



Development of Iron (III) Selective Coated Graphite Electrode Based on Schiff Base N, N'-BIS (2,4-Dimethoxybenzilidene) Ethylenediamine

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Abstract

A graphite electrode coated with a PVC-based membrane was developed for the potentiometric detection of Fe^{3+} ions, incorporating the Schiff base ligand N, N'-bis(2,4-dimethoxybenzilidene) ethylenediamine (L). The optimized membrane composition included 4% L, 2.5% NaTPB, 51% NPOE, and 42.5% PVC. This sensor effectively detected Fe^{3+} ions across a concentration range of 2.5×10^{-7} to 1.0×10^{-1} M, with a detection limit as low as 7.8×10^{-8} mol L⁻¹ and a response time of just 12 seconds. Stability tests revealed that the electrode maintained consistent performance for over 90 days, without significant degradation. The sensor also showed high selectivity towards Fe^{3+} ions, remaining effective in the presence of potential interfering species. Additionally, it functioned reliably within a pH range of 3.0 to 7.0 and was compatible with non-aqueous solvents (up to 20% v/v). The electrode was effectively utilized as an indicator for potentiometric titration of Fe^{3+} with EDTA and for accurate determination of Fe^{3+} ions in various sample matrices.

Keywords: Schiff base Coated graphite electrode, PVC membrane, Potentiometry, EDTA.

1. Introduction

Iron is a crucial trace mineral in the body, playing a key role in essential biological processes such as electron transport, storage, and oxygen movement [1,2]. It forms the foundation of critical molecules, including hemoglobin, myoglobin, and various haemenzymes, which are vital for enzyme functions. A deficiency in iron is a well-known cause of anemia [3-7], while elevated iron levels can contribute to an increased risk of heart disease, cancer, and conditions like hemochromatosis. Therefore, determining iron concentrations is important across industrial, pharmaceutical, clinical, and environmental settings [8,9]. Several methods, including atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP), and emission absorption spectrometry, can detect iron ions. While these techniques provide accurate results, they are expensive and not ideal for routine, real time analysis. On the other hand, potentiometric analysis using ion-selective electrodes offers a more practical, cost-effective, and efficient alternative for on-site analysis of materials.

Ion-selective electrodes (ISEs) with polymer-based membranes incorporating ionophores are essential tools for analytical applications in clinical, chemical, and environmental fields. They provide fast response, high selectivity, ease of operation, and cost efficiency, allowing precise detection of target ions across a wide concentration spectrum. Potentiometric sensors for cations and anions can be developed using specific metal–ligand interactions, which are



significant recognition mechanisms [10-17]. Numerous ionophores with great selectivity for Fe^{3+} ions have been produced to date for their selective determination in various samples. Numerous PVC membrane electrodes for various ions, including iron, have been documented [18-30].

In this article, we have made attempts to construct PVC based coated graphite electrodes of Schiff bases N, N'-bis (2,4-dimethoxybenzilidene) ethylenediamine (L) as ionophore. Membrane having different compositions of PVC, a plasticizer and anionic additive with ionophore L was coated on the graphite surface and investigated it as Fe (III) selective electrodes.

2. Experimental

Chemicals and reagents

The chemicals used in this study were of reagent grade and included oleic acid (OA), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP), benzyl acetate (BA), o-nitrophenyloctyl ether (o-NPOE), dioctyl phthalate (DOP), dioctyl sebacate (DOS), dibutyl sebacate (DBS), tributyl phosphate (TBP), tetrahydrofuran (THF), and potassium tetrakis(4-chlorophenyl) borate (KTpClPB). High molecular weight polyvinyl chloride (PVC) was also utilized. These materials were procured from E. Merck (Germany) and used directly without further purification. Additionally, o-phenylenediamine, ethylenediamine, and salicylaldehyde, all of reagent grade, were obtained from Loba Chemie (Mumbai, Maharashtra, India). A 0.1 M stock solution of metal ions was prepared using double-distilled water, and subsequent dilutions were made to achieve the desired concentrations. Where necessary, solution standardization was performed to ensure accuracy.

Apparatus

Potentiometric measurements were carried out at a controlled temperature of $25 \pm 0.1^\circ\text{C}$ using a digital pH/mV meter (ESICO International Digital Potentiometer, Model-118) in combination with a double-junction Ag/AgCl reference electrode. The pH values of the solutions were measured using a digital pH meter (ESICO International Digital pH Meter, Model-101), which utilized a glass electrode for pH detection and a calomel electrode as the reference.

3. Synthesis of Chelating Compound

Schiff bases L was synthesized according to the previously reported methods [31] as discussed here and the reaction schemes are shown in Figures 1.

Synthesis of N, N'-bis(2,4-dimethoxybenzilidene) ethylenediamine (L)

A reaction solution was prepared by dissolving 0.2 mL (3 mmol) of ethylenediamine and 1 g (6 mmol) of 2,4-dimethoxybenzaldehyde in 20 mL of absolute ethanol. The mixture was then heated under reflux at 80°C for a duration of 3 hours. After completion of the reaction, the resulting solid product was collected by vacuum filtration and subsequently dried under vacuum overnight. The synthetic scheme for the ligand (L) is illustrated in Figure 1.

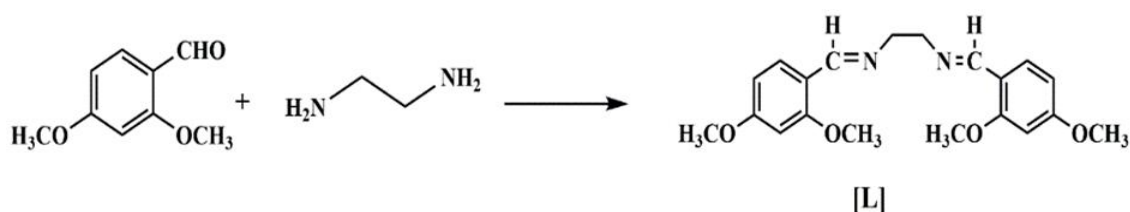


Figure 1: Scheme of synthesis of Schiff–base N, N'-bis (2,4-dimethoxybenzilidene) ethylenediamine (L) as ionophore.

Preparation of coated graphite electrode

Coated graphite electrodes employed in this study were prepared as described before [32]. A solution was prepared by dissolving the membrane components (ionophore, anion additives, PVC, and plasticizers) in 5 mL of tetrahydrofuran, which was then concentrated by evaporation. A copper wire was attached to one end of a polished graphite electrode (5 mm in diameter and 15 mm in length), and the opposite end was dipped into the concentrated

membrane solution. The electrode was left overnight to allow the solvent to evaporate, resulting in the formation of a thin PVC film on the electrode surface. Finally, the graphite electrode was placed inside a glass tube and sealed with epoxy resin to make it portable.

Conditioning of membranes and potential measurements

Prior to conducting potential measurements, all prepared electrodes were equilibrated to achieve stable and consistent potential readings. The graphite electrodes coated with the solution of 1 mM Fe (NO₃)₃ were allowed to equilibrate for four days before commencing the measurements. The potentials were then recorded across a broad concentration range (1.0 x 10⁻⁹ – 1.0 x 10⁻¹ M) of metal salt solution using the coated graphite electrode (CGE) in conjunction with an Ag/AgCl reference electrode on a digital potentiometer (Electronic India) at room temperature, following this cell setup:

Coated graphite electrode || Test solution || Hg/Hg₂Cl₂ | KCl (saturated)

The activity coefficients were computed using the Debye-Hückel equation, given as:

$$\log \gamma = -0.511 z^2 \left[\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} - 0.2\mu \right]$$

In this formula, γ stands for the activity coefficient, μ represents the ionic strength, and z indicates the ion's valency.

4. Results and Discussion

Determination of stability constants

Studies show that the Schiff base N, N'-bis(2,4-dimethoxybenzylidene) ethylenediamine (L) can interact with metal ions to form complexes. These complexes are with varied metals. Certain metal complexes of (L) have stability constants. Constants were identified by sandwich membrane method [33, 34]. These are detailed in Table 1. Formation constants values (Table 1.0) were obtained. They are for ion-ionophore complexes. The obtained values were collected using the sandwich membrane method. These values reveal an interesting pattern. The value of formation constant is the highest for Fe³⁺ complex. The ligand in this complex is L. The value is 5.94. None of the other metal ions matched this high value. We make an inference from these results. The ligand creates stable complexes with Fe (III). Conversely the stability with other metal ions is significantly lower. The high affinity of the ligand towards Fe³⁺ ion is evident. This prompted us to consider it for an important role in specific preparation. The preparation of a selective electrode. The electrode is specifically for Fe³⁺.

Table 1: Formation constants of ion-ionophore complex of (L) ionophore with different metal ions.

Cations	Formation constant (logβ _{IL_n}) ± S.D.
Ba ²⁺	2.21 ± 0.12
Ca ²⁺	2.12 ± 0.02
Ni ²⁺	2.96 ± 0.15
Cu ²⁺	2.23 ± 0.13
Co ²⁺	2.22 ± 0.04
Cd ²⁺	2.39 ± 0.14
Zn ²⁺	2.21 ± 0.09
Pb ²⁺	2.61 ± 0.13
Fe ³⁺	5.94 ± 0.12
Ce ³⁺	2.44 ± 0.02
Cr ³⁺	2.63 ± 0.07
Na ⁺	1.45 ± 0.05

Optimization of the Membrane Composition

Numerous investigations have demonstrated that ISE's performance characteristics are greatly impacted by the membrane's composition [35,36]. In order to determine which composition produced the greatest results across all



potentiometric properties, various membrane compositions were tested. Several electrodes were fabricated by adjusting the amounts of membrane materials, and their potentiometric properties were evaluated using a Fe^{3+} ion solution within a concentration range of 1.0×10^{-9} to 1.0×10^{-1} molL⁻¹. This study examines the performance of an electrode based on Schiff base L in combination with various plasticizers, such as o-NPOE, DOP, DBP, TBP, BA, DOS, and DBS, as shown in Table 2. It is well-documented that plasticizers enhance membrane sensor performance by altering the polarity of the membrane phase [37]. The findings of this investigation reveal that plasticized electrodes offer improved working concentration ranges and slopes. Among the different plasticizers tested, the coated graphite electrode C2 with o-NPOE exhibited the best results, including a slope of 19.8 mV/decade, a linear operating range of 2.5×10^{-7} to 1.0×10^{-1} M, and a lower detection limit of 7.8×10^{-8} M, as summarized in Table 2.

In neutral carrier-based cation selective electrodes, it is well known that an anion additive gives the electrode permselectivity by removing anion interference [38, 39]. Thus, two distinct anion additions (NaTPB and KTpCIPB) were added to the membrane composition in order to further examine the impact on these electrodes' performance. The findings showed that the electrodes based on L performed better when the lipophilic additive NaTPB was present, whereas the coated membrane electrode's performance characteristics significantly declined when KTpCIPB was present. Additionally, the electrode made without NaTPB (C13) had a non-Nernstian slope, a high detection limit, and a comparatively small working concentration range. These electrodes' altered performance could be the result of interacting ions in the test solution. Prior research has demonstrated that the highest electrode performance is achieved when a specific concentration of the lipophilic anion additive is used in the membrane phase. According to L, this investigation shows that 2.5% (w/w) NaTPB works well for all electrodes.

Additionally, the impact of ionophore concentration on these electrodes' performance was noted. Their potentiometric response was highly impacted by altering the ideal concentration of ionophore L (4%, w/w) in the corresponding electrode. The results make it evident that while electrodes C10 and C12 with lower ionophore concentrations provide inferior potentiometric responses, electrode C11 with higher ionophore concentrations than the ideal exhibits no improvement in performance.

Table 2: Membrane formulations of CGEs utilizing L and their potentiometric behavior as electrodes selective for Fe(III) ions

CGE No.	Composition of membrane (wt %)				Slope (mV/decade)	Linear working range (M)	Detection limit (M)
	Ionophore	Plasticizer	Additive	PVC			
C1	4		2.5,NaTPB	93.5	33.0	5.8×10^{-5} - 1.0×10^{-1}	3.2×10^{-5}
C2	4	51,NPOE	2.5,NaTPB	42.5	19.8	2.5×10^{-7} - 1.0×10^{-1}	7.8×10^{-8}
C3	4	51,DOP	2.5,NaTPB	42.5	32.5	1.7×10^{-6} - 5.0×10^{-2}	9.6×10^{-7}
C4	4	51,TBP	2.5,NaTPB	42.5	32.0	3.5×10^{-6} - 1.0×10^{-1}	1.8×10^{-6}
C5	4	51,DBP	2.5,NaTPB	42.5	28.0	5.0×10^{-6} - 1.0×10^{-2}	7.8×10^{-6}
C6	4	51,BA	2.5,NaTPB	42.5	25.0	7.3×10^{-6} - 5.0×10^{-2}	4.6×10^{-6}
C7	4	51,OA	2.5,NaTPB	42.5	23.0	4.8×10^{-6} - 5.0×10^{-2}	2.1×10^{-6}
C8	4	51,DOS	2.5,NaTPB	42.5		1.3×10^{-5} - 1.0×10^{-1}	8.4×10^{-6}
C9	4	51,NPOE	2.5,KTpCIPB	42.5	24.0	1.4×10^{-6} - 1.0×10^{-1}	8.2×10^{-7}
C10	3	51,NPOE	2.5,NaTPB	43.5	22.0	8.9×10^{-6} - 1.0×10^{-2}	6.1×10^{-6}
C11	5	51,NPOE	2.5,NaTPB	41.5	26.0	7.8×10^{-7} - 1.0×10^{-1}	6.7×10^{-7}
C12	-	51,NPOE	2.5,NaTPB	46.5	33.0	6.9×10^{-4} - 1.0×10^{-2}	4.4×10^{-4}
C13	4	51,NPOE	-	45.0	20.2	5.0×10^{-6} - 1.0×10^{-2}	2.5×10^{-6}

Potentiometric Characteristics of Fe^{3+} Selective Electrode

The calibration curves of the Fe (III) selective electrode was presented in Figure 3., which showed that the electrode no. C2 based on L displays Nernstian slope (19.8 ± 0.07 mV/decade) in the range of 2.5×10^{-7} - 1.0×10^{-1} M with a lower detection limit of 7.8×10^{-8} M.



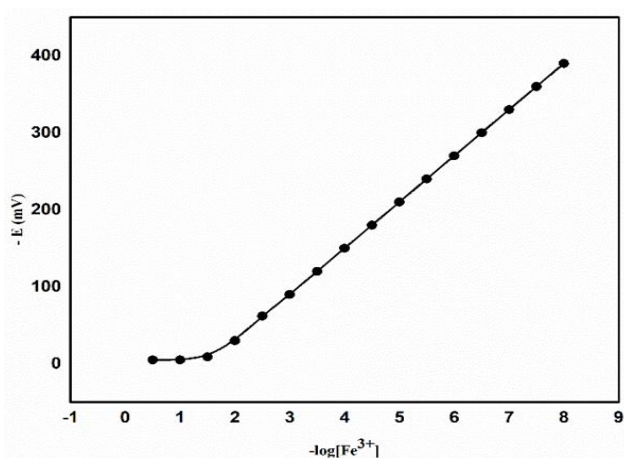


Figure 2: Calibration curves of the Fe (III) selective electrode CGE-C2.

Effect of pH Change

The effects of pH on the electrode's potential response at $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Fe}^{3+}$ ion solutions across a pH range of 1.0 to 10.0 were examined, and the findings are displayed in Figure 3. The pH of the test solution was adjusted using 0.1 M HNO₃/NaOH in order to investigate the operating pH range. For the electrode B2 based on L, the pH-potential curve showed that the potential stays constant as the pH changes between 3.0 and 7.0. Potential changes beyond this electrode pH range could be caused by ionophore protonation and iron hydrolysis.

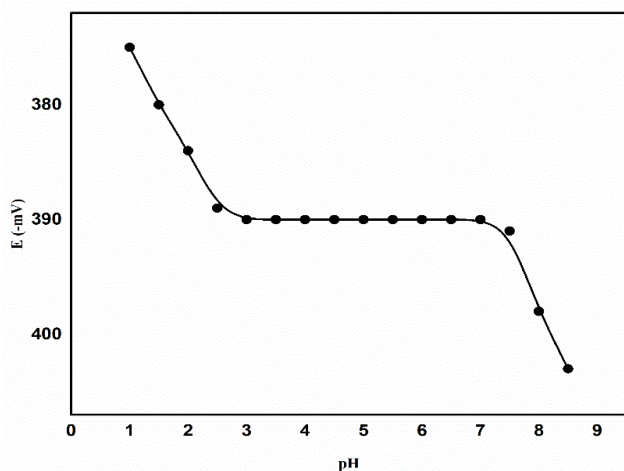


Figure 3: Effect of pH on the potential response of the electrode (C2) at $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Fe}^{3+}$ ion solution.

Potentiometric Selectivity of the Electrodes

Potentiometric selectivity is a critical parameter for ion-selective sensors, as it governs the sensor's ability to measure a specific ion accurately while minimizing interference from other ions. In this study, the potentiometric selectivity coefficient ($K_{A,B}^{Pot}$) of the proposed coated graphite electrode (C2) was determined for various cations (Mn⁺) using the Fixed Interference Method. This method evaluates the selectivity coefficients based on the following expression [40].

$$K_{Fe^{3+},B}^{Pot} = \frac{a_{Fe^{3+}}}{a_B^{Z_{Fe^{3+}}/Z_B}} \quad (3)$$

The selectivity coefficients determined by FIM are presented in Table 3. As shown in Table 3, the selectivity coefficients for the electrode are in the range of 10^{-3} M or lower, suggesting that the electrode is highly selective for Fe³⁺ ions compared to a variety of alkali, alkaline earth, transition, and rare earth elements (Na⁺, K⁺, Al³⁺, Ag⁺, Cr³⁺,

Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Sr^{2+} , Ca^{2+} , Co^{2+}). The stability of the ion-ionophore complex is also responsible high selectivity of these CGEs to Fe^{3+} ions over other secondary ions.

Table 3: Selectivity coefficients of Fe^{3+} selective electrode based on L

Interferent ion (B)	Selectivity Coefficients ($K_{Fe,B}^{Pot}$)
	(L) CGE-C2
Cr^{3+}	1.4×10^{-3}
Cu^{2+}	1.1×10^{-4}
Cd^{2+}	8.3×10^{-3}
Co^{2+}	3.0×10^{-4}
Ni^{2+}	1.0×10^{-4}
Na^+	6.0×10^{-3}
Pb^{2+}	6.9×10^{-3}
Hg^{2+}	1.4×10^{-4}
Sr^{2+}	5.7×10^{-5}
Ca^{2+}	6.9×10^{-5}
Al^{3+}	6.9×10^{-4}
Ag^+	1.7×10^{-4}
Zn^{2+}	2.3×10^{-4}
K^+	1.2×10^{-4}

Response Time of the Proposed Coated Graphite Electrodes

The usefulness of an ion-sensitive electrode in a measurement is largely determined by its response time. To predict the likelihood of success for novel ISEs, a thorough assessment of response time is necessary. In our study, we determined the average time it took for the electrode to stabilize at its final equilibrium potential after being immersed in Fe^{3+} solutions with concentrations between 1.0×10^{-2} M and 1.0×10^{-7} M, each differing by a factor of ten. This was done using the dipping method [40]. The concentration range for the potential measurement series was 1.0×10^{-2} M to 1.0×10^{-7} M. Figure 4. makes it clear that the electrodes' approximate response time to provide a steady potential 14 seconds is the duration of the full concentration range.

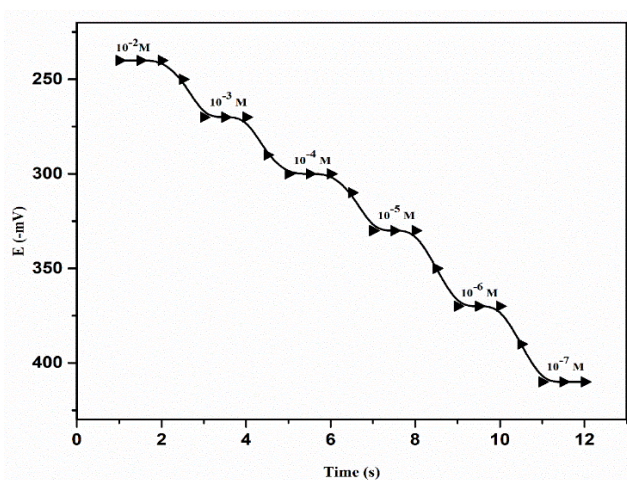


Figure 4: Dynamic response time of the Fe(III) electrode CGE-C2 based on L for ten-fold step changes in concentration.

Effect of non-Aqueous Media on the Performance of the Electrodes

In partially non-aqueous media, the electrode's performance has also been examined using mixtures of acetonitrile and water, methanol and water, and ethanol at varying concentrations (10%, 15%, 20%, 25%, and 30%, v/v). The potential response data is summarized in Table 4. It was observed that up to 20% (v/v) non-aqueous content did not significantly affect the electrode's (C2) performance. However, their performance began to decline at 20% non-aqueous content, as seen by a constant shift in their potential response. This was mostly because the membrane elements were lost to the organic phase at high non-aqueous content. The electrodes can therefore only be used in non-aqueous solvents up to a 20% (v/v) maximum limit.

Table 4: Influence of partially non-aqueous medium on the performance of Fe³⁺ electrode based on L

Non-aqueous content (vol %)	CGE-A2	
	Slope (mV/decade)	Detection Limit (M)
0	19.8	7.8×10 ⁻⁸
Acetonitrile		
10	19.8	7.8×10 ⁻⁸
15	19.5	8.3×10 ⁻⁸
20	19.4	8.9×10 ⁻⁸
25	18.1	5.6×10 ⁻⁷
30	16.7	8.8×10 ⁻⁶
Methanol		
10	19.8	7.8×10 ⁻⁸
15	19.8	8.9×10 ⁻⁸
20	19.5	8.2×10 ⁻⁸
25	17.3	4.5×10 ⁻⁷
30	16.8	3.9×10 ⁻⁶
Ethanol		
10	19.8	8.9×10 ⁻⁸
15	19.8	8.8×10 ⁻⁸
20	19.6	8.6×10 ⁻⁸
25	18.2	3.9×10 ⁻⁷
30	16.2	6.4×10 ⁻⁶
0	19.8	7.8×10 ⁻⁸

5. Analytical Applications

The electrode proved to be effective for the direct measurement of iron levels in water samples. Before conducting the potentiometric analysis, the samples were treated with 0.1 N HNO₃ to set the pH at 6.0 and to ensure the conversion of iron into its Fe (III) state. Triplicate measurements were conducted, and the results were compared with those from atomic absorption spectrometry (AAS). As presented in Table 5.0, there is a strong correlation between the results from both methods, validating the electrode's capability for direct Fe (III) determination in real-world samples.

Table 5: Analysis of iron in water samples using AAS and proposed Fe³⁺ selective electrode.

Sample	AAS(μg/mL)	CGE C2 (μg/mL)
Tap water	3.9	4.1
Mineral water1	1.7	1.9
Mineral water 2	0.9	1.1



The potentiometric performance of the electrode was evaluated in the laboratory, where it was utilized as an indicator electrode for the volumetric determination of Fe^{3+} ions using EDTA. The end point of the titration was identified to assess the electrode's applicability. In this experiment, 25 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Fe}^{3+}$ ion solution was titrated with a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ EDTA solution at pH 5.5. The resulting titration curve, presented in Figure 5.0, exhibited a sigmoidal shape, indicating that the electrode demonstrates high selectivity for Fe^{3+} ions. The inflection point observed on the curve correlates with a 1:1 stoichiometric ratio in the Fe^{3+} -EDTA complex, thereby confirming that the electrode is suitable for use as an indicator electrode in potentiometric determinations of Fe^{3+} ions.

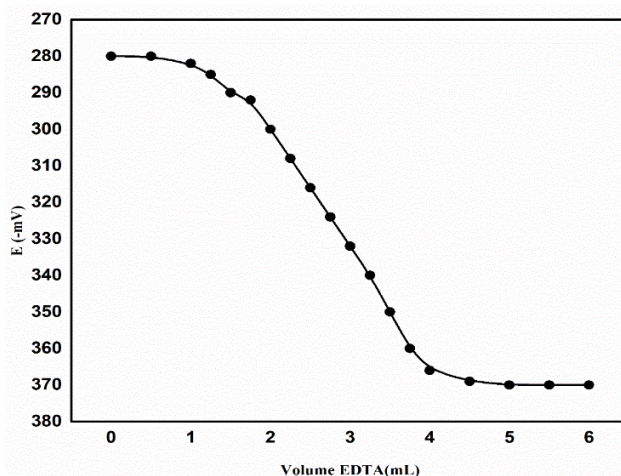


Figure 5: Potentiometric titration curves of CGE-C2 for 25 mL of $1.0 \times 10^{-3} \text{ M Fe}^{3+}$ ion solution was titrated against $1.0 \times 10^{-2} \text{ M EDTA}$ solution at pH 5.5

6. Conclusion

A coated graphite electrode was developed using various membrane compositions, and it was found that electrode C2, based on composition L, which had a membrane ingredient ratio of L:NaTBP: PVC: NPOE as 4:2.5:42.5:51 (% w/w), demonstrated the best overall performance. It exhibited a Nernstian response across a broad linear concentration range from 2.5×10^{-7} to $1.0 \times 10^{-1} \text{ M}$, with a detection limit of $7.8 \times 10^{-8} \text{ M}$ and an optimal pH range of 3.0 to 7.0. Additionally, it displayed a rapid response time of 12 seconds and maintained stability in solutions containing up to 20% (v/v) non-aqueous solvents. The electrode functioned effectively as an indicator electrode in the potentiometric titration of Fe (III) with EDTA and was successfully utilized for Fe (III) quantification in water samples.

Acknowledgement

The authors are thankful to M. S. College, Saharanpur and IIC, and Roorkee, for assistance to complete this work.

Funding

Nil

Conflict of Interests

The author declares no conflict of interests.

References

- [1]. Goyer RA, Clarkson TW. Toxic effects of metals, in: Casarett & Doull's toxicology: the basic science of poisons. McGraw-Hill. 1996; 5: 811-867.
- [2]. Greentree WF, Hall JO. Iron toxicosis, in: Kirk's current therapy XII small animal practice. Philadelphia PA and W.B. Saunders Co. 1995; 240-242.
- [3]. Wintrobe, Maxwell M. Clinical hematology. Philadelphia: Lea & Febiger. 1961; 5:143-149.



- [4]. John B, Porter MD, Maciej Garbowski MD. The Pathophysiology of Iron Overload. *Hematol Oncol Clin North Am.* 2005; 19:7-12. doi: <https://doi.org/10.1016/j.hoc.2014.04.003>.
- [5]. Andrews NC. Disorders of iron metabolism. *The New England Journal of Medicine.* 1999; 341(26): 1986-1995. doi: 10.1056/NEJM199912233412607.
- [6]. Cabantchik Z, Breuer W, Zanninelli G, Cianciulli P. LPI-labile plasma iron in iron overload. *Best Practice & Research Clinical Haematology.* 2005; 18: 277-287. doi: <https://doi.org/10.1016/j.beha.2004.10.003>
- [7]. Weinberg ED. The role of iron in cancer. *Eur J Cancer Prev.* 1996; 5(1):19-36.
- [8]. Jingfeng W, Edward AB. Determination of iron in seawater by high-resolution isotope dilution inductively coupled plasma mass spectrometry after Mg (OH)₂ coprecipitation. *Analytica Chimica Acta.* 1998; 367(1-3): 183-191. doi: [https://doi.org/10.1016/S0003-2670\(98\)00145-7](https://doi.org/10.1016/S0003-2670(98)00145-7).
- [9]. Obata H, Karatani H, Nakayama E. Automated determination of iron in seawater by chelating resin concentration and chemiluminescence detection. *Analytical Chemistry.* 1993; 65(11):1524-1528. doi: <https://doi.org/10.1021/ac00059a007>.
- [10]. Zolgharnein J, Abdollahi H, Jaefarifar D, Azimi GH. (2002). Simultaneous determination of Fe (II) and Fe (III) by kinetic spectrophotometric H-point standard addition method. *Talanta.* 2002; 57(6): 1067-1073. doi: [https://doi.org/10.1016/S0039-9140\(02\)00133-9](https://doi.org/10.1016/S0039-9140(02)00133-9).
- [11]. Shampur T, Sheikhshoae I, Mashhadizadeh MH. (2005). Flame atomic absorption spectroscopy (FAAS) determination of iron (III) after preconcentration on to modified analcime zeolite with 5-((4-nitrophenylazo)-N-(2', 4'-dimethoxyphenyl)) salicylaldehyde by column method. *Journal of Analytical Atomic Spectrometry.* 2005; 20(5): 476-478. doi: <https://doi.org/10.1039/B416097E>
- [12]. Ganjali MR., Norouzi P, Gol-Mohammadi M, Mizani F, Poursaberi T, Salavati-Niasari, M, Shamsipur M, Hosseini M, Javanbakht M. Sulfate-selective PVC membrane electrode based on a strontium Schiff's base complex. *Annali di chimica.* 2003; 93(7-8): 679-690.
- [13]. Mitchell-Koch JT, Malinowska E, Meyerhoff ME. Gallium (III)-Schiff Base Complexes as Novel Ionophores for Fluoride Selective Polymeric Membrane Electrodes. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis.* 2005;17(15-16):1347-53. doi: <https://doi.org/10.1002/elan.200503284>
- [14]. Kumar KG, John KS, Indira CJ. A chloride ion-selective potentiometric sensor based on a polymeric schiff base complex., *Ind. J. Chem. Techno.* 2006;13(1):13-16. doi: <http://nopr.niscpr.res.in/handle/123456789/6988>
- [15]. Ye G, Chai Y, Ruo Y, Zhou L, Li Y, Zhang L. Salicylate ion-selective electrode based on new tetranuclear copper complexes of O-vannilin-methionine as neutral carriers. *Analytical sciences.* 2007;23(2):171-176. doi: <https://doi.org/10.2116/analsci.23.171>.
- [16]. Hutchins RS, Bachas LG. Nitrate-selective electrode developed by electrochemically mediated imprinting/doping of polypyrrole. *Analytical Chemistry.* 1995;67(10):1654-1660. doi: <https://doi.org/10.1021/ac00106a002>
- [17]. Bühlmann P, Pretsch E, Bakker E. Carrier-based ion-selective electrodes and bulk optodes. 2. Ionophores for potentiometric and optical sensors. *Chemical Reviews.* 1998;98(4):1593-688.
- [18]. Wang TY, Shih JS. Iron (III) Ion Selective Electrode Based on Dithia 12-Crown-4. *Journal of the Chinese Chemical Society.* 1988;35(6):405-10. doi: <https://doi.org/10.1002/jccs.198800060>
- [19]. Hassan SS, Marzouk SA. A novel ferriin membrane sensor for potentiometric determination of iron. *Talanta.* 1994;41(6):891-9. doi: [https://doi.org/10.1016/0039-9140\(94\)E0042-P](https://doi.org/10.1016/0039-9140(94)E0042-P)
- [20]. Teixeira MF, Aniceto C, Fatibello-Filho O. Ion-selective electrode for the determination of iron (III) in vitamin formulations. *Journal of the Brazilian Chemical Society.* 1998; 9:506-10.
- [21]. doi: <https://doi.org/10.1590/S0103-50531998000500017>.
- [22]. Saleh MB. Iron (III) ionophores based on formylsalicylic acid derivatives as sensors for ion-selective electrodes. *Analyst.* 2000;125(1):179-83. doi: <https://doi.org/10.1039/A905530D>.



- [23]. Pejčić B, De Marco R. Impedance measurements of a chalcogenide membrane iron (III)-selective electrode in contact with aqueous electrolytes. *Electrochimica acta*. 2004;49(21):3525-43. doi: <https://doi.org/10.1016/j.electacta.2004.03.029>.
- [24]. Mashhadizadeh MH, Shoaie IS, Monadi N. A novel ion selective membrane potentiometric sensor for direct determination of Fe (III) in the presence of Fe (II). *Talanta*. 2004 Nov 15;64(4):1048-52. doi: <https://doi.org/10.1016/j.talanta.2004.05.005>.
- [25]. Sil A, Ijeri VS, Srivastava AK. Coated-wire iron (III) ion-selective electrode based on iron complex of 1, 4, 8, 11-tetraazacyclotetradecane. *Sensors and Actuators B: Chemical*. 2005 May 13;106(2):648-53. doi: <https://doi.org/10.1016/j.snb.2004.09.013>.
- [26]. Ekmekci G, Uzun D, Somer G, Kalaycı Ş. A novel iron (III) selective membrane electrode based on benzo-18-crown-6 crown ether and its applications. *Journal of membrane science*. 2007 Feb 1;288(1-2):36-40. doi: <https://doi.org/10.1016/j.memsci.2006.10.044>.
- [27]. Mahmoud WH. Iron ion-selective electrodes for direct potentiometry and potentiometric titrimetry in pharmaceuticals. *Analytica Chimica Acta*. 2001 Jun 12;436(2): 199-206. doi: [https://doi.org/10.1016/S0003-2670\(01\)00892-3](https://doi.org/10.1016/S0003-2670(01)00892-3).
- [28]. Fakhari AR, Alaghemand M, Shamsipur M. Iron (III)-selective membrane potentiometric sensor based on 5, 10, 15, 20-tetrakis-(pentafluorophenyl)-21H, 23H-porphyrin. *Analytical letters*. 2001 Apr 30;34(7):1097-106. doi: <https://doi.org/10.1081/AL-100104956>.
- [29]. Ekmekci G, Uzun D, Somer G, Kalaycı Ş. A novel iron (III) selective membrane electrode based on benzo-18-crown-6 crown ether and its applications. *Journal of membrane science*. 2007 Feb 1;288(1-2):36-40. doi: <https://doi.org/10.1016/j.memsci.2006.10.044>.
- [30]. Pooyamanesh MJ, Zamani HA, Rajabzadeh G, Ganjali MR, Norouzi P. Fe (III) ion-selective membrane electrode based on 4-Amino-6-methyl-3-methylmercapto-1, 2, 4-triazin-5-one. *Analytical letters*. 2007 Jun 1;40(8):1596-609. doi: <https://doi.org/10.1080/00032710701380632>.
- [31]. Gupta VK, Jain AK, Agarwal S, Maheshwari G. An iron (III) ion-selective sensor based on a μ -bis (tridentate) ligand. *Talanta*. 2007 Mar 30;71(5):1964-1968. doi: <https://doi.org/10.1016/j.talanta.2006.08.038>.
- [32]. Radfard R, Abedi A. Synthesis and characterization of new Schiff bases of ethylenediamine and benzaldehyde derivatives, along with their iron complexes. 2015;9(2): 59-65.
- [33]. Mi Y, Bakker E. Determination of complex formation constants of lipophilic neutral ionophores in solvent polymeric membranes with segmented sandwich membranes. *Analytical chemistry*. 1999 Dec 1;71(23): 5279-87. doi: <https://doi.org/10.1021/ac9905930>.
- [34]. Shultz MM, Stefanova OK, Mokrov SB, Mikhelson KN. Potentiometric estimation of the stability constants of ion-ionophore complexes in ion-selective membranes by the sandwich membrane method: Theory, advantages, and limitations. *Analytical chemistry*. 2002 Feb 1;74(3): 510-517. doi: <https://doi.org/10.1021/ac015564f>.
- [35]. Mi Y, Mathison S, Goines R, Logue A, Bakker E. Detection limit of polymeric membrane potentiometric ion sensors: how can we go down to trace levels. *Analytica chimica acta*. 1999 Oct 4;397(1-3): 103-111. doi: [https://doi.org/10.1016/S0003-2670\(99\)00396-7](https://doi.org/10.1016/S0003-2670(99)00396-7).
- [36]. Meier PC, Morf WE, Läubli M, Simon W. Evaluation of the optimum composition of neutral-carrier membrane electrodes with incorporated cation-exchanger sites. *Analytica chimica acta*. 1984 Jan 1; 156:1-8. doi: [https://doi.org/10.1016/S0003-2670\(00\)85531-2](https://doi.org/10.1016/S0003-2670(00)85531-2).
- [37]. Shawish HM, Saadeh SM, Al-Dalou AR, Ghalwa NA, Abou Assi AA. Optimization of tramadol-PVC membrane electrodes using miscellaneous plasticizers and ion-pair complexes. *Materials Science and Engineering: C*. 2011 Mar 12;31(2):300-6. doi: <https://doi.org/10.1016/j.msec.2010.09.014>.
- [38]. Morf WE, Ammann D, Simon W. Elimination of Anion Interference In Neutral Carrier Cation-Selective Membrane Electrodes. *Chimia*. 1974 Jan 1;28(2):65-7.



- [39]. Żubrowska M, Wróblewski W, Wojciechowski K. The effect of lipophilic salts on surface charge in polymeric ion-selective electrodes. *Electrochimica acta*. 2011 Jul 1;56(17): 6114-6122.doi: <https://doi.org/10.1016/j.electacta.2011.04.070>.
- [40]. Umezawa Y, Bühlmann P, Umezawa K, Tohda K, Amemiya S. Potentiometric selectivity coefficients of ion-selective electrodes. Part I. Inorganic cations (technical report). *Pure and Applied Chemistry*. 2000 Jan 1;72(10): 1851-2082.doi: <https://doi.org/10.1351/pac200072101851>.
- [41]. Maccà C. Response time of ion-selective electrodes: Current usage versus IUPAC recommendations. *Analytica Chimica Acta*. 2004 Jun 11;512(2):183-90.doi: <https://doi.org/10.1016/j.aca.2004.03.010>.

