Iron (III)-Selective Sensor Based on Modified Glassy Carbon Electrode

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Abstract:
The aim of this work is intended to make a comparison between the effects of the presence of potassium ferricyanide ($K_3[Fe(CN)_6]$) / potassium ferrocyanide $K_4[Fe(CN)_6]$ and the absence of any redox couple for iron (III) determination in aqueous solution using modified Glassy Carbon Electrode. Benzo-18-crown-6 is employed as ionophores for preparing PVC-based membrane sensors selective to iron (III), plasticized with Di-n-octyl phthalate, Tetrabutylammonium tetraphenylborate was used as additive. The measurements performed and characterized by square wave voltammetry methods. Agents were optimized for iron (III) stripping analysis and optimal condition was frequency of 20 Hz, step potential of 6 mV, amplitude of 40 mV, the modified glassy carbon electrode immersed in standard solutions of Fe(III) at PH 2.0. The square wave voltammograms showed a sharp peak around positive potentials + 0.260 V that was used for construction of the calibration curve in a work range from $10^{-10}$ until $10^{-6}$ mol L$^{-1}$ of iron, exhibiting a linear correlation coefficient of 0.99, a detection limit of $10^{-10}$ mol L$^{-1}$ and sensibility of 9.87 μA/mol L$^{-1}$, especially, those obtained by the presence of redox couple better than the absence of external redox.

Key words: square wave voltammetry, iron (III) determination, sensor, benzo-18-crown-6, PVC membrane sensor

Introduction:
It is well known that iron is very important for environmental studies because is the metal in the first transition series [1].

In this paper we present the comparison between the effects of the presence of potassium ferricyanide ($K_3[Fe(CN)_6]$) / potassium ferrocyanide $K_4[Fe(CN)_6]$ Redox Couple and the absence of any external redox for iron (III) determination in aqueous solution using modified Glassy Carbon Electrode. Benzo-18-crown-6 is employed as ionophores for preparing PVC-based membrane sensors selective to iron (III), plasticized with Di-n-octyl phthalate, Tetrabutylammonium tetraphenylborate was used as additive. Agents were optimized for iron (III) stripping analysis and optimal condition was frequency of 20 Hz, step potential of 6 mV, amplitude of 40 mV, the modified glassy carbon electrode immersed in standard solutions of Fe(III) at PH 2.0. The measurements are performed in 0.1M NaNO$_3$ and 0.1 M HCl (pH 7). The modified glassy carbon electrode immersed in standard solutions of Fe(III) at PH 2.0.

Results and Discussions:
We observe that the presence of ionophore in the polymeric membrane induce the stability and lead to the best response with optimized PVC; Di-n-octyl phthalate; TBATPB and benzo-18-crown-6 wt.% ratio of 29; 67; 2 and 2 respectively. Figure 1. depict the SWV performance of Fe (III) in 0.1M NaNO$_3$ and 0.1 M HCl (pH 7) and the calibration curve for Fe (III) selective electrode in the absence of any external redox The related linear regression equation was:
ip/μA = 3.08 C Fe (III)/ mol L⁻¹ + 4.66 ...........(1)
and correlation coefficient was R² = 0.99. The detection limit of this electrode was 10⁻³ mol L⁻¹.

Figure 2 depicts the SWV performance of Fe (III) in 0.1M NaNO₃ and 0.1 M HCl (pH 7) and the calibration curve for Fe (III) selective electrode in the presence of potassium ferricyanide (K₃[Fe(CN)₆]) / potassium ferrocyanide K₄[Fe(CN)₆]).
The peak currents were extracted and plotted versus concentration (Fig 2). The related linear regression equation was:
\[ ip/\mu A = 7.78 \ C \text{ Fe (III)/ mol L}^{-1} + 4.81 \] .................(2)
and correlation coefficient was R² = 0.99. The detection limit of this electrode was 10⁻³ mol L⁻¹.

The working electrode was prepared by mixing 2 mg ionophore, 67 mg Di-n-octyl phthalate, 29 mg of Polyvinyl chloride and 2 mg of TBATPB.
It should be mentioned that the accuracy of data obtained by the presence of potassium ferricyanide (K₃[Fe(CN)₆]) / potassium ferrocyanide K₄[Fe(CN)₆]) is better than those obtained by the absence of redox couple. The reason of this interesting behaviour is that when solutions of Fe³⁺ and [Fe(CN)₆]³⁻ are mixed.
The iron is low spin and facilely reduced to the linked ferrocyanide ion [Fe(CN)₆]²⁻, which is a ferrous (Fe²⁺) derivative. This redox couple is reversible and necessitates no action or fraction of Fe-C bonds [2].

\[ [\text{Fe(CN)}₆]^{3⁻} + e⁻ \rightarrow [\text{Fe(CN)}₆]^{2⁻}. \]

**Conclusions**

Iron (III)-Selective Sensor Based on Modified Glassy Carbon Electrode was elaborated.
The measurements performed and characterized by square wave voltammetry methods. The comparison between the effects of the presence of potassium ferricyanide (K₃[Fe(CN)₆]) / potassium ferrocyanide K₄[Fe(CN)₆]) and the absence of any external redox couple were studied. The results demonstrated that sensor could be used for the determination of Fe(III) in the absence and in the presence of redox couple, the better results in the presence of potassium ferricyanide (K₃[Fe(CN)₆]) / potassium ferrocyanide K₄[Fe(CN)₆]) Redox Couple, because Fe(III) was reduced to Fe(II) leaving the surface, it will be seen that in the absence of redox couple have smaller slopes. The preparation of the electrode is simple and the membrane composition including (PVC; Di-n-octyl phthalate; TBATPB and benzo-18-crown-6 wt % ratio of 29; 67; 2 and 2 respectively).

**References**