All-Solid-State PVC Membrane Fe (III) Selective Electrode based on 2-Hydroxymethyl-15-crown-5

Omer Isildak, Omer Durgun

Abstract— A novel potentiometric sensor based on ionophore (2-Hydroxymethyl-15-crown-5) for the determination of Fe^{3+} ions is developed. The Fe^{3+}-selective membrane sensor demonstrates high sensitivity and short response time. The detection limit of the Fe^{3+}-selective membrane sensor was about 1.2×10^{-6} mol L^{-1} and the response time was shorter than 8 s. The linear dynamic range of the Fe^{3+}-selective membrane sensor was between 1.0×10^{-1} and 8.0×10^{-6} mol L^{-1} Fe^{3+} concentration. The Fe^{3+}-selective membrane sensor exhibited good operational stability for at least two month keeping in dry conditions at 4–6 °C. It had a reproducible and stable response during continuous standard deviation of 0.34% (n = 30).

Index Terms— Iron (III), ionophore, potentiometric analysis, solid-state sensor.

I. INTRODUCTION

Iron is an important element of metabolic processes indispensable for plants and animals and it is generally available in environmental and biological materials [1]-[3]. The abundancy of it is the fourth in the earth's crust, it is present especially in a variety of rock and soil minerals in the form of iron (II) and iron (III) [1], [3], [4]. The availability of various forms of iron in natural waters depends upon geological area and chemical components in the environment. The iron is essentially present as a pollutant in water because iron alloys are widely used as containers and pipelines all over the world [5]. Besides, iron and its compounds are ingredients of various industrial processes and so interferes natural sources through the discharge of wastes [5].

The inevitable constitution of iron brings about its determination need at low cost and high accuracy which is very important issue due to that it is necessary in environmental and health monitoring [5]. In the past decades, trace levels of iron have been successfully determined [2]-[7] and the new insights into the properties of specific trace element compounds with appropriate analytical techniques become challenging.

Among the analysis techniques, flow-injection analysis (FIA) is well accepted because of its high sample throughput, cost effective performance, versatility, flexibility, and ease of operation [5]. FIA is much compatible with a wide range of detection techniques [5], [8], [9]. FIA was in general operated with spectrophotometric detectors for the determination of iron (III) [3], [5]. The colored complex formed with various chromogenic reagents was investigated through

spectrophotometric detector to measure the absorbance of iron analytes [2], [7], [10]-[23].

There are also kinetic approaches for speciation purposes [3], [24]. Obata et al., determined Fe (III) and Fe (II) with high sensitivity and selectivity using chemiluminescence, their method suffered from the working conditions of the concentration steps [3], [24], [25]. Opto-electrochemical detection was operated for simultaneous detection of the two redox species in spiked tap water by Haghighi and Safavi. The detection limits was about 20 and 200 mg L^{-1} for Fe (III) and Fe (II) respectively [3], [26].

Potentiometric sensors have been developed through immobilizing a membrane matrix on all-solid-state contact. It was for sample monitoring without any reagent consumption and at a very short analysis time [3], [27]. The all-solid-state contact mixture electrode of graphite-epoxy resin was prepared in suitable ratio where the sensing membrane adhered to the surface of all-solid-state contact electrode without an internal reference solution. As a result life-time of the electrode increased without any loss in its potentiometric response property and thus electrode became more stable. All-solid-state membrane electrodes are cost effective because they are very easily prepared in miniaturized construction. In this work, all-solid-state PVC membrane Fe^{3+}-selective electrode as shown in Figure 1 based on 2-Hydroxymethyl-15-crown-5 was developed. Analytical characteristics of the sensor such as response time, sensitivity, and limit of detection, selectivity, dynamic range, usage stability, and storability were investigated.
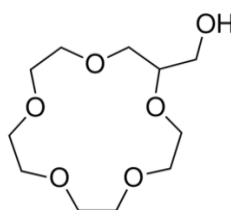

Figure 1. The Structure of the ionophore

II. MATERIAL AND METHOD

A. Apparatus

Potentiometric measurements were performed at room temperature (20 ±1 °C) by using a home-made multi-channel potentiometric system controlled by a computer. The potential values as steady-state responses of the Fe^{3+}-selective membrane sensor were performed for different concentrations of standard solutions of Fe^{3+} respectively. Throughout the measurements, a micro-sized solid silver/silver chloride

Omer Isildak, Department of Chemistry, Faculty of Science and Arts, Gaziosmanpasa University, 60240, Tokat, Turkey, +90356 252 16 16,
Omer Durgun, Department of Chemistry, Faculty of Science and Arts, Gaziosmanpasa University, 60240, Tokat, Turkey, +90356 252 16 16

electrode (provided by Isedo medical instruments, Turkey) was used as reference electrode with the Fe^{3+}-selective membrane sensor. To investigate the potentiometric characteristics of the prepared Fe^{3+}-selective membrane sensor, measurements of the potential differences between two points which is the cause of electrical currents were taken in the following cell assembly:

Micro-sized solid silver/silver chloride reference electrode / test solution / Fe^{3+}-selective membrane sensor membrane / all solid-state contact material / Cu wire.

B. Materials

The reagents used were at analytical reagent grade and deionized water was double distilled with a DI 800 Model deionize water system. High molecular mass poly (vinylchloride) (PVC), potassium tetrakis (p-chlorophenyl) borate (KTpClPB), dibütil ftalat (DBF), [Bis(2-etilhekzil)]sebakat (BEHS), o-nitrophenyl octylether (o-NPOE), tetrahydrofuran (THF) and graphite were from Fluka Company. Epoxy resins (Macroplast Su 2227) and hardener (Desmodur RFE) was from Henkel and Bayer Company respectively. Fe^{3+}-selective ionophore (2-Hydroxymethyl-15-crown-5) was from Merck Company.

A stock Fe^{3+} solution (1.0×10^{-1} mol L^{-1}) was prepared in distilled deionize water. The diluted solutions (1.0×10^{-1} to 1.0×10^{-6} mol L^{-1}) of Fe^{3+} were prepared by an appropriate dilution of the stock solution. All of the other reagents used were of analytical reagent grade. Twice-distilled deionize water was used throughout the study.

C. Design of all solid-state contact Fe^{3+}-selective membrane sensor

The potentiometric all solid-state contact Fe^{3+}-selective membrane sensor was prepared as previously described in our work [28]. The graphite was bound in epoxy resin mixture in the all solid-state contact of the sensor and a hardener in THF solvent was added in the proportion of 1.0:0.5 w/w. The 1.0:1.0 w/w ratio of powdered graphite to epoxy resin was used. After mixing, the solvent was casted for 20-30 min in air. When the appropriate viscosity was obtained, a plastic covered copper wire was dipped into the mixture several times to obtain solid-state contact uniformly coated and allowed to stand overnight in an oven at 40 °C.

The Fe^{3+}-selective membrane solution comprised ionophore (4 %, w/w), plasticizer (65.0 %, w/w), KTpClPB (1 %, w/w) and PVC (30 %, w/w) was dissolved in 5 ml of THF.

The solid-state contact was dipped into the Fe^{3+}-selective membrane solution at least three times and then the coated membrane was allowed to dry in the air for at least 3 hours. Finally, the prepared all solid-state contact Fe^{3+}-selective membrane sensor was soaked in a 0.01 M KCl solution for at least 3 hours before use. The potentiometric performance characteristics of the all solid-state contact Fe^{3+}-selective membrane sensor were tested in steady-state conditions.

III. RESULTS AND DISCUSSION

A. Potentiometric performance of the all solid-state contact PVC membrane Fe^{3+}-selective electrode

The crown ethers were expected to determine heavy and transition metal ions selectively because of oxygen donor atoms in the rigid and lipophilic micro cyclic ring [29]-[31]. Therefore, we prepared all-solid-state PVC membrane Fe^{3+}-selective electrode using crown ether compound as neutral carriers and initially measured the potential response of electrode to a variety of metal ions. Potentiometric performance of the Fe^{3+}-selective membrane sensor was accounted for optimization of membrane composition. The potentiometric results of Fe^{3+}-selective membrane compositions were tabulated in Table 1.

Table 1. Membrane compositions

Parameter	Fe^{3+}-sensitive membrane sensor
Detection limit (mol/L)	1.2×10^{-6}
Linear range (mol/L)	$1.0 \times 10^{-1} – 8.0 \times 10^{-6}$
Response time (s)	<8
Linear equation	y= - 34.6x + 2664.2
Correlation coefficient (r^2)	0.9904

2-Hydroxymethyl-15-crown-5 compound is a superior neutral carrier in PVC membrane, and all-solid-state PVC membrane Fe^{3+}-selective electrode based on 2-Hydroxymethyl-15-crown-5 demonstrates excellent selectivity against to Fe^{3+} ions. KTClPB is essentially included to increase the selectivity and conductivity of the membrane [29], [32], [33]. Some plasticizers (o-NPOE, BEHS and DBP) commonly used in PVC membrane systems were examined for suitability. Among these plasticizers, BEHS gave a best sensitivity in a linear range. It is explained by the high polarity of BEHS leading to be better compatibility to PVC membrane electrodes based on neutral ionophore [29], [34], [35].

Potentiometric selectivity of all-solid-state PVC membrane Fe^{3+}-selective electrode toward Fe^{3+} cation relative to other metal cations were investigated by using the fixed interference method [29], [36]. The potentiometric selectivity coefficients of all solid-state Fe^{3+}-selective membrane sensor in respect to many cations were evaluated by the separate solutions method according to the IUPAC recommendation [37]. The selectivity coefficients expressed as $-Log\ k^{pot}_{Fe^{3+},M^{2+}}$ are presented in Figure 2. There was distinguished decrease in the selectivity for Fe^{3+} relative to other metal ions (see Figure 3). From the shown Figure 2, it is quite obvious that the proposed Fe^{3+}-selective sensors are highly selective with respect to other ions.
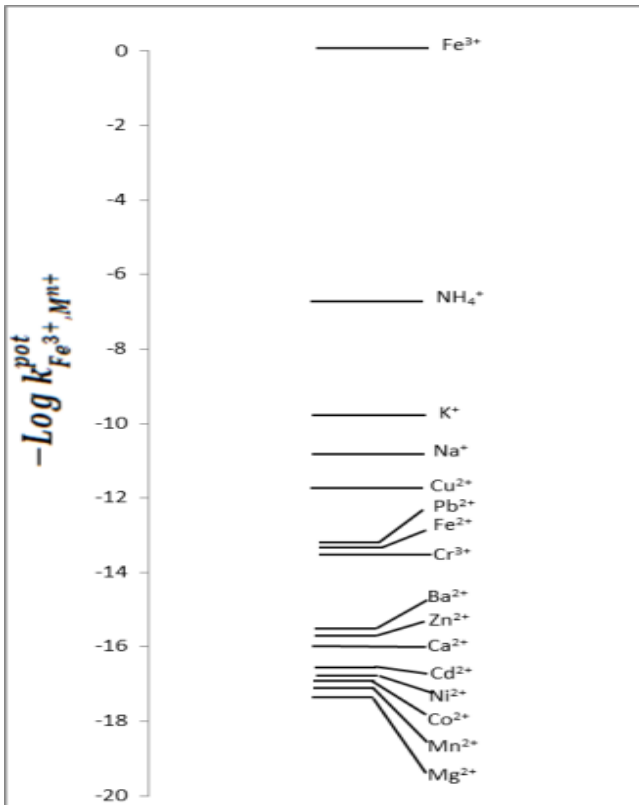
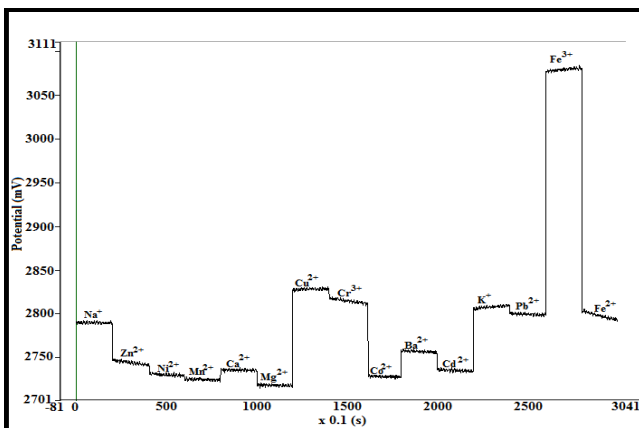**Figure 2.** Selectivity coefficients of all solid-state PVC membrane Fe^{3+}-selective electrode

Figure 3. Potential difference for 10^{-2} M metal solutions of Fe^{3+}-selective membrane sensor

The response time ($t_{95}\%$) is known as the time period for the presented potential of electrode to reach equilibrium with the sensible part of the membrane. The Fe^{3+} concentration was rapidly increased from 10^{-5} to 10^{-1} M and the $t_{95}\%$ values was measured. The response time obtained was always less than 8 s. The pH dependence of the electrode response was examined using in 10^{-1} M solution adjusted with hydrochloric acid and sodium hydroxide. The all-solid-state PVC membrane Fe^{3+}-selective electrode showed a potential changed against Fe^{3+} concentration range of 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} in this acidic and basic mediums (see Figure 4 and 5). Figure 4 show that electrode can work in both acidic and basic media. According to Figure 5, the decrease in the potential of the electrode is due to the formation of $Fe(OH)_3$ compound when the pH is above 10 and Fe^{3+} concentration is below 10^{-3} M.
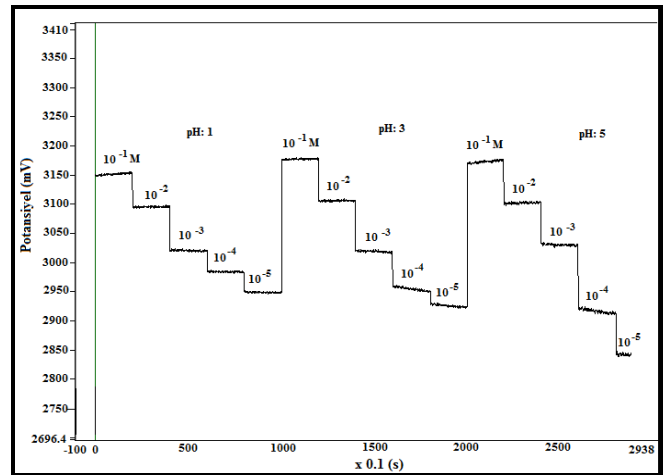

Figure 4. Potential changes against Fe^{3+} concentration in acidic mediums of Fe^{3+}-selective membrane sensor
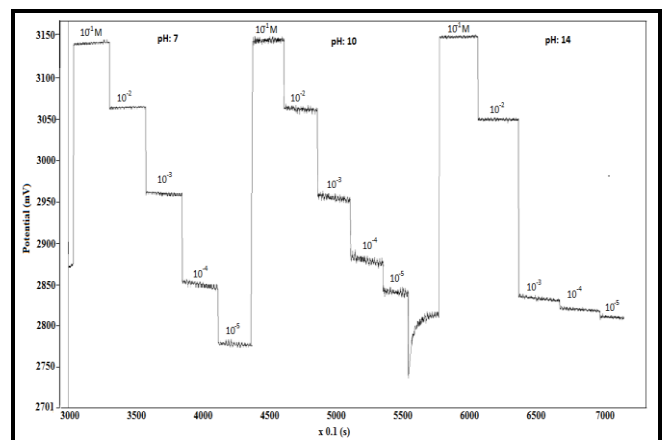

Figure 5. Potential changes against Fe^{3+} concentration in basic mediums of Fe^{3+}-selective membrane sensor

The highest sensitivity of potentiometric Fe^{3+}-sensor was observed when 4.0 % (w/w) ionophore was loaded. When the amount of ionophore loading is increased the diffusion resistance for the ions increases and then the sensor response decreases. On the other hand, if the ionophore concentrations lower than 1.0 % (w/w), there is no enough ionophore involved in the reaction which leads only a slight potential variation. As a result, the ionophore ratio of 4.0 % (w/w) was used to obtain optimum membrane composition for further experiments.

B. Analytical characteristics of the all solid-state contact PVC membrane Fe^{3+}-selective electrode

When the change of potential according to metal ion concentrations was monitored, Fe^{3+} ion was observed to change the potential at maximum that is, the electrode is found the most selective to Fe^{3+} ion. The change values in potential are consistent with Nernst equation. The linear correlation of the electrode detected according to the concentration changes of metal ions between $1x10^{-1}$ and $5x10^{-5}$ M could be seen in Figure 6.
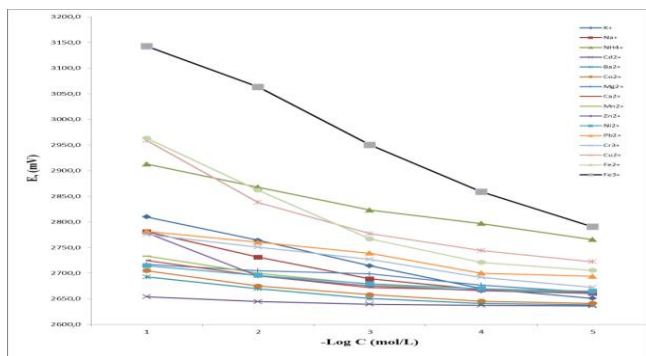
Figure 6. Potentiometric response of all solid-state PVC membrane Fe^{3+}-selective electrode

Using the optimum conditions determined in the above studies, calibration curve of the Fe^{3+}-selective membrane electrode was obtained over Fe^{3+} concentration range of 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1}. As shown in Figure 7, the Fe^{3+}-selective membrane sensor exhibited a linear response, the graph of the linear response was defined by the equation of $y = -90.92x + 2233.8$ with a correlation coefficient $r^2 = 0.994$. The Fe^{3+}-selective membrane electrode reached to a steady-state rapidly and its detection limit was 1.0×10^{-6} mol L^{-1}.
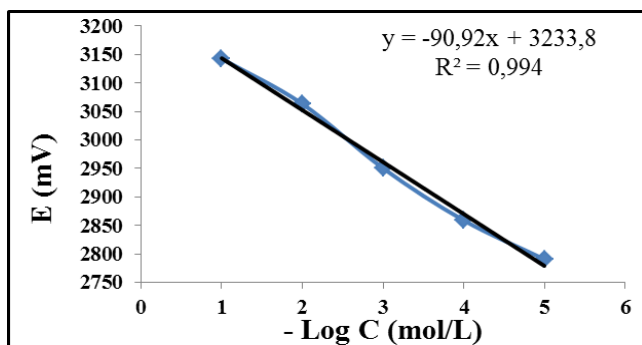

Figure 7. Calibration curve of all solid-state PVC membrane Fe^{3+}-selective membrane electrode obtained over Fe^{3+} concentration range of 10^{-1} to 10^{-5} mol L^{-1}

The all-solid-state PVC membrane Fe^{3+}-selective electrode showed that exhibit to results can be fairly repeatedly. Figure 8 depicts the reusability of Fe^{3+} selective electrode in 10^{-2}, 10^{-3}, and 10^{-4} M Fe^{3+} concentrations. The average potential values were calculated as 3050.3 ± 15.5; 2945.8 ± 11.2, and 2847.3 ± 9.3 mV in the repeated measurements.
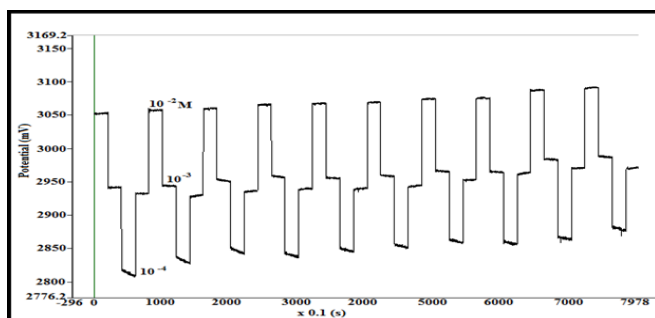

Figure 8. The reusability of all solid-state PVC membrane Fe^{3+} selective electrode

An investigation about long term storage stability of Fe^{3+}-selective membrane sensor, kept in dry at 4–6 °C, the calibration curve was recorded every day and the potentials were measured. The sensor demonstrated good storage stability for at least two month to standard Fe^{3+} concentration change.

Fe^{+3} selective electrodes presented a high potential difference for Fe^{+3} among the other metal ions which show electrode selectivity towards Fe^{3+} ions. Besides the potential values obtained in the solutions consisting of all the metal ions (3035.0 mV in 10^{-1} M solution and 2905.0 mV in 10^{-3} M solution) represents the selectivity of our electrodes toward Fe^{3+} ions (see Figure 9). When the potential values in Figure 6 is investigated, potential values of almost all the metal ions (except NH_4^+, Fe^{2+} and Cu^{2+}) in 10^{-1} M concentrations showed lower values than 2790.3 mV measured in 10^{-5} M Fe^{3+} solution which means that the electrode is able to measure Fe^{3+} ions at 10^{-4} M Fe^{3+} solutions in the presence of the other ions.
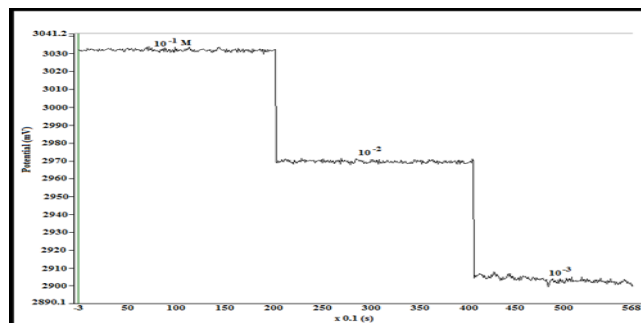

Figure 9. The potential values obtained in the solutions consisting of all the metal ions

IV. CONCLUSIONS

A novel potentiometric sensor based on all sold state contact is developed for fast and simple analysis of iron (III). Composite Fe^{3+} selective sensor could easily be prepared and economic. Its response time is considerable. Also composite Fe^{3+} selective censor can be miniaturized and used in mobile. The developed sensor is suitable for production of a detector cell with micro liter dead volume and therefore suitable to be used in the chromatography systems. Therefore the expensive measurements could be achieved at low cost. Additionally, we believe this work imparts an important contribution to the present literature.

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Dr Omer Isildak has a master degree in chemistry and PhD in Analytical Chemistry at Gaziosmanpasa University of Turkey. He has been a research and education staff since 1993 at Gaziosmanpaşa university of Turkey. He has plurality papers of ion analysis, heavy metal determination, and sensors. He has mainly interested in biosensors and chemical sensors.

Omer Durgun has a Master of Science degree in chemistry at Gaziosmanpaşa university of Turkey. He has experience on chemical sensors.