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Electroanalytical Studies on Fe(III) Ion-Selective Sensors Based on 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one Ionophore.

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A new Fe(III) ion-selective screen-printed and carbon paste sensors based on 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (MMCHH) has been developed. The electrodes displayed a linear potential response over the wide concentration range from 4.3×10^{-7} to 1×10^{-2} and 1×10^{-7} to 1×10^{-2} mol L^{-1} with a detection limit of 4.3×10^{-7} and 1×10^{-7} mol L^{-1} for modified carbon paste (MCPEs; electrodes I and II) and screen-printed sensors (MSPEs; electrodes III and IV), respectively. The slopes of the calibration graphs are 18.5±0.9 and 19.3±0.5 for MCPEs with tricresylphosphate (TCP) (sensor I) and *o*-nitrophenyloctylether (*o*-NPOE) (sensor II) as plasticizers, respectively. Also, the MSPEs show good potentiometric slopes of 19.1±0.2 and 19.8±0.05 mV decade^{-1} with TCP (sensor III) and *o*-NPOE (sensor IV), respectively. The electrodes show stable and reproducible potential over a period of 55, 70, 130 and 150 days for sensors (I), (II), (III) and (IV), respectively. The sensors possessed some advantages such as short conditioning time, very fast response time (<12, 10, 7 and 5 s for sensors (I), (II), (III) and (IV), respectively) and especially good discriminating ability towards Fe(III) ions over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. The potential response of the proposed sensors was independent of the pH of the test solution within the pH working range from 1.8 to 6.0, 1.5 to 6.0, 1.5 to 6.5 and 1.5 to 6.5 for sensors (I), (II), (III) and (IV), respectively. The optimized sensors were used successfully for direct and indirect determination of free iron species in some different spiked real water samples with satisfactory results. The results compared satisfactory with those obtained with atomic absorption spectrometry.

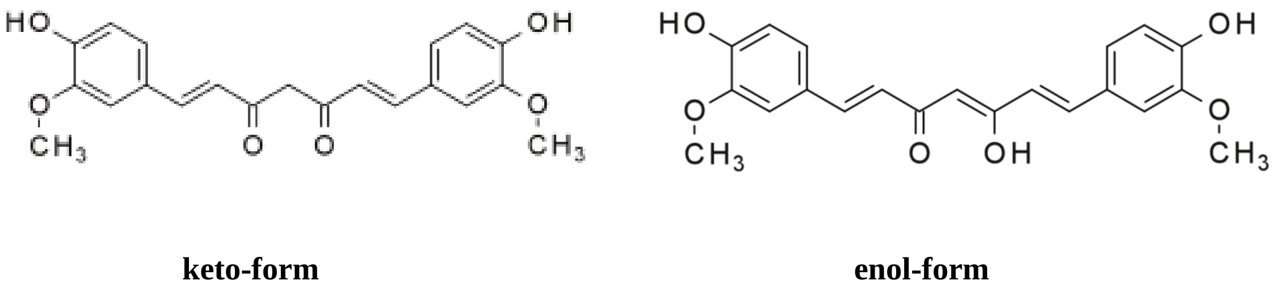
Keywords: Modified screen-printed sensor; Modified carbon paste sensor; Determination of iron(II); 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (MMCHH); Water Samples.

1. INTRODUCTION

Iron is believed to be the sixth most abundant element in the universe and the fourth most abundant on earth. The iron concentration in the layers of the earth structure ranges from high (probably greater than 80%, perhaps even nearly pure iron crystal) at the inner core, to only 5% in the outer crust. Iron is second in abundance to aluminium among the metals and fourth in abundance in the crust. It is the most abundant element by mass of our entire planet, consisting 35% of the earth mass as a whole. It is also one of the most important elements in the biological systems, playing a significant role in the oxygen transport, storage and in the electron transport. It is a fact that, with only a few possible exceptions in the bacterial world, there would be no life without iron [1-3]. On the one hand, if the iron concentration exceeds the normal level in the body, it may become a potential health hazard as iron deficiency leads to anemia. Excess iron in the body causes liver and kidney damage (hemochromatosis). Some iron compounds are suspected to be carcinogens [4-10].

Although ion selective electrodes could be very useful for routine determination of iron, there are only few reports of ion selective iron electrodes in the literature [11-15]. While some of them were prepared with ion exchangers [16-18] and a few of them with ionophores [19-23] and some of them were prepared as solid state electrodes [24,25]. Most of them were less selective and had long response time; their stability was also not good. Some electrodes have been prepared using porphyrins as ionophores and crown ether derivatives for different varieties of membrane sensors [14,15,26-30].

2-Methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one ionophore (MMCHH) (Scheme 1) is an important commercial crop grown for its aromatic rhizomes. It has been used as a condiment, preservative and traditional medicine for treating certain diseases since 4000 B.C. India is the largest MMCHH producer, importer and exporter. However, many other Asian, Latin American and Caribbean countries now produce 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one. Global 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one production is approximately 1100,000 t/year [31-33]. Today, it is used primarily as a natural coloring agent to replace synthetic dyes in chutneys, pickles, mustard, butter and cheese among other products [34,35]. Most importantly, MMCHH is employed in the preparation of curry.



Scheme 1. Structure of MMCHH.

In this study, we were also motivated to investigate the fabrication and characterization of a new modified carbon paste and screen-printed sensors based on 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (MMCHH) as a suitable ionophore (Scheme 1). The electrodes were applied for the determination of iron ions in spiked real water samples with satisfactory results in comparison with atomic absorption spectrometry.

2. EXPERIMENTAL

2.1. 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 electrodes was used. Digital burette was used for the field measurement of Fe(III) ion under investigation. 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.

2.2. Reagents

All chemicals used were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Ferric chloride [$FeCl_3.6H_2O$] was supplied from Koch Light, Ethylenediaminetetraacetic acid (EDTA) was supplied from El Nasr pharmaceutical chemical company and 2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (MMCHH) was supplied from BDH. For making ISEs the following reagents were used: *o*-nitrophenyloctylether (*o*-NPOE) was supplied from Fluka, while di-n-octyl phthalate (DOP), dibutylphthalate (DBP) and dioctyl sebacate (DOS) were supplied from BDH. In addition, tricresylphosphate (TCP), polyvinylchloride (PVC relative high molecular weight) and graphite powder (synthetic 1–2μm) were supplied from Aldrich was used for the fabrication of different electrodes.

2.2.1. Samples

Different water samples were collected. They included formation water (Amry deep (7), sample 1 and Falak (11), sample 2, from Western Desert, Agiba Petroleum Company, Egypt and Karama, al-Wahhat-al-Bahhriyah, Qarun Petroleum Company, sample 3, Egypt), tab water (sample 4), river water (sample 5; Mansoura, El-Dakahlia, Egypt) and sea water (Marsa Matrouh in Mediterranean Sea area, sample 6, Egypt).

2.3. Procedures

2.3 1. Preparation of modified carbon paste sensors (MCPEs)

A 500 mg pure graphite powder and 5-12.5 mg MMCHH ionophore are transferred to mortar and mixed well with plasticizer (0.2 mL of *o*-NPOE, TCP, DOP, DBP or DOS). The modified paste is filled in the electrode body and kept in distillated water for 24 h before use [14,36,37]. A fresh surface was obtained by gently pushing the stainless-steel screw forward and polishing the new carbon-paste surface with filter paper to obtain a shiny new surface.

*2.3.2. Preparation of the modified screen-printed sensors (M*SPS)

Modified SPEs were printed in arrays of six couples consisting of the working and the reference electrodes (each 5 × 35 mm) following the procedures previously described [36-42]. A polyvinyl chloride flexible sheet (0.2 mm) was used as a substrate which was not affected by the curing temperature or the ink solvent and easily cutted by scissors. The working electrodes were prepared depending on the method of fabrication. The working electrodes were printed using homemade carbon ink (prepared by mixing 5-12.5 mg of MMCHH ionophore, 450 mg TCP, 1.25 g of polyvinyl chloride (8%) and 0.75 g carbon powder). They were printed using homemade carbon ink and cured at 50 ^{o}C for 30 min. A layer of an insulator was then placed onto the printed electrodes, leaving a defined rectangular shaped (5 × 5 mm) working area and a similar area (for the electrical contact) on the other side. Fabricated electrodes were stored at 4 ^{o}C and used directly in the potentiometric measurements.

2.3.3. Calibration of the new electrodes

The new MSPEs and MCPEs were calibrated by immersion in conjunction with a reference electrode in a 25-mL beaker containing a 2.0 mL of acetate buffer solution of pH 3. Then 10 ml aliquot of iron solution of concentrations ranging from 1×10^{-7} to 1×10^{-2} mol L^{-1} was added with continuous stirring and the potential was recorded after stabilization to ±1 mV. A calibration graph was then constructed by plotting the recorded potentials as a function of -log [Fe(III)]. The resulting graph was used for subsequent determination of unknown iron concentration [14,15].

2.3.4. Determination of iron in spiked real water samples

About 5 ml water samples were transferred to a 25 ml beaker, definite concentration of iron solution was added and the pH was adjusted to 3. The content was estimated via potentiometric calibration using MCPEs and MSPEs as sensing electrodes. The method was repeated several times to check the accuracy and reproducibility of the proposed method [14,15,43].

3. RESULTS AND DISCUSSION

2-methyl-6-(4-methylenecyclohex-2-en-1-yl)hept-2-en-4-one (MMCHH) is used as an effective ionophore for the construction of iron-selective MCPEs (sensors I and II) and MSPEs (sensors III and IV). Response characteristics of modified CPEs and SPEs were investigated as shown in Table 1. The MCPEs were found to have linear response over wide concentration range of 4.3×10^{-7}-1×10^{-2} mol L^{-1} (for electrodes I and II) and 1×10^{-7}-1×10^{-2} mol L^{-1} (for electrodes III and IV) of Fe(III) ion with trivalent cationic slopes of 18.5±0.9, 19.3±0.5, 19.1±0.2 and 19.8±0.05 mV decade^{-1} for sensors (I), (II), (III) and (IV), respectively.

Table 1. Response characteristics of MCPEs (electrodes I, II) and MSPEs (electrodes III, IV).

Parameter	MCPEs		MSPEs	
	I	II	III	IV
Slope (mV/decade)	18.5±0.9	19.3±0.5	19.1±0.2	19.8±0.05
Standard deviation (SD)[a]	0.47	0.29	0.31	0.15
Relative standard deviation (RSD%)[a]	1.02	0.86	0.79	0.63
Concentration range (mol/L)	4.3×10^{-7} - 1×10^{-2}		1×10^{-7} - 1×10^{-2}	
Limit of detection (mol/L)	4.3×10^{-7}		1×10^{-7}	
Limit of quantification (mol/L)	12.9×10^{-7}		3.0×10^{-7}	
Working temperature range (ºC)	(10-60)		(10-60)	
Working pH range	1.8-6	1.5-6	1.5-6.5	1.5-6.5
Response time (sec)	12	10	7	5
Correction coefficient, r	0.995	0.998	0.998	0.999
Life time (days)	55	70	130	150
Accuracy (%)	98.70	99.00	99.35	99.90

3.1. Effect of the electrode composition

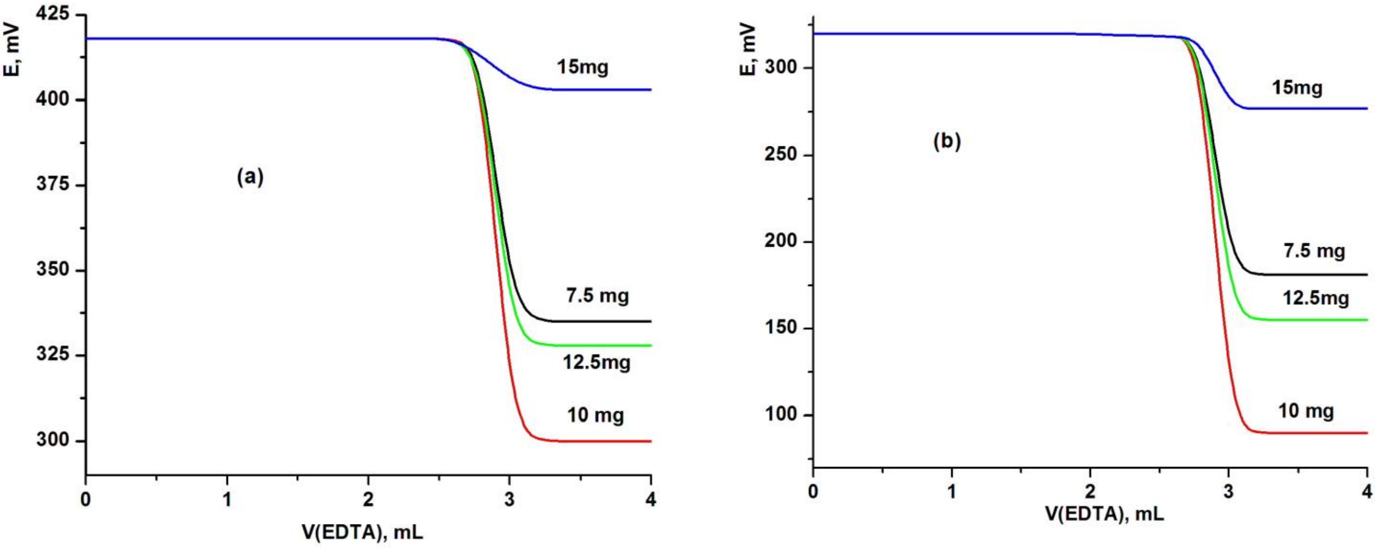


Figure 1. Effect of MMCHH ionophore contents on (a) MCPE and (b) MSPE sensors using TCP plasiticizer.

It is well known that the sensitivity and selectivity obtained for a given ionophore depend significantly on the paste composition and the nature of solvent mediator and additives used. Thus, the influences of the paste composition, nature and amount of plasticizer, and amount of MMCHH as ionophore additive on the potential response of the Fe(III) electrodes were investigated. Thus, four MCPEs and four MSPEs sensors were fabricated in order to determine the best electrode composition. The weights of MMCHH were varied as 7.5, 10, 12.5 and 15 mg (w/w%). The potentiometric titration was carried out for each electrode and the resulting potential breaks at the end point were found to be 74, 110, 81 and 7 mV mL^{-1} and 133, 223, 158 and 41 mV mL^{-1} for MCPEs and MSPEs sensors, respectively. These electrodes give sharp and reproducible inflection at the end point (110 and 223 mV mL^{-1} for MCPEs and MSPEs sensors, respectively). These results indicate that the highest potential break at the end point was evaluated using 10 and 10 mg of MMCHH ionophore for MCPEs and MSPEs sensors, respectively. But increasing the amount of MMCHH ionophore over 10 mg, the total potential change decreased as shown in Figure 1. It should be noted that the presence of a lipophilic anion in cation-selective electrodes not only diminishes 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 electrodes.

3.2. Effect of plasticizer

The influence of solvent mediator (plasticizer) type and concentration on the characteristics of the Fe(III) modified carbon paste and screen-printed sensors were investigated using five solvents with different polarities namely *o*-NPOE, TCP, DOP, DBP and DOS. The presence of plasticizers not only improves the workability of the sensor, but also contributes significantly to the improvement of the working concentration range, stability and life span of the electrode. The potential break at the end point of the electrodes (MCPEs and MSPEs) were as measured and found to be 139, 110, 90, 73 and 51 mV mL^{-1} and 253, 223, 169, 101 and 63 mV mL^{-1} for MCPEs and MSPEs, respectively (Figure 2). The results show that the best performance is attributed to the electrodes which are prepared using *o*-NPOE and TCP plasticizers which have the highest dielectric constant.

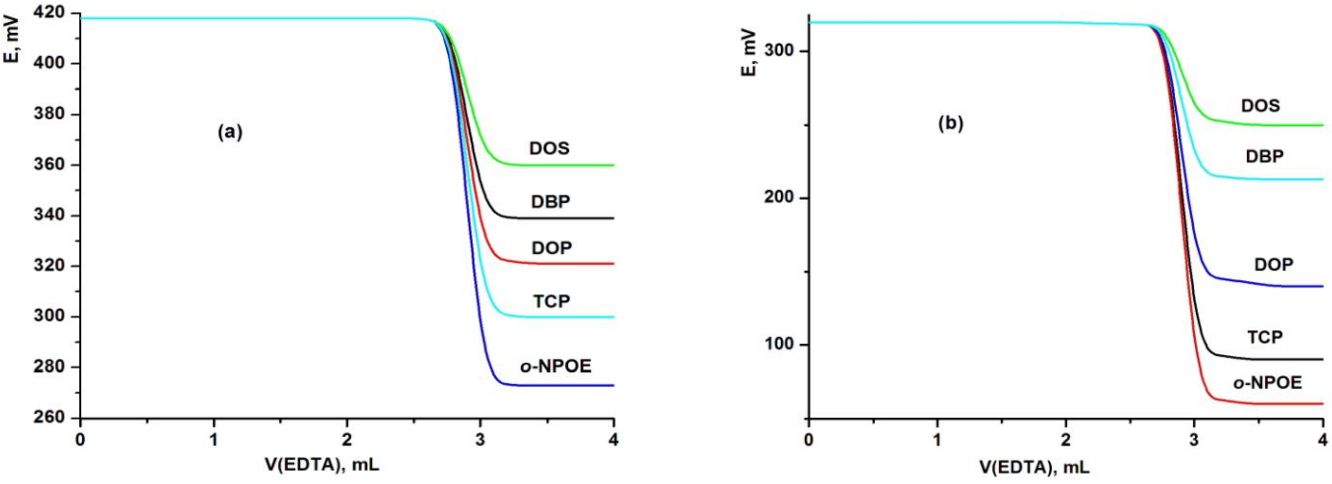


Figure 2. Effect of plasticizer type on the performance of (a) MCPE and (b) MSPE sensors.

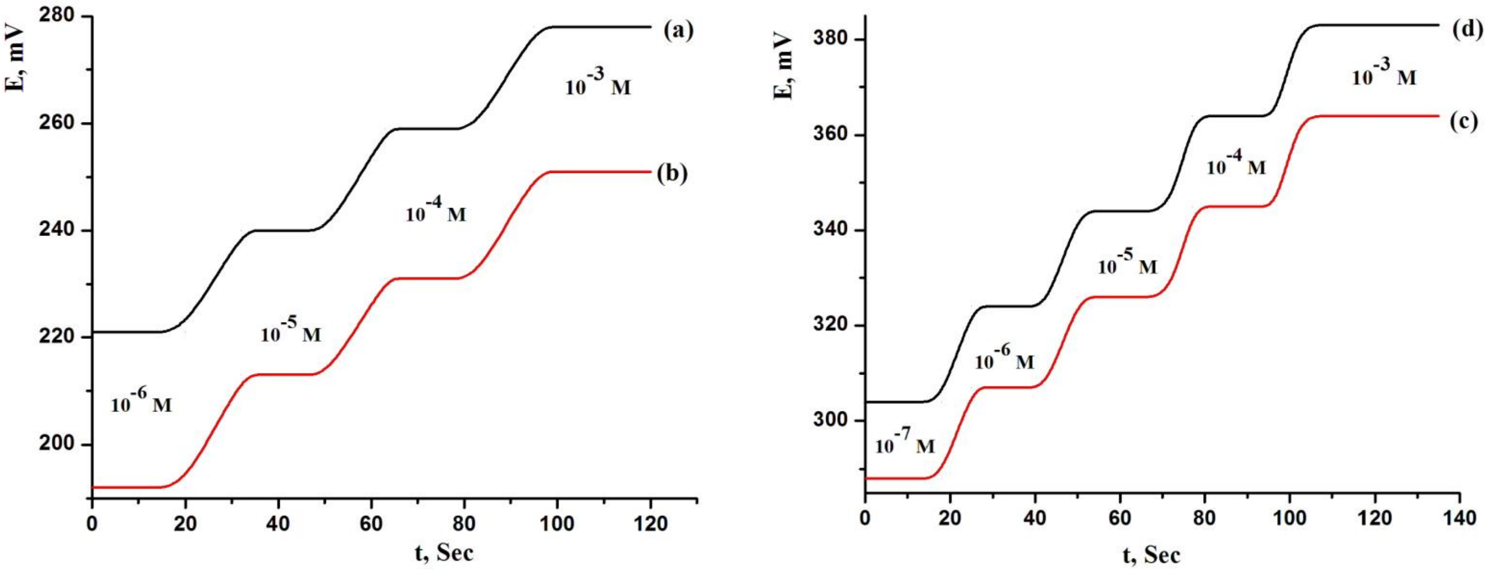


Figure 3. Dynamic response time of Fe(III) sensors of MCPEs [(a) electrode (I) and (b) electrode (II)] and MSPEs [(c) electrode (III) and (d) electrode (IV)].

3.3. Response Time

The response time of the electrodes (I-IV) was measured after successive immersion of the electrode in a series of iron solutions, in each of which the Fe(III) concentration was increased 10-fold, from 1.0×10^{-7} to 1.0×10^{-3} mol L^{-1}. The static response time thus obtained was 12, 10, 7 and 5s (for electrodes I, II, III and IV) of 1.0×10^{-3} mol L^{-1} Fe(III) concentration. At lower concentrations, however, the response time was longer and reached 17, 14, 10 and 7 s (for electrodes I, II, III and IV) of 1.0×10^{-6} (for electrodes I and II) and 1.0×10^{-7} (for electrodes III and VI) mol L^{-1} Fe(III) concentration. The actual potential versus time traces is shown in Figure 3. The potentials remained constant for approximately 3 min, after which a very slow change within the resolution of the meter was recorded. The sensing behavior of the MCPEs and MSPEs electrodes did not depend on whether the potentials were recorded from low to high concentrations or vice versa.

3.4. Lifetime of Fe(III) sensors

The response of Fe(III) carbon paste (electrodes I and II) and screen-printed (electrodes III and IV) sensors were examined at regular intervals to check the reproducibility and lifetime of the sensors (Figure 4). It was observed that during the long time period of 55, 70, 130 and 150 days, the slope of the sensor drifts only by 1.2 mV decade^{-1} from 18.5–17.3, 19.3–18.1, 19.1-17.9 and 19.8–18.6 mV decade^{-1} (for electrodes I, II, III and IV), respectively and detection limit is increased by a small factor. But after five months, the electrode characteristics significantly drifted away from the Nernstian behavior. This may be attributed to the decrease in the quantity of ionophore and the plasticizer in the paste due to migration of these components. Therefore, MCPEs and MSPEs can be used over a period of two and five months without any considerable change in the value of the slope, working concentration range and detection limit [44].

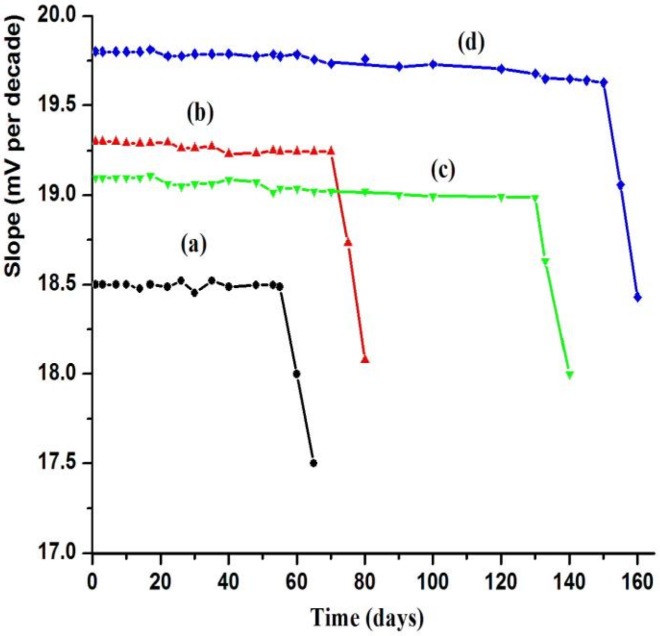
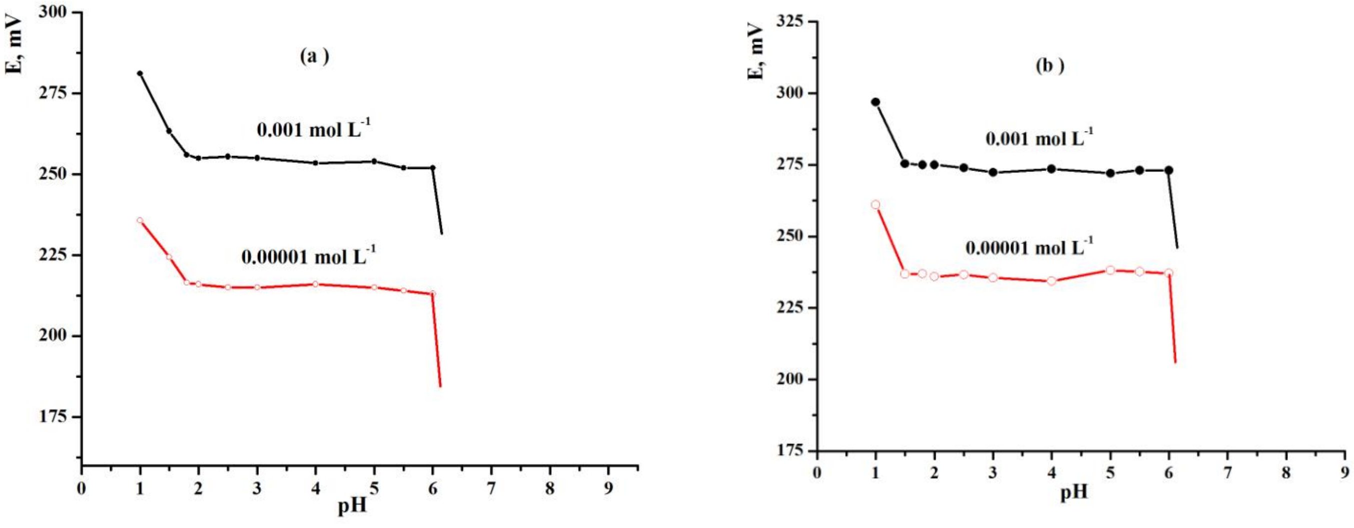


Figure 4. Life time of Fe(III) ion selective electrodes: MCPEs [(a) electrode (I) and (b) electrode (II)] and MSPEs [(c) electrode (III) and (d) electrode (IV)].

3.5. Effect of pH

The pH dependence of response of the electrodes (I, II, III and VI) have been tested in the range of 1.0 - 9.0 at two Fe(III) concentrations of 1.0×10^{-3} and 1.0×10^{-5} mol L^{-1} Fe(III) ions. The pH was adjusted with dilute nitric acid and sodium hydroxide solutions. The potential of the sensors were determined as a function of pH and the results are shown in Figure 5. The potential remains constant over the pH range of 1.8-6.0, 1.5-6.0, 1.5-6.5 and 1.5-6.5 for electrodes (I, II, III and VI), respectively, which may be taken as the working pH range of the sensors assembly.



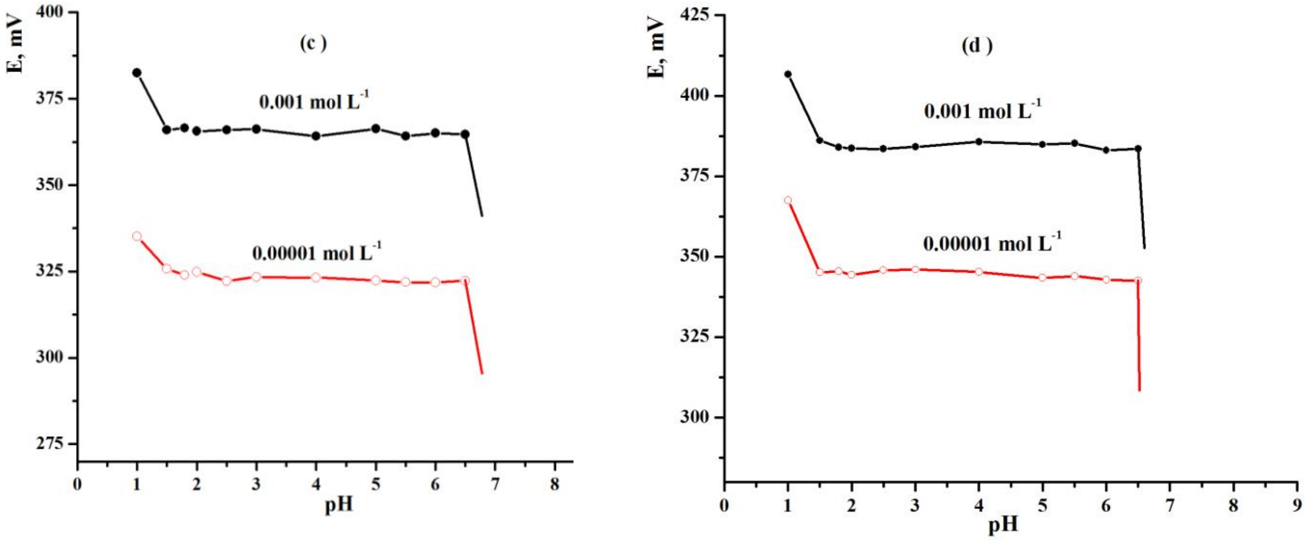


Figure 5. Effect of pH of the test solution on MCPEs [(a) electrode (I) and (b) electrode (II)] and MSPEs [(c) electrode (III) and (d) electrode (IV)].

At pH lower than 1.5, the interference of H^+ ions is more which is due to the high rate of diffusion of H^+ ions from sample solution to membrane matrix (extract H^+ ion) where they interact with carrier and its protonation takes place resulting in decreased selectivity of Fe(III) ions. In this case, the sensors then respond to hydrogen ions. At pH higher than 6.5, the deviation in the electrode response is due to the formation of some hydroxyl complexes of Fe(III) ion in solution [14,15,45,46].

3.6. Effect of temperature

On the test solution, calibration graphs (electrode potential (E_{elec}) versus p[Fe(III)]) were constructed at different test solution temperatures (10 - 60 ^{o}C). For the determination of the isothermal coefficient (dE/dt) of the electrodes, calibration graphs [E^{o}_{cell} versus p[Fe(III)] were constructed at different test solution temperatures covering the range of 10- 60 °C. The electrodes exhibit good Nernstian behavior in the temperature range. E^{o}_{cell} at different temperatures were obtained from calibration graphs as the intercepts at p[Fe(III)] = 0 (after subtracting the values of the standard electrode potential of the Ag/AgCl electrode at these temperatures) and was plotted versus (t-25), where t was the temperature of the test solution in ^{o}C . A straight line plot is obtained according to Andropov's equation [[12,14,19-23,39,41]]:

$$E^{o}_{Cell} = E^{o}_{Cell(25)} + (dE^{o}/dt)_{Cell}\ (t-25)$$

where $E_{(25)}$ is the standard electrode potential at 25 ^{o}C, t is the temperature in unit celsius, and the slope of the straight-line obtained represents the isothermal coefficient of the electrodes. The electrodes (I), (II), (III) and (IV) were found to have isothermal coefficient of 0.00293, 0.00287, 0.00253 and 0.00189 mV/ºC, respectively (Figure 6). The values of the obtained isothermal coefficient of the electrodes indicate that electrodes (III) and (IV) have high thermal stability within the investigated temperature range than electrodes (I) and (II). The investigated electrodes were found to be usable up to 60 ^{o}C without noticeable deviation from the Nernstian behavior of the sensors (I), (II), (III) and (IV), respectively.

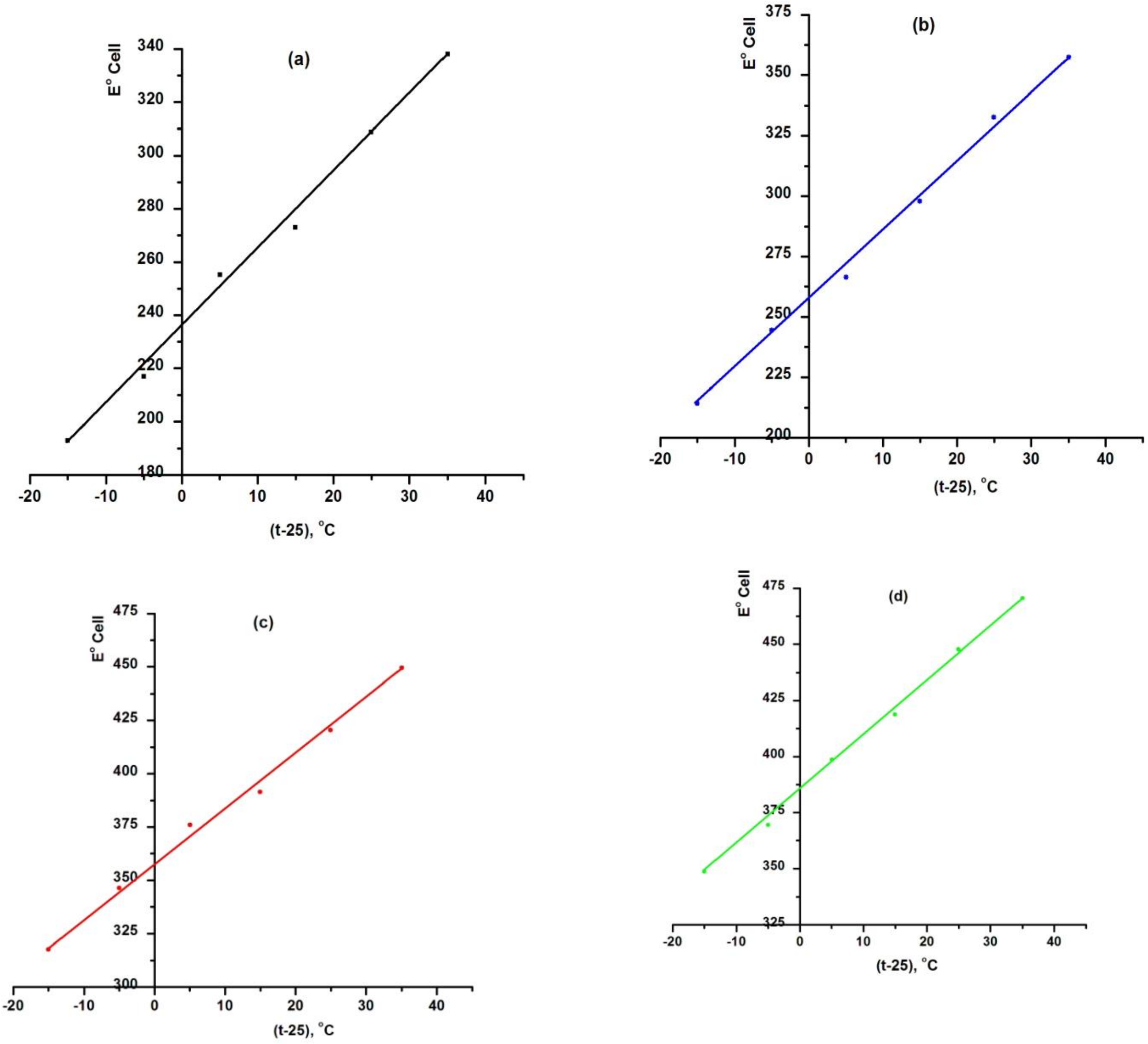


Figure 6. Effect of temperature on the performance of MCPEs [(a) electrode (I) and (b) electrode (II)] and MSPEs [(c) electrode (III) and (d) electrode (IV)].

3.7. Potentiometric selectivity

One of the most important characteristic of any ion electrode was its response to the target ion to be measured over other ions and species present in the solution. This characteristic was expressed in terms of the potentiometric-selectivity coefficient. In this study, potentiometric-selectivity coefficients for some cations and anions tested were determined by the mixed-solution method (MSM) [12]. A fixed concentration of Fe(III) (1×10^{-3} mol L^{-1}) and different amounts of interfering species (x) were used to check the selectivity coefficients in accordance with Eq. (1).

$$K^{pot}_{Fe(III),\,x}\; a_x^{(1/n)} = a_{Fe(III)} \left[\exp(E_2 - E_1)\, \frac{F}{RT} \right] - a_{Fe(III)} \qquad (1)$$

where, E1 and E2 were the electrode potentials for the solution of iron(III) alone and for the solution containing interfering species and iron(III), respectively. The potentiometric selectivity coefficient values ($K^{Pot}_{Fe(III),\, x}$) could be evaluated from the slope of the graph of $a_{Fe(III)}\{\exp(E_2{-}E_1)\,F/RT\}{-}a_{Fe(III)}$ versus $a_x^{(1/n)}$. The resulting selectivity coefficients are summarized in Table 2. It is clear from these data that the electrodes (I-IV) have a high selectivity for Fe(III) but Fe(II) interfere seriously so the electrode can detect the total iron.

Table 2. Potentiometric selectivity coefficients of some interfering ions using MCPEs (electrodes I and II) and MSPEs (electrodes III and IV).

Interfering ions (x)	$K_{Fe(III),\, x}$			
	MSM			
	I	II	III	IV
Ni^{2+}	5.2×10^{-4}	5.1×10^{-4}	3.8×10^{-4}	1.5×10^{-4}
Fe^{2+}	0.96	0.94	0.91	0.92
Mn^{2+}	6.3×10^{-4}	6.1×10^{-4}	5.2×10^{-4}	1.4×10^{-4}
Co^{2+}	8.3×10^{-4}	5.1×10^{-4}	3.1×10^{-4}	2.9×10^{-4}
Cu^{2+}	9.3×10^{-3}	9.8×10^{-3}	1.9×10^{-3}	0.8×10^{-3}
Mg^{2+}	7.0×10^{-3}	6.2×10^{-3}	2.1×10^{-3}	1.1×10^{-3}
Pb^{2+}	8.3×10^{-3}	7.1×10^{-3}	3.7×10^{-3}	8.9×10^{-4}
Sr^{2+}	6.5×10^{-4}	4.3×10^{-4}	3.1×10^{-4}	1.4×10^{-4}
Hg^{2+}	5.3×10^{-3}	5.0×10^{-3}	9.2×10^{-4}	9.7×10^{-4}
Ca^{2+}	4.7×10^{-3}	4.1×10^{-3}	2.2×10^{-3}	2.6×10^{-3}
Al^{3+}	5.7×10^{-5}	4.9×10^{-5}	2.8×10^{-5}	1.1×10^{-5}
Ce^{3+}	7.4×10^{-5}	7.1×10^{-5}	4.3×10^{-5}	3.2×10^{-5}
Ba^{2+}	4.1×10^{-5}	4.5×10^{-5}	3.7×10^{-5}	3.0×10^{-5}
Na^{+}	4.4×10^{-4}	4.1×10^{-4}	1.9×10^{-4}	0.7×10^{-4}
K^{+}	9.2×10^{-4}	8.8×10^{-4}	5.8×10^{-4}	3.4×10^{-4}
Ag^{+}	5.1×10^{-5}	3.6×10^{-5}	3.3×10^{-5}	1.7×10^{-5}
Cl^{-}	7.2×10^{-5}	7.1×10^{-5}	5.8×10^{-5}	5.1×10^{-5}

3.8. Analytical applications

In order to test the analytical applicability of the proposed sensors system, it has been applied for the determination of iron in river, formation water, tap water and sea water samples. The 5 mL of H_2O_2 solution (1 N) and 5 mL of HNO_3 solution (1 N) were added to each sample to oxidize Fe(II) to

Fe(III). Then, the resulting solution was diluted with distilled water in a 100 mL volumetric flask. The pH was adjusted to 3 with the use of concentrated HNO_3. The Fe(III) concentration in the spiked real water samples was determined directly by using the calibration and titration methods. The results were also determined by atomic absorption spectroscopy (AAS). The data obtained by potentiometry are in good agreement with the AAS data (Tables 3, 4).

Table 3. Potentiometric determination of Fe(III) in spiked real water samples using MCPEs (electrodes I and II) and MSPEs (electrodes III and IV) using calibration method.

Sample No.	[Fe(III)] mg/mL	[Fe(III)] mg/mL					RSD(%)				
	Taken	AAS	I	II	III	IV	AAS	I	II	III	IV
1	0.50	0.487	0.492	0.496	0.498	0.499	1.153	1.095	1.062	0.956	0.628
2	0.26	0.253	0.256	0.258	0.259	0.260	1.509	1.989	1.585	1.284	1.164
3	0.50	0.492	0.493	0.498	0.501	0.496	1.949	1.751	1.336	1.261	1.122
4	0.25	0.245	0.247	0.249	0.250	0.251	1.204	1.991	1.472	1.255	1.073
5	0.50	0.486	0.487	0.499	0.501	0.503	1.175	1.011	1.433	1.990	1.170
6	1.00	0.989	0.991	0.995	0.998	1.001	1.141	1.063	1.003	1.136	0.990
SD values for water samples (AAS= 0.025- 0.078), (electrode I = 0.055- 0.130) (electrode II = 0.033-0.108), (electrode III = 0.060- 0.199) and (electrode IV = 0.003- 0.037). Recovery% = (AAS = 97.2- 98.9), (electrode I = 98.4- 99.1) (electrode II = 99.2-99.8), (electrode III = 99.6-100.2) and (electrode IV = 99.20-100.6)											

Table 4. Potentiometric determination of Fe(III) in spiked real water samples using MCPEs (electrodes I and II) and MSPEs (electrodes III and IV) using titration method.

Sample No.	[Fe(III)] Found mg/mL					RSD(%)			
	[Fe(III)] Taken (mg/mL)	I	II	III	IV	I	II	III	IV
1	0.50	0.495	0.496	0.499	0.50	2.21	2.27	1.3	1.35
2	1.00	1.03	1.02	0.994	0.999	2.22	2.30	1.38	1.41
3	0.50	0.494	0.497	0.498	0.503	2.16	2.12	1.19	1.25
4	1.00	0.991	0.996	0.999	1.00	2.44	2.56	1.41	1.53
5	0.50	0.483	0.490	0.50	0.499	2.37	2.49	1.2	1.24

6	1.00	0.990	0.997	0.996	1.00	2.26	2.33	1.12	1.19
SD values for water samples (electrode I = 0.050- 0.098) (electrode II = 0.034-0.110), (electrode III = 0.042- 0.090) and (electrode IV = 0.023- 0.086). Recovery% = (electrode I = 96.6- 100.3) (electrode II = 98.0-102.0), (electrode III = 99.4- 100.0) and (electrode IV = 99.8- 100.6).									

3.8. Comparison study

Data reported in Table 5 compare several reported Fe(III)-selective electrodes with those of the proposed electrodes with respect to slope, response time, pH, linear range and detection limit [14,15,43,45-47]. It is noteworthy that the selectivity coefficients, linear range, slope and response time of the proposed electrodes are considerably improved with respect to those of the previously reported Fe(III)-selective electrodes (Table 5).

Table 5. Comparing some of the Fe(III)-MCPEs and Fe(III)-MSPEs characteristics with some of the previously reported Fe(III)-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (days)	Linear range (mol L^{-1})	Detection limit (mol L^{-1})
Proposed electrode(I)	18.5	12	1.8 - 6.0	55	4.3×10^{-7} - 1.0×10^{-2}	4.3×10^{-7}
(II)	19.3	10	1.5 - 6.0	70	4.3×10^{-7} - 1.0×10^{-2}	4.3×10^{-7}
(III)	19.1	7	1.5 - 6.5	130	1.0×10^{-7} – 1×10^{-2}	1.0×10^{-7}
(IV)	19.8	5	1.5 - 6.5	150	1.0×10^{-7} – 1×10^{-2}	1.0×10^{-7}
[14]	19.20	7	3.0 – 7.5	180	1.0×10^{-7} – 2.5×10^{-2}	1.57×10^{-7}
[15]	20.3	15	1.8 - 3	74	1.0×10^{-6} - 1.0×10^{-2}	6.4×10^{-7}
[15]	21.0	9	1.8 – 3.5	95	1.0×10^{-6} – 1.0×10^{-2}	4.8×10^{-7}
[43]	20.0	15	3.5 - 5.5	60	6.3×10^{-6} - 1.0×10^{-2}	5.0×10^{-6}
[45]	19.6	<10	1.6 - 4.3	72	1.0×10^{-7} - 1.0×10^{-2}	6.8×10^{-8}
[46]	20.2	<10	1.8 – 5.6	60	3.0×10^{-7} - 1.0×10^{-2}	2.0×10^{-7}
[46]	19.9	<10	1.8 – 5.8	60	6.9×10^{-7} - 1.0×10^{-2}	3.9×10^{-7}
[47]	19.9	<12	3.0 – 6.3	60	1.0×10^{-7} - 1.0×10^{-1}	5.0×10^{-8}

4. CONCLUSIONS

Determination of Fe(III) is important; therefore, this work describes a simple method for the determination of Fe(III) ion. The electrodes (I-IV) have a fast response time, good Nernstian behavior over wide concentration range and good selectivity. The paste is mechanically and chemically stable. The electrodes were successfully applied as an end point indicator electrodes in potentiometric titration. Table 5 compares the reported electrodes with other previous published electrodes.

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