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Research Article

A new potentiometric electrode based on indole derivative molecule for the determination of Fe (III) ions

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ABSTRACT

A new solid state electrode based indole diamine (ionophore) was developed that acted towards the iron (III) ion selectively. After calculating the membrane composition of developed electrode, the potentiometric performances were studied. In this study, the results indicated that the electrode has a near-Nernstian response at 43.00 ± 5 mV/decade and low detection limit (6.5×10^{-7} M) in the wide linear concentration range (1.0×10^{-6} - 1.0×10^{-2} M). The potentiometric pH response of the electrode is in a wide range such as 2-11 and the time it gives to the solutions is as short as <20 s. In addition, the obtained electrode exhibited high selectivity towards iron (III) ions in a solution containing various cations. The advanced electrode has a potential to be used in wastewater and fruit juices for determining iron (III) as a potentiometric method with fast, low-cost, on-site analysis.

Keywords: PVC membrane, potentiometric sensor, iron (III)-selective, indole derivative.

1. INTRODUCTION

The organic compound synthesis is an important field of science.[1-4] Because organic compounds constitute the basis of life and are widely used in medicine, agriculture, food, and cosmetics as well as sensory.[5-8] Chemosensors have been used commonly in many fields such as medicine, environmental science, aerospace, and national security.[9] Generally, various chemical iron forms exist in water sources depending on geological areas and chemical compounds. At the same time, ion forms of iron can be found at the center of the entire living system. Fe^{3+} exists in several enzymes in the human body and plays an important role in the nervous system.[10] Further, Fe^{3+} is an essential micronutrient in basic needs such as photosynthesis and respiration in plants.[11-12] On the other hand, Fe^{3+} is both a crucial element for the human body and as much as present at a certain rate in the body. Because entering more or less iron into the human body causes many diseases such as liver and kidney damage. Some methods including MS-ICP-MS,[13] ion chromatography,[14] ICP-AES[15] have been used commonly to detect Fe^{3+} in the samples. These methods require a long time and high-cost equipment. The quantitative analysis of iron ions in environmental samples is crucial. So, ion-selective electrodes can be effectively used to determine the iron ions. In this study, indole diamine molecule as an ionophore was used in different water samples and fruit juices for the detection of Fe^{3+} ions. The structure of this molecule we use is given in Figure 1. The synthesis protocol was presented in literature.[16]

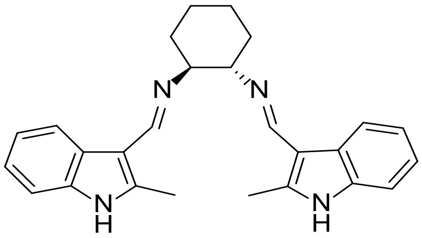

Fig. 1. Structure of indole diamine (ionophore).

2. EXPERIMENTAL

2.1. Chemicals

The chemicals were analytical degree and used without further purification. The chemicals were purchased from Sigma Aldrich and Bayer AG (Darmstadt, Germany).

2.2. Instruments

Potentiometric analysis was executed by a potentiometric device (Medisen Ar-Ge, Türkiye) composed of a special software program, computer-controlled, high input impedance, and multi-channel. All the potentials of the electrodes were evaluated using an Ag/AgCl reference electrode (Thermo Orion™) saturated with 3 M KCl. pH of solutions was detected using a pH meter (S220-K, Mettler Toledo) integrated with a pH electrode pH/mV. The potential of the membrane, selective to Fe^{3+} was performed using a serial solution having different Fe^{3+} concentrations.

2.3. Preparation of PVC membrane

PVC membrane preparation used in the composition of the electrode was conducted in two stages. Firstly, all of the solid-state contacts containing (%, w/w) graphite (50.0), hardener (15.0), and epoxy (35.0) for electrodes were prepared. Thereafter, the solid-state material was homogenized in 3 mL of THF, and the wire (approximately 0.5-1 mm thickness, 5-15 cm length) was covered with the resulting mixture 4-5 times and left at room temperature overnight. Briefly, the preparation of PVC membrane electrode procedure can be summarized as follows. A mixture containing 33% of powdered PVC (w/w), 63.0 mg of plasticizer (genius), 1.0 mg of conductivity improver (KTpClPB), and 3.0 mg of ionophore (cyclohexane-1,2 -diamine) was prepared and homogenized in THF (4.0 mL). The mixture was boiled slowly to yield a gel-like concentrated. Finally, electrodes prepared as solid contacts were immersed in the solution for 5 seconds, hence a transparent membrane with a thickness of about 0.3 mm was yielded. The electrodes coated with the solid contact were kept at rt for 24 h. Finally, the electrodes were immersed in 1.0×10^{-2} mol L^{-1} Fe^{3+} solution to were conditioned in a dark place for 3-4 h. The other prepared membrane components and their optimizations are summarized in Table 1.

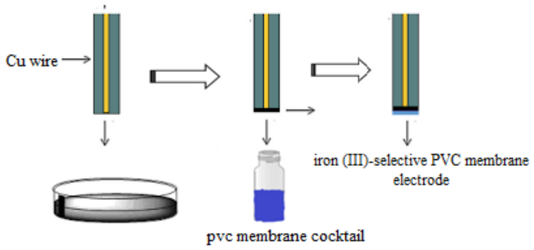

Figure 2. Schematic illustration of PVC membrane and their coating on the surface of electrodes.

Table 1. The ingredients of membranes and their optimizations.

	Ionophore (mg)	PVC (mg)	KTpClPB (mg)	DBF (mg)	DEHA (mg)	BEHS (mg)	R^2
1	2.5	33.0	1.0	63.5	-	-	0.9887
2	3.0	33.0	1.0	63.0	-	-	0.9801
3	4.0	33.0	1.0	62.0	-	-	0.9885
4	2.5	33.0	1.0	**-**	63.5	**-**	0,9901
5	**3.0**	**33.0**	**1.0**	**-**	**63.0**	**-**	**0.9994**
6	4.0	33.0	1.0	-	62.0	-	0.9975
7	2.5	33.0	1.0	-	-	63.5	0,9890
8	3.0	33.0	1.0	-	-	63.0	0,9881
9	4.0	33.0	1.0	-	-	62.0	0,9080

Among the PVC membrane compositions prepared in Table 1, it was determined that the membrane number 5, which exhibits the best linear behavior towards Fe(III) ion and has the best determination constant (R^2). PVC membrane electrode with this composition was used in all measurements.

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2.4. Potentiometric measurements

The emf analysis conducted with polymeric membrane coated electrodes (PVC) and made with the setup shown schematically below. The measurements taken at the room conditions were carried out by regulating the following cell preparations.

Ag/AgCl; KCl (saturated) ‖Fe^{3+} sample solution│Fe^{3+} selective PVC membrane

3. RESULTS AND DISCUSSION

The electrode response time is significant for the usability of the electrode. In this study, the response time of the new iron-selective PVC membrane electrode changed rapidly in the certain concentration range (1.0×10^{-2} - 1.0×10^{-6} mol L^{-1}). The potentiometric measurements were accomplished in iron nitrate solutions. The calibration curve, potentiometric response and linear equation of the electrode were calculated using the formula E= -43,5(-log [Fe^{3+}]) +1719,8 and R^2 = 0,9994 (**Figure 4**). The developed electrode did not demonstrate a Nernstian behaviour but displayed a linear potential difference (43.0 mV±5.0).

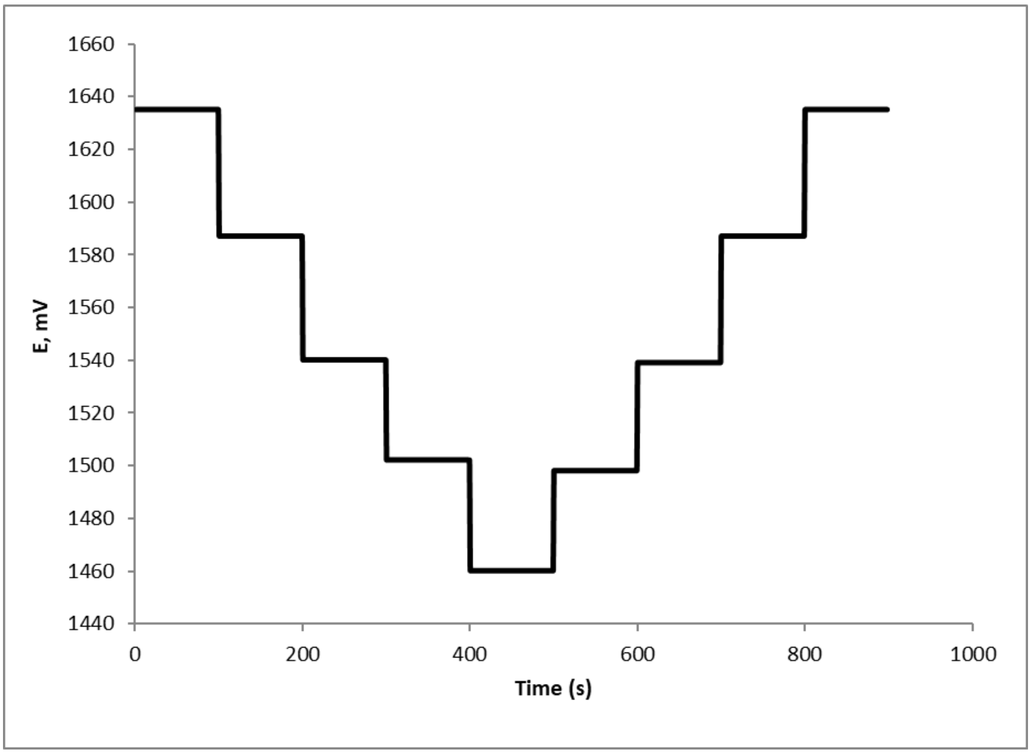

Fig. 4 Potentiometric response and calibration curve of electrode (1.0×10^{-2} – 1.0×10^{-6} mol L^{-1}).

3.1. Selectivity of PVC membrane electrode to iron (III)

The detection of the target ion with the selective electrode is one of the most vital features of the potentiometric sensor in the presence of different ions interfering in any solution environment. The coefficients of the prepared electrode were calculated by separate solution method (SSM) for several heavy metal ions.[17]

Hence, the selectivity of the iron-selective PVC membrane electrode towards interfering ions was calculated using the following equation according to a solution method proposed by IUPAC: [18]

$$\log k^{pot}_{A,B} = \frac{(E_{B} - E_{A})Z_{A}F}{RT\ln 10} + (1 - \frac{Z_{A}}{Z_{B}})\log a_{A}$$

In this study, various ions of mono, di, and trivalent cations as interference ions were studied. The coefficients of the electrode were calculated using the potential values corresponding to each ion solution having 1.0×10^{-3} mol L^{-1} concentration. As can be seen in Table 2 and Figure 5, the obtained electrode is 10^3 times more selective towards Fe^{3+} compared to silver and bismuth ions, which are the two species that interfere most closely with Fe^{3+}.

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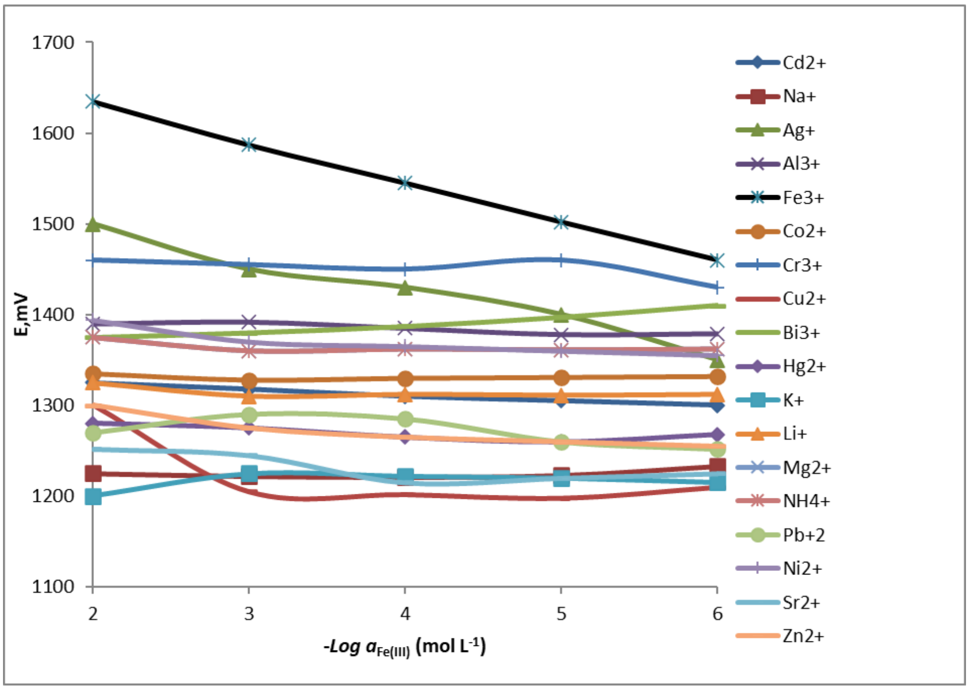

Fig.5. Potentiometric response of the all-solid state contact iron- selective PVC membrane electrode to cations.

Table 2. Selectivity coefficients of various interference metal ions.

Interfering ions	**Selectivity coefficient,** $logk^{pot}_{Fe^{3+},M^{n+}}$	**Selectivity coefficient** $k^{pot}_{Fe^{3+},M^{n+}}$	**Interfering ions**	**Selectivity coefficient,** $logk^{pot}_{Fe^{3+},M^{n+}}$	**Selectivity coefficient,** $k^{pot}_{Fe^{3+},M^{n+}}$
Cd^{2+}	-12.65	2.25×10^{-13}	**K^{+}**	-14.37	4.29×10^{-15}
Na^{+}	-14.52	3.02×10^{-15}	**Li^{+}**	-10.05	8.82×10^{-11}
Ag^{+}	-2.95	1.12×10^{-03}	**Mg^{2+}**	-10.52	3.04×10^{-11}
Al^{3+}	-9.89	1.28×10^{-10}	**NH_4^{+}**	-7.52	3.04×10^{-08}
Co^{2+}	-12.14	7.22×10^{-13}	**Pb^{+2}**	-14.07	8.52×10^{-15}
Cr^{3+}	-6.70	2.01×10^{-07}	**Ni^{2+}**	-10.01	9.77×10^{-11}
Cu^{2+}	-18.38	4.15×10^{-19}	**Sr^{2+}**	-16.35	4.44×10^{-17}
Bi^{3+}	-10.50	3.14×10^{-11}	**Zn^{2+}**	-14.83	1.48×10^{-15}

The reusability of iron (III)-selective PVC membrane electrode

The reusability of the Fe^{3+} selective electrode was conducted by using $Fe(NO_3)_3$ solution having concentrations 1.0 x 10^{-2}, 1.0 x 10^{-3} ve 1.0 x 10^{-4} mol L^{-1}. The potential time graph shown in Figure 6 displayed that the results given by the developed iron selective electrode can be easily reused. Also, Figure 6 shows that the electrode is reusable, these obtained values reveal that the reusability of the electrode is quite good.

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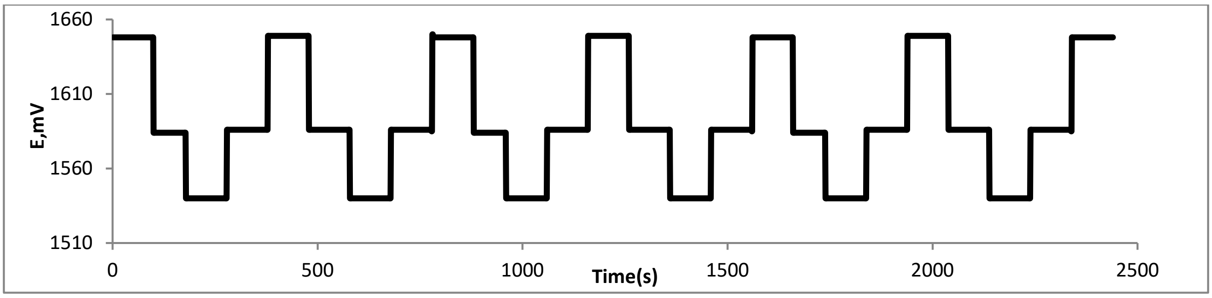

Figure 6. The reusability of iron(III)-selective PVC membrane electrode.

3.2. Response time of electrode

One of the important parameters used in the determination of the ion-selective electrode is the response time. In this research, the transition times from 1.0 × 10^{-2} to 1.0 × 10^{-6} mol L^{-1} Fe^{3+} concentration of the solutions were investigated to evaluate the response time of the electrode. The response time was detected to be between 15 and 20 seconds. It was found that the electrode reached equilibrium relatively quickly.

3.3. The pH dependence of iron (III)-selective PVC membrane electrode

The effect of pH on the membrane electrode potential stability was determined by measuring the behaviour of iron (III) solution (1.0×10^{-2} mol L^{-1}) in acidic and basic solutions. The potential change of the developed electrode in the pH range of 1.0 to 14.0 revealed that the electrode is potentially sensitive and not affected much by the pH of the environment. For measurements, pH solutions between 1.0 and 14.0 were prepared by diluting the hydrochloric acid (1.0×10^{-1} mol L^{-1}) and sodium hydroxide (1.0×10^{-1} mol L^{-1}) stock solutions. The pH of 1.0×10^{-2} mol L^{-1} Fe^{3+} solutions formed at various pH levels was measured. Potential deviation occurred as a result of the effect of hydronium ion below pH 2.0 and the precipitation of $Fe(OH)_3$ in the above 11.0. The working pH range of the produced electrode was determined as 2.0 to 11.0, and the results are shown in Figure 7.

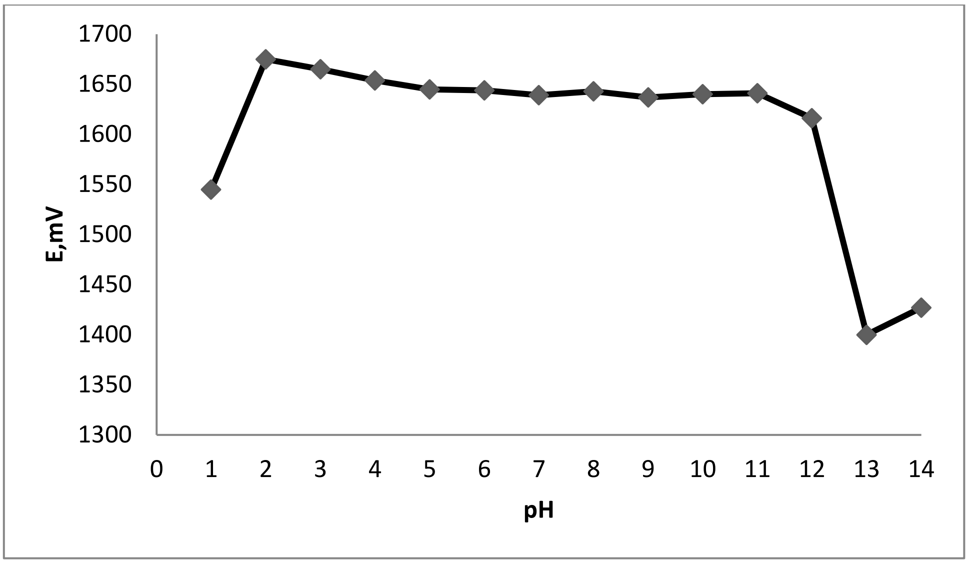

Figure 7. Effect of pH on the potential response of electrode.

3.4. Potentiometric titration

Fe^{3+} selective electrode was used as an indicator electrode in the potentiometric titration of Fe^{3+} solution against EDTA. It was titrated by adding 0.2 mL (1.0 x 10^{-1} mol L^{-1} EDTA) to 50 mL of 1.0 x 10^{-2} mol L^{-1} Fe^{3+} solution. The sharp break point of the sigmoid shape corresponds that this sensor can be used for the potentiometric determination of Fe^{3+} in solutions. In the experiments, the endpoint of the titration was determined as 25.7 mL. Fe^{3+} -selective electrode has been successfully used as an indicator electrode (Figure 8).

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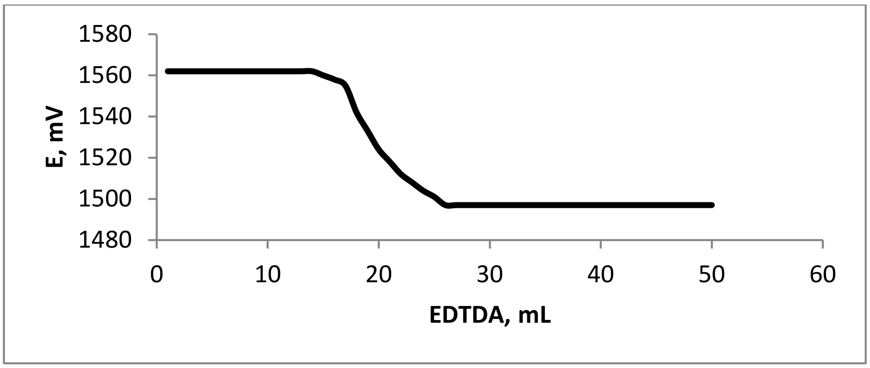

Figure 8. Titration curve for 50.0 mL of 1.0 x 10^{-3} mol L^{-1} iron(III) with 1.0 x 10^{-2} mol L^{-1} ethylene diamine tetra acetic. acid.

3.5. Comparison with other sensors

In comparison of the developed Fe^{3+} -selective sensor with the reported sensors, the developed one has a wide range of pH and faster response time (Table 3). Moreover, the sensor exhibited ideal Nernst behaviour, when real samples were evaluated such as in fruit juices and wastewater.

Table 3. Comparison of proposed iron- selective sensor with reported sensor.

Ionophore	Linear range (mol $L^{-1)}$	Response time (s)	pH	Detection limit (mol L-1)	Slope (mV per decade)	Lit.
1S,2S,N1,N2)-N1,N2-bis((2-methyl-1H-indol-3-yl)methylene)cyclohexane-1,2-diamine	1.0×10^{-2}-1.0×10^{-6}	<20	2-11	6.5×10^{-7}	43.00	this work
Bis-benzilthiocarbohydrazide	1.0×10^{-2}-1.0×10^{-7}	<10	2-5	8,6×10^{-8}	19.6	19
Di-tert-butylazodicarboxylate	1.0×10^{-1}-1.0×10^{-6}	<10 s	2.3–3.4	4.8×10^{-8}	18.70	20
Ethylacenaphtho[1,2-b]quinoxaline	5.0×10^{-2}-2.3×10^{-7}	25	2.9-7.1	9.6×10^{-8}	15.9	21
Morin-Fe^{2+} shiff-base complex	1.0×10^{-1}-1.0×10^{-6}	<10	5.0-10.0	4.5×10^{-7}	56.14	22
(E)-N'-((2-hydroxynaphthalen-3-yl)methylene)benzohydrazide	1.0×10^{-2}-5.0×10^{-9}	10	2.4-4.0	1.0×10^{-9}	19.9	23
µ-bis(tridentate) ligand	6.3×10^{-1}-1.0×10^{-6}	15	3.5–5.5	5.0×10^{-6}	20.0	24
2-[(thiophen-2-yl)methyleneamino]isoindoline-1,3-dione	1.0×10^{-2}-1.0×10^{-6}	10	2.3-4.8	5.0×10^{-7}	20.1	17

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3.6. Recovery and Determination of İron (III) Ions in Real Samples

The electrode has been effectively applied in the detection of Fe^{+3} ions. Recovery experiments were carried out by adding a certain amount of Fe^{+3} ions to different samples. The accuracy and precision of the developed electrode were established using the addition method. Data and recoveries obtained from the graph and percentage relative standard deviation (%RSD) values are shown in Table 4. The results obtained in Table 4 show that the electrode can be used to measure Fe^{3+} ions in environmental samples.

Table 4. Potentiometric determination of Fe^{3+} in different real samples using iron- selective PVC membrane electrode. (n:3).

	Found (mol $L^{-1)}$	**Added (mol L^{-1})**	**%R**	**%R.S.D**
Cherries	1.02×10^{-3}	1.00×10^{-3}	96,71	0,01
Cherries	1.19×10^{-4}	1.00×10^{-4}	83,78	0,02
Cherries	1.33×10^{-5}	1.00×10^{-5}	74,54	0,01
Apricot	1.13×10^{-3}	1.00×10^{-3}	86,96	0,06
Apricot	1.25×10^{-4}	1.00×10^{-4}	76,20	0,04
Apricot	1.15×10^{-5}	1.00×10^{-5}	69,43	0,01
Water	1.02×10^{-3}	1.00×10^{-2}	92,15	0,01
Water	1.09×10^{-4}	1.00×10^{-3}	92,44	0,01
Water	1.06×10^{-5}	1.00×10^{-4}	94,53	0,04

4. CONCLUSION

In this study, a new membrane sensor with solid-state contact for ferrous metal is developed. The ionophore was employed at first in this study. This situation gives different originality to our work. According to the results, the optimum membrane composition [ionophore:PVC:BEHS:KTpClPB] was determined to be 3:33.0:63:1 (mg). The prepared electrode detects Fe^{3+} in a short time of response time <20 seconds and shows appropriate performance characteristics. The electrode has a broad working concentration range from 1.0×10^{-6} to 1.0×10^{-2} at 43.0 ± 5.0 mV/decade. As all sensor materials (except ionophores) are special and contain various compositions, this sensor exhibits high selectivity towards iron (III) ions. It also indicates good selectivity for Fe^{+3} in the presence of foreign ions and an extensive pH range of 2-11. The PVC-based sensor works much faster and in a broader pH range than other iron sensors. The developed electrode displayed good reproducibility and was successfully used as an indicator electrode in the potentiometric titration of Fe^{+3} against EDTA. In addition, the sensor has been successfully used for the determination of iron(III) ions in different water samples.

Conflict of interests

The authors disclose they have no financial or non-financial interests that are directly or indirectly related to the work submitted for publication.

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