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RESEARCH ARTICLE

STRONTIUM ION SELECTIVE ELECTRODES – PREPARATION AND APPLICATIONS

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ABSTRACT

A heterogeneous precipitates have been used as ion carriers for the preparation of strontium (II) selective membrane sensor. The electrodes give near-Nernstian responses in linear concentration range of 1M to 1×10^{-5} M with detection limits of the order of 10^{-5} M. The stable potentiometric signals are obtained within a short time period of 15 seconds and stable upto 3 month. The effect of pH, and the effect of medium have been studied found to give a better response. Selectively coefficient values were evaluated using fixed interference method. The sensor was used for the determination of strontium ion in some real samples.

Key words:

Strontium (II), Araldite –matrix,
Potentiometry, Polyvinylchloride,
Semicarbozone.

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INTRODUCTION

Consuming 75% of production, the primary use for strontium is in glass for cooler television cathode ray tubes. It prevents X-ray emission. All parts of the CRT (Cathode ray tube) tube have to absorb X-rays. The amount of strontium used for the production of cathode ray tube is declining because the CRTs are replaced by other display methods. This decline has a significant influence on the mining and refining of strontium Health effects¹. Most strontium compounds are regarded as harmless to plants and animals. A few, such as strontium chloride (SrCl_2) and Strontium Iodide (SrI_2), are somewhat toxic. An Ion-Selective Electrode (ISE), also known as a Specific Ion Electrode (SIE), is a transducer that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode. Ion-selective electrodes are used in biochemical and biophysical research, where measurements of ionic concentration in an aqueous solution are required, usually on a real time basis (Bakker *et al.*, 1997; Chandra, *et al.*, 2005). Potentiometry is an analytical technique, much used since 1966. Potentiometry can be described as the measurement of a potential in an electrochemical cell. Direct potentiometric measurements provide a rapid and convenient method for

determining the activity of various cations and anions. The technique requires only a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution, with its potential when immersed in one or more standard solution of known analyte concentration (Laksh, 2003). The most important consideration in using potentiometric technique is the type of indicator electrodes to be used. Depending on the application a variety of electrodes are available, each with inherent advantages and disadvantages. The use of potentiometry increased with the development of several new types of ion selective electrodes i.e.; electrodes that responds more or less selectivity to various ions.

Preparation of Semicarbazone & Benzamide membrane based ion selective electrode

Chemicals required

Polyvinyl chloride, di-n-butyl phthalate, sodium tetra phenyl borate, tetra hydro furan, Semi Carbazide hydrochloride, Sodium acetate, 4 – methoxy acetophenone, Benzamide, NaOH were obtained from E.Merck. the standard stock solutions 1M strontium chloride were prepared using distilled water. Working solutions were made by dilution of the stock solution. A digital potentiometer (EQUIP-TRONICS EQ 602) with Ag/AgCl electrode as a reference electrode was used for this study.

Preparation of ionophore - I

About 10 ml of water is added to 3g of semicarbazide hydrochloride followed by 3g of anhydrous sodium acetate and

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a mixture is warmed gently until a clear solution is obtained. Then a solution of 3 ml of the 4- methoxyacetophenone is added to it and warmed on a water bath. Crystals of semicarbazone separated on cooling (Fig 1).

Preparation of Ionophore – II

1g of substance (benzamide) is mixed with 10 ml of 10% NaOH solution. Heated for 30 mins till the evolution of ammonia gas. The solution is then cooled and acidified with concentrated HCl. The precipitated acid is filtered and washed with cold water.

Preparation of membrane Ion selective electrode

The membrane electrode was prepared by 0.3g of ionophore, 0.1g of PVC, predetermined ratio of DOP and NaTPB was dissolved in 3 ml THF and the clear solution was evaporated slowly. Then it was mixed with araldite and spread uniformly over whatmann filter paper No.42 to attain 0.7 mm thicknesses of the electro active membrane. The membrane was air dried for 48 h. A circular piece from each of the membrane was cut and fixed with resin at one end of hollow glass tubes of diameter 2 cm and length 10 cm. The tubes were filled with 1M solution of strontium chloride. Reference copper metal wire of diameter 0.5 mm and length 12 cm was inserted through the other end of tube in such a way, that it remains dipped in the 1 M solution of strontium Chloride. The electrodes were conditioned for 48 hours to attain equilibrium in 1M SrCl₂ solution.

RESULTS AND DISCUSSION

CHARACTERIZATION

In order to absorb infrared radiation a molecule must undergo a net change in dipole moment, as a consequence of its vibrational motion. The FT-IR spectrum of semicarbazone of 4- methoxyacetophenone was recorded using FTIR spectrometer (Model: Testscan Shimadzu Prestige-21 series) in the region 4000–500 cm⁻¹ and the spectrum is shown in Fig. 1. Below 1400 cm⁻¹ the region is called finger print region. There is an intense sharp peak at 3462 cm⁻¹, assigned to the free hydrogen bonded N–H stretch. The broad envelope between 2859 and 3351.2 cm⁻¹ is due to overlapping of peaks of hydrogen bonded N–H and aromatic C–H stretching modes. The symmetric and asymmetric C–H stretching modes of –CH₃ group appear as a shoulder just below 3000 cm⁻¹ in the broad envelope. The C =O stretch of semicarbazide moiety is observed at 1686.4 cm⁻¹. The aromatic ring skeletal vibrations are observed at 1577cm⁻¹. The –CH₃ bending modes are positioned at 1432 and 1307cm⁻¹.

Electrode response

The two electrodes were first conditioned in 1M solution of SrCl₂ for 3 days till it attained stable equilibrium which are then used for the determination of their characteristic study. The potential of the electrodes were studied by noting its E.M.F from the series of standard solutions of SrCl₂ of concentration ranging from 1M to 1x10⁻⁵M. The following are the E.M.F values obtained for electrode I (Table.1), electrode II (Table 2).

The EMF measurements were carried out using the following cell assembly,

Internal Reference Electrode (Cu wire)	Internal Reference(1M SrCl ₂ Solution)	Electro Active Membrane	Sample Solution	External Reference Electrode (Ag/AgCl)
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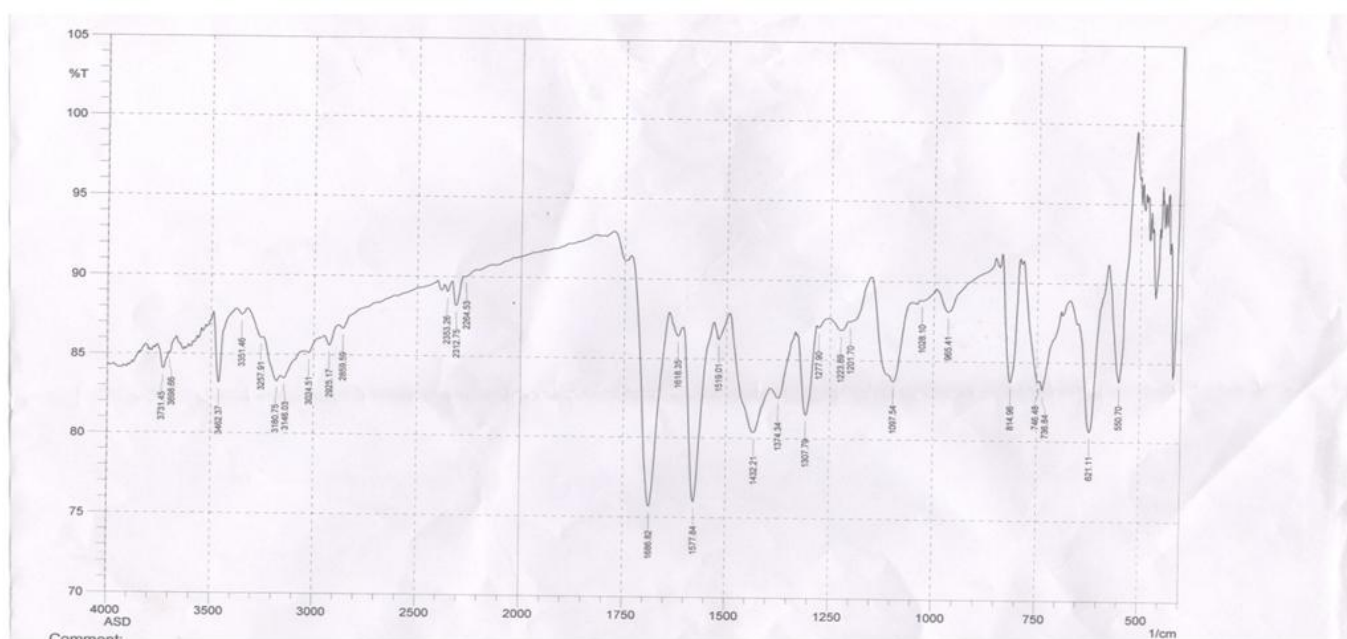


Fig.1. FT- IR Spectrum of semicarbazone of methoxyacetophenone

Table 1. Electrode I electrode response

Concentration of SrCl ₂ (M)	EMF In volts
1	0.250
1x10 ⁻¹	0.233
1x10 ⁻²	0.214
1x10 ⁻³	0.203
1x10 ⁻⁴	0.195
1x10 ⁻⁵	0.184

Table 2. Electrode II Electrode response

S.No	Concentration of SrCl ₂ solution (M)	EMF (Volts)
1	1	0.219
2	1x10 ⁻¹	0.202
3	1x10 ⁻²	0.184
4	1x10 ⁻³	0.174
5	1x10 ⁻⁴	0.166
6	1x10 ⁻⁵	0.166

The two electrodes behaves according to the Nernst equation.

Electrode II
Electrode Response

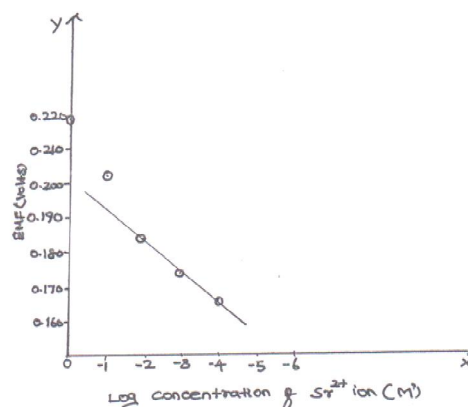


Fig .3 Plot of Log concentration of Sr(II) ion (M) Vs EMF (volts)

Electrode I
Electrode Response

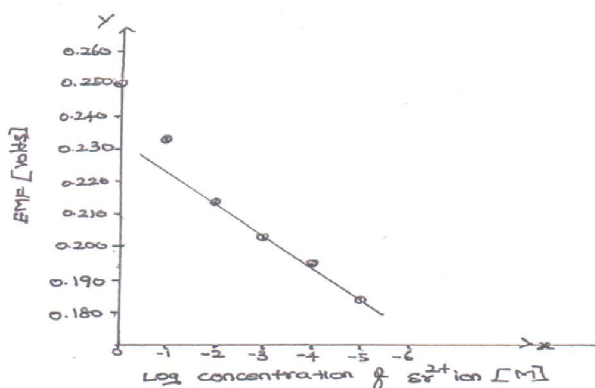


Fig .2 Plot of Log concentration of Sr(II) ion (M) Vs EMF (volts)

Effect of pH on electrode response

The effect of pH on the response of electrode was studied in this work. The electrode potential of standard Sr(II) solution of varying pH had been measured. It was found that the electrodes worked well over a wide pH range of 4 to 7.

Electrode I : Table – 3. Effect of pH for Sr²⁺ions

Concentration of SrCl ₂ (M)	pH4	pH7
1M	0.249	0.249
1x10 ⁻¹ M	0.231	0.229
1x10 ⁻² M	0.216	0.217
1x10 ⁻³ M	0.204	0.202
1x10 ⁻⁴ M	0.194	0.191
1x10 ⁻⁵ M	0.183	0.182

Electrode II : Table 4. Effect of pH for Sr²⁺ions

S.No	Concentration of the SrCl ₂ solution (M)	pH 4	pH 7
1.	1	0.222	0.225
2.	1x10 ⁻¹	0.205	0.202
3.	1x10 ⁻²	0.184	0.185
4.	1x10 ⁻³	0.178	0.175
5.	1x10 ⁻⁴	0.166	0.167
6.	1x10 ⁻⁵	0.166	0.166

Table 5. Electrode I Effect of medium for Sr²⁺ions

S.No	Conc. of the SrCl ₂ Solution (M)	Ethanol			Acetone			DMF		
		25%	50%	75%	25%	50%	75%	25%	50%	75%
1.	1	0.249	0.248	0.258	0.249	0.248	0.249	0.249	0.250	0.248
2.	1x10 ⁻¹	0.232	0.229	0.228	0.231	0.229	0.229	0.232	0.229	0.227
3.	1x10 ⁻²	0.216	0.217	0.218	0.217	0.216	0.216	0.216	0.218	0.216
4.	1x10 ⁻³	0.204	0.202	0.204	0.201	0.201	0.203	0.204	0.203	0.204
5.	1x10 ⁻⁴	0.193	0.193	0.193	0.196	0.191	0.192	0.193	0.194	0.193
6.	1x10 ⁻⁵	0.182	0.182	0.181	0.183	0.182	0.183	0.182	0.183	0.182

Table 6. Electrode II Effect of medium for Sr²⁺ions

S.No	Concentration of the SrCl ₂ solution (M)	Ethanol			Acetone			DMF		
		25%	50%	75%	25%	50%	75%	25%	50%	75%
1.	1	0.220	0.226	0.225	0.223	0.221	0.223	0.225	0.222	0.223
2.	1x10 ⁻¹	0.202	0.209	0.206	0.206	0.204	0.205	0.205	0.202	0.203
3.	1x10 ⁻²	0.185	0.189	0.184	0.189	0.188	0.187	0.184	0.185	0.187
4.	1x10 ⁻³	0.174	0.179	0.174	0.175	0.176	0.174	0.176	0.174	0.176
5.	1x10 ⁻⁴	0.166	0.170	0.166	0.169	0.169	0.166	0.168	0.167	0.168
6.	1x10 ⁻⁵	0.166	0.169	0.166	0.167	0.167	0.167	0.166	0.166	0.167

Effect of medium on electrode response on the electrode I and II:

To study the effect of medium, a standard solution containing 1M Sr (II) ion in a series of 25%, 50%, 75% Ethanol, acetone and dimethyl formamide was added. It was found that the potential of electrode I and II remains unchanged in the above medium.

Interference study

Selectivity is one of the most important characteristic of a chemical sensor. The influence of interfering ion and response behaviour of ion selective electrode is usually described in terms of selectivity coefficient. The potential response of the strontium ion selective electrode to different ion have been investigated by determining the selectivity coefficient of the electrode using Fixed Interference Method (FIM) based on semi empirical Nicolskii – Eisenman equation and the concentration of interfering ion was set to 1M. It was found that the potential of electrode I remains unaffected in the presence of a series of various cations like Na, Mn, Ca, K, and anions I, Br, NO₃²⁻, and Cl and also found that the potential of electrode II remains unaffected in the presence of various cations like Na⁺, Mg²⁺, Cu²⁺, K⁺, NH₄ and anions like I, Br, NO₃²⁻ and Cl.

Analytical application

Determination of strontium by direct potentiometric methods

The proposed electrodes was found to work well under the laboratory conditions. To assess the applicability of the sensors to real sample an attempt was made to determine strontium ion in vegetable (Beetroot). The recovery of strontium ion in sample analysis was found to be quantitative with the maximum recovery of electrode I was found to be 98% and the recovery of electrode II was 97%.

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