

## PVC Membrane Sensor for Nd (III) Based on N<sup>1</sup>, N<sup>2</sup>-Bis (Salicylidine) Butane-1, 4 -Diamine

Beena Saraswathyamma<sup>a\*</sup> and Krishnapillai Girish Kumar<sup>b</sup>

<sup>a</sup> Dept.of Chemistry, Amrita School of Arts and Sciences,  
Amrita Vishwa Vidyapeetham, Amrita University, Kollam, India

<sup>b</sup> Department of Applied Chemistry, Cochin University of Science and Technology,  
Kerala, Kochi, India  
*beenasdec25@gmail.com, giri@cusat.ac.in*

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**Abstract:** N<sup>1</sup>, N<sup>2</sup>-bis(salicylidine)butane-1,4-diamine (SAB ) based PVC membrane sensor was fabricated for Nd(III). The developed sensor showed nernstian response in the concentration range of 1.0×10<sup>-6</sup> to 1.0×10<sup>-1</sup> M. Nernstian slope of the proposed sensor was found to be 20.6±0.3 mV/decade in the pH range 3.0 to 7.5. The developed sensor displays a response time of <15 s. The proposed sensor can be used over a period of 7 weeks without any significant changes in its Nerstian behaviour. The sensor showed good selectivity for neodymium when compared with other metal ions such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, La<sup>3+</sup>, and Gd<sup>3+</sup>. This electrode was used as an indicator electrode in the potentiometric titration of neodymium ions with EDTA and was also applied in the determination of neodymium in binary mixture.

**Keywords:** PVC membrane Sensor; Neodymium ions; Ion-selective electrode; N<sup>1</sup>, N<sup>2</sup>-bis(salicylidine)butane-1,4-diamine; Potentiometry.

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### 1. INTRODUCTION

Neodymium is the second most abundant of the rare earths. Neodymium is largely used in the production of neodymium-iron-boron (Nd<sub>2</sub>-Fe-B) permanent magnets which is the strongest permanent magnet commercially available. Oxides of lanthanides are extensively used in the fabrication of glass fibers for optical purposes, optical glasses, gasoline-cracking catalysts, polishing compounds and carbon arcs, and in the iron and steel industries to remove sulfur [1]. Neodymium is discarded in to the environment by petroleum producing industry and also when house hold equipments are thrown away. So the trace level monitoring of rare earth elements in environmental and in biological materials has received increasing attention [2].The analytical techniques that have been reported for the determination of Nd<sup>3+</sup> ions are X-ray fluorescence [3] (AAS), neutron activation analysis [4], isotopic dilution method [5], inductively coupled plasma atomic emission spectroscopy (ICP AES)[6]and inductively coupled plasma mass spectroscopy[7-8]. Although these methods are sensitive and precise, they require multiple sample preparation and are expensive. Potentiometric sensors offer a sensitive, selective and cost effective method for the determination of metal ion even from a complex matrix of samples. This paper introduces a highly selective and sensitive PVC membrane sensor based on N<sup>1</sup>, N<sup>2</sup>-bis(salicylidine)butane-1,4-diamine for neodymium.

### 2. EXPERIMENTAL

#### 2.1. Reagents

1, 4 diaminobutane, Salicylaldehyde, dioctyl phthalate (DOP), dioctyl sebacate (DOS), dibutyl phthalate (DBP), dioctyl adipate (DOA), and sodium tetra phenyl borate (NaTBP) were purchased from Lancaster (UK) and were used as such. Lanthanide salts were obtained from IRE Ltd (INDIA) and other metal salts, high molecular weight PVC and dibutyl sebacate (DBS) were purchased from Merck. S.D. fine-chem. Ltd, India was the supplier for tetrahydrofuran (THF) and methanol and was distilled before use. Double distilled water was used for the preparation of all metal salts solutions and solutions of different concentrations were made by serial dilution of the 1×10<sup>-1</sup> M stock solution.

#### 2.2. Synthesis of Ionophore

The Schiff's base N<sup>1</sup>,N<sup>2</sup>-bis(salicylidine)butane-1,4-diamine(SAB-Fig.1) was prepared by refluxing (0.02mol) salicylaldehyde and (0.01mol) butane-1,4-diamine in 20 mL methanol for 3hrs.The yellow

product that separated out was filtered and recrystallized from dichloromethane. The formation of the ionophore was confirmed by elemental analysis and spectroscopic techniques and results are given below.

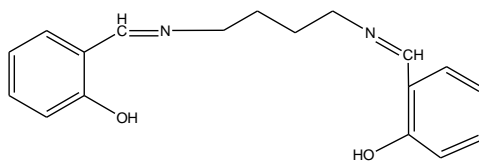


Fig1. Structure of SAB

### 2.3. CHN Analysis

Found (%): C - 72.44, H - 6.30, N - 9.25

Calcd (%): C - 72.95, H - 6.80, N - 9.45

### 2.4. Spectroscopic Analysis

IR (KBr,  $\text{cm}^{-1}$ ): 1604 (CH=N, S), 1581, 1528, 3565, 2885, 1352, 149, 1282, 1223, 1047, 942, 893, 744, 750, 659.

$^1\text{H}$ NMR (DMSO): 8.5 (2H, s, CH=N), 7.49 (2H, d, Ar-H), 7.3 (2H, t, Ar-H), 6.9 (2H, m, Ar-H), 6.7(2H, m, Ar-H), 3.5(4H, t,  $\text{CH}_2$ ), 11.29 (2H, s, OH).

### 2.5. Preparation of PVC Membrane Electrode

The PVC membrane was prepared by thoroughly mixing ionophore, PVC, DBS and NaTBP in the ratio 3:32:62:3 in 6-7 mL THF. The resulting solution was then poured into glass ring resting on smooth glass plate. The solvent was then allowed to evaporate at room temperature. The transparent membrane obtained was then cut to size and attached to one end of a Pyrex glass tube with araldite. The tube filled with internal solution ( $1.0 \times 10^{-1}$  M  $\text{NdCl}_3$ ) was conditioned for 24 hrs by soaking in  $1.0 \times 10^{-1}$  M  $\text{NdCl}_3$  solution.

### 2.6. EMF Measurements

Emf measurements were carried out by using the following cell assembly Ag, AgCl| KCl || test solution | membrane | internal solution ( $1.0 \times 10^{-1}$  M  $\text{NdCl}_3$ ) || KCl | AgCl, Ag. Potentials were measured using a Metrohm 781 ion meter at  $25 \pm 0.1^\circ\text{C}$

## 3. RESULTS AND DISCUSSION

The structure of the ionophore (SAB) was confirmed by  $^1\text{H}$  NMR, IR, and elemental analysis (CHN). The data is given in the experimental section. The  $\nu_{\text{max}}$ /cm at 1604 and  $\delta$  at 8.5 indicates the presence of CH=N in the structure of SAB. The close agreements between the theoretically and experimentally obtained CHN values also confirm the formation of SAB.

The presence of four donor atoms (two nitrogen and two oxygen) in the structure of SAB is expected increase the stability and selectivity of its complexes with lanthanide ions rather than alkali and alkaline metal ions [9]. So, in preliminary experiments, SAB was used as a potential neutral ion carrier to prepare PVC membrane electrodes for a number of metal ions and potential response of the resulting sensors are shown in Fig 2. As it is seen, neodymium ion demonstrates most sensitive response to the ionophore and is suitably determined by the developed sensor.

### 3.1. Optimization of Membrane Composition

The key factors which influence the sensitivity, selectivity and linearity of the membrane sensors are the nature of ionophore, membrane composition and nature of plasticizer [10-20]. The performance characteristics of different membranes having ingredients of different proportions are summarized in Table 1. As expected, the amount of ionophore was found to affect the sensitivity of the PVC membrane sensor. The calibration slope of the membrane sensor was found to be increased when ionophore percentage varied from 2-3% and further addition of the ionophore resulted in a decrease in determination range of the sensor, probably due to some inhomogeneity and possible saturation of the membrane. The nature of plasticizer influences the dielectric constant of the membrane phase and state of the ligand [21-25]. Of the four plasticizer studied, membrane with DBS as plasticizer

displayed in best slope (SA<sub>3</sub>). The effect of both OA and NaTPB, as suitable lipophilic additives, on the response characteristics of the proposed PVC membrane was also investigated, and the results are also included in Table1. The sensor, SA<sub>3</sub>, with NaTBP as additive gave better slope than oleic acid. 3% NaTBP was found to be the optimum amount and further variation of NaTBP from 3% to 5% resulted in a super nernstian slope. Thus optimized membrane composition which resulted in best performance was found to be 3: 32: 62: 3 (SAB: PVC: DBS: NaTBP).

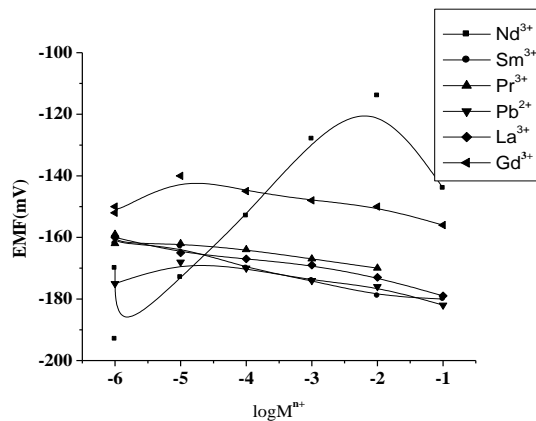


Fig2. Potential response of various PVC membrane ion selective electrodes based on SAB

Table1. Optimization of membrane composition

| Membrane no.    | Composition (%) |     |             |                            | Slope (mV/decade) | Concentration range ( M)             |
|-----------------|-----------------|-----|-------------|----------------------------|-------------------|--------------------------------------|
|                 | Ionophore       | PVC | Plasticizer | Additives NaTBP/oleic acid |                   |                                      |
| SA <sub>1</sub> | 2               | 32  | DBP, 63     | 3                          | 13.3±0.4          | 10 <sup>-6</sup> to 10 <sup>-3</sup> |
| SA <sub>2</sub> | 2               | 32  | BEA, 63     | 3                          | 10.9±0.5          | 10 <sup>-5</sup> to 10 <sup>-2</sup> |
| SA <sub>3</sub> | 2               | 32  | DBS, 63     | 3                          | 16.7±0.4          | 10 <sup>-6</sup> to 10 <sup>-2</sup> |
| SA <sub>4</sub> | 2               | 32  | BEP, 63     | 3                          | 12.5±0.6          | 10 <sup>-6</sup> to 10 <sup>-4</sup> |
| SA <sub>5</sub> | 2               | 32  | DBS, 58     | 3*                         | 10.9±0.3          | 10 <sup>-5</sup> to 10 <sup>-2</sup> |
| SA <sub>6</sub> | 3               | 32  | DBS, 62     | 3                          | 20.6±0.3          | 10 <sup>-6</sup> to 10 <sup>-2</sup> |
| SA <sub>7</sub> | 4               | 32  | DBS, 61     | 3                          | 21.3±0.4          | 10 <sup>-4</sup> to 10 <sup>-1</sup> |
| SA <sub>8</sub> | 3               | 32  | DBS, 60     | 5                          | 25.3±0.4          | 10 <sup>-5</sup> to 10 <sup>-2</sup> |

\*Oleic acid

The surface structure of the membrane was studied using SEM image. The SEM image of the membrane SA<sub>6</sub> is presented in the Figure 3. This image gives an idea of the homogeneity of the membrane which is a main factor affecting the response characteristics of the sensor. It is clear from the figure that the surface of the optimized membrane is smooth and homogeneous.

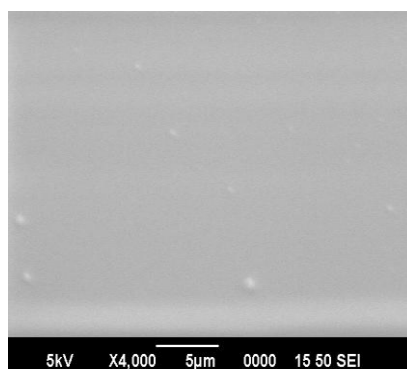
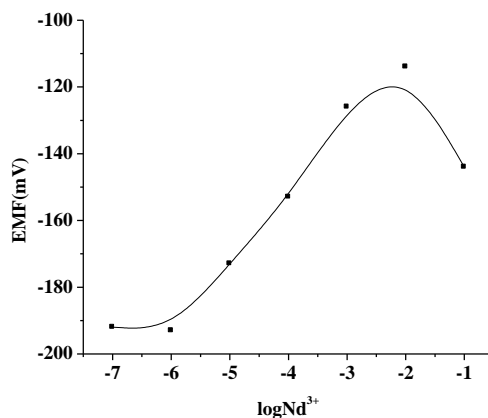


Fig3. SEM image of the polymeric membrane of SA<sub>6</sub> sensor

### 3.2. Calibration Curve and Statistical Data

The optimum equilibration time for the membrane sensor in the presence of  $1.0 \times 10^{-1}$  M  $\text{NdCl}_3$  was found to be 24 hrs. The sensor showed linear response in the range  $1.0 \times 10^{-6}$  -  $1.0 \times 10^{-1}$  M (Fig 4). The slope of the calibration graph is found to be  $20.6 \pm 0.3$  mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph is found to be  $8.7 \times 10^{-7}$  M. The membrane sensor could be used for at least 7 weeks without any measurable divergence from Nernstian response.



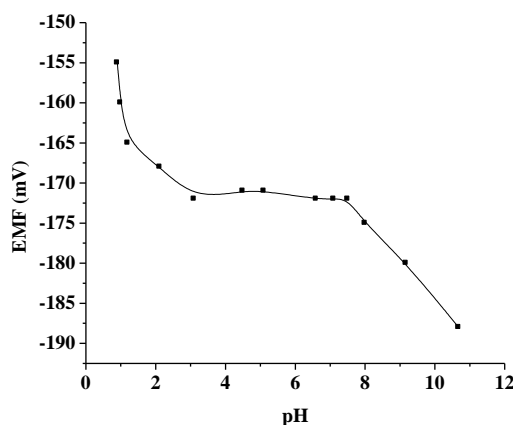
**Fig4.** Calibration graph for Nd (III) selective PVC membrane sensor based on SAB ( $\text{SA}_6$ )

### 3.3. Response Time

Dynamic response time is an important factor of any ion selective electrode [26]. The response time of the membrane sensor was recorded by changing the  $\text{Nd}^{3+}$  concentration from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M and was measured as  $< 15$ s over the entire concentration range.

### 3.4. Effect of pH

The pH dependence of the membrane sensor has been tested using  $1 \times 10^{-4}$  M  $\text{NdCl}_3$  solution over the pH range from 1 to 11 and results are shown in the figure 5. It was found that potential remains constant in the pH range 3.0 to 7.5. Beyond this pH, a drift in potential is observed which may be due to the formation of hydroxide of  $\text{Nd}^{3+}$  at higher pH and interference by hydrogen ion at lower pH.



**Fig5.** The effect of pH of test solution ( $1 \times 10^{-4}$  M  $\text{NdCl}_3$ ) on the response of Nd (III) membrane sensor  $\text{SA}_6$

### 3.5. Selectivity

The influence of the interfering ions on the response characteristics of the sensor is expressed in terms of selectivity coefficient K. Potentiometric selectivity coefficients of neodymium membrane sensor were evaluated by fixed interference method (FIM) [27- 29] at  $10^{-2}$  M concentration of interfering ions using the equation  $K_{A,B}^{\text{pot}} = a_A / (a_B)^{Z_A/Z_B}$  Where  $K_{A,B}^{\text{pot}}$  is the selectivity coefficient;  $a_A$  is the value obtained from the intersection of the extrapolated linear portions of the plot of EMF values versus the logarithm of the activity of the primary ion;  $a_B$  is the activity of the interfering ion which is fixed;  $Z_A$

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and  $Z_B$  are the charge numbers of the primary ion, A, and of the interfering ion, B. The experimental conditions employed and the resulting values obtained are given in Table 2. The selectivity coefficients are on the order of  $10^{-3}$  to  $10^{-2}$ , which seems to indicate that these cations have negligible effect on the functionality of the neodymium sensors. The relatively good selectivity of the electrodes for neodymium ions arose from the stronger tendency of the carrier molecule for complexing with  $Nd^{3+}$  compared to other cations.

**Table2.** Selectivity coefficients for  $SA_6$  and  $Sb_6$  sensors using fixed interference methods of interfering ions

| Interfering Ions ( $10^{-2}$ M) | $K_{set}$             |
|---------------------------------|-----------------------|
| $Na^+$                          | $3.16 \times 10^{-2}$ |
| $K^+$                           | $3.53 \times 10^{-2}$ |
| $Mg^{2+}$                       | $2.77 \times 10^{-2}$ |
| $Pb^{2+}$                       | $2.23 \times 10^{-2}$ |
| $Ag^+$                          | $3.48 \times 10^{-2}$ |
| $Ca^{2+}$                       | $5.67 \times 10^{-2}$ |
| $Gd^{3+}$                       | $9.68 \times 10^{-3}$ |
| $Sm^{3+}$                       | $1.02 \times 10^{-2}$ |
| $La^{3+}$                       | $6.55 \times 10^{-3}$ |
| $Pr^{3+}$                       | $8.55 \times 10^{-3}$ |

### 3.6. Analytical Applications

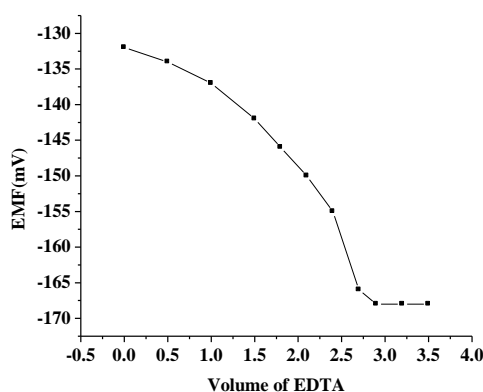
The utility of the developed sensor was investigated in the determination of neodymium ions in various binary mixtures and the results are presented in Table 3. It was observed that the recoveries of Nd (III) ions are quantitative in all cases and the sensors can be used for the determination of Nd (III) in real samples having different analytical matrixes.

**Table3.** Determination of Neodymium in binary mixtures

| Nd <sup>3+</sup> (M) taken | Added cation (M)                   | Nd <sup>3+</sup> found (M)* |
|----------------------------|------------------------------------|-----------------------------|
| $5.0 \times 10^{-4}$       | $La^{3+}$ ( $5.0 \times 10^{-4}$ ) | $4.8 \times 10^{-4}$        |
| $5.0 \times 10^{-4}$       | $Pr^{3+}$ ( $5.0 \times 10^{-4}$ ) | $5.1 \times 10^{-4}$        |
| $5.0 \times 10^{-4}$       | $Pb^{2+}$ ( $5.0 \times 10^{-4}$ ) | $4.9 \times 10^{-4}$        |
| $5.0 \times 10^{-4}$       | $Gd^{3+}$ ( $5.0 \times 10^{-4}$ ) | $5.2 \times 10^{-4}$        |
| $5.0 \times 10^{-4}$       | $Na^+$ ( $5.0 \times 10^{-4}$ )    | $4.7 \times 10^{-4}$        |

\*Average of six replicates

The developed sensor has been successfully applied as an indicator electrode in the titration of Nd (III) with EDTA at pH 7. The titration curve for the sensor is shown in the figure 6. A very good inflection point which corresponds to 1:1 stoichiometry of EDTA complex was observed from the titration curve. Hence, the amount of neodymium ions in solution can be accurately determined with the developed sensor.



**Fig6.** Potentiometric titration curve of 25 mL of  $1 \times 10^{-3}$  M  $NdCl_3$  with  $1 \times 10^{-2}$  M EDTA for the membrane sensor  $SA_6$

### 3.7. Comparative Study of the Developed Sensor with some of the Reported Sensors

Table 4 represents comparative study of characteristics of the proposed sensor with some of the reported sensors. The presently developed sensors are highly comparable with all the reported sensors [9, 30-36].

**Table4.** Comparison of the response characteristics of the developed sensors with other reported neodymium sensors

| Sens. No | Working conc. range (M)  | pH               | Response time(s) | Slope (mV/decade) | Reference        |
|----------|--|------------------|------------------|-------------------|------------------|
| 1        | $5.0 \times 10^{-7}$ - $1 \times 10^{-2}$                            | 4.0 – 8.0        | 10               | 19.8±0.3          | 30               |
| 2        | $1 \times 10^{-6}$ - $1 \times 10^{-2}$                              | 3.7 – 8.3        | <10s             | 19.7±0.4          | 31               |
| 3        | $1 \times 10^{-6}$ - $1 \times 10^{-2}$                              | 3.0 – 7.0        | <15s             | 19.4±0.3          | 32               |
| 4        | $1 \times 10^{-5}$ - $1 \times 10^{-2}$                              | 3.5 – 8.5        | <10s             | 19.7±0.3          | 35               |
| 5        | $1 \times 10^{-5}$ - $1 \times 10^{-2}$                              | 4.0 – 8.0        | 15s              | 19.6±0.3          | 34               |
| 6        | $1 \times 10^{-6}$ - $1 \times 10^{-2}$                              | 4.0 – 6.5        | <5s              | 20.1              | 33               |
| 7        | $1 \times 10^{-6}$ - $1 \times 10^{-2}$                              | 2.4 – 8.5        | 7                | 21.2±0.2          | 9                |
| 8        | $5.0 \times 10^{-6}$ - $1 \times 10^{-2}$                            | 2.9– 9.2         | <10s             | 19.5±0.4          | 36               |
| <b>9</b> | <b><math>1 \times 10^{-6}</math> - <math>1 \times 10^{-2}</math></b> | <b>3.0 - 7.5</b> | <b>&lt;15s</b>   | <b>20.6±0.3</b>   | <b>This work</b> |

### 4. CONCLUSIONS

PVC membrane sensor based on N<sup>1</sup>, N<sup>2</sup>-bis(salicylidine)butane-1,4-diamine as ionophore was developed for the determination of Nd (III). This sensor showed a good Nernstian response over a wide concentration range with a fast response time. pH range of the developed sensor was found to be 3.0-7.5. The electrode showed better selectivity, working concentration range, slope and pH range in comparison to other Nd (III) selective sensors reported in literature (Table 4). The proposed sensor can be successfully applied for the direct determination of neodymium in binary mixtures.

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#### AUTHORS BIOGRAPHY



**Beena Saraswathyamma**, obtained her Masters Degree in chemistry in 2002. She received her Ph. D in Analytical chemistry from Cochin University of Science and Technology in 2011. Her Ph. D work on Fabrication of Potentiometric sensors for lanthanide Ions was performed under the supervision of Prof. Girish Kumar. She also worked in the area of voltammetric sensors based on self assembled monolayer for pharmaceuticals under the guidance of Prof. Jerzy Radecki and Prof. Hanna Radecka, Polish Academy of Sciences, Poland. At present she is working as Asst. Professor in the department of chemistry, Amrita University. Her research interest includes fabrication of potentiometric sensors for metal ions, biosensors for Cholesterol, DNA bases and DNA.



**Dr. K Girish Kumar**, received his Bachelor and Post Graduate degree in Chemistry from University of Kerala in 1982 and 1984 respectively. He obtained his Ph.D in Analytical Chemistry from University of Kerala in 1989. In 1999 he joined the Dept. of Applied Chemistry, Cochin University of Science and Technology as Reader in Analytical Chemistry. He has been a Visiting Professor at the Dept. of Chemistry, Sultan Qaboos University, Muscat, Sultanate of Oman. He has research collaboration with Dept. of Biosensors in Food, Institute of Animal Reproduction and Food Research, POLAND. Having supervised 15 Ph.Ds he has been conferred with the One-Time Research Grant of the UGC in 2014. He has 26 years of teaching experience and has been actively involved in research for 29 years. His research interests include Development of optical/fluorescent sensors, Fabrication of electrochemical sensors for determination of metal ions, pharmaceuticals, biologically active molecules and food additives, Spectrophotometric methods for pharmaceuticals, Trace analysis of metals, Ion removal studies, Electrode modification using carbon nanotubes, conducting polymers, metal nanoparticles and self- assembled monolayers and Fabrication of Biosensors. He has over 78 research publications in Indian and international journals. He has undertaken many research projects from various agencies like UGC, CSIR, DRDO, KSCSTE and DST.