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Modified Carbon Paste Ion Selective Electrodes for the Determination of Iron (III) in Water, Soil and Fish Tissue Samples

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The construction, performance characteristics, and application of iron(III) sensors based on (5,5'-(propane-1,3-diylbis(sulfanediyl))bis(3-benzyl-4H-1,2,4-triazol-4-amine) (ionophore A), 5,5'-(butane-1,4-diylbis(sulfanediyl))bis(3-benzyl-4H-1,2,4-triazol-4-amine) (ionophore B), 7,8,16,17-tetrahydrodibenzo[e,m] [1,4,8,11]dioxadiazacyclotetra-decine (ionophore C) and [3{(1E)-2-[3-2-[3-[(1E)-2-aza-2-(3-carboxyphenyl)vinyl]phenoxy}-ethoxy)phenyl1]-1-azavinyl} benzoic acid (ionophore D) are reported in this paper. The sensors are prepared by incorporating of A, B, C and D ionophores into a plasticized carbon paste electrodes to form electrodes I, II, III and IV, respectively. Under the optimized conditions, the electrodes reveal Nernstian slopes of 20±0.32, 20.3±0.46, 19.2±0.62 and 21±0.25 mV decade^{-1} over a wide concentration range from 1×10^{-6} to 1×10^{-2} mol L^{-1} with a detection limit of 6.4×10^{-7}, 6.4×10^{-7}, 1×10^{-6} and 4.8×10^{-7} mol L^{-1} at pH range from 1.8- 3, 1.8- 3, 2- 3.5 and 1.8- 3.5 for electrodes I, II, III and IV, respectively. The sensors are stable for 86, 74, 66 and 95 days for electrodes I, II, III and IV, respectively. without any measurable divergence in the potential characteristics and exhibit good selectivity with respect to alkali, alkaline earth and transition metal ions (e.g. Na(I), K(I), Ba(II), Ca(II), Zn(II), Cd(III), Co(II), Mn(II), Ni(II), Cu(II), Pb(II) and Al(III)). This method is successfully applied for potentiomertric determination of Fe(III) in water, soil and fish tissue samples, and the results obtained agreed with those obtained with atomic absorption spectrometer (AAS).

Keywords: Modified carbon paste electrode, Ferric chloride, Potentiometric determination, Ionophores, Water samples.

1. INTRODUCTION

Iron is widely distributed in nature and it is one of the most important elements in environmental and biological systems. Iron plays a crucial role in a variety of cellular events and indeed no life form is possible without this element with a few possible exceptions in bacterial world [1- 2]. Though it is an essential element for all living systems, the gradual accumulation of iron leads to a number of diseases [3- 9]. Excess of iron in body causes liver and kidney damage (haemochromatosis), whereas its deficiency adversely affects the health leading to anaemia [10- 12]. Moreover, iron compounds are also potential carcinogens.

Several methods for the determination of iron are available, including inductively coupled plasma–mass spectrometry, neutron activation analysis, atomic absorption spectrometry and emission spectrometry. However, most of them require several time-consuming manipulation steps, sophisticated instruments and special training [13- 14].

Ion-selective sensors are used for the potentiometric determination of iron in chemical, biological, industrial and environmental samples as they provide a simplest method, offers several advantages such as fast and easy preparation procedures, simple instrumentation, relatively fast response time, wide concentration range, reasonable selectivity, low cost and may also be suitable for online analysis [15- 28]. Some of them were prepared with ion exchangers [29], neutral carriers [30-31] and a few of them with ionophores [32- 33].

Among the various iron chelators reported till date, siderophores are the naturally occurring powerful iron(III) chelating agents produced by microorganisms and present unique chemical and physiochemical properties [34]. One of the most studied siderophore for the designing of biomimic synthetic chelators for iron(III) is enterobactin, which produced and excreted by bacteria in iron deficient media in order to bind and assimilate extracellular iron [35,36].

The objective of this work is to demonstrate the ability of A, B, C and D as excellent ionophores in the construction of novel carbon paste electrodes and the use of these modified electrodes as electrochemical sensors for Fe(III) determination. The characteristics and analytical performance of CPEs like influence of different plasticizers, ionophores content, pH range, temperature and effect of the interfering cations have been investigated.

2. EXPERIMENTAL

2.1. Reagents and Chemicals

Analytical grade reagents are used in this study. Distilled water was used throughout all experiments. Ferric chloride [$FeCl_3.6H_2O$] was supplied from Koch Light. *o*-Nitrophenyloctylether (*o*-NPOE) was supplied from Fluka. Dioctylphthalate (DOP), dibutylphthalate (DBP) and dioctylsebacate (DOS) were supplied from BDH. Tricresylphosphate (TCP), and graphite powder (synthetic 1 – 2µm) were supplied from Aldrich. Chloride salts of copper, magnesium, cadmium, strontium, zinc, nickel, calcium, potassium, manganese, lead, barium, cobalt, sodium, ferrous and aluminum are used as interfering materials.

2.2. Apparatus

Laboratory potential measurements were performed using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrode was used. pH measurements were done using Thermo- Orion, model Orion 3 stars, USA. Prior to analysis, all glassware used were washed carefully with distilled water and dried in the oven before use.

2.3. Preparation of A-D ionophores

5,5'-(propane-1,3-diylbis(sulfanediyl))bis(3-benzyl-4H-1,2,4-triazol 4-amine) (ionophore A) and 5,5'-(butane-1,4-diylbis(sulfanediyl))bis(3-benzyl-4H-1,2,4-triazol-4-amine) (ionophore B) were prepared according to the previous reported methods [37, 38]. While, preparation of 7,8,16,17-tetrahydrodibenzo[e,m] [1,4,8,11]dioxadiazacyclotetradecine (ionophore C) and 3{(1E)-2-[3-2-[3-[(1E)-2-aza-2-(3-carboxyphenyl)vinyl]phenoxy}ethoxy)-phenyl1]-1-azavinyl}benzoic acid (ionophore D) were prepared according to the previously published methods [39].

2.4. Preparation of modified carbon paste electrodes

Modified carbon paste electrodes (I to IV) were prepared by matrices compositions 10 mg [A, B and D] + 250 mg carbon powder + 100 μl *o*-NPOE and 7.5 mg [C] + 250 mg carbon powder + 100 μl *o*-NPOE for electrodes I, II, IV and III, respectively. This matrix was thoroughly mixed in the mortar and the resulted paste was used to fill the electrode body [40-48]. The sensors were used directly for potentiometric measurements without preconditioning. A fresh surface of the paste was obtained by squeezing more out. The surplus paste was wiped out and the freshly exposed surface was polished on a paper until the surface showed shiny appearance.

2.5. Preparation of sample solution

10 ml aliquots of 10^{-7}- 10^{-2} mol L^{-1} Fe(III) solution were transferred into 25 ml beaker at 25 ^{0}C, The pH of each solution adjusted to 2.5 using NaOH/HCl, followed by immersing the modified electrodes I, II, III and IV in conjugation with Ag/AgCl reference electrode in the solution. The potential change was plotted against the logarithm of Fe(III) concentration from which the calibration curves were constructed.

2.6. Determination of iron in water samples

About 10 ml water samples (Table 1) were transferred to a 25 ml beaker and adjusted to pH 2.5 then content was estimated via potentiometric calibration using CPEs as sensing electrodes. The method was repeated several times to check the accuracy and reproducibility of the proposed method.

2.7. Determination of iron in Soil samples

Soil samples (Table 1) are dried and then treated with diethylene triamine pentaacetic acid [DTPA] solution, stirred for 2 hours, filtrated with Whatman filter paper No. 42 [49]. Take 10 ml of the prepared soil solution and adjust pH to 2.5, iron is determined by potentiometric calibration as described above.

2.8. Determination of iron in fish tissue samples

Iron is determined in fish tissue samples (Table 1) after their preparation and digestion according to the previously reported method [50]. A 10 ml sample is transferred to 25 ml beaker and adjusted to pH 2.5 using NaOH/HCl. Iron is determined by potentiometric calibration as mentioned before.

3. RESULT AND DISCUSSION

Compounds A, B, C and D are used as effective ionophores for the construction of iron(III) selective carbon paste electrodes I, II, III and IV, respectively. The effect of membrane composition, selectivity, working range, pH of the media and life time of electrodes were investigated. The sensors plasticized with *o*-NPOE were calibrated against a double junction Ag/AgCl reference electrode, at 25± 1°C, using the direct calibration technique. The potential response of the electrodes are determined and found to have a linear response over wide concentration range from 1×10^{-6}-1×10^{-2} mol L^{-1} of Fe(III) with a trivalent cationic slope of 20±0.32, 20.3±0.46, 19.2±0.62 and 21±0.25 mV $decade^{-1}$ and exhibit detection limit of 6.4×10^{-7}, 6.4×10^{-7}, 1×10^{-6} and 4.8×10^{-7} mol L^{-1} for electrodes I, II, III and IV, respectively. The electrodes show stable and reproducible potential over a period of 86, 74, 66 and 95 days for electrodes I, II, III and IV, respectively.

3.1. Effect of ionophore content

Membrane composition is a significant parameter for an electrode, when the amount of the electroactive material in the matrix is sufficient to achieve reasonable ionic exchange (selective extraction of the target ion), chemical equilibrium at the membrane or electrode/solution interface will be responsible for the electrode potential. The influence of the A, B, C and D content (sensing material) on the electrode performance was studied. For this purpose, five electrodes were prepared containing different amounts of the ionophores (2.5- 12.5) mg of A, B, C and D ionophores. It was obvious that, the optimum ionophores content were found to be 10, 10, 7.5 and 10 mg for electrodes I, II, III and IV, respectively, as indicated in Table (2). As the ionophore content increases, the slope of calibration curve increases till certain point then decreases for all types of the studied electrodes. This is also supported by the high slope values of the calibration curve in the tested concentration range from 10^{-7}–10^{-2} mol L^{-1} which are 20± 0.32, 20.3± 0.46, 19.2± 0.62 and 21± 0.25 mV decade^{-1} for electrodes I, II, III and IV, respectively.

Table 1. Types and location of water, soil, plant, fish tissue and formation water samples.

Water Samples			**Soil Samples**		
Sample No.	Type	Location, Egypt	Sample No.	Type	Location, Egypt
1	Drain water	El- Omoom Drain	1	Drain soil	El- Omoom Drain
2	Drain water	El- Gharbeya Drain	2	Drain soil	El- Gharbeya Drain
3	Drain water	Sendbees Drain	3	Drain soil	Sendbees Drain
4	Canal water	El- Nokra Canal	4	Canal soil	El- Nokra Canal
5	Canal water	El- Ibrahiumeya Canal	5	Canal soil	El- Ibrahiumeya Canal
6	Canal water	El- Sharkaweya Canal	6	Canal soil	El- Sharkaweya Canal
7	Canal water	El- Basoseya Canal	7	Canal soil	El- Basoseya Canal
8	Nile water	Nile River (Shobra)	8	Nile soil	Nile River (Embaba)
9	Nile water	Nile River (Embaba)	9	Nile soil	Nile River (Shobra)
10	Nile water	Nile River (Helwan)	10	Nile soil	Nile River (Embaba)
Fish Tissue Samples			Formation water Samples		
Sample No.	Type	Type	Sample No.	Type	Location, Egypt
1	Drain fish	El- Omoom Drain			
2	Drain fish	El- Gharbeya Drain	1	Formation water	Karama Petroleum, al-Wahhat-al-Bahhriyah
3	Drain fish	Sendbees Drain			
4	Drain fish	Abo- Hamad Drain	2	Formation water	Qarun Petroleum Company
5	Drain fish	El-Nazaz El- Ayman Drain			
6	Canal fish	El- Twaysa Canal			
7	Canal fish	El- Sersaweya Canal			
8	Canal fish	El- Nokra Canal			
9	Canal fish	El- Sharkaweya Canal			
10	Canal fish	El- Basoseya Canal			

Table 2. Effect of ionophores content on the performance characteristics of Fe(III) electrodes (I, II, III and IV).

Electrode Type	Ionophores Content (mg)	Concentration range mol L^{-1}	Slope mV decade^{-1}	Recovery %	Total potential change, mV
I	2.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	16.2±0.61	97.57	76
	5	$6.4\times 10^{-7}- 1\times 10^{-2}$	17.1±0.32	98.87	80
	7.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	18.3±0.29	98.95	86
	10	$6.4\times 10^{-7}- 1\times 10^{-2}$	19.2±0.21	99.95	90
	12.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	17.5±0.53	98.15	82
II	2.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	17.1±0.73	98.56	80
	5	$6.4\times 10^{-7}- 1\times 10^{-2}$	18.3±0.63	99.12	86
	7.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	19±0.45	99.36	89
	10	$6.4\times 10^{-7}- 1\times 10^{-2}$	19.9±0.32	99.99	93
	12.5	$6.4\times 10^{-7}- 1\times 10^{-2}$	18.7±0.62	98.96	88
III	2.5	$1.0\times 10^{-6}- 1\times 10^{-2}$	16.4±0.82	98.36	77
	5	$1.0\times 10^{-6}- 1\times 10^{-2}$	17.4±0.16	99.06	82
	7.5	$1.0\times 10^{-6}- 1\times 10^{-2}$	18.8±0.53	99.98	88
	10	$1.0\times 10^{-6}- 1\times 10^{-2}$	17.7±0.45	99.56	84
	12.5	$1.0\times 10^{-6}- 1\times 10^{-2}$	16.6±0.29	98.82	79
IV	2.5	$4.8\times 10^{-7}- 1\times 10^{-2}$	17.1±0.36	99.01	83
	5	$4.8\times 10^{-7}- 1\times 10^{-2}$	18.2±0.79	99.47	85
	7.5	$4.8\times 10^{-7}1\times 10^{-2}$	19.2±0.54	99.96	90
	10	$4.8\times 10^{-7}- 1\times 10^{-2}$	20.1±0.37	99.99	94
	12.5	$4.8\times 10^{-7}- 1\times 10^{-2}$	17.1±0.31	98.69	83

3.2. Effect of plasticizer type

Plasticizer is an important constituent of the electrode and influences the detection limit, sensitivity, selectivity of the electrodes and mobility of the electroactive cation in the membrane. The improvement in the performance was attempted by the addition of plasticizers to the membranes. The addition of plasticizers not only improves the workability of the membranes, but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor. The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure, adequate viscosity and dielectric constant and high capacity to dissolve the substrate and other additives present in the membrane. In the present study, the effect of five plasticizers of different polarities such as *o*-NPOE, TCP, DBP, DOP and DOS were studied.

The obtained calibration graphs using different plasticizers indicates that the electrode plasticized with *o*-NPOE showed the highest sensitivity clarified by the highest slope values which are found to be 20±0.32, 19.2±0.21,18.5±0.15, 18±0.18 and 17.3±0.31; 20.3±0.46, 19.9±0.32, 19±0.25, 18.1±0.76 and 17.5±0.55; 19.2±0.21, 18.8±0.53, 18.1±0.45, 17.7±0.48 and 17.1±0.66 and 21±0.25, 20.1±0.37, 19.5±0.52, 19±0.68 and 18.1±0.43 mV decade^{-1} for electrodes I, II, III and IV plasticized with *o*-NPOE, TCP, DBP, DOP and DOS, respectively, as indicated in Figure (1).

3.3. Effect of soaking time

The performance characteristics of the iron-selective membrane electrodes were studied as a function of soaking time in which freshly prepared electrodes must be soaked to activate the surface of the carbon paste layer to form an infinitesimally thin gel layer at which ion exchange occurs. For this purpose CPEs were soaked in 10^{-4} mol L^{-1} Fe(III) solution and the calibration curves were plotted from which the total potential changes are recorded after 0, 15, 30, 45, 60, 120 min. and 6, 12, 24 h. The optimum soaking time was found to be 0 min, where the highest total potential change and slope of the calibration curves are obtained at 25 °C. They decreased with increasing soaking time as indicated in Tables (3 and 4). Soaking is not recommended because it can be assumed that the concentration of the plasticizer and the ionophore in the membrane is likely reduced during this contact period with the CPE. This reduction of the concentration is likely due to the leaching of the ion pairs on the electrode surface.

3.4. Effect of PH

Table 3. Effect of soaking time on the performance characteristics of Fe(III) electrodes (I and II).

Soaking Time	Electrode Type	Concentration range mol L^{-1}	Slope mV decade^{-1}	Recovery %	Total potential change, mV
Without	I	6.4×10^{-7}- 1×10^{-2}	19.2±0.36	99.75	90
5 min		6.4×10^{-7}- 1×10^{-2}	18.47±0.42	99.63	86
10 min		6.4×10^{-7}- 1×10^{-2}	18.14±0.25	99.31	84
15 min		6.4×10^{-7}- 1×10^{-2}	17.79±0.75	99.45	83
30 min		6.4×10^{-7}- 1×10^{-2}	17.57±0.25	99.00	82
45 min		6.4×10^{-7}- 1×10^{-2}	17.2±0.52	98.90	81
60 min		6.4×10^{-7}- 1×10^{-2}	16.59±0.36	98.85	78
120 min		6.4×10^{-7}- 1×10^{-2}	15.91±0.21	98.83	75
6 h		6.4×10^{-7}- 1×10^{-2}	15.2±0.45	98.45	72
12 h		6.4×10^{-7}- 1×10^{-2}	14.0±0.56	98.26	66
24 h		1.0×10^{-5} 1×10^{-2}	12.22±0.46	97.56	58
Without	II	6.4×10^{-7}- 1×10^{-2}	19.9±0.75	99.99	93
5 min		6.4×10^{-7}- 1×10^{-2}	19.36±0.65	99.52	91
10 min		6.4×10^{-7}- 1×10^{-2}	18.76±0.52	99. 43	88
15 min		6.4×10^{-7}- 1×10^{-2}	18.1±0.63	99.20	85
30 min		6.4×10^{-7}- 1×10^{-2}	17.75±0.42	99.00	84
45 min		6.4×10^{-7}- 1×10^{-2}	17.13±0.66	99.20	81
60 min		6.4×10^{-7}- 1×10^{-2}	16.49±0.43	98.68	78
120 min		6.4×10^{-7}- 1×10^{-2}	15.38±0.62	98.23	73
6 h		6.4×10^{-7}- 1×10^{-2}	14.59±0.52	98.00	69
12 h		6.4×10^{-7}- 1×10^{-2}	13.82±0.43	97.76	65
24 h		1.0×10^{-5} 1×10^{-2}	12.22±0.55	97.63	58

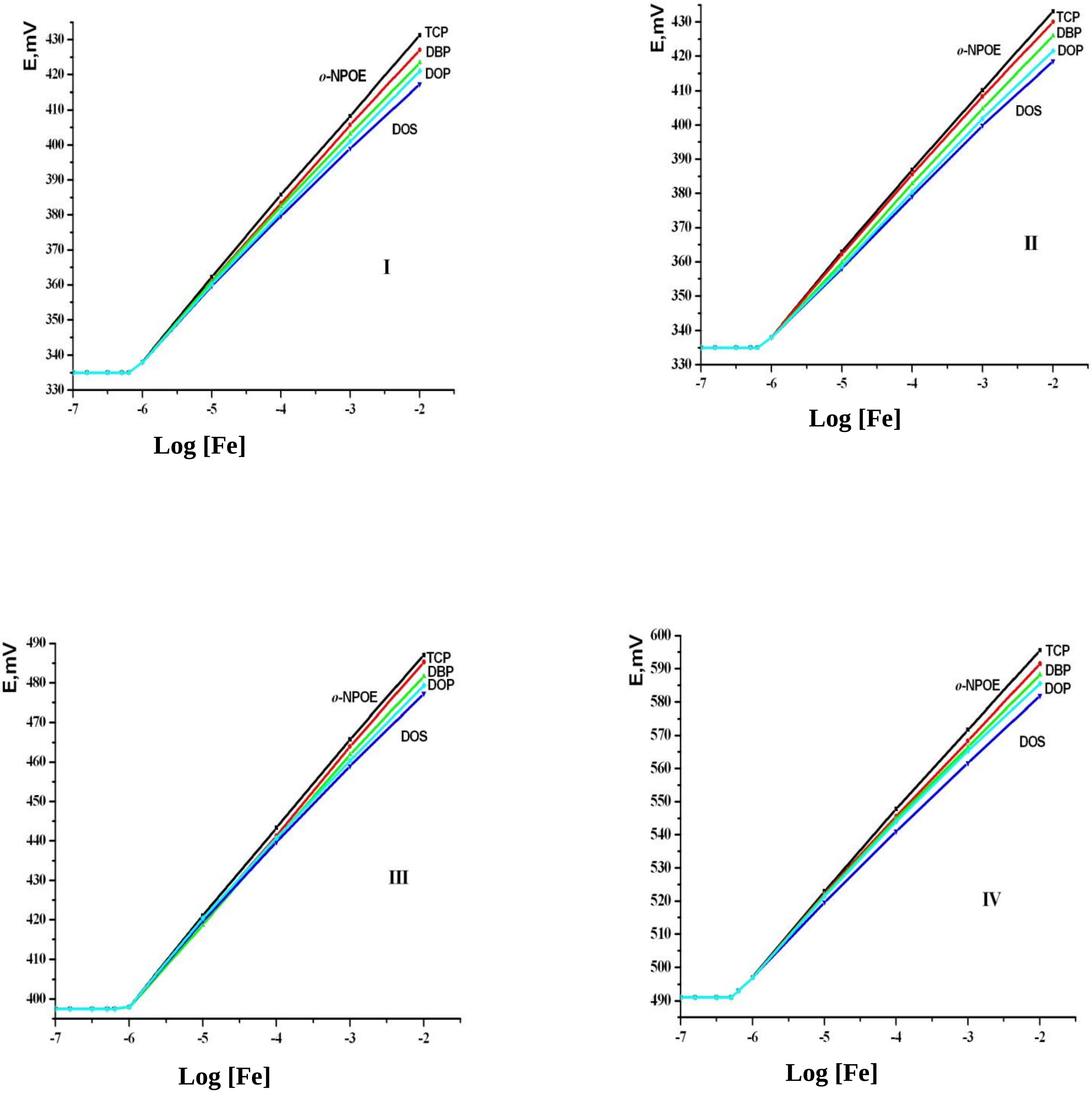

Figure 1. Effect of plasticizer types on the performance of Fe(III) electrodes (I, II, III and IV).

The effect of pH of the test solutions on the electrode potentials was studied. The variation in potential with pH change was followed by the addition of small volumes of HCl and/or NaOH to the test solutions 1× 10^{-4} and 1× 10^{-2} mol L^{-1} For each pH value, the potential was recorded and thus the potential-pH curves for two Fe(III) concentrations were constructed. It was obvious that at pH range from 1.8- 3, 1.8- 3, 2- 3.5 and 1.8- 3.5 for electrodes I, II, III and IV, respectively. Potential are practically independent on pH as shown in Figure (2). At lower or higher pHs, a drift is observed which may attribute to the formation of hydroxide form of iron.

Table 4. Effect of soaking time on the performance characteristics of Fe(III) electrodes (III and IV).

Soaking Time	Electrode Type	Concentration range mol L^{-1}	Slope mV $decade^{-1}$	Recovery %	Total potential change, mV
Without	III	1.0×10^{-6}- 1×10^{-2}	18. 8±0.25	99.86	88
5 min		1.0×10^{-6}- 1×10^{-2}	18.09±0.37	99.71	85
10 min		1.0×10^{-6}- 1×10^{-2}	17.85±0.41	99.75	84
15 min		1.0×10^{-6}- 1×10^{-2}	17.24±0.44	99.36	82
30 min		1.0×10^{-6}- 1×10^{-2}	16.52±0.32	98.43	78
45 min		1.0×10^{-6}- 1×10^{-2}	16.03±0.19	98.36	76
60 min		1.0×10^{-6}- 1×10^{-2}	15.33±0.14	98.22	73
120 min		1.0×10^{-6}- 1×10^{-2}	14.39±0.25	98.00	68
6 h		1.0×10^{-6}- 1×10^{-2}	13.85±0.37	97.76	65
12 h		1.0×10^{-6}- 1×10^{-2}	13.05±0.38	97.62	61
24 h		1.0×10^{-6}- 1×10^{-2}	11.45±0.21	97.60	55
Without	IV	4.8×10^{-7}- 1×10^{-2}	20.1±0.25	99.99	94
5 min		4.8×10^{-7}- 1×10^{-2}	19.73±0.25	99.64	92
10 min		4.8×10^{-7}- 1×10^{-2}	19.36±0.43	99.31	91
15 min		4.8×10^{-7}- 1×10^{-2}	18.69±0.29	99.12	88
30 min		4.8×10^{-7}- 1×10^{-2}	17.67±0.28	99.33	83
45 min		4.8×10^{-7}- 1×10^{-2}	16.99±0.42	98.75	80
60 min		4.8×10^{-7}- 1×10^{-2}	16.06±0.44	98.46	77
120 min		4.8×10^{-7}- 1×10^{-2}	14.98±0.76	98.12	70
6 h		4.8×10^{-7}- 1×10^{-2}	14.39±0.55	97.64	68
12 h		4.8×10^{-7}- 1×10^{-2}	13.41±0.39	97.42	63
24 h		1.0×10^{-5} 1×10^{-2}	11.35±0.42	96.67	54

3.5. Effect of temperature

To investigate the thermal stability of the electrode, The isothermal temperature coefficient of the electrode (dE^{o}/dt) and the standard electrode potentials (E^{o}) were determined from the calibration graphs as the intercepts at p(Fe) = 0, of electrodes at different temperatures range from 10 to 60 ºC and plotted versus (t-25), where (t) is the temperature of the experiment in degree centigrade with the aid of the following equation [51],

$$E^{o} = E^{o}\,(25) + [(\, dE^{o}/dt\,]\,(t-25)]$$

The electrodes exhibits good Nernstian behaviour in the temperature range and a straight line is obtained where its slope represents the isothermal coefficient of the electrode. The isothermal temperature coefficient (dE^o /dt) values were found to be 0.097, 0.1002, 0.1181 and 0.1025 mV °C for electrodes I, II, III and IV, respectively as illustrated in Figure (3).

The low isothermal coefficient value of Fe(III) CPEs the electrodes in the tested temperature range revealed a reasonable thermodynamic ionic exchange process at the membrane/Fe(III) solution interface with good mechanical stability up to 60 ^oC. The investigated electrodes were found to be usable up to 60 °C without noticeable deviation from the Nernstian behaviour.

3.6. Response Time

It is clear that the experimental conditions, like the stirring, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrodes were exposed before performing the experiment measurement, any previous usages or preconditioning of the electrodes, and the testing temperature, are effective on the experimental response time of a sensor.

The average time required for the Fe(III) electrodes to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Fe(III) solutions, each having a 10-fold difference in concentrations, were measured. The average static response times 13, 15, 20 and 9 s for electrodes I, II, III and IV sensors, respectively, were obtained when contacting different Fe(III) solutions from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}, (Figure 4).

3.7. Selectivity and interference

The selectivity behaviour is one of the most important characteristics of ion-selective sensors, determining whether a reliable measurement in the target sample is possible. To investigate the selectivity of the four sensors of iron, their potential responses were assessed in the presence of some inorganic cations using mixed solution method (MPM). Fixed concentration of 1×10^{-3} mol L^{-1} of both iron and the interfering solutions incorporated as their chloride salts were mixed at pH 2.5. The potentials of these solutions were measured and the selectivity coefficients values $K^{Pot}_{Fe(III),B}$ are summarized in Table (5), The results shown in Table (5) indicate that the modified electrodes III and IV are highly selective for Fe(III) ion and there is no interference from the studied cations, but ferrous ion shows high selectivity coefficient with electrodes I and II. The high interference of ferrous ions indicates that the modified carbon paste electrodes I and II can be used for the determination of total iron.

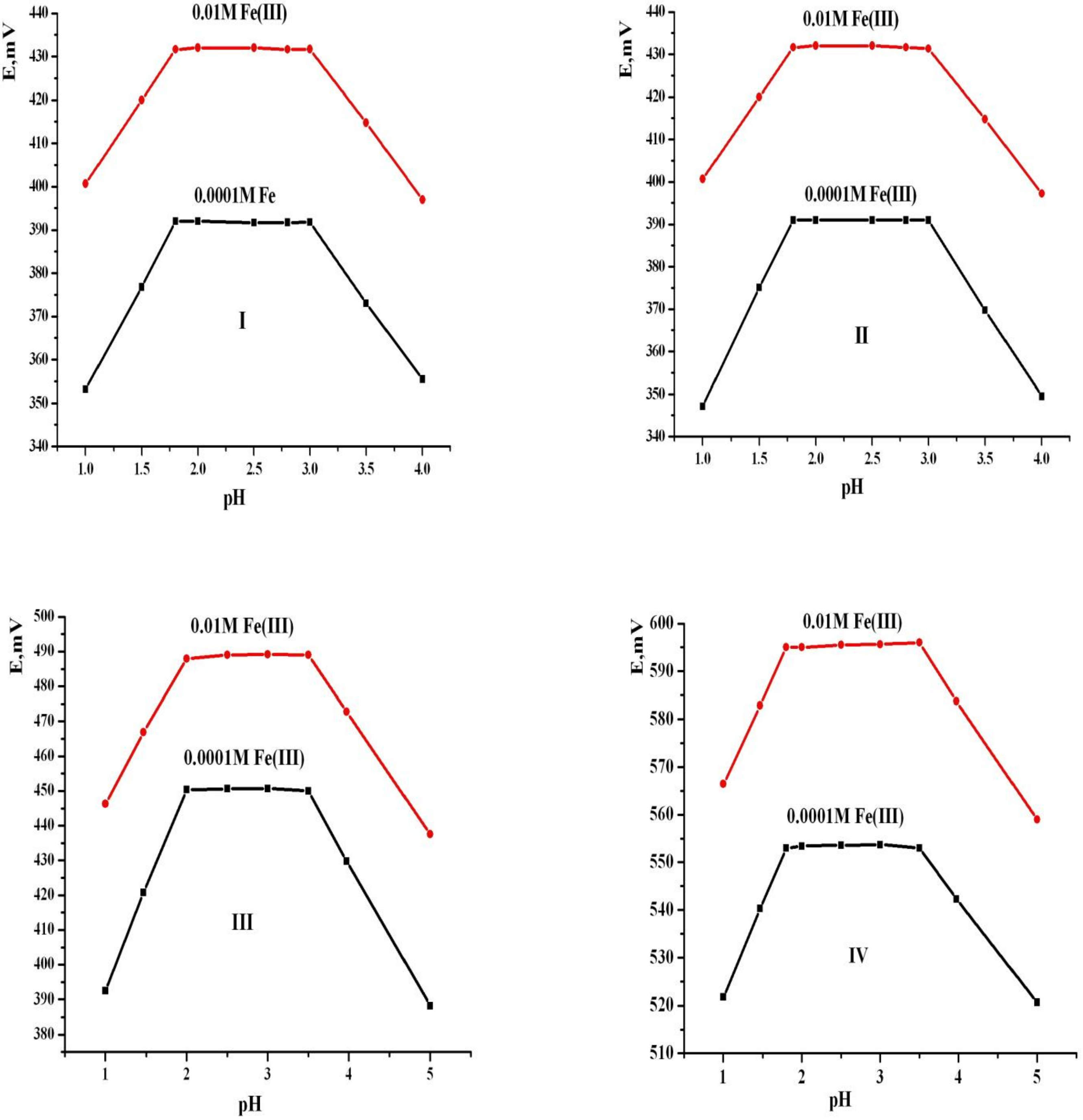

Figure 2. Effect of pH on the performance characteristics of Fe(III) electrodes (I, II, III and IV).

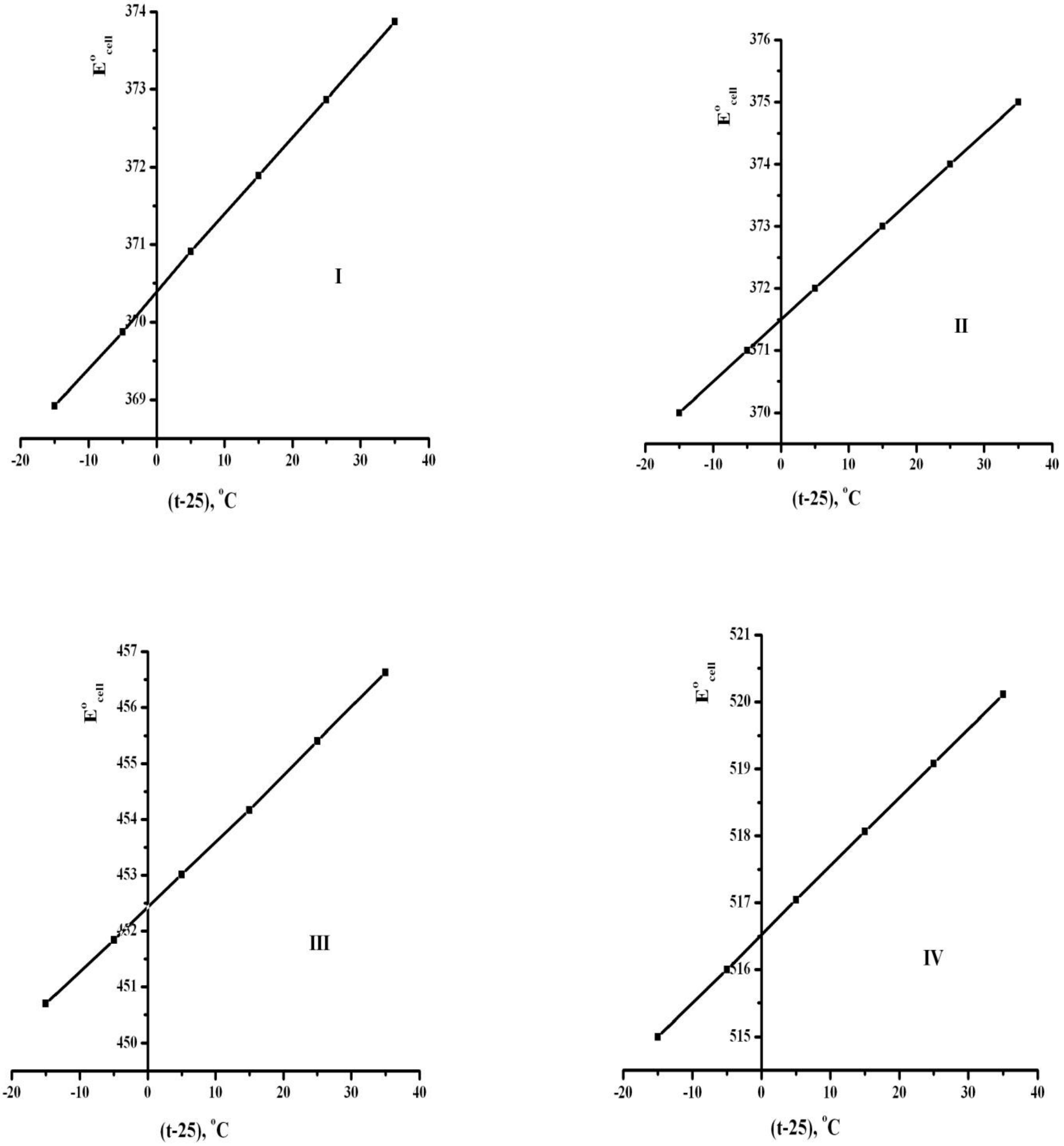

Figure 3. Effect of temperature on the performance characteristics of Fe(III) electrodes (I, II, III and IV).

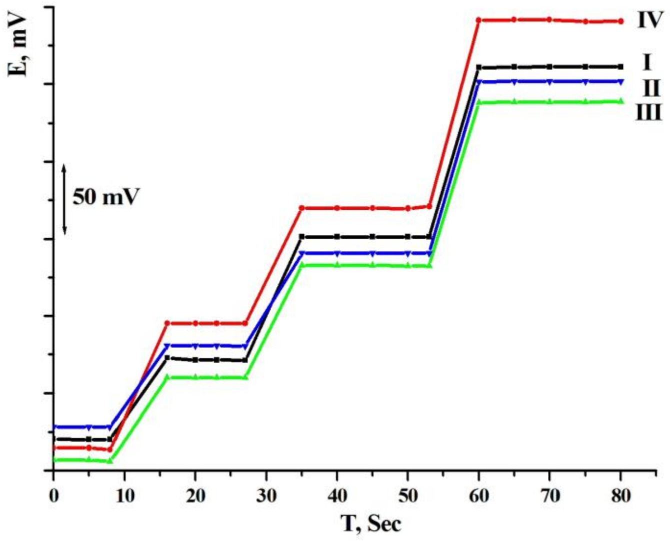

Figure 4. Dynamic response time of different Fe(III) sensors

Table 5. Potentiometric selectivity coefficients of some interfering ions using Fe(III) electrodes(I, II, III and IV).

Interfering ions (B)	$\log K^{pot}_{Fe(III), B}$			
	I	II	III	**IV**
K^+	4.25×10^{-5}	1.51×10^{-4}	4.08×10^{-5}	**2.58×10^{-4}**
NH_4^+	3.65×10^{-5}	1.71×10^{-4}	3.52×10^{-5}	**3.66×10^{-7}**
Na^+	2.22×10^{-4}	3.24×10^{-5}	2.15×10^{-4}	**5.29×10^{-6}**
Mg^{2+}	1.72×10^{-5}	2.55×10^{-5}	1.63×10^{-5}	**1.54×10^{-4}**
Mn^{2+}	5.01×10^{-6}	8.54×10^{-6}	4.98×10^{-6}	**2.22×10^{-5}**
Pb^{2+}	7.12×10^{-3}	3.03×10^{-5}	7.08×10^{-3}	**3.69×10^{-5}**
Ba^{2+}	3.63×10^{-6}	4.59×10^{-6}	3.52×10^{-6}	**3.87×10^{-6}**
Co^{2+}	1.95×10^{-4}	2.39×10^{-4}	2.15×10^{-4}	**7.52×10^{-3}**
Ni^{2+}	2.85×10^{-5}	1.48×10^{-3}	2.55×10^{-5}	**6.38×10^{-4}**
Ca^{2+}	7.12×10^{-3}	3.21×10^{-3}	7.38×10^{-3}	**4.51×10^{-6}**
Sr^{2+}	4.15×10^{-4}	2.33×10^{-6}	4.25×10^{-4}	**6.08×10^{-5}**
Zn^{2+}	3.69×10^{-6}	2.17×10^{-3}	3.82×10^{-6}	**4.28×10^{-4}**
Cd^{2+}	1.85×10^{-4}	8.52×10^{-5}	2.04×10^{-4}	**1.73×10^{-3}**
Al^{3+}	3.46×10^{-3}	8.58×10^{-5}	3.57×10^{-3}	**2.76×10^{-5}**
Cu^{2+}	3.89×10^{-6}	7.3×10^{-4}	4×10^{-6}	**6.72×10^{-4}**
Fe^{2+}	**0.92**	**0. 85**	**3.82×10^{-5}**	**1.29×10^{-6}**

3.8. Analytical applications

The proposed CPEs sensors were found to work well under laboratory conditions. In order to test the analytical validity of this approach, the membrane electrodes with *o*-NPOE have been applied as indicator electrodes for the determination of iron in different samples (water, soil, fish tissue and formation water samples) by direct potentiometry using the calibration graph and atomic absorption spectrometer (AAS) methods. The result obtained by potentiometric calibration are presented in Tables (6 and 7), and were compared with those obtained by Atomic Absorption Spectrometer (AAS) which showed good agreement with them.

3.9. Precision and accuracy

For precision and accuracy study, the calibration curves were constructed. The repeatability and reproducibility of the CPEs method were studied by performing successive calibrations with the same modified electrodes on the same day (intra-day) (n = 5) and on different days (inter-day) (n = 5). The data reveal that the average slope with standard deviation ranges from (0.015- 0.325), (0.047- 0.456), (0.044- 0.142) and (0.036- 0.175) and relative standard deviation value ranges from (0.56- 1.87), (0.68- 1.64), (0.69- 1.91) and (0.64- 2.11) for intra- and inter-days measurements in water and soil samples using electrodes I, II, III and IV, respectively, (Tables (8 and 9). The low values of the relative standard deviation (RSD) and standard deviation (SD) also indicate repeatability, reproducibility and precision of the modified carbon paste electrodes in the determination of iron.

4. CONCLUSION

The proposed iron selective membrane electrodes based on (A, B, C and D) ionophores display a Nernstian response in a wide concentration range from 1×10^{-6} - 1×10^{-2} mol L^{-1} with a detection limit of 6.4×10^{-7}, 6.4×10^{-7}, 1×10^{-6} and 4.8×10^{-7} mol L^{-1} and a slope of 20±0.32, 20.3±0.46, 19.2±0.62 and 21±0.25 mV decade^{-1} for electrodes I, II, III and IV, respectively. It was obvious that electrode IV is the best electrode as it has the highest performance characteristics, Nernstian slope and working pH range. Iron CPEs show advantages over other methods (inductively coupled plasma–mass spectrometry, neutron activation analysis, atomic absorption spectrometry and emission spectrometry) as high performance, selectivity, sensitivity in a wide range of activities, long-term stability (86, 74, 66 and 95 days for electrodes I, II, III and IV, respectively), wide pH range, fast and easy preparation procedures, simple instrumentation, low cost and higher calibration graph slope. Electrodes I and II can be used for the determination of total iron but electrodes III and IV are highly selective and sensitive for the determination of Fe(III). This method can be used for the determination of iron in water, soil, fish tissue and formation water samples.

Table 6. Potentiometric determination of Fe(III) in water and soil samples using electrodes (I, II, III and IV).

Sample No.	**[Fe(III)] mg/L**					**RSD(%)**				
	AAS	I	II	III	IV	AAS	I	II	III	IV
Water Samples										
1	0.95	0.943	0.942	0.946	0.949	1.974	1.098	0.995	1.671	0.895
2	0.86	0.855	0.854	0.857	0.862	1.439	1.050	0.981	1.780	0.456
3	1.0	0.991	0.995	0.989	1.02	1.921	1.056	1.078	2.001	0.860
4	0.75	0.741	0.745	0.738	0.746	1.078	0.978	1.053	1.930	0.672
5	0.69	0.692	0.683	0.685	0.688	0.988	0.936	0.922	0.909	0.842
6	0.71	0.701	0.709	0.705	0.711	0.962	1.067	1.007	1.028	0.952
7	0.83	0.822	0.825	0.826	0.821	1.045	1.001	0.966	1.061	1.064
8	0.28	0.276	0.271	0.274	0.273	1.672	0.789	0.999	2.009	1.009
9	0.25	0.25	0.251	0.243	0.247	1.099	0.932	1.078	2.011	0.999
10	0.26	0.251	0.256	0.254	0.253	1.004	1.059	1.029	1.979	1.004
SD values for water samples (AAS= 0.867- 1.092), (electrode I = 0.375- 0.832) (electrode II= 0.379- 0.753), (electrode III= 0.920- 1.213), (electrode IV= 0.054- 0.182)										
Soil Samples										
1	1.25	1.246	1.249	1.244	1.252	1.782	1.564	0.892	2.043	0.951
2	1.43	1.425	1.456	1.421	1.429	2.050	1.349	1.129	2.120	0.942
3	1.22	1.215	1.219	1.214	1.225	1.920	1.860	1.082	1.972	0.678
4	0.86	0.855	0.853	0.852	0.853	2.029	1.067	1.180	2.121	0.910
5	0.96	0.961	0.953	0.957	0.96	1.620	0.980	0.933	2.045	1.003
6	1.02	1.018	1.012	1.015	1.02	1.499	1.061	1.410	1.850	1.012
7	1.11	1.09	1.05	1.06	1.1	2.025	1.189	0.880	1.001	1.041
8	0.38	0.375	0.372	0.379	0.375	1.944	1.040	1.290	2.196	0.910
9	0.42	0.719	0.411	0.413	0.410	1.909	0.859	0.730	2.010	0.621
10	0.51	0.509	0.508	0.501	0.508	2.049	1.056	1.051	1.956	0.811
SD values for soil samples (AAS = 1.002- 1.421), (electrode I = 0.609- 1.225) (electrode II= 0.742- 1.035), (electrode III= 0.899- 1.601), (electrode IV= 0.429- 1.053)										

Table 7. Potentiometric determination of Fe(III) in fish tissue and formation water samples using electrodes (I, II, III and IV).

Sample No.	**[Fe(III)] mg/L**					**RSD(%)**				
	AAS	I	II	III	IV	AAS	I	II	III	IV
Fish Tissue Samples										
1	0.99	0.982	0.988	0.984	0.992	1.022	1.217	0.762	1.220	0.452
2	0.98	0.981	0.976	0.972	0.976	0.956	1.178	0.878	1.055	0.335
3	0.88	0.876	0.875	0.877	0.879	0.911	1.255	1.005	1.038	0.602
4	1.05	1.04	1.042	1.049	1.041	1.220	1.055	1.026	0.995	0.099
5	1.10	1.09	1.05	1.08	1.01	0.889	2.020	1.045	1.388	0.325
6	0.63	0.625	0.626	0.628	0.631	0.763	1.563	0.822	1.115	0.794
7	0.68	0.677	0.679	0.675	0.671	0.844	0.955	0.933	2.001	0.433
8	0.63	0.625	0.625	0.628	0.624	0.782	1.355	1.070	1.945	0.722
9	0.71	0.706	0.708	0.706	0.705	0.864	1.034	1.067	1.555	0.255
10	0.35	0.343	0.345	0.349	0.347	0.921	1.199	0.955	2.011	0.212
SD values for fish tissue samples (AAS = 0.099- 0.632), (electrode I = 0.175-0,925), (electrode II = 0.222-1.031), (electrode III = 0.002- 0.420), (electrode IV= 0.782- 1.220)										
Formation Water Samples										
1	1.47	1.498	1.462	1.384	1.499	2.005	1.172	1.422	2.046	1.075
2	2.98	2.879	2.890	2.801	2.997	1.539	1.074	1.185	1.951	1.026
SD values for formation water samples (AAS = 1.023- 1.320), (electrode I = 1.027- 1.398), (electrode II = 1.032- 2.018), (electrode III = 1.056- 1.385), (electrode IV = 0.851- 0.972)										

Table 8. Evaluation of intra- and inter-days precision and accuracy of electrodes (I, II, III and IV) in water samples.

Sample No.	**Electrode type (plasticizer used)**	**[Fe(III)] Taken, (mg mL^{-1})**	**Intra day**				**Inter day**			
			[Fe(III)] Found, (mg mL^{-1})	Recovery* (%)	SD	RSD %	[Fe(III)] Found, (mg mL^{-1})	Recovery* (%)	SD	RSD %
9	I (*o*-NPOE)	0.25	0.245	98.00	0.015	0.89	0.249	99.60	0.067	0.97
5		0.69	0.693	100.43	0.046	0.67	0.665	96.38	0.315	1.54
3		1.00	0.995	99.50	0.051	1.51	0.985	98.50	0.132	1.36
9	II (*o*-NPOE)	0.25	0.243	97.20	0.054	1.33	0.245	98.00	0.094	1.24
5		0.69	0.685	99.28	0.221	1.87	0.663	96.09	0.087	0.97
3		1.00	0.989	98.90	0.273	0.96	0.986	98.60	0.063	0.87
9	III (*o*-NPOE)	0.25	0.240	96.00	0.043	0.78	0.243	97.20	0.047	0.68
5		0.69	0.679	98.41	0.048	1.05	0.669	96.96	0.094	0.79
3		1.00	0.981	98.10	0.165	1.61	0.985	98.50	0.065	1.06
9	IV (*o*-NPOE)	0.25	0.253	101.20	0.058	0.56	0.251	100.40	0.456	1.33
5		0.69	0.696	100.87	0.097	0.69	0.669	96.96	0.076	1.54
3		1.00	1.020	102.00	0.325	1.23	1.000	100.00	0.066	1.64

Table 9. Evaluation of intra- and inter-days precision and accuracy of electrodes (I, II, III and IV) in soil samples.

Sample No.	**Electrode type (plasticizer used)**	**[Fe(III)] Taken, (mg mL^{-1})**	**Intra day**				**Inter day**			
			[Fe(III)] Found, (mg mL^{-1})	Recovery* (%)	SD	RSD %	[Fe(III)] Found, (mg mL^{-1})	Recovery* (%)	SD	RSD %
8	I (*o*-NPOE)	0.38	0.372	97.89	0.135	0.97	0.375	98.68	0.084	0.99
2		0.86	0.847	98.49	0.142	0.96	0.854	99.30	0.063	0.82
4		1.43	1.422	99.44	0.068	1.44	1.415	98.95	0.043	0.79
8	II (*o*-NPOE)	0.38	0.375	98.68	0.047	1.57	0.369	97.11	0.074	1.54
2		0.86	0.849	98.72	0.098	1.66	0.856	99.53	0.054	0.64
4		1.43	1.420	99.30	0.067	1.78	1.427	99.79	0.059	1.88
8	III (*o*-NPOE)	0.38	0.369	97.11	0.085	0.92	0.370	97.37	0.048	1.37
2		0.86	0.845	98.26	0.045	0.69	0.850	98.84	0.036	1.54
4		1.43	1.390	97.20	0.044	1.67	1.399	97.83	0.175	2.11
8	IV (*o*-NPOE)	0.38	0.378	99.47	0.078	1.55	0.379	99.74	0.089	1.81
2		0.86	0.852	99.07	0.063	1.91	0.852	99.07	0.067	1.52
4		1.43	1.433	100.21	0.125	1.85	1.443	100.91	0.054	1.67

References

1. S. Jagadevan, M. Jayamurthy, P. Dobson, I.P. Thompson, *Water Research*, 46 (2012) 2395.
2. W.W.J.M. de Vet, I.J.T. Dinkla, L.C. Rietveld, M.C.M. van Loosdrecht, *Water Research*, 45 (2011) 5389.

3. V. Antharama, J.F. Collingwood, J. Bullivant, M.R. Davidson, S. Chandra, A. Mikhaylova, M.E. Finnegan, C. Batichc, J.R. Forderg, J. Dobson, *NeuroImage*, 59 (2012) 1249.
4. B. Novotna, P. Jendelova, M. Kapcalova, P. Rossner, K. Turnovcova, Y. Bagryantseva, M. Babic, D. Horak, E. Sykova, *Toxicol. Lett.*, 210 (2012) 53.
5. K. Gkouvatsos, G. Papanikolaou, K. Pantopoulos, BBA- GEN. Subjects, 1820 (2012) 188.
6. C. Huanga, M. Hub, *Food and Chem. Toxicol.*, 49 (2011) 1381.
7. P. Arosio, S. Levi, *BBA- GEN. Subjects*, 1800 (2010) 783.
8. M. Haase, R. Bellomo, A. Haase-Fielitz, *J. Am. Coll. of Cardiology*, 55 (2010) 2024.
9. A. Corti, T.L. Duarte, C. Giommarelli, V. De Tata, A. Paolicchi, G.D.D. Jones, A. Pompella, *Mutat. Res.*, 669 (2009) 112.
10. T. Meroño., P. Sorroche, L.A.G. Rosso, L. Casañas, L.E. Boero, J.A. Arbelbide, F.D. Brites, *Clin. Biochem.*, 43 (2010) 416–423.
11. D.O. Okonko, A. K.J. Mandal, C.G. Missouris, P.A. Poole-Wilson, Disordered Iron Homeostasis in Chronic Heart Failure : Prevalence, Predictors, and Relation to Anemia, Exercise Capacity, and Survival J. Am. Coll. of Cardiology, Volume 58 (2011) 1241.
12. T.W. Lee, M.R. Kolber, R.N. Fedorak, S.V.V. Zanten, *J. Crohn's and Colitis*, 6 (2012) 267.
13. Ç.A. Şahin, İ. Tokgöz, S. Bektaş, *J. Hazard. Mater.*, 181 (2010) 359.
14. F.A. Aydin, M. Soylak, *J. Hazard. Mater.*, 173 (2010) 669.
15. H.A. Zamani, M.R. Ganjali, F. Faridbod, M. Salavati-Niasari, *Mater. Sci. Eng. C*, 32 (2012) 564.
16. F. Xie, G. Liu, F. Wu, G. Guo, G. Li, *Chem. Eng. J.*, 2012, 183, 372–380.
17. M. Masrournia, H.A. Zamani, H.A. Mirrashid, M.R. Ganjali, F. Faridbod, *Mater. Sci. Eng. C*, 31 (2011) 574.
18. V.K. Gupta, B. Sethi, N. Upadhyay, S. Kumar, R. Singh, L.P. Singh, *Int. J. Electrochem. Sci.*, 6 (2011) 650.
19. B.K. Bera, S.K. Sahoo, M. Baral,B. K. Kanungo, *Bull. Korean Chem. Soc.*, 32 (2011) 3592.
20. M.G. Motlagh, M.A. Taher, A. Ahmadi, *Electrochimica Acta*, 55 (2010) 6724.
21. K. Huanga, Y. Suna, D. Niua, W. Xiea, W. Wangb, *Colloid Surface B*, 78 (2010) 69.
22. A. Babakhanian, M.B. Gholivand, M. Mohammadi, M. Khodadadian, A. Shockravi, M. Abbaszadeh, A. Ghanbary, *J. Hazard. Mater.*, 177 (2010) 159.
23. M.A. Karimi, M.M. Ardakani, R.B. Ardakani, M.H. Mashhadizadeh, M.R. Monfared, M. Tadayon, *J. AOAC Int.*, 93 (2010) 327.
24. M.M. Zareh, I.S.F.A. Ismail, M.H. Abd El-Aziz, *Electroanal.*, 2010, 22, 1369.
25. H.A. Zamani, M.R. Ganjali, H. Behmadi, M.H. Behnajady, *Mater. Sci. Eng. C*, 29 (2009) 1535.
26. M. Pooyamanesh, H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, P. Norouzi, *Anal. Lett.*, 40 (2007) 1596.
27. A. Sil, V.S. Ijeri, A.K. Srivastava, *Sens. Actuators B*, 106 (2005) 648.
28. V.K. Gupta, A.K. Jain, S. Agarwal, G. Maheshwari, *Talanta*, 71 (2007) 1964.
29. M. Naushad, *Bull. Mater. Sci.*, 31 (2008) 957.
30. H.A. Zamani, M.R. Abedi, M.R. Ganjali, *J. Chil. Chem. Soc.*, 54 (2009) 186.
31. G. Ekmekci, D. Uzunb, G. Somer, S. Kalaycıb, *J. Membrane Sci.*, 288 (2007) 36.
32. R. Maleki, R. Hosseinzadeh, H. Mehrabi, A. Hosseinzadeh, K. Fadrhadi, *Turk J Chem.*, 33 (2009) 1.
33. M.H. Zamani, M.T. Hamed-Mosavian, E. Hamidfar, M.R. Ganjali, P. Norouzi, *Mater. Sci. Eng. C*, 28 (2008) 1551.
34. S.S. M. Hassan, S.A.M. Marzouk, *Talanta*, 41 (1994) 891.
35. Z. Chem, X. Yang, X. Lu, *Electroanal.*, 10 (1998) 567.
36. M.B. Saleh, *Analyst*, 125 (2000) 179.
37. A.H.M. Elwahy, A.A. Abbas, Y.A. Ibrahim, *J. Chem. Res. (s)*, 182 (1996) 1066.
38. A.H.M. Elwahy, A.A. Abbas, R.M. Kassab, *Heteroatom*, 14 (2003) 551.

39. A.B. Kamel, Title of [Ph.D] Thesis, Chemistry Department, Faculty of Science, Ain Shams University, 2011.
40. Gehad G. Mohamed, Tamer Awad Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, E. Khaled, *Anal. Chim. Acta* 673 (2010) 79.
41. E.Y.Z. Frag, Tamer Awad Ali, Gehad G. Mohamed, Y.H.H. Awad, *Int. J. Electrochem. Sci.*, 7 (2012) 4443.
42. E.Y.Z. Frag, Gehad G. Mohamed, W.G. El-Sayed, *Bioelectrochem*., 82 (2011) 79.
43. E.Y.Z. Frag, G.G. Mohamed, F.A. Nour El-Dien, M.E. Mohamed, *Analyst*, 136 (2011) 332.
44. Gehad G. Mohamed, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, Tamer Awad Ali, *Analyst*, 136 (2011) 1488.
45. Gehad G. Mohamed, Tamer Awad Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, *Electroanal.*, 22 (2010) 2587.
46. E. Khaled, G.G. Mohamed, T. Awad, *Sens. Actuators, B*, 135 (2008) 74.
47. Gehad G. Mohamed, Tamer Awad Ali, M.F. El-Shahat, M.A. Migahed, A.M. Al-Sabagh, *Drug test. Anal.*, (2012) in press.
48. W. Lindasy, W.A. Norvell, *Soil Sci. Soc. Am. J.*, 42 (1978) 421.
49. M.W. Finerty, J.D. Madden, S.H. Feagly, R.M. Grodner, *Arch. Environ. Contam. Toxicol.*, 19 (1990) 94.
50. H.H. Bauer, G.D. Christian, J.E. O'Reilly, Ed., Allyn and Bacon Inc., Boston, Mass, USA, *Instrumental Analysis*, (1978) 750.