $5.0 \times 10^{-2}$	$9.6 \times 10^{-8}$
16	33	NPOE,57	5	NaTPB,5	18.9	$4.5 \times 10^{-7}$ - $2.0 \times 10^{-2}$	$1.5 \times 10^{-7}$

As is obvious from Table 2, membrane number 15 with PVC: NPOE: L: NaTPB percent ratio of 33: 58: 5: 4 resulted in the Nernstian behavior of the membrane electrode over a wide concentration range the PME.

### 3.4. Effect of internal solution concentration

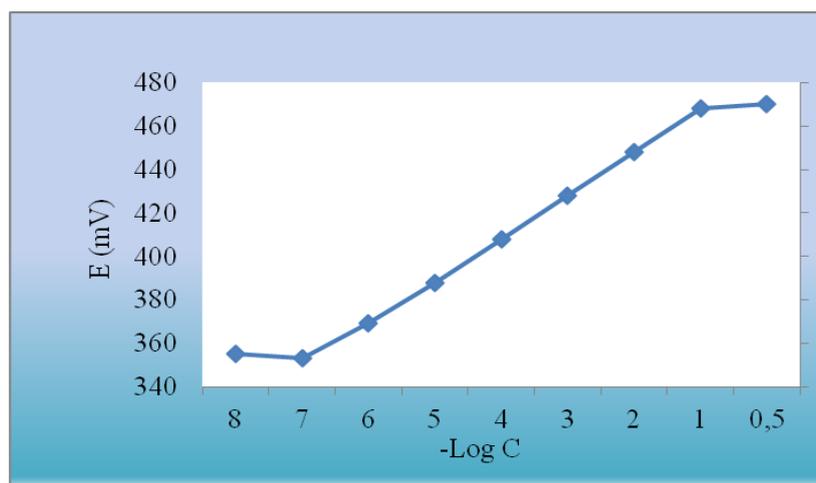
The proposed electrode was also used at different concentrations of the internal reference solution. The  $\text{Fe}^{3+}$  concentrations were changed from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-2}$  M and the emf-p  $\text{Fe}^{3+}$  plot was obtained (Fig 3). It was found that the variation of the concentration of the internal  $\text{Fe}^{3+}$  solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian plots. However, a  $1.0 \times 10^{-3}$  M concentration of the reference solution found to be quite appropriate for smooth functioning of the system. The optimum conditioning time for the membrane electrode in a  $1.0 \times 10^{-3}$  M  $\text{Fe}^{3+}$  was 24 h, after which it generates stable potentials in contact with  $\text{Fe}^{3+}$  solutions.



**Figure 3.** The effect of different concentrations of the internal reference solution, A)  $1.0 \times 10^{-4} \text{M}$ , B)  $1.0 \times 10^{-4} \text{M}$ , C)  $1.0 \times 10^{-4} \text{M}$  of the  $\text{Fe}^{3+}$  as internal solutions respectively

### 3.5. Linear concentration range and detection limit

Under the optimized position, the linear response to the activity of  $\text{Fe}^{3+}$  ion was investigated for the prepared PME and the resulting plot is shown in Fig. 4. As is obvious from Fig. 4 Nernstian response is obtained in very broad concentration ranges of  $2.3 \times 10^{-7}$  to  $5.0 \times 10^{-2} \text{M}$ . The resulting limit of detection (LOD) for PME obtained from the intersection of the two linear parts of the calibration plots, were found to be  $9.6 \times 10^{-7}$ .

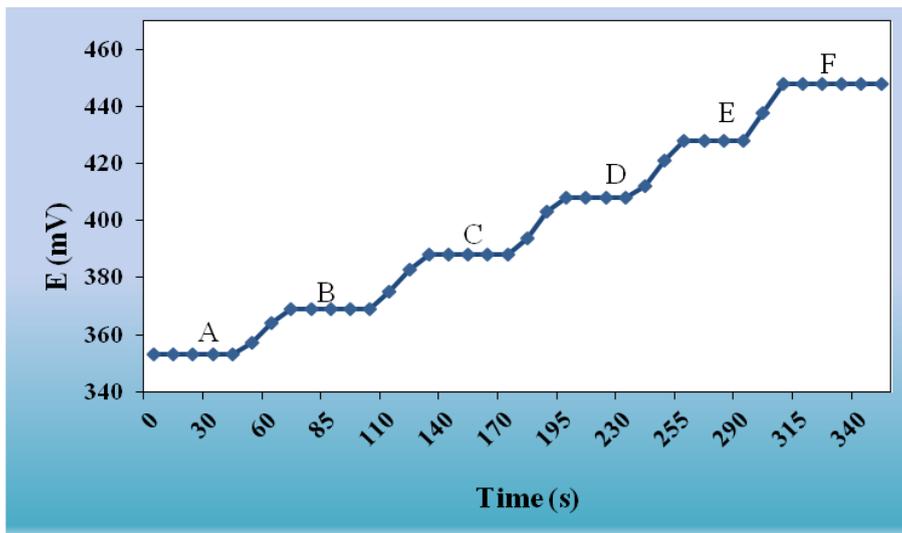


**Figure 4.** Calibration curve  $\text{Fe}^{3+}$  ion-selective electrode based on EANQ

### 3.6. Response time

For analytical applications, the response time of a membrane sensor is an important factor. The static response time of the electrode tested by measuring the average time required to achieve a

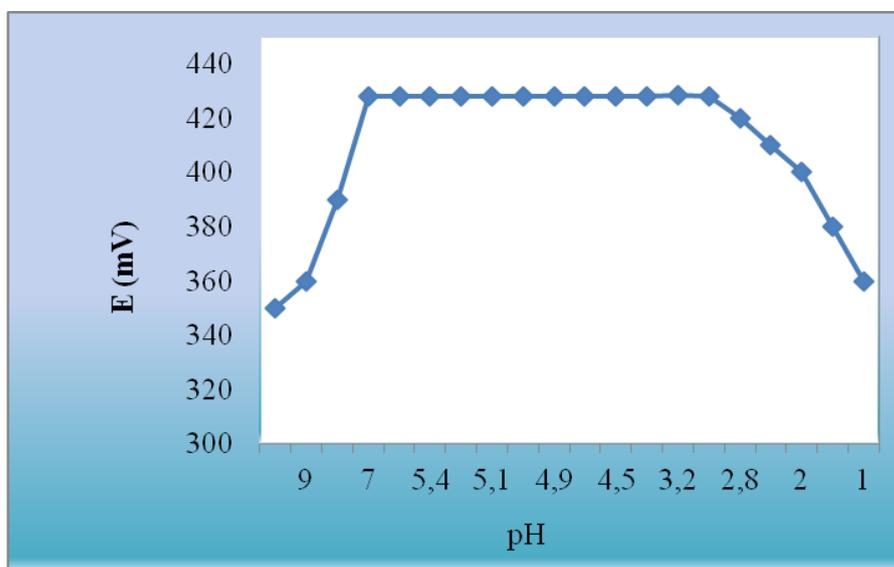
potential within  $\pm 1\text{mV}$  of the final steady state potential upon successive immersion of a series of  $\text{Fe}^{3+}$  ions, each having a tenfold difference in concentrations, was within  $<25$ . (Fig. 5)



**Figure 5.** Dynamic response time of the proposed sensor for step changes in the concentration of  $\text{Fe}^{3+}$  (M): A)  $1.0 \times 10^{-7}$ , B)  $1.0 \times 10^{-6}$ , C)  $1.0 \times 10^{-5}$ , D)  $1.0 \times 10^{-4}$ , E)  $1.0 \times 10^{-3}$ , F)  $1.0 \times 10^{-2}$

### 3.7. pH effect on the electrode response

The influence of pH of the test solution on the potential response of the membrane electrode was tested in the pH range of 2-10, and the results are shown in Fig. 6. As seen, the potential remained constant from pH 2.9 to 7.1, beyond which the potential changed considerably.



**Figure 6** Influences of pH of the test solution on the potential response of electrode in the presence of  $1.0 \times 10^{-3} \text{ M Fe}^{3+}$

At higher pH values hydroxy complexes of  $\text{Fe}^{3+}$  can be formed on the other hand, at lower pH values the decrease in potential is due to the protonations of ionophore.

### 3.8. Potentiometric selectivity

The selectivity behavior is obviously one of the most important characteristics of a membrane sensor, determining whether a reliable measurement in the target sample is possible. In this work, the influence of several transition and heavy metal ions on the potential response of the Ferric-selective electrode was tested by determining the potentiometric selectivity coefficients of the electrodes by the separate solution method (SSM) [50,51]. In this method, the potential of a cellprising an ion selective electrode and a reference electrode is measured with two separate solutions.

One contains the ion of interest  $i$  at the activity  $a_i$  (but no  $j$ ) and the other containing the interfering ion  $j$  at the same activity  $a_j=a_i$  (but no  $i$ ). In this method the values are the selectivity coefficient can be derived from the following equation:

$$K_{ij}^{pot} = \frac{(E_2 - E_1)}{2.303RT/Z_i F} + \left(1 - \frac{Z_i}{Z_j}\right) \log a_i$$

Where  $E_1$ ,  $E_2$  and  $Z_i$ ,  $Z_j$  are the respective measured potentials and charges on the ions  $i$  and  $j$

The resulting  $\log K_{\text{Fe(III)},M_i}^{pot}$  values obtained are summarized in Table 3. It is seen that, in all cases, the log selectivity coefficients are in the order of -3.5 and lower, indicating negligible interference in the performance of the membrane sensor assemblies.

In Table 4, the slope, response time, detection limit, linear range and life time of the proposed PME are compared with the corresponding values for the best previously reported Ferric ion-selective electrodes based on different neutral ion carries [23-30].

**Table 3.** The selectivity coefficients of various interfering cations for the membrane sensor

$M^{n++}$	$\text{Log } K_{\text{Fe(III)},M}^{pot}$	$M^{n++}$	$\text{Log } K_{\text{Fe(III)},M}^{pot}$
$\text{Co}^{2+}$	-3.5	$\text{Zn}^{2+}$	-4.6
$\text{Cu}^{2+}$	-3.7	$\text{Na}^+$	-4.7
$\text{Ni}^{2+}$	-3.8	$\text{K}^+$	-4.7
$\text{La}^{3+}$	-4.1	$\text{Rb}^+$	-4.9
$\text{Be}^{2+}$	-4.1	$\text{Ni}^{2+}$	<-5.0
$\text{Ag}^+$	-4.2	$\text{Hg}^{2+}$	<-5.0
$\text{Fe}^{2+}$	-4.5	$\text{Mg}^{2+}$	<-5.0
$\text{Ca}^{2+}$	-4.6	$\text{Pb}^{2+}$	<-5.0
$\text{Al}^{3+}$	-4.6		

From the data given in Table 4 it is immediately obvious that the slope, detection limit, linear range and life time of the proposed sensor is superior to those reported before.

**Table 4.** Comparison of the slope, response time, detection limit, linear range and life time of present work and previous studies of other research groups

No.	Slope (mV/decade)	Response time(s)	Detection Limit (M)	Linear range (M)	Life times	Ref.
1	19.4 ± 0.5	≈ 15	6.8 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> - 1.0 × 10 <sup>-1</sup>	9 weeks	[23]
2	28.5	≈ 15	-	3.5 × 10 <sup>-6</sup> - 4.0 × 10 <sup>-2</sup>	2 months	[24]
3	20.0	15	5.0 × 10 <sup>-6</sup>	6.3 × 10 <sup>-6</sup> - 1.0 × 10 <sup>-1</sup>	2 months	[25]
4	60.0	25 - 30	-	1.0 × 10 <sup>-6</sup> - 1.0 × 10 <sup>-2</sup>	3 months	[26]
5	30.5 - 32	8 - 15	1.0 × 10 <sup>-6</sup> - 4 × 10 <sup>-8</sup>	5.0 × 10 <sup>-7</sup> - 1.0 × 10 <sup>-2</sup>	≈ 3 months	[27]
6	19.4 ± 0.5	-	3.6 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> - 1.0 × 10 <sup>-2</sup>	2 months	[28]
7	57.0	30	1.0 × 10 <sup>-6</sup>	1.0 × 10 <sup>-4</sup> - 1.0 × 10 <sup>-1</sup>	2 months	[29]
8	20	20	1.3 × 10 <sup>-6</sup>	1.0 × 10 <sup>-5</sup> - 1.0 × 10 <sup>-1</sup>	2 months	[30]
9	19.5 ± 0.3	25	9.6 × 10 <sup>-8</sup>	2.3 × 10 <sup>-7</sup> - 5.0 × 10 <sup>-2</sup>	5 months	This work

### 3.9. Stability and lifetime

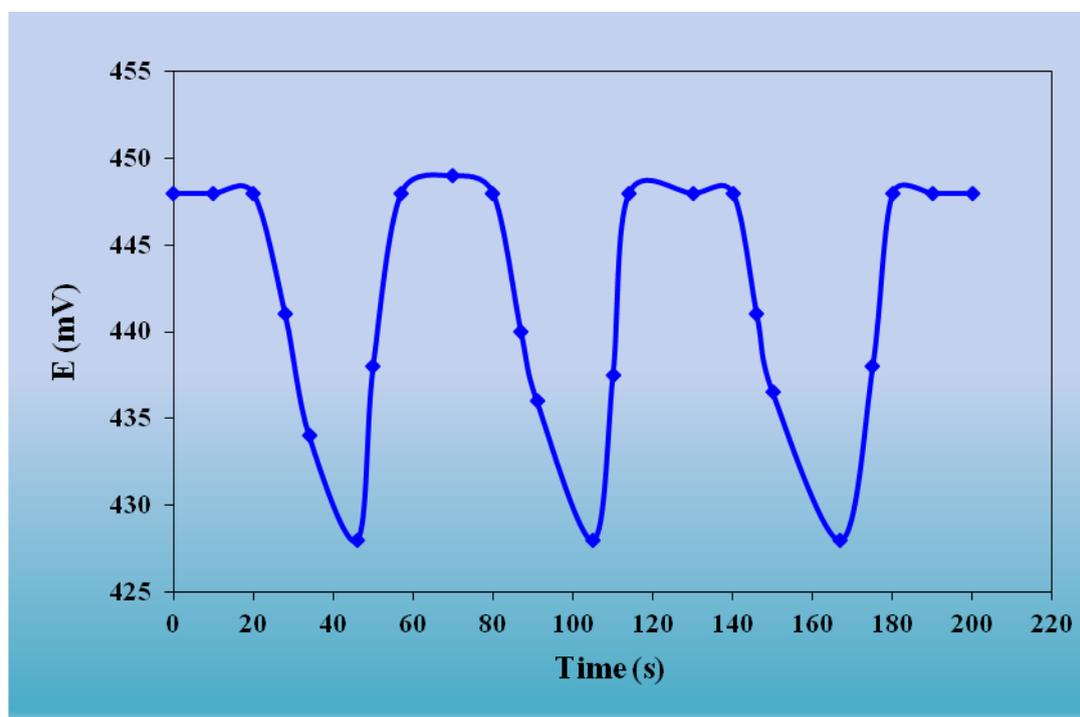
For the investigation of the stability and lifetime of the Fe(III) membrane sensor, two electrodes were tested over a period of 25 weeks and the results are in Table 5. The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 20 weeks (use of 1 hour daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 20 weeks changes were observed in the slope and detection limit (from 19.5 to 16.5 mV decade<sup>-1</sup> and 9.6 × 10<sup>-8</sup> to 1.0 × 10<sup>-7</sup> M or less, respectively).

**Table 5.** Lifetime of Fe(III) selective membrane sensor

Week	Slope (mV decade <sup>-1</sup> )	Detection Limit (M)
1	19.5 ± 0.3	9.6 × 10 <sup>-8</sup>
3	19.2 ± 0.2	9.9 × 10 <sup>-8</sup>
5	19.4 ± 0.4	9.8 × 10 <sup>-8</sup>
7	19.1 ± 0.3	1.1 × 10 <sup>-7</sup>
9	18.9 ± 0.3	2.5 × 10 <sup>-7</sup>
11	19.0 ± 0.4	4.3 × 10 <sup>-7</sup>
13	18.7 ± 0.6	2.9 × 10 <sup>-7</sup>
15	18.5 ± 0.5	5.6 × 10 <sup>-7</sup>
17	18.8 ± 0.4	6.6 × 10 <sup>-7</sup>
19	18.5 ± 0.7	8.5 × 10 <sup>-7</sup>
21	16.5 ± 0.5	1.5 × 10 <sup>-6</sup>
23	14.2 ± 0.8	5.2 × 10 <sup>-6</sup>

### 3.10. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-3}$  M) sample concentrations and the results showed that, the potentiometric responses of the electrode was reversible; although the time needed to reach equilibrium values (25 s) were longer than that of low-to-high sample concentrations [52] (Fig.7).



**Figure 7.** Dynamic response characteristics of the  $\text{Fe}^{3+}$  membrane sensor for several high-to-low sample cycles.

### 3.11. Analytical applications

#### 3.11.1 Determination of Fe(III) in real samples

In order to test the analytical validity of this approach, the electrode has been used for the determination of iron in pharmaceutical samples (Feriron, Darou Pakhsh, Iran) and water samples (tap water Qazvin, Iran and mineral water, Damavand, Iran).

Pharmaceutical sample was prepared by dissolving one tablet of Feriron in 10 mL HCl and heated to dryness. After that, the sample was dissolved in 10 mL distilled water, filtered and transferred to a 25 mL standard flask and this volume was completed with distilled water. Atomic absorption spectrometer was also used for the determination of iron contents in these samples. The results obtained are presented in table 6 and pared with those obtained by using AAS. The sensor is found to be in satisfactory agreement with that obtained from atomic absorption spectrometer (AAS).

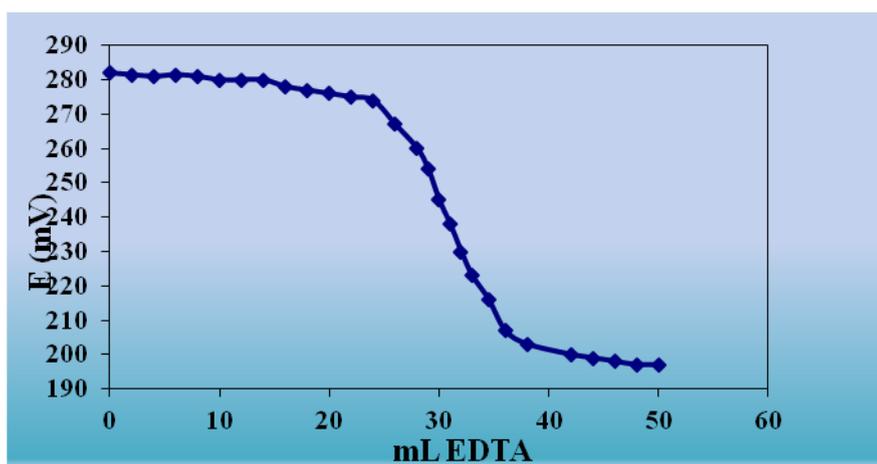
These observations and results have been confirmed that present electrode can be used for practical analysis.

**Table 6.** Determination of Fe (III) in real samples using AAS and proposed sensor

Sample	Adjusted pH	Labeled amount	AAS	Proposed sensor
Feriron	3.5	50 mg/tablet	49.5 ± 0.05mg/tablet	49.3 ± 0.02 mg/tablet
tap water	3.5	-	3.9 ± 0.04mg L <sup>-1</sup>	4.1 ± 0.05 mg L <sup>-1</sup>
mineral water	3.5	-	1.8 ± 0.08mg L <sup>-1</sup>	2.0 ± 0.05 mg L <sup>-1</sup>

3.11.2. Potentiometric titration

The other analytical application of Fe<sup>3+</sup> sensor based on EANQ was tested by the potentiometric titration of Fe<sup>3+</sup> with EDTA solution. A 30 ml (10<sup>-3</sup>M) of testing solution was titrated with 10<sup>-3</sup>M EDTA solution. With the addition of EDTA solution into the testing solution, the Fe<sup>3+</sup> concentration and the output voltage were decreased because of the formation of Fe-EDTA complex as shown in figure 8. In figure 8, which exhibits that the end point represent the stoichiometric formulation of Fe-EDTA complex and it also suggests that the almost all of the iron ions are used up in the formation of Fe-EDTA complex and so after the equivalent point, the potential response was found to almost be constant. It is therefore suggested that the proposed sensor based on EANQ can successfully be used as an indicator electrode for the determination of Fe<sup>3+</sup> by potentiometric titration



**Figure 8.** Titration curve of 30mL of 1.0×10<sup>-3</sup>M Fe<sup>3+</sup> with 0.01M EDTA solution

4. CONCLUSION

The membrane assembly prepared using 9- ethylacenaphtho [1,2-b]quinoxaline (EANQ)as membrane ingredient with plasticizers (NPOE) and anion excluder (NaTPB) exhibited linearity over a wide concentration range (2.3×10<sup>-7</sup>-5.0×10<sup>-2</sup> M) with Nernstian slope (19.5±0.3 mV/decade of

activity), fast response time (25s), long lifetime (five months) and selectivity (of the order of  $10^{-4}$  and  $10^{-5}$ ) over a number of cations. The iron ion-selective electrode can be employed as an indicator electrode in potentiometric titration and the determination of iron ions in Pharmaceutical sample and water samples.

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