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STUDY AND APPLICATION OF COPPER ION SELECTIVE ELECTRODE IN ENVIRONMENTAL SAMPLE

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ABSTRACT

Mixed silver-copper sulfide precipitates have been prepared between metal ions (Ag^+ ; Cu^{2+}) reversible to sulfide ion and tested for their suitability as Cu^{2+} ion-selective electrode (ISE). Characterization of coated wire electrode has been carried out by potentiometry and pHmetry. Explanations for Nernstian response are also discussed. Some potentiometric characteristics such as: Nernstian slope, calibration curves, detection limits, pH range and time response of the electrode are also discussed. Applicability of this electrode is checked with respect to determination of copper (heavy metal) in lake water samples used for drinking purposes. These findings offer a novel approach to understanding the response mechanism of electrodes based on mixed metal sulfides.

KEYWORDS: copper (II), Ion Selective Electrode (ISE), Potentiometry, Lake water samples.

INTRODUCTION

Potentiometric measurements using ion-selective electrodes (ISE) for determination of the respective metal ions is advantageous due to speed, wide dynamic ranges, and no requirement for pretreatment of sample. The development of highly specific ion-selective electrodes for application in industrial, environmental, clinical, and laboratory analysis is an ongoing challenge.

Due to many applications of copper in industry, biological and medical systems, and its widespread occurrence in diverse samples, fast and accurate determination of copper is important. Hence preparation of ion selective electrodes for determination of Copper have received much interest, and many different organic compounds were prepared and investigated as sensing ionophores for copper (II) ion. Bühlmann et al. summarized the ionophores for Cu^{2+} sensors and recently Cu^{2+} ionophores have also been reported.

Ion-selective electrodes (ISEs) are established tools that are capable of determining the activities of many analytes. Since Ross and Frant introduced the use of metal sulfide membranes for Ion selective electrodes as sensors for copper (II), cadmium (II) and lead (II) ions, many authors have published different methods for the preparation of Cu^{2+} ion-selective electrodes. The characteristic of these electrodes will depend on

two main aspects, i.e. the way of preparing the electro active material and the way in which this material is applied to construct the actual working electrode [1, 2].

Although, different materials were used for preparation of copper-selective electrode, chalcogenide glass [5] and ionophores are the most common. Commercial copper ISE are those based on mixed metal sulfides, mainly silver-copper sulfides. However, limited information is available regarding electrodes used for determination of Cu^{2+} based on the other silver-copper compounds which are prepared by simultaneously precipitations of mixed metal salts with Na_2S at different mole ratio. Electrochemical properties and limitation in potentiometric characteristics observed at these electrodes can be helpful in understanding response mechanism and origin of mentioned limitations. In this study, Cu^{2+} ion-selective electrodes (ISE), prepared by co-precipitation of mixed metals ions (Cu^{2+} , Ag^+) and S^{2-} (from Na_2S), were fabricated and characterized by potentiometric and pH metric techniques. Nernstian response, narrowed linear range and detection limit have also been determined [2]

MATERIALS AND METHODS

Reagents

All chemicals were of Analytical Reagent Grade. All solutions were prepared with double distilled water. Standard Cu²⁺ solution (0.1 M) was prepared using AR grade Copper (II) Sulfate in a calibrated volumetric standard flask. Dilutions were carried out using double distilled water. Common stock solution was used for the preparation of series of standard solutions. Sodium sulfide solution was prepared by dissolving Sodium sulfide (Na₂S) in double distilled water.

Preparation of electrode materials

Copper (II) sulfate, Silver nitrate (AgNO₃) and Sodium sulfide (Na₂S) were used for the preparation of electro active materials by simultaneous precipitation of copper (II) sulfide and silver (I) sulfide [8].

Electrode is fabricated from a mixture of copper sulfide and silver sulfide.

Potentiometric measurements

Potentiometric measurements were carried out using Equiptronic Digital Potentiometer (Model EQ – 606) with saturated calomel (Equiptronic EQ-705) as external Reference Electrode. The potential build up across the electrode was measured using the following electrochemical cell assembly: External reference electrode | test solution | ISE). The potential was recorded after addition of standard Cu²⁺ solution. The investigated concentration range was from 1.0 × 10⁻⁵M to 1.0 × 10⁻¹ M [8].

RESULTS AND DISCUSSION

The Cu(II) – sensitive ion selective electrode gave a linear response in the concentration range of 1.0 × 10⁻⁵M to 1.0 × 10⁻¹ mol/dm³ and slope of the graph of potential in mV against –logarithm of activity of copper ion was found to be 22.0±3 per decade change in concentration. [8,9].

3.1. Table 1: Linear Response

Sr No.	Concentration of standard Cu in mol/dm ³	Electrode Potential in mV
01	1.0x10 ⁻⁵	90.0
02	1.0x10 ⁻⁴	112
03	1.0x10 ⁻³	125
04	1.0x10 ⁻²	164
05	1.0x10 ⁻¹	184
06	Lake Water	74.0

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02	1.0x10 ⁻⁴	112
03	1.0x10 ⁻³	125
04	1.0x10 ⁻²	164
05	1.0x10 ⁻¹	184
06	Lake Water	74.0

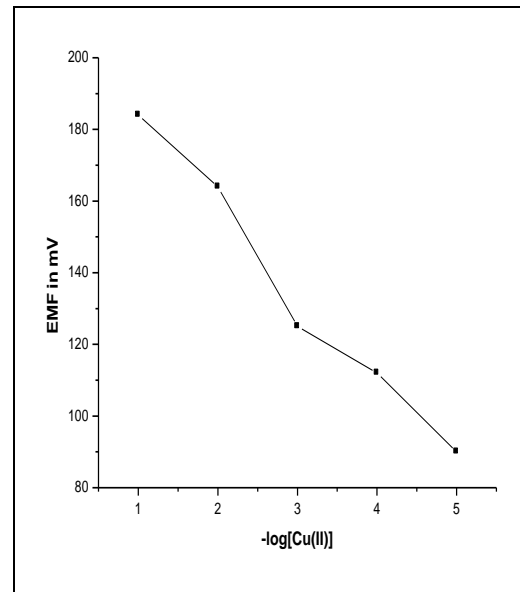


Figure: Graph of potential in mV Vs –log[Cu(II)]

3.2. Table 2: Amount of Copper in Lake Water

Sr.No.	Environmental Sample	Concentration of Copper by ISE	Concentration of Copper by UV-visible Spectrophotometry	WHO $\mu\text{g/ml}$	BIS $\mu\text{g/ml}$
01	Lake Water	0.369ppm	0.400ppm	2.0	1.5

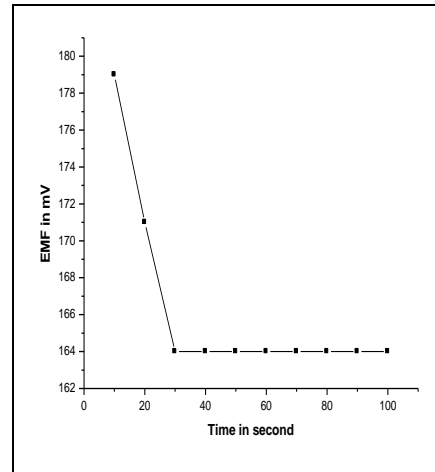


Figure.3.1: Graph of potential in mV Vs Time

Response Time:

There is fall in potential for 30 seconds after which a steady potential is attained which indicates the response time. Response time for 95% steady potential in Cu (II) electrode was 30 seconds.

Effect of pH:

The plot was made between electrode potential and pH values. It is found that there is decrease in potential from pH 1.0 to 3.0, after which it attains a constant potential up to pH10.0. Hence the working pH range of Cu (II) electrode is 3.0 to 6.0. This working range of pH was determined from the limit where the potential remained constant.

3.3. Table 3: Time response of the electrode

Sr No.	Time in Seconds	Potential in mV
01	10	179.0
02	20	171.0
03	30	164.0
04	40	164.0
05	50	164.0
06	60	164.0
05	70	164.0
06	80	164.0
05	90	164.0
06	100	164.0

3.4. Table 4: Effect of pH on Cu (II) electrode

Sr No.	pH	Potential in mV
01	1	298.0
02	2	280.0
03	3	262.0
04	4	262.0
05	5	262.0
06	6	262.0

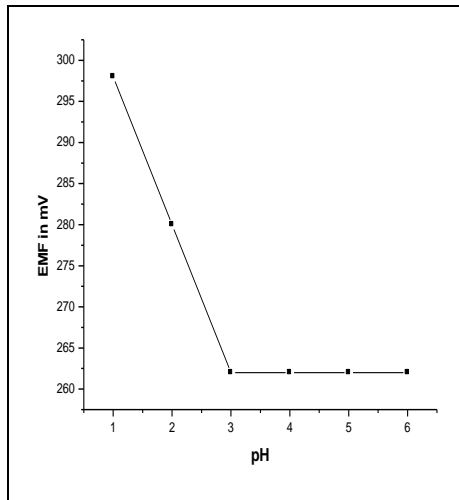


Figure 3.2: Graph of electrode potential Vs pH

CONCLUSION

The amount of Copper present in lake water was determined by measuring the potential by using Cu (II) ion selective electrode. The amount of copper in the lake water was found to be lower than the standards prescribed by WHO and BIS. This indicates that the lake water is not contaminated with heavy metal copper and that it is safe for drinking [6, 7].

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