



ISSN: 0975-833X

RESEARCH ARTICLE

DEVELOPMENT OF STRONTIUM (II) SELECTIVE ELECTRODE BASED ON LARIAT ETHER
DERIVATIVE AS AN IONOPHORE

¹Gyanendra Singh and ²*Gaurav Kumar

¹Department of Chemistry M.M.H. College Ghaziabad U.P. 201001 India

²Department of Chemistry Mewar University Chittorgarh Rajasthan 312901, India

ARTICLE INFO

Article History:

Received 09th March, 2014

Received in revised form

16th April, 2014

Accepted 26th May, 2014

Published online 25th June, 2014

ABSTRACT

A lariat ether derivative N,N-bis[(1-benzothiophen-4-yl)methyl]-4,13-diaza-18-crown-6 has been synthesized and used as neutral carrier for the selective determination of strontium. The electrode works in a linear concentration range of 1.8×10^{-7} M – 1.0×10^{-1} M of Sr(II) ion with a slope of 30.57 mV/decade of activity. The electrode works successfully in a pH range of 3.0 – 10 and has fast response time (8s). The electrode was also used as an indicator electrode in potentiometric titration of Sr(II) with EDTA solution.

Key words:

Ion-selective electrode,
Strontium, Lariat ether,
Selectivity coefficient

Copyright © 2014 Gyanendra Singh and Gaurav Kumar. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Strontium is a soft, silvery metal. When cut it quickly turns a yellowish colour due to the formation of strontium oxide (SrO). Strontium is never found free in nature. The principle strontium ores are Celestine (Strontium sulphate, SrSO₄) and strontianite (strontium carbonate, SrCO₃) (Izzat *et al.*, 1995). The non-radioactive isotope of strontium is non-toxic to human beings. However, the radioactive isotope ³⁸Sr⁹⁰ created by fission of uranium nuclei is incorporated into the bones. The α-particles emitted by this isotope may produce bone cancer (Mohapatra *et al.*, 2004). It may also cause anaemia and oxygen shortages. It is used in a variety of optical materials, paints, plastics, bricks, tiles and ferrite magnets (Baumann, 1975). Various methods such as atomic absorption spectrometry (AAS) (Shamsipur *et al.*, 2001), flame photometry (Bondareva *et al.*, 1991), ICP-AES (Tarun *et al.*, 2002) etc. have been reported for the determination of strontium. These methods required large infrastructure back up, relatively expensive and time consuming. Thus ion-selective electrodes due to its simple preparation, high selectivity, high sensitivity, wide concentration range and fast response time are the effective analytical device for the determination of strontium in solution (Singh *et al.*, 2013; Faridbod *et al.*, 2008; Cozzi, 2004; Jain *et al.*, 1998; Ganjali, *et al.*, 2001; Akbari *et al.*, 2003; Katsu *et al.*, 2001).

Lariat ethers belong to a special class of crown ethers with covalently linked side arm(s). The cation-binding behavior of lariat ethers will depend upon both the size of cavity and the donor groups on the flexible arm (Covadonga Rodri *et al.*, 2001). The macrocyclic ring of crown ether forms nesting complex or a sandwich complex depending on the size of cation. The flexible arms of the crown ether provide three dimensional complexation. The cation-binding behavior of lariat ethers will depend upon both the size of cavity and the donor groups on the flexible arm (Gupta *et al.*, 2009; Soledad García *et al.* 2011). In the present work, the lariat ether derivative based on 18-crown-6 was synthesized and used as ionophore for the selective determination of strontium in various samples. The selectivity coefficient of membrane electrode was calculated by match potential method (MPM) and the response characteristics of electrode were also compared with previously reported electrodes.

Experimental section

Chemicals used

18-crown-6 and 3-(chloromethyl)-1-benzothiophene were purchased from (Sigma-Aldrich). High molecular weight Poly(Vinyl Chloride) (PVC), oleic acid (OA), dibutylbutyl phosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), tris(2-ethylhexyl)phosphate (TEP), sodium tetraphenyl borate and (NaTPB), acetone, chloroform and tetrahydrofuran (THF) were purchased from Merck. All metal nitrates were also purchased from Fischer Scientific

*Corresponding author: Gaurav Kumar

Department of Chemistry Mewar University Chittorgarh Rajasthan
312901, India

India. Doubled-distilled water was used to prepare the metal nitrate solutions.

Synthesis of lariat ether derivative

To a mixture of 4,13-diaza-18-crown-6 (3 mmol) and K_2CO_3 (10 mmol) in DMF (5 mL), 1.82 g 3-(chloromethyl)-1-benzothiophene (10 mmol) in DMF (5 mL) were added and stirred under nitrogen at 60 °C overnight. After cooling to room temperature, the mixture was poured into 30 mL of ice-cold saturated NH_4Cl solution. It was then filtered and the solvent was removed from the filtrate in a rotary evaporator. Addition of cold diethyl ether to the oily residue led to the deposition of a white precipitate of N,N-bis[(1-benzothiophen-4-yl)methyl]-4,13-diaza-18-crown-6 (Fig. 1). Yield: (64%). The 3D structure of ionophore is shown in Figure3.

1H NMR (200 MHz, $CDCl_3$); δ =7.63 (m, 4H, arH), 7.60 (m, 4H, arH), 7.43 (s, 2H, arH), 3.76 (s, 4H, N- CH_2 -ar), 3.72 (t, 8H, $-CH_2O-$), 3.64 (s, 8H, $-CH_2-O-$), 2.72 (t, 8H, N- CH_2-).
 ^{13}C NMR (200 Mz, $CDCl_3$); δ =153.00, 133.36, 130.18, 127.23, 124.61, 120.26, 72.74, 68.19, 58.67, 54.99.

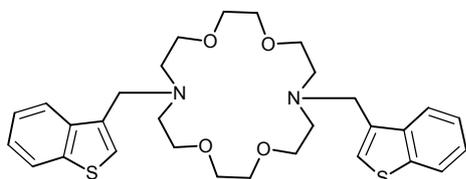


Figure 1. N,N-bis[(1-benzothiophen-4-yl)methyl]-4,13-diaza-18-crown-6

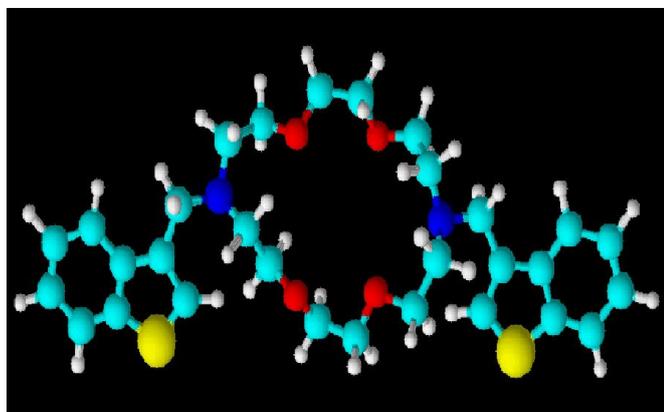


Figure 2. 3D-structure of ionophore

Development of membrane

The various membranes of ionophore (L) with different plasticizers i.e., DBP, DBBP, DOP, TEP and OA were prepared using PVC as binder material and NaTPB as anionic additive, by the method of Craggs *et al.* All the membrane components were dissolved in 15 ml of THF. The resulting solution was stirred well and poured in a glass casting ring on a smooth glass plate. The THF was allowed to evaporate at room temperature for 24 hours in order to obtain the uniform membrane. A membrane sheet about 0.5 mm of thickness and 8 mm diameter was cut away from inner edge and glued it to one end of a glass tube.

Potential measurements

The membrane electrode was finally conditioned by soaking in a 0.1 M $Sr(NO_3)_2$ solution for 2 days. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. Potential measurements were performed with the help of a digital potentiometer at $25 \pm 0.1^\circ C$ by following cell assembly.

Internal reference electrode	Internal reference solution (0.01 M Sr^{2+})	Strontium Selective Membrane	Test solution	External reference electrode
------------------------------	---	------------------------------	---------------	------------------------------

RESULTS AND DISCUSSION

Optimization of membrane components

The composition of membrane components significantly affects the sensitivity and selectivity of membrane electrodes therefore membranes with different compositions were prepared and the response characteristics were studied. After several experimental results it was observed that the membrane with the composition of PVC : Plasticizer: ionophore: NaTPB of 30: 62: 5: 3 (w/w) shows the best possible results of linear concentration range, detection limit, response time, slope of calibration curve etc. (Table 1)

Linear concentration range and detection limit

The presence of plasticizers as the membrane component significantly enhances the selectivity and sensitivity of membrane electrodes. In the present study membranes of different plasticizers was prepared and their potential

Table 1. optimization of membrane components

Electrode No.	Membrane Composition (%)				Linear working range (M) ^a	Slope (mV/dec. of activity) ^a	Response Time (sec)
	PVC	Additive	Plasticizer	Ionophore			
1	30	3, NaTPB	62, DBP	5	1.8×10^{-7} - 1×10^{-1}	30.57 ± 0.5	8
2	30	3, NaTPB	62, DBBP	5	2.3×10^{-6} - 1×10^{-1}	26.8 ± 0.5	17
3	30	3, NaTPB	62, DOP	5	1.7×10^{-6} - 1×10^{-1}	25.4 ± 0.5	18
4	30	3, NaTPB	62, TEP	5	5.0×10^{-6} - 1×10^{-1}	24.6 ± 0.5	20
5	30	3, NaTPB	62, OA	5	6.2×10^{-6} - 1×10^{-1}	24.7 ± 0.5	18
6	34	3, NaTPB	58, DBP	5	1.0×10^{-6} - 1×10^{-1}	30.55 ± 0.5	8
7	28	3, NaTPB	64, DBP	5	1.8×10^{-7} - 1×10^{-1}	30.57 ± 0.5	8
8	30	3, NaTPB	60, DBP	7	1.8×10^{-7} - 1×10^{-1}	30.56 ± 0.5	8
9	60	10, NaTPB	0.00	30	2.0×10^{-4} - 1×10^{-1}	18.6 ± 0.5	30

responses were investigated (Fig. 3). The data presented in Table 1 and Figure 3 clearly indicates that the membrane with DBP as plasticizer shows the wide linear concentration range ($1.8 \times 10^{-7} \text{ M} - 1.0 \times 10^{-1} \text{ M}$), low detection limit $5.0 \times 10^{-8} \text{ M}$, fast response time of about 8s as compared to other membranes. This is because of the high polarity of DBP which provides the best possible environment for ligand ion complexation kinetic. The membrane without plasticizer has the linear concentration range of $2.0 \times 10^{-4} \text{ M} - 1.0 \times 10^{-1}$, with lower detection limit of $5.2 \times 10^{-5} \text{ M}$ for Sr(II) ion.

Effect of pH and non-aqueous contents

The effect of PH of test solution on the potential response of membrane electrode no. 1 was studied over the range of 1.0 – 12.0 for A ($1.0 \times 10^{-2} \text{ M}$), B ($1.0 \times 10^{-3} \text{ M}$) and C ($1.0 \times 10^{-4} \text{ M}$) solution of Sr^{2+} ion. The pH of the test solution was adjusted by adding dil. HNO_3 and NaOH .

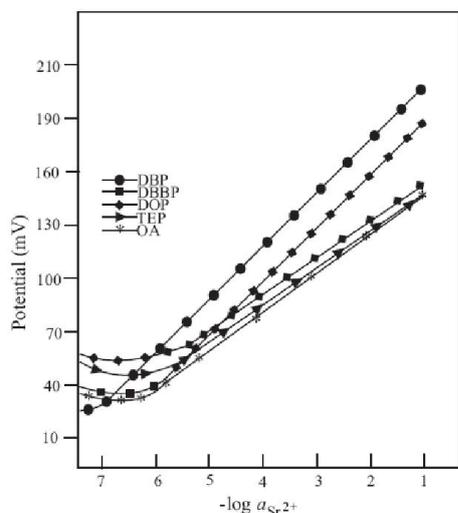


Figure 2. Calibration curve of membrane electrode with different plasticizers

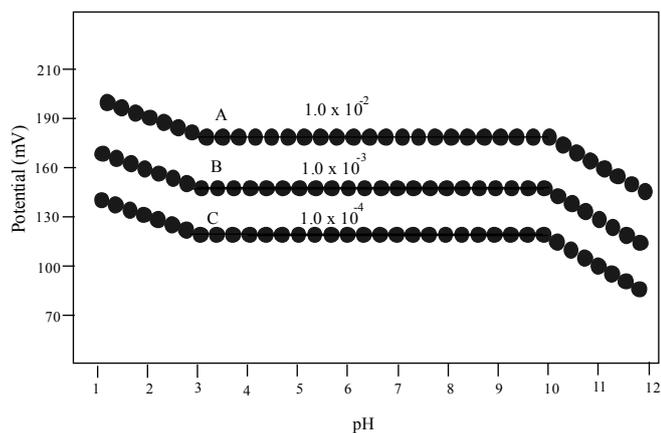


Figure 3. Effect of pH on potential response of electrode no. 1

The data presented in Figure 4 indicates that the potential stays constant from pH 3.0 to 10.0, thus this pH range is taken as the optimum pH range of electrode assembly. However beyond this pH range a sharp increase in potential is observed, which may be due to competition kinetics between Na^+ and Sr^{2+} or due to the formation of hydroxyl complex of Sr(II). The observed sharp change in potential response below pH 3 might be due to the interference caused by H^+ .

Table 2. Effect of partially non-aqueous contents on response characters of electrode no.1

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. Range (M)	Response time (Sec)
0	30.57 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
Methanol			
10	30.57 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
20	30.53 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
30	30.47 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	9
40	27.34 ± 0.5	$6.3 \times 10^{-7} - 1.0 \times 10^{-1}$	12
50	25.45 ± 0.5	$8.2 \times 10^{-7} - 1.0 \times 10^{-1}$	14
Ethanol			
10	30.57 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
20	30.50 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	9
30	30.42 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	9
40	26.83 ± 0.5	$6.5 \times 10^{-7} - 1.0 \times 10^{-1}$	12
50	24.65 ± 0.5	$8.6 \times 10^{-7} - 1.0 \times 10^{-1}$	15
Acetone			
10	30.57 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
20	30.35 ± 0.5	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	8
30	30.27 ± 0.5	$1.9 \times 10^{-7} - 1.0 \times 10^{-1}$	9
40	26.13 ± 0.5	$8.3 \times 10^{-7} - 1.0 \times 10^{-1}$	13
50	24.62 ± 0.5	$9.1 \times 10^{-7} - 1.0 \times 10^{-1}$	15

The performance of electrode no. 1 based N,N -bis[(1-benzothiophen-4-yl)methyl]-4,13-diaza-18-crown-6 as ionophore and DBP as plasticizer was also studied in partially non-aqueous media (methanol-water and ethanol-water and acetone –water mixtures) and the results are compiled in Table 3. The non-aqueous contents up to 30% do not have any appreciable change on response characters of the electrode. Above 30% non-aqueous content, the working concentration range and slope of the calibration curve are considerably shortened. Thus the electrode no. 1 can be used in mixtures having up to 30% (v/v) non-aqueous content for the selective determination of Sr(II) ion.

Dynamic Response time and life time

The dynamic response time of ion selective electrode is defined as the time taken to reach a static potential by the electrode assembly. In present study the response time was calculated for $1.0 \times 10^{-4} \text{ M}$ and $1.0 \times 10^{-2} \text{ M}$ solution of Sr(II) ion (Fig.5). It was observed that the electrode no. 1 reached the equilibrium value in a very short time of about 8s.

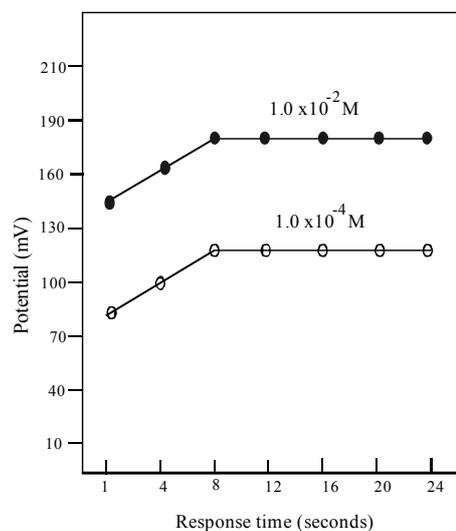


Figure 4. Response time curve for electrode no. 1

The check the reversibility of membrane electrode the response time was also calculated by change the concentration of test solution from lower to higher ($1.0 \times 10^{-7} - 1.0 \times 10^{-1}$) and from higher to lower ($1.0 \times 10^{-1} - 1.0 \times 10^{-7}$). It was observed that the response time remains almost same for whole concentration range. This indicates that the proposed electrode is sufficiently reversible for Sr(II) ion. The life time of the proposed electrode assembly was calculated in terms of change in slope of calibration curve and detection limit. The slope of calibration curve and detection limit found to be reproducible (up to 95%) over a period of 7 months (Table 3). After this period significance decrease in slope and increase in detection limit was observes.

Table 3. Life time of Sr(II) selective electrode no. 1

Time (months)	Slope (mV/decay)	Detection limit (M)
1	30.57 ± 0.5	5.0×10^{-8}
3	30.0 ± 0.5	4.95×10^{-8}
5	29.65 ± 0.5	4.80×10^{-8}
6	29.32 ± 0.5	4.72×10^{-8}
7	29.10 ± 0.5	4.63×10^{-8}
8	27.20 ± 0.5	5.0×10^{-8}
9	25.62 ± 0.5	5.0×10^{-8}

Selectivity coefficient: The selectivity of ion-selective electrode is one of the most important characteristics which detect the selectivity of electrode towards Sr(II) over other cations and determine the practical utility of the electrode. In the present the potential response of electrode was investigated in the presence of various interfering foreign cations using the matched potential method (MPM) [30] recommended by IUPAC (Bakker *et al.*, 2000; Viteri and Diamond, 1994). The selectivity coefficient was determined by the following equation:

$$K_{Sr^{2+}, M^{n+}} = \frac{a_2 - a_1}{a_{M^{n+}}}$$

where a_2 is the activity of Sr(II) in presence of interfering ion, a_1 is the initial activity of primary ion and $a_{M^{n+}}$ is the activity of interfering ion. The values of selectivity coefficient were calculated for different mono, bi and trivalent cations and the results are summarized in table 4.

Table 4. Selectivity coefficient calculated by MPM method for electrode no. 1

Interfering ions	Selectivity coefficient ($K_{Sr^{2+}, M^{n+}}$) (MPM)
Na ⁺	1.7×10^{-3}
K ⁺	1.6×10^{-3}
Rb ⁺	2.1×10^{-3}
Cs ⁺	2.3×10^{-3}
Ag ⁺	4.5×10^{-3}
Mg ²⁺	1.2×10^{-4}
Ca ²⁺	2.3×10^{-3}
Ba ²⁺	2.8×10^{-3}
Ni ²⁺	2.5×10^{-3}
Co ²⁺	3.2×10^{-3}
Pb ²⁺	1.8×10^{-3}
Cu ²⁺	4.6×10^{-3}
Cd ²⁺	4.5×10^{-3}
Zn ²⁺	1.6×10^{-3}
Hg ²⁺	5.2×10^{-3}
Al ³⁺	3.1×10^{-3}
Cr ³⁺	2.8×10^{-3}
Fe ³⁺	2.3×10^{-3}
La ³⁺	1.7×10^{-3}

The performance of proposed electrode was also compared with the previously reported Sr(II) selective electrodes. The comparison of response characteristics are listed in table 5. The data presented in the table 5 indicates the proposed electrode no. 1 is superior in terms of concentration range, detection limit and response time as compared to previously reported electrodes.

Table 5. Comparison of response characters of proposed electrode with previously reported electrodes

Reference	Concentration range (M)	Lower detection limit (M)	Slope (mV/decay of activity)	Response time (sec)	pH-range
This work	$1.8 \times 10^{-7} - 1.0 \times 10^{-1}$	5.0×10^{-8}	30.57	8	2.5 - 10.0
Chandra, <i>et al.</i> , 2012	$1.0 \times 10^{-7} - 1.0 \times 10^{-2}$	2.7×10^{-8}	29.4	<10	2.5 - 10.5
Zanjanchi <i>et al.</i> , 2009	$8.0 \times 10^{-7} - 1.0 \times 10^{-1}$	7.5×10^{-7}	29.1	11	3.0 - 10.0
Arbab-Zavar <i>et al.</i> , 2009	$1.0 \times 10^{-7} - 1.0 \times 10^{-2}$	-	27.35	20 - 25	-
Jain <i>et al.</i> , 2004	$3.2 \times 10^{-5} - 1.0 \times 10^{-1}$	-	30	10	3.0 - 10.0
Shamsipur <i>et al.</i> , 2007	$1.6 \times 10^{-6} - 1.0 \times 10^{-3}$	6.3×10^{-7}	30	<15	4.3 - 9.4

Analytical applications

In order to investigate the analytical use of the proposed electrode no.1, the electrode was successfully applied as an indicator electrode for Sr²⁺ and EDTA titration. The titration was carried in 15 ml solution of Sr²⁺ (0.001 M) against 0.01 M EDTA solution. During the titration the pH (9.5) of the solution was maintained by using ammonia buffer. The potential responses of the titration are shown in Figure 5. The titration curve shown in Figure 6 is not a standards sigmoid curve, but has a sharpe inflation point corresponds to 1:1 stoichiometry of Sr (II) and EDTA. Thus the electrode can be used for the determination of Sr(II) (Fig.6) in solution.

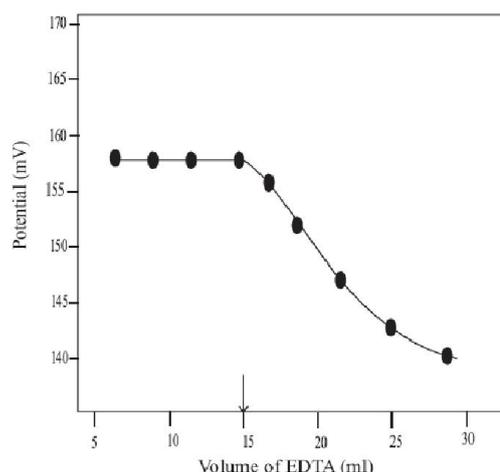


Figure 5. Titration curve of Sr(II) with EDTA solution

Conclusion

A lariat ether derivative based on 18-crown-6 was synthesized and used as ionophore for constricting Sr(II) selective

membrane electrode. The electrode no. 1 based on DBP as plasticizer has a detection limit of 5.0×10^{-8} M in a linear concentration range of 1.8×10^{-7} – 1.0×10^{-1} with a slope of calibration curve of 30.57 mV/decade of activity for Sr(II) ion. The proposed electrode shows good selectivity for Sr(II) over a wide range of mono-, di- and trivalent cations. The electrode was successfully in a pH range of 3.0 – 10.0 and has fast response time of about 8s.

REFERENCES

- Akbari, A; Mousavi, M.F; *Talanta*; 2003, 60, 853.
- Arbab-zavar, M.H; Rounaghi, G.H; and Fahmideh-rad, E; *Asian Journal of Chemistry* Vol. 21, No. 3 (2009), 2224-2232
- Bakker, E; Pretsch, E; Bühlmann, P; *Anal. Chem.*, 2000, 72, 1127–1133.
- Baumann, E.W; *Anal. Chem.*, 1975, 47,959.
- Bondareva, N.V and Zolotoritskaya, E.; *Zhavod. Lab.*; 1991,57, 36 .
- Covadonga Rodríguez-Infante, S; David Esteban, D; Fernando Avecilla, F; Andre's de Blas; Rodríguez-Blas, T; Mahi, J; Macedo, A.L; Geraldes, C.F.G.C; *Inorganica Chimica Acta*; 2001, 317, 190–198.
- Cozzi, P.G; *Chem. Soc. Rev.*; 2004, 33, 410-421.
- Chandra, S; Sharma, K; Kumar, A; 2012, doi:10.1016/j.jscs.2011.11.002
- Faridbod, F; M.R. Ganjali, M.R; et. al., *Sensors*, 2008, 8, 1645-1703.
- Ganjali, M.R, et. al, *Sensor Journal, IEEE*, 2001,7,4, 544.
- Gupta, V.K; Pal, M.K; Singh, A.K; *Anal Chim Acta.* 2009, 12, 161-9.
- Izzat, R.M; Bradshaw, J.S; Bruening, R. L; Tarbet, B.J and M.L. Bruening, M.L; *Pure Appl. Chem.*, 1995, 67, 1069.
- Jain, A.K; Gupta, V.K; Singh, L.P; Khurana,U; *Talanta*, 1998, 46, 6, 1453.
- Jain, A.K; Vinod K. Gupta, A.K; and Raisoni, J.R; *Sensors* 2004, 4, 115-124
- Mohapatra, P.K; Pathak, P.N; Kelkar, A and Manchanda, V.K; *New J. Chem.*, 2004,28, 1004.
- M Soledad García, M.S; Ortuño, J.A; Albero, M.I; and Abuherba, M,S; *Sensors* 2009, 9, 4309-4322;
- Mojtaba Shamsipur, M; Kazemi, S.Y; and Sharghi, H; *Sensors* 2007, 7, 438-447
- Shamsipur M; Mojtaba, R and Raufi, F *Mikrochim. Acta*, 2001, 137, 163.
- Singh, S; Rani,G; Singh, G; and Agarwal, H; *Electroanalysis*, 2013, 25, 475-485.
- Singh, G; Rani, G; and Singh, S; *Sensor letters*, 2013, 11,11, 2072 – 2076.
- Xu, D; Katsu, T; *Electroanalysis*, 2001, 13, 10, 868 – 871.
- Tarun, D.K. and M. Sarin, *Geostd. Newslett.*, 26, 301 (2002).
- Viteri, Sa'ez de; Diamond, F.J.D; *Analyst*, 1994, 119, 749–758.
- Zanjanchi, M.A; Arvand, M; Mahmoodi, N,O; Islamnezhad, A; *Electroanalysis*, 2009, 21, 16, 1816 – 1821.
