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Low-cost Pencil-Graphite Multi-electrodes for Simultaneous Detection of Iron and Copper

Tugba OZER[1*]

[1] Yildiz Technical University, Department of Bioengineering, Faculty of Chemical and Metallurgical Engineering, Istanbul, 34220, Turkey

Abstract: Herein, two novel ion-selective electrodes are reported for simultaneous potentiometric determination of Fe^{3+} and Cu^{2+} ions. The liquid polymeric membrane components were optimized and the resulting pencil graphite electrodes gave Nernstian slopes of 20.7 mV/decade and 31.2 mV/decade with lower detection of limit of 1×10^{-6} mol L^{-1} and 2×10^{-6} mol L^{-1}, and wide pH range of 1.5-3.5 and 2.0-4.7 for Fe^{3+} and Cu^{2+} ions, respectively. The electrodes exhibited very fast response time (<6 s). In addition, the electrodes exhibited high selectivity for Fe^{3+} and Cu^{2+} ions against different cations, which were tested by matched potential method. The sensing platform using the optimized electrodes were integrated with the Internet of Things concept are suitable for simultaneous monitoring of Fe^{3+} and Cu^{2+} in real samples with high accuracy and precision.

Keywords: Potentiometric determination, ion selective electrode, copper, iron, internet of things, simultaneous determination.

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***Corresponding author. E-mail:** tozer@yildiz.edu.tr.

INTRODUCTION

Heavy metals have been widely used in a variety of industries such as petrochemicals, metal processing, organic chemicals, pharmaceuticals, pesticides, and plastics (1). Due to the discharge of industrial effluents into natural waters, heavy metal ions adversely affect environment and human health (2). Among the heavy metals, Fe and Cu are the first and second most widely used industrial metals worldwide (3). Fe^{3+} plays a significant role in various metabolic processes including oxygen transport, enzyme catalysis, DNA and RNA synthesis, and hemoglobin synthesis (4). Although Fe^{3+} is necessary for living organisms at low concentrations, biological disorders such as Alzheimer's, Parkinson's, and Huntington's diseases and, renal failure are seen with uptake of Fe^{3+} at high concentrations (5). Similarly, excess copper causes anemia, bone disorders, diarrhea, infertility, hepatic and renal damages, and neurological disorders, thus, permissible limits of copper in ground water and drinking water are set as 3 mg L^{-1} and 2 mg L^{-1}, respectively, by United States Environmental Protection Agency (EPA) and The World Health Organization (WHO) (6). In addition, the concentration of copper should not surpass 100-150 μg dL^{-1} (15.7-23.6 μmol L^{-1}) in human blood according to WHO. Thus, there is a need for a continuous and simultaneous sensing system for copper and iron to ensure water safety and public health.

There are many conventional techniques such as atomic absorption spectroscopy, atomic fluorescence spectrometry, chromatography, inductively coupled plasma mass spectrometry and ultraviolet-visible spectrophotometry for quantitative determination of heavy metals (7). Although these methods are highly sensitive and selective, they have several disadvantages such as labor-intensive and time-consuming experimental steps, the need of expensive and bulky instruments and specialized personnel (8). On the other hand, potentiometric method based on ion selective electrodes (ISEs) have been widely employed for quantitative and in-situ determination of target ion activity in aqueous samples owing to their advantages including simplicity, low-cost, rapid response, miniaturization, portability and low energy consumption (9). There have also been various reports of liquid membrane-based ISEs consisting of a plasticizer, a polymer (mostly polyvinyl chloride, PVC), an ionic additive, and an ionophore (10). Due to the semipermeable nature of PVC, it has been widely used for ISEs application (11). While the ionophore complexes with the metal ion of interest, the plasticizer enhances solubility and mobility of the ionophore in the membrane (12). In addition, lipophilic anionic additives such as sodium tetraphenyl borate and potassium tetrakis(4-chlorophenyl)borate (KTChPB) are utilized to enhance ISE sensitivity and selectivity while decreasing membrane resistance (11). Various ionophores such as calixarenes, crown ethers, macrocyclic polyethers, cyclic tetrapeptides, and thiophenes have been applied for the fabrication of Cu^{2+} and Fe^{3+} selective ISEs (13). Previously reported electrodes have drawbacks including higher limit of detection or interferences from other cations.

Porphyrins, which are a class of heterocyclic macromolecular compounds, can be utilized as ionophores for constructing cation-selective electrodes by grafting functional groups to the porphyrin ring (14). Recently, Chen et al. synthesized Gd-(5,10,15,20-tetrakis (4 carboxyphenyl) porphyrin to detect Fe^{3+} using colorimetric and fluorometric methods (15). Although low detection limits were achieved with the use of a polymer-based probe, their methods require bulky instruments an UV-visible spectrometer and fluorescence spectrometer, and they are not suitable for online monitoring of Fe^{3+}. In addition, their assay showed a limited linear range of 10^{-4} and 0.5×10^{-6} mol L^{-1}. In our study, a new membrane consisting of Fe(III) octaethylporphyrin chloride ($C_{36}H_{44}ClFeN_4$) as an ionophore was used to develop low-cost and disposable ISEs for the first time. Selectivity and detection limits of the fabricated Fe^{3+} and Cu^{2+} selective electrodes were improved due to the optimization of membrane components including lipophilic additives and plasticizers. The electrodes had fast response time (≤6 s) and showed selectivity over various interfering cations. Also, the Internet of Things (IoT) concept was tested for on-site and simultaneous environmental monitoring of Cu^{2+} and Fe^{3+} using our developed ISEs. The sensing platform exploits the IoT approach to transmit the data to smartphones through a cloud service for the end-users. Furthermore, the characteristics of the electrodes were compared with the previous literature reports. The developed multi-analyte sensor is advantageous over various methods due to their low-cost, fast response time, ease of fabrication, and applicability for the simultaneous quantification of iron and copper in water samples.

EXPERIMENTAL SECTION

Reagents and Chemicals

All chemicals and reagents were of analytical grade and utilized as received. Tetrahydrofuran (THF), KTChPB, Fe (III) octaethylporphyrin chloride, high molecular weight PVC and plasticizers, o-nitrophenyloctyl ether (NPOE), dioctylsebacate (DOS), dibutyl phthalate (DBP), dioctyl phthalate (DOP) were obtained from Fluka (Bucks, Switzerland). An 8B pencil graphite (2 mm, Koh-i Noor) was purchased from a local store and used without any pre-treatment. Ultrapure water (~18.2 MΩ·cm, 25 ºC, ELGA LabWater, UK) was utilized to prepare all solutions of metal ions from their nitrate salts. Sodium hydroxide and nitric acid solutions with concentration between 0.1-1 mol L^{-1} were used for adjusting solution pH.

Apparatus

The potentiometric measurements were conducted using a portable multi-channel potentiostat (sensitivity: ± 0.1mV) connected a smartphone through a WiFi module based on our previous study (16). A Ag/AgCl electrode (MF2052 model, BASi) was used as reference electrode (RE) during electrochemical measurements. Solution pH was tested with HI9126 (Hanna Instruments) portable pH/mV meter. All measurements were carried out at room temperature (25°C). Debye-Hückel equation was used to calculate the ion activity coefficients (17). The weight loss of the membrane was investigated as a function of temperature using a thermal gravimetric analyzer (TGA–DTA, TA Instruments, New Castle, DE, USA). Electrode holders were 3D printed (Formlab, USA). Modified electrodes and the Ag/AgCl electrode were mounted onto the 3D-printed holder for electrochemical measurements.

Procedure

To prepare membrane cocktails, the ionophore, KTChPB and DOS, DBP, DOP or NPOE plasticizers were dissolved in THF (18). The cocktail solution was let evaporate at room temperature. 20 µL of membrane cocktail was dropped on the surface of each pencil graphite electrode and left at ambient temperature for 2 h to allow the THF to evaporate. Finally, the electrodes were equilibrated into a 10^{-2} mol L^{-1} solution of each ion for 12 h before use. The ion-selective electrodes along with Ag/AgCl reference electrode were assembled using a fabricated 3D-printed holder. The potentiometric sensors and the reference electrode connected to the multi-channel potentiostat were dipped into 10 mL of the test solution in an electrochemical cell to perform potentiometric measurements as shown in Figure 1.

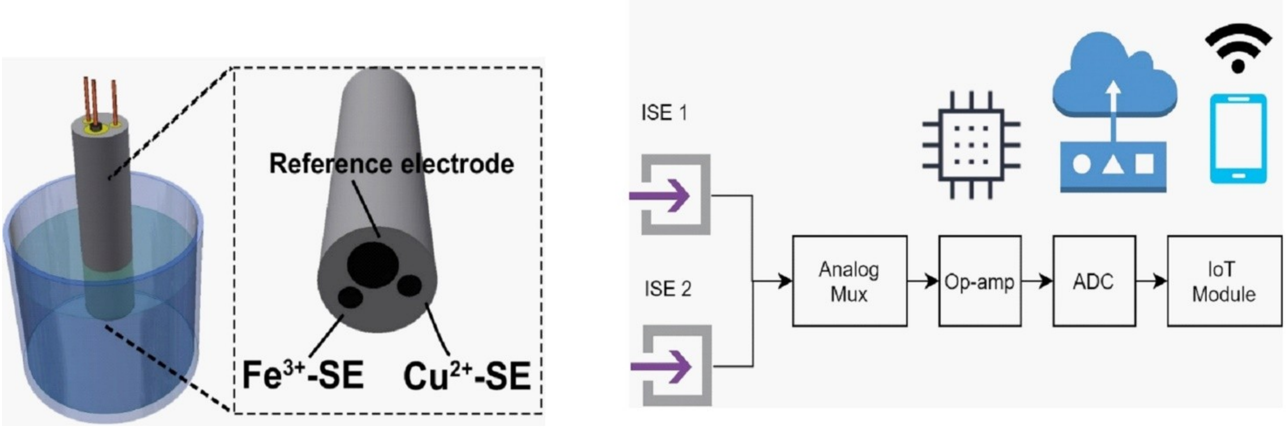

Figure 1: Schematic representation of the electrochemical measurement cell and diagram of the IoT data acquisition process.

RESULTS AND DISCUSSION

To investigate the potentiometric behavior of the electrodes towards different cations, the developed electrodes were submerged into nitrate/chloride solutions of corresponding cations, which were adjusted to pH=3, for overnight. The slopes of the corresponding potential values versus logarithmic activity of ion plots exhibited much lower than the Nernstian slopes excepting Fe^{3+} and Cu^{2+} ions, respectively (Figure 2a and 2b). Therefore, Fe(III) octaethylporphyrin chloride was selected for preparation of Fe^{3+} and Cu^{2+}-selective membranes.

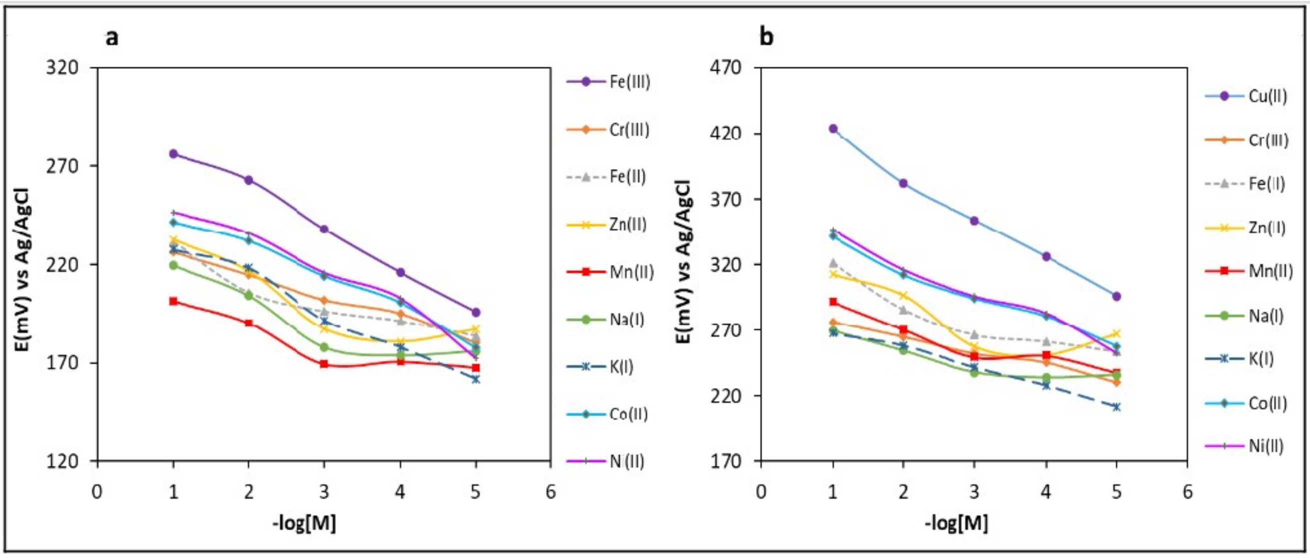

Figure 2: The EMF signals of (a) Fe^{3+}-selective electrode (b) Cu^{2+}- selective electrode towards different ions.

Optimization of the Proposed Electrodes

The properties and component amounts for the membrane have significant effect on the performance of an ISE due to rapid interfacial reaction of a target metal ion at the membrane-aqueous interface. After various compositions of the membrane were prepared, their potentiometric responses were recorded as a function of primary ions concentration. Ion-selective membrane was prepared using (by weight) 0.3% KTChPB, 1% ionophore, 65.8% plasticizer, and 32.9% PVC in THF. DOS and NPOE were used as plasticizers for preparation of iron-selective and copper-selective membrane, respectively. 200 mg of the membrane components were mixed in 2 mL of THF in a glass vial and homogenized using an ultrasonicator for 5 min. The optimized membrane composition was used to prepare the electrodes as presented in the experimental section. Then, a Mututoya digital micrometer (Japan) was used to measure the thickness of the membrane and was found to be 0.20 ± 0.09 mm.

The potential response values of the electrodes were recorded in different activities of Fe^{3+} and Cu^{2+} solutions and a calibration curve was plotted for each ion (Figure 3a and 3b). Nernstian slope, which is the function of different activity of analytes, is shown as the slope of the calibration curve.

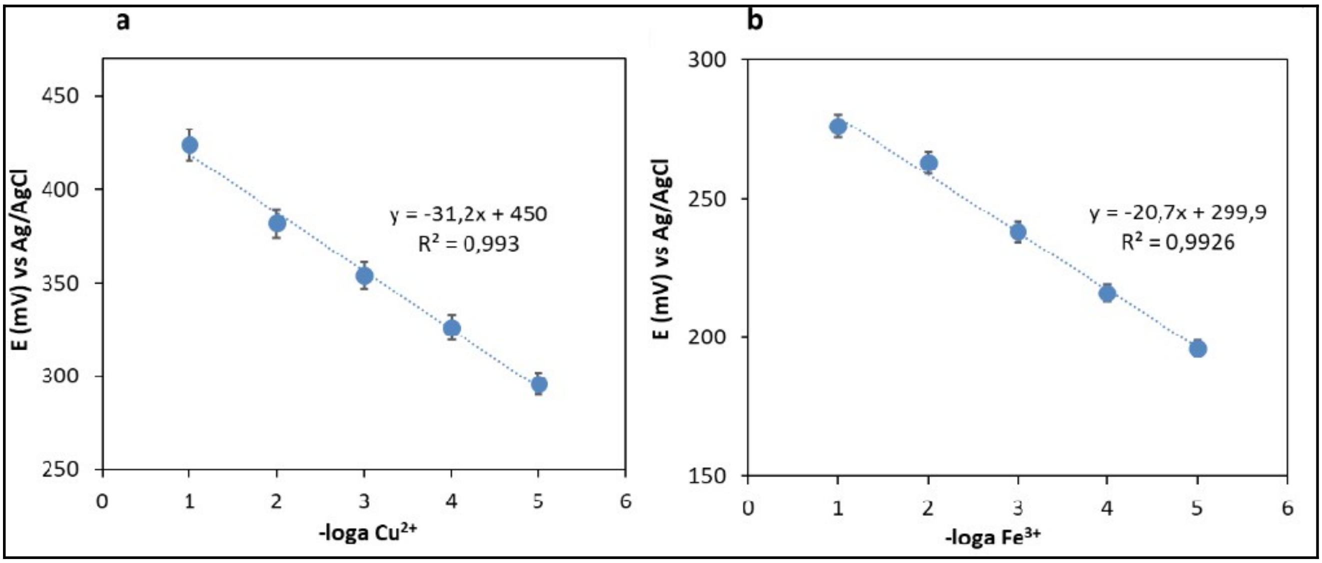

Figure 3: Calibration curve of the solid-contact (a) Cu^{2+} ISE and (b) Fe^{3+} ISE. Each error bar represents one standard deviation for three measurements.

For Fe^{3+}-selective electrode, the membrane composition (M5) including 1% ionophore, 65.8% DOS, 0.3% KTChPB and 32.9% PVC showed a slope of 20.7 mV/decade, which shows the ideal Nernstian slope for trivalent ions, and a limit of detection (LOD) of 1×10^{-6} mol L^{-1} calculated from intersection of two slope lines. The relationship between the potential response of the Cu^{2+}-selective electrode consisting of membrane M7 and logarithm of ion activity was linear from 1×10^{-5} mol L^{-1} to 1×10^{-1} mol L^{-1} with a slope of 31.2 mV/decade showing Nernstian response and a LOD of 2×10^{-6} mol L^{-1}. According to the results presented in Table 1, it was observed that the presence of KTpClPB in the membrane enhanced the calibration curve slope. The Donnan exclusion was improved by increased amount of KTpClPB to 30 mol% (19). Plasticizer NPOE is suitable for ISEs for detection of divalent ions (11). Moreover, a polymeric membrane including more polar plasticizer, NPOE (ε = 24), exhibited an increased potential response slope and a lower detection limit for Cu^{2+} compared to the membrane consisting of PVC-DOS (ε = 4.8). Similarly, better sensitivity and enhanced detection limit were obtained using PVC-DOS membrane for Fe^{3+} detection compared to membranes containing other types of plasticizers. According to these results, it was observed that the composition of ion selective membrane has significant impact on LOD values and sensitivity of the electrodes.

Table 1: Composition and characterization of Cu^{2+} ISE and Fe^{3+} ISE having PVC:Plasticizer (1:2) Membrane consisting of 1 wt % ionophore and KTChPB (mol %)

Electrode	KTChPB (mol %)	Plasticizer	Cu^{2+} ISE Slope (mV/dec)	Cu^{2+} ISE Detection limit (mol L^{-1})	Fe^{3+} ISE Slope (mV/dec)	Fe^{3+} ISE Detection limit (mol L^{-1})
M1	10	NPOE	27.3	7×10^{-6}	17.5	6×10^{-4}
M2	50	NPOE	35.4	1×10^{-6}	18.6	5×10^{-4}
M3	10	DOS	23.1	3×10^{-5}	18.9	3.2×10^{-5}
M4	50	DOS	27.3	5×10^{-5}	18.5	1×10^{-5}
M5	30	DOS	27.7	5×10^{-5}	20.1	1×10^{-6}
M6	-	DOS	-	-	15.2	5.4×10^{-4}
M7	30	NPOE	31.2	2×10^{-6}	18.7	6.5×10^{-5}
M8	30	DOP	26.5	1×10^{-4}	18.4	2.3×10^{-4}
M9	30	DBP	25.3	1×10^{-4}	18.2	5×10^{-4}
M10	-	NPOE	20.6	6.2×10^{-4}	-	-

Effect of pH

The pH effect on the potentiometric response of the electrodes was investigated at a fixed concentration

(1×10^{-3} mol L^{-1}) in the pH range between 1.0 and 8.0. The potential values are plotted in Figure 4a and 4b. It was observed that the potential response of the electrodes were constant at pH values in the range of 1.5-3.5 and 2.0-4.7, which could be considered as the working pH range of iron- and copper-selective electrodes, respectively. Due to the binding of H^+/OH^-, the potential changes might be observed with high acidity or alkalinity of the solution. Potential responses were not independent at pH lower than 1.5 and pH higher than 3.5 because of protonation of the ionophore and formation of ferric hydroxide in the solution, respectively. Similarly, change in equilibrium potential below 4.7 and above 2.0 could be due to hydrolysis of Cu^{2+} resulting in formation of more H^+ ions competing with Cu^{2+} (20).

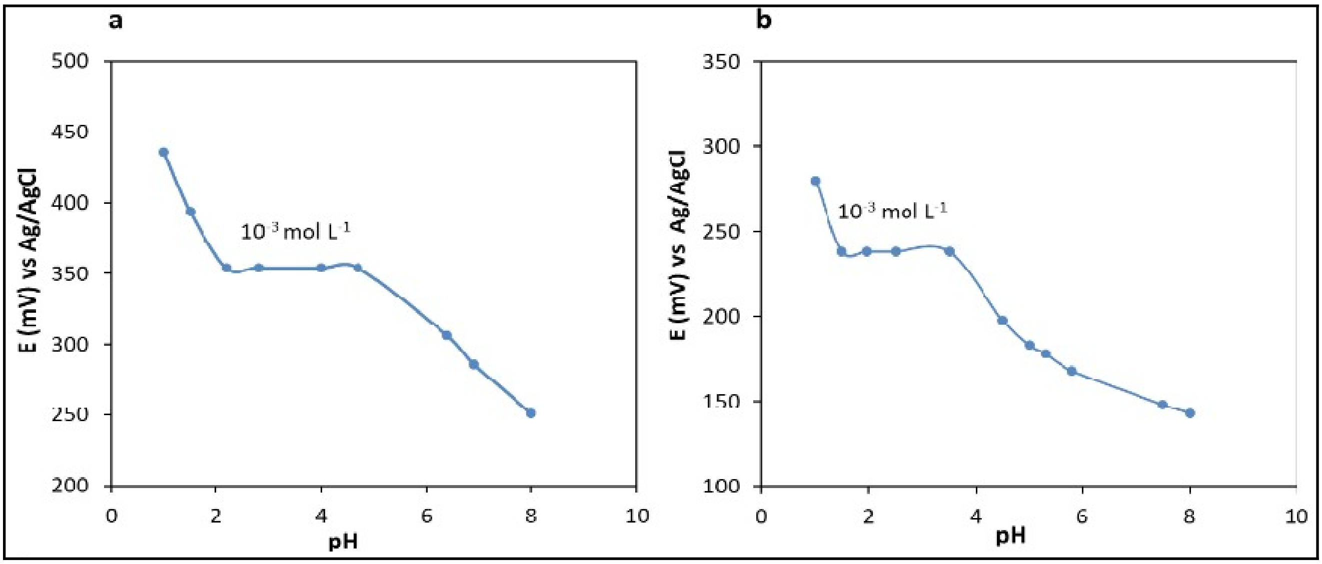

Figure 4: pH effect of the solutions to the EMF signals of (a) Cu^{2+} ISE and (b) Fe^{3+} ISE.

Response Time, Repeatability, Reproducibility, and Stability of the Electrodes

Electrodes response times were recorded with the time required to achieve 95% of final equilibrium electromotive force (EMF) signal after successive immersion of the test solutions within the concentration from 1.0×10^{-6} mol L^{-1} to 1.0×10^{-2} mol L^{-1}. The electrode response times were obtained as 6 s and 4 s for detection of Fe^{3+} and Cu^{2+}, respectively (Figure 5a and 5b), which is suitable for *in-situ* detection. The short response time of the electrodes was the result of the fast exchange kinetics between association and dissociation of ions with the porphyrin derivative ionophore at the membrane surface. It is necessary to obtain consistent performance after utilization of the electrodes repeatedly for real-time monitoring water. Thus, the repeatability and reproducibility tests (n=5) of the electrodes were performed in 1.0×10^{-3} mol L^{-1} Fe^{3+} and Cu^{2+} solutions. While RSDs (relative standard deviations) have been calculated as 2.4% and 2.7% for repeatability of Fe^{3+} and Cu^{2+} selective electrodes, respectively, RSDs were found as 3.2% and 3.0% for reproducibility of the electrodes. Moreover, long-term stability of the electrodes were investigated using same electrodes during eight weeks and the calibration plot slopes were decreased by 5% and 7% for Fe^{3+} and Cu^{2+} selective electrodes, respectively. Since the change were not significant, they could be used during this period.

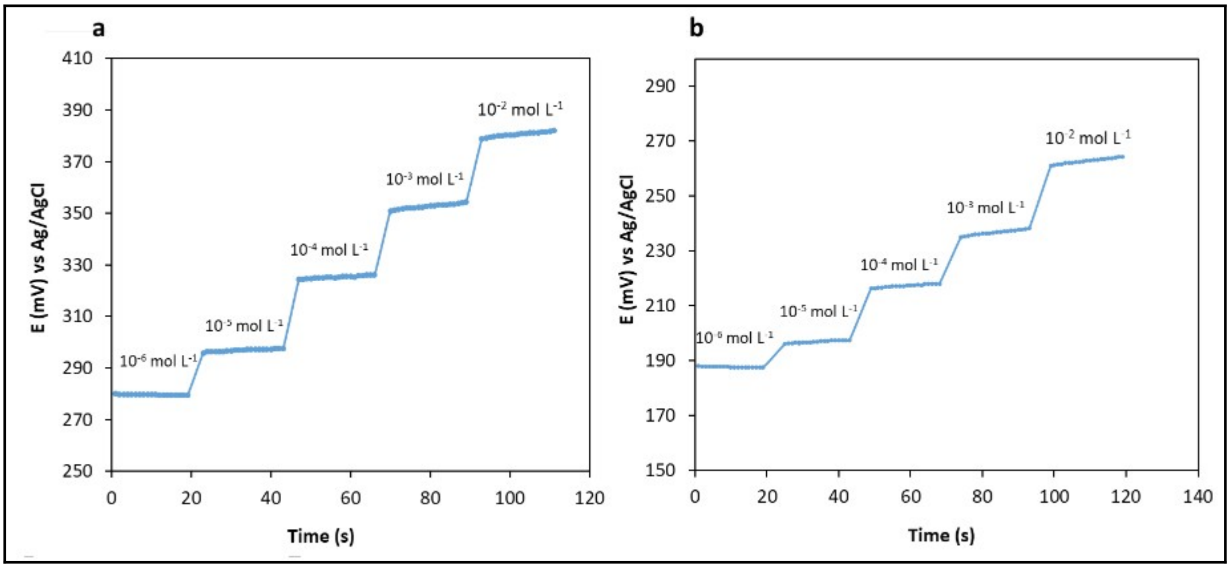

Figure 5: Response time of (a) Cu^{2+} ISE and (b) Fe^{3+} ISE for step change in concentrations.

Interference Study

The interference effect of other cations to the response of developed electrodes were investigated since selectivity coefficient represent the ability of the electrode to discriminate the target ion in the presence of interfering ions. For determination of the selectivity coefficients, the matched potential method (MPM) was used (21). The potential response (ΔE) value was recorded while the activity of primary ions changed from $a_A = 5\times10^{-4}$ mol L^{-1} to $a_A' = 5\times10^{-3}$ mol L^{-1}. Until the same ΔE was obtained, 0.1 mol L^{-1} solution of the interfering ion (a_B) was added to primary ion solution. The values of the sensor selectivity coefficient are evaluated using the equation (Equation 1) and presented in Table 2.

$$K_{A,B} = (a'_A - a_A)/a_B \qquad (1)$$

It can be seen in Table 2 that interferences with metal ions including Na^+, K^+, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} Fe^{2+}, and Cr^{3+} are negligible for the developed electrodes since the selectivity coefficient values were lower than 1 (22).

Table 2: Potentiometric selectivity coefficients of the developed ISEs.

	Log $K_{i,j}^a$	**Log $K_{i,j}^a$**
Ion	**Cu^{2+} ISE**	**Fe^{3+} ISE**
Na^+	-3.6	-4.3
K^+	-3.8	-4.4
Mn^{2+}	-2.8	-2.4
Zn^{2+}	-2.5	-2.4
Fe^{2+}	-3.0	-3.2
Cu^{2+}	-	-3.5
Ni^{2+}	-2.8	-2.9
Co^{2+}	-2.7	-2.2
Fe^{3+}	-3.5	-
Cr^{3+}	-4.5	-3.1

[a] Average value obtained from the three corresponding pairs of concentrations of Cu^{2+}, Fe^{3+} and the respective interfering cation.

Thermogravimetric Analysis

The results of the thermal analysis of the PVC/ionophore/NPOE and PVC/ionophore/DOS membranes are presented in Figure 6a and Figure 6b, respectively. Weight loss of the membranes started to be seen at 293 and 295 °C, respectively. At temperatures which the initial mass loss was observed, the loss of mass was equal to 11.68% and 14.59% for the slow decomposition of the material in the TGA measurement. The inorganic contents of the component underwent degradation based on the curve which was at 455 °C onwards. A single large peak was found at ~295 °C, which indicate the exothermic reaction in the composite in the DTGA curve (Figure 6b). The thermal decomposition of the polymeric membrane showed the similar general weight loss pattern to the reported values of 200-350 °C and 450-600 °C (23). These results include that the membranes are thermally stable and can be used at higher temperatures.

Analytical Applications

10 mL aliquot samples of tap water were spiked with standard Fe^{3+} or Cu^{2+} solutions at pH=3. For each increment, the concentration of Fe^{3+} or Cu^{2+} sample solution was calculated using the change in potential responses (mV). Next, the environmental water sample was used for application of the developed sensing platform integrated with WiFi to an IoT based web server (ThingSpeak.com) and the real-time data was validated with standard addition method and exhibited in Table 3. In addition, the electrodes were utilized to determine Fe^{3+} and Cu^{2+} ion concentration in spiked tap water with standard addition method (Table 3). There were no significant differences between the determination results of the developed electrodes. Since the results obtained using Fe^{3+}-ISE and Cu^{2+}-ISE are in good agreement with added values, the proposed methodology has great promise for accurate and simultaneous quantification of Fe^{3+} and Cu^{2+} ions in water samples.

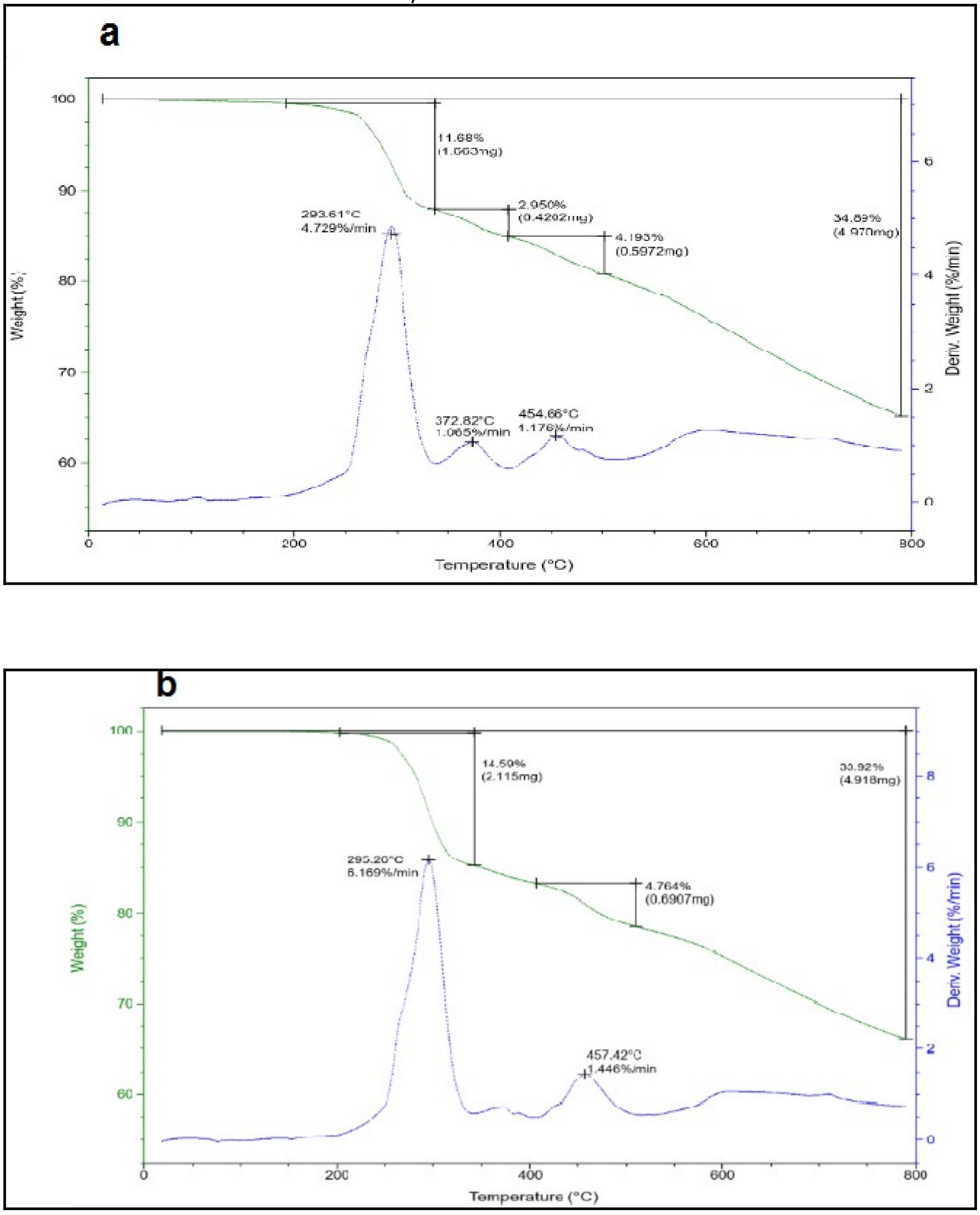

Figure 6: TGA spectra of (a) PVC/ionophore/NPOE and (b) PVC/ionophore/DOS up to 800 °C in nitrogen atmosphere.

Table 3: The results for the simultaneous detection of Cu^{2+} and Fe^{3+} in water samples using developed ISEs.

Sample	Added (μmol L^{-1})	Cu^{2+} ISE (measured value, μmol L^{-1})	Recovery (%)	Fe^{3+} ISE (measured value, μmol L^{-1})	Recovery (%)
Tap water 1	10	10.06±0.09	100.6	10.08±0.09	100.8
Tap water 2	20	20.3±0.1	101.5	19.9±0.1	99.5
Tap water 2	50	49.3±0.1	98.6	50.1±0.2	100.2
Environmental water	50	49.40±0.1	98.8	49.8±0.2	99.6

Comparison of the Fe^{3+} and Cu^{2+} Ion-Selective Electrodes with other ISEs

The response characteristics of other Fe^{3+} and Cu^{2+}-ISEs in the literature ions are compared with the proposed electrodes in Tables 4 and 5. Consequently, the developed electrodes for detection of Fe^{3+} and Cu^{2+} ions show better LOD and wider linear concentration ranges compared to the most of previous works.

CONCLUSION

It is important to detect metal ions in environmental samples to protect human health and ecosystem. The routine analysis of iron and copper are typically performed using bulky instruments such as atomic absorption spectroscopy, inductively coupled plasma-optical emission spectrophotometry, inductively coupled plasma mass spectrometry, and spectrophotometry, which require trained personnel to operate, large amount of samples/reagents and transportation of samples to the laboratory. On the other hand, the electrochemical sensors integrated with IoT provide autonomous decisions along with the obtained data, allowing rapid response time of sensing platforms in a user-friendly manner. The utilization of smart technology is crucial for in-field applications of environmental samples.

In this study, a new low-cost IoT-based sensing platform using disposable pencil graphite electrodes is developed for simultaneous and sensitive detection of Fe^{3+} and Cu^{2+} ions. Fe (III) octaethylporphyrin chloride was used as ionophore for the polymeric membrane Fe^{3+}-ISE and Cu^{2+}-ISE for the first time. The membrane components were optimized and resulted in improved Nernstian responses towards Fe^{3+} and Cu^{2+}, slope of 20.7 mV/decade and 31.2 mV/decade with LOD of 1×10^{-6} mol L^{-1} and 2×10^{-6} mol L^{-1}, respectively. The results demonstrate that the fabricated ISEs are able to be employed in a pH range of 1.5-3.5 and 2.0-4.7 for Fe^{3+} and Cu^{2+} ions respectively, with rapid response, good reversibility, and a long-time stability. The electrodes had no interference in the presence of common ions. High thermal membrane stability was observed in TGA studies. Furthermore, the ISEs were successfully used to detect Fe^{3+} and Cu^{2+} in spiked and real water samples with good recoveries. The proposed system is suitable for real-time monitoring of Fe^{3+} and Cu^{2+} ions in water.

Table 4: The developed Fe^{3+}-selective electrode compared to other electrodes in the literature.

Ionophore	**Linear Range (mol L^{-1})**	**LOD (mol L^{-1})**	**Response time (s)**	**pH range**	**Ref.**
1) Phosphorylated Calix-6-Arene Derivative	1.0×10^{-2}- 1.0×10^{-4}	1.0×10^{-5}	5	4.0-7.0	(24)
2) norfloxacin	1.0×10^{-1}- 1.0×10^{-5}	5.0×10^{-6}	10	3.0–8.0	(25)
3) morin-Fe^{2+} schiff-base complex	1.0×10^{-1}- 1.0×10^{-6}	4.5×10^{-7}	<10	5.0-10.0	(26)
4) Iron (II) Phthalocyanines	1.0×10^{-1}- 1.0×10^{-6}	1.8×10^{-7}	<7	3.5-5.7	(18)
5) Iron(III) phosphate and silver sulfide	1.0×10^{-2}- 3.97×10^{-5}	2.41×10^{-5}	Not tested	1	(27)
6) Fe(III) octaethylporphyrin chloride	1.0×10^{-1}- 1.0×10^{-5}	1×10^{-6}	6	1.5-3.5	This work

Table 5. The developed Cu^{2+}-selective electrode compared to other electrodes in the literature.

Ionophore	**Linear Range (mol L^{-1})**	**LOD (mol L^{-1})**	**Response time (s)**	**pH range**	**Ref.**
1) 1-ethyl-3-methyl imidazolium chloride	1.0×10^{-1} - 1.0×10^{-7}	3.2×10^{-8}	5–10	2.5–6.0	(28)
2) Rhodamine 6g	1.0×10^{-2} - 4.3×10^{-7}	4.3×10^{-7}	15	4.0−7.5	(3)
3) phenanthroline–tetraphenyl borate	1.0×10^{-2} – 1.0×10^{-6}	1.0×10^{-6}	8	3.8 – 5	(29)
4) thiohydrazone and thiosemicarbazone ligands	1.0×10^{-2} – 1.0×10^{-5}	2.5×10^{-6}	2–18	-	(30)
5) cyclic tetrapeptide derivatives	1.0×10^{-2} – $3.1.0\times10^{-6}$	2.1×10^{-6}	<15	4.5 – 7	(31)
6) Fe (III) octaethylporphyrin chloride	1.0×10^{-1}- 1.0×10^{-5}	2×10^{-6}	4	2.0-4.7	This work

CONFLICT OF INTEREST

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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