

A NEW MODIFIED FE(III)-SELECTIVE SOLID MEMBRANE ELECTRODE

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ABSTRACT

In this study, a Fe(III)-selective solid state membrane electrode based on $\text{AgFeS}_2\text{-FeS}_x$ ($x=2-3$) mixture was developed. This electrode exhibited a linear Nernstian response over the range 10^{-2} - 10^{-5} M of iron(III) with a slope of 18.7 ± 0.8 mV per p[Fe] . The effects of the pH and the lifetime of the electrode were investigated. The selectivity coefficients for some common cations were calculated by the mixed-solution method. The preparation procedure of the electrode is easy and inexpensive. Moreover, the proposed electrode was applied for the determination of iron in standard reference materials.

Keywords: Iron(III), Sulfur based membrane, Ion-selective electrode, Potentiometry

1. INTRODUCTION

In recent decades, many intensive studies about ion-selective electrodes (ISE) have been reported. In spite of increasing studies dealing with ISE, the reports about iron-selective electrodes are relatively scarce [1-6]. In these studies the different types of electrodes were prepared such as poly(vinyl chloride) membrane electrodes, coated wire electrodes and solid-state

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electrodes were used for the determination of iron.

As is known, membranes which sensitive towards metal ions can be made by using $\text{Ag}_2\text{S-MS}$ (M=metal) mixture. Silver ion must be present in these membranes to conduct electricity because divalent ions are immobile in crystals. On the other hand silver ions are sufficiently mobile to conduct electricity through the solid medium. The sensitivity of these types of membranes towards Fe(III) ions was reported for the first time by Fung and Fung in 1977 /6/. In that study a copper-selective electrode with a membrane of mixed $\text{Ag}_2\text{S-CuS}$ is used to measure Fe(III) ions in aqueous solutions. In order to increase the sensitivity of the membrane towards Fe(III) ions AgFeS_2 was used instead of CuS in our study.

2. EXPERIMENTAL

Potential measurements were carried out with a Jenway 3040 ion Analyzer pH-ionmeter. The reported potential values are given against a Ag/AgCl reference electrode. Measurements were made with the electrodes immersed to a depth of 1.5 cm in a sample solution being stirred by a magnetic stirrer. All of the experimental works were carried out at $20 \pm 1^\circ\text{C}$ and pH values were determined using a combined glass-pH electrode (Ingold U402-S7/120 402.3311)

All of the chemicals were analytical grade and used without further purification. All of the solutions were prepared using deionized water. The 1M stock Fe(III) solution was prepared from ferric nitrate and adjusted according to the Zimmermann Reinhardt method /8/. Solutions of 1×10^{-1} to 1×10^{-6} M were freshly diluted from the 1 M stock solution of iron(III).

The proposed electrode was applied to determine iron in a standard ion sample. Standard reference material (Schwefelkies IX: 46.47% S, 40.82% Fe, 0.21% Cu, 0.82% Pb, 0.43% Zn and 0.52% As) was obtained from Dr. Hoefner's Subztanz Firm. A suitable amount was taken from the standard reference material and was dissolved by using nitric acid. Then it was diluted to a certain volume.

The membrane was prepared in a similar method given for AgFeS_2 preparation in literature /7/. 12.5 g of anhydrous K_2CO_3 , 7.65 g of AgNO_3 , 2.50 g of iron powder and an excessive amount of elemental sulfur were slowly heated from 60°C to 550°C in a 60×200 mm pyrex cylindrical vessel

under $\text{H}_2\text{S} + \text{N}_2$ atmosphere for 4 hours and then cooled to room temperature. The mixture was then taken out, the heterogeneous parts were cleaned off and the remaining black homogenous part was crushed into a powder. The excessive sulfur was separated by washing with 10 mL CS_2 at 50°C for 6 - 7 times. Then it was washed with ethyl alcohol and dried at 80°C . The dry powder was put in a press and subjected to 800 mPa pressure for 5 minutes. The discs were then removed and one side was polished to prepare a membrane. The copper wire was attached the unpolished side of membrane for electrical contact. The disc was then mounted onto a glass tube 1 cm diameter. The electrode was instantly ready for use.

The following electrochemical cell was established with the prepared iron(III)-selective electrode:

$\text{Ag,AgCl} / \text{KCl (sat.)} / \text{Sample solution} / \text{Membrane} / \text{Cu wire}$

Potassium, silver, iron and sulfur in the prepared membrane were analyzed by atomic absorption spectrometric method and classical analytical methods /8/. The results have been given as %Ag 6.82, %Fe 34.66, %S 58.40. Potassium was seen to trace. According to these results the membrane is thought to be of $\text{AgFeS}_2\text{-FeS}_x$ ($x=2-3$) structure.

3. RESULTS AND DISCUSSION

The potentiometric response of the prepared iron(III)-selective solid state membrane electrode was investigated against the iron(III) ion concentration. For this purpose, appropriate aliquots of stock solution of iron(III) were introduced to the cell and the corresponding potentials were determined. For a fixed ionic strength, all of the measurements were made in a 0.5 M sodium perchlorate because of its well-known weak tendency of forming a complex with iron(III).

The pH values of these solutions were adjusted to 2.3 using HClO_4 and NaOH . The potential readings were plotted against $-\log$ of iron(III) concentration. Over the concentration range $10^{-2} - 10^{-5}$ mol/L of iron(III) in the calibration solution, the electrode potential response was linear with the concentration of iron(III), (Fig 1). The calibration curve slope was 18.7 ± 0.8 mV / p[Fe] and the detection limit, calculated as recommended by the IUPAC, was 5.1×10^{-6} M /9/.

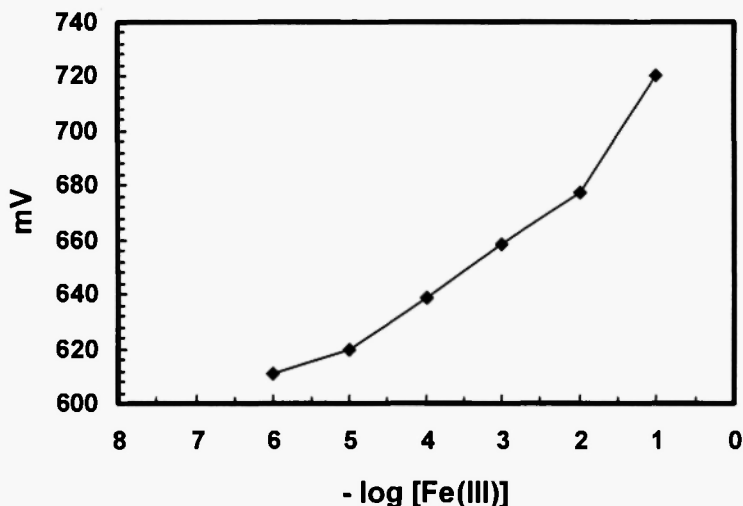


Fig. 1: The calibration curve of the proposed iron(III)-selective electrode at pH 2.3

The effect of the pH on the prepared electrode potential response was studied. The pH of the solution was changed between 1.5 and 3.0 by adding suitable volumes of perchloric acid to 1.0×10^{-3} M iron(III) solution and measure potentiometrically with the combined glass-pH electrode. When these pH values were plotted against pH, it was observed that the potential remains constant at the pH range 2.2 - 2.4, (Fig 2). At pHs higher than 2.4, iron(III) ions started to hydrolyze by forming iron(III) hydroxide from the sample solution. At pHs lower than 2.2, the potential values decrease as pH values decrease because of the interference effects of the hydrogen ions in the test solutions. Therefore, the pH values of the solutions were kept at 2.3.

The lifetime of the electrode was determined by recording its potentials at the optimum pH value and plotting its calibration curve each day for a period of a year. It was observed that there was no significant change in the slope of the electrode on the following day. At the end of a month, the slope of the electrode was found to be 17.9 mV; however it increased to its first value after conditioning the electrode in 10^{-3} M $\text{Fe}(\text{NO}_3)_3$ solution for 30 minutes. After one year the electrode was still working and its slope was seen to remain stable by conditioning. According to our observations, we can claim that the lifetime of the electrode is quite long.

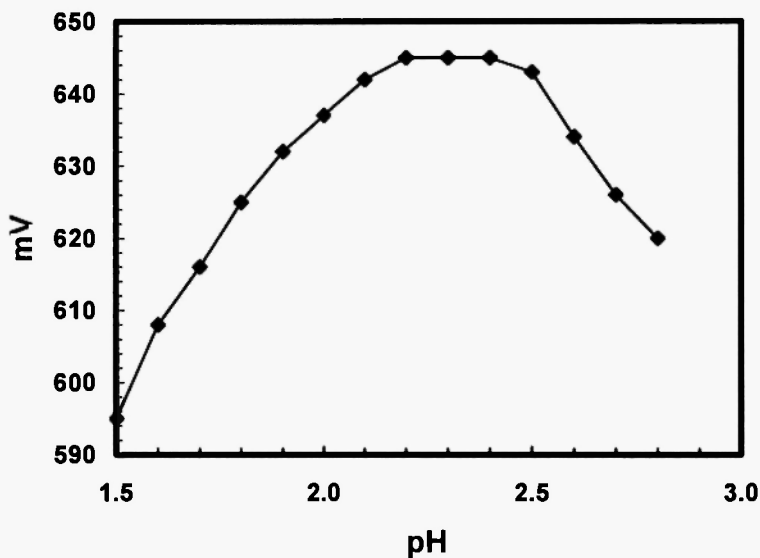


Fig. 2: The determination of optimum working pH range of the proposed iron(III)-selective electrode

The selectivity coefficients (K_{FeX}) of the iron(III)-selective electrode were calculated by the mixed solution method /10, 11/ from potential measurements of solutions prepared with a fixed iron(III) concentration and varying concentration of the interference ion. In this work, interference studies were made for Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and Pb(II) ions. As can be seen from Table 1, the most interfering cations to the electrode are Ag(I), Cu(II) and Mn(II). This is the case for most of the studies discussed in the literature /5, 13/. However, the selectivity coefficients of the iron(III)-selective electrode against the other cations investigated are in good compliance with the literature data.

These results show that the iron(III)-selective electrode which we prepared is superior to most of the iron(III)-selective electrodes mentioned in the literature as regards to the detection limit and the life time /4-6/.

The proposed electrode was applied to determine iron in a standard reference material. For this purpose, the solutions prepared from standard reference material were potentiometrically titrated with EDTA by using the proposed iron(III)-selective electrode as an indicator electrode (Fig 3). The

obtained results were compared with those obtained by the Zimmermann-Reinhardt method /8/ and the results are given in Table 2. As can be seen from Table 2, it is obvious that the results of iron determination in a standard reference material using these two methods are compatible within the 95% confidence level.

Table 1
The potentiometric selectivity coefficients of the proposed
Fe(II)-selective electrode.

X	$K_{Fe,X}$
Ag ⁺	12,6 ± 0,401
Co ²⁺	0,41 ± 0,030
Pb ²⁺	0,43 ± 0,062
Zn ²⁺	0,46 ± 0,087
Ni ²⁺	0,47 ± 0,082
Cu ²⁺	5,97 ± 0,303
Fe ²⁺	0,40 ± 0,053
Mn ²⁺	1,05 ± 0,138
Cr ³⁺	0,0093 ± 4,8 × 10 ⁻⁴

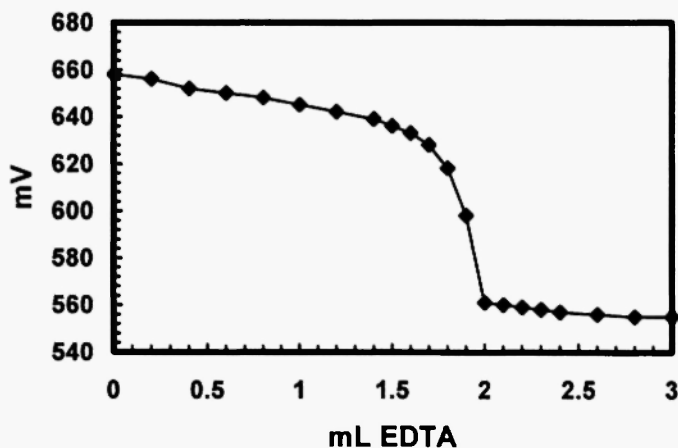


Fig. 3: The potentiometric titration curve of the solution of the standard reference material with EDTA obtained using the proposed iron(III)-selective electrode.

Table 2
 Results of the determination of iron in standard reference material with the proposed iron(III)-selective electrode and Zimmermann-Reinhardt method at 95% confidence level (mean value and confidence limit for the mean of 5 replicate determinations)

μ	The proposed electrode				Zimmermann-Reinhardt method				Comparison of the two experimental means	
	$\bar{x}_1, \%$	s	N	$\mu - \bar{x}_1 < \frac{ts}{\sqrt{N}}$	$\bar{x}_2, \%$	SS	N	$\mu - \bar{x}_2 < \frac{ts}{\sqrt{N}}$	$\bar{x}_1 - \bar{x}_2$ (tsb)	$\sqrt{\frac{N_1 + N_2}{N_1 \cdot N_2}}$
% 40,82	40,64	0,42	5	0,18 < 0,52	40,71	0,32	5	0,11 < 0,40		0,07 < 0,33

\bar{x}_1 : The experimental mean of the analyses by iron(III)-selective electrode

\bar{x}_2 : The experimental mean of the analyses by Zimmermann-Reinhardt method

s : Standard deviation

N : The number of analyses

μ : The true value, 40,82%

$\mu - \bar{x}_1 < \frac{ts}{\sqrt{N}}$: Comparison of the experimental mean with true value

$\mu - \bar{x}_2 < \frac{ts}{\sqrt{N}}$: Comparison of the experimental mean with true value

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