Int. J. Electrochem. Sci., 2 (**2007**) 832 - 847

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Novel Copper(II)-Selective Electrode Based on 2,2': 5',2''-Terthiophene in PVC Matrix

Rakesh Kumar Mahajan[*] *and Pallavi Sood*

Department of Chemistry, Guru Nanak Dev University, Amritsar-143005, India
[*]E-mail: rakesh_chem@yahoo.com

Received: 20 June 2007 / *Accepted:* 12 September 2007 / *Online published:* 5 October 2007

A new copper(II) ion-selective liquid polymeric membrane electrode based on 2,2': 5',2''-Terthiophene has been developed. When optimized, this electrode exhibits a linear Nernstian response over the range of 5.0×10^{-6}-1.0×10^{-1}M of copper(II) ion, with a slope of 29.88 mV per decade and detection limit was 2.34×10^{-6}M. The effect of several parameters, such as content of ionophore in the membrane, pH of the sample solution and internal reference solution was investigated. The electrode is selective for Cu(II) ions over Li^+, Na^+, K^+, Cs^+, NH_4^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, UO_2^{2+}, Fe^{3+} and their potentiometric selectivity coefficients were calculated. The preparation procedure of the electrode is very easy and inexpensive. Moreover, the proposed electrode was applied as an indicator electrode in potentiometric titration of copper ion with EDTA solution.

Keywords: neutral carrier: Terthiophene, poly(vinyl chloride), Nernstian slope, potentiometry, copper(II) ion-selective electrode

1. INTRODUCTION

The environmental and health effects of metal ion pollution are important and complex problems. From the broad point of view, almost every metal or metallic compound encountered in manufacturing industry presents some type of ecological hazard. From the more realistic point of view, lead, mercury, arsenic, chromium, cadmium, antimony, copper and their compounds cause the principal health hazards. Natural sources of copper exposure include windblown dust, volcanoes, decaying vegetation, forest fires and sea spray. Copper possesses high electrical, thermal conductivity and resists corrosion. Copper is widely used in cooking utensils and water distribution systems as well as fertilizers, bactericides, fungicides, algaecides and antifouling paints. It is also used in animal feed additives and growth promoters as well as for disease control in livestock and poultry. Copper is used in industry as an activator in froth floatation of sulfide ores, production of wood preservatives, electroplating, azo-dye manufacture, as a mordant for textile dyes, in petroleum refining and the manufacture of copper compounds. The mean daily dietary intake of copper in adults ranges between 0.9 and 2.2 mg. In some cases, drinking water may make a substantial additional contribution to the total daily intake of copper, particularly in households where corrosive waters have stood in copper pipes. Effects of single exposure following suicidal or accidental oral exposure have been reported as metallic taste, epigastric pain, headache, nausea, dizziness, vomiting and diarrhea, tachycardia, respiratory difficulty, haemolytic anemia, haematuria, massive gastrointestinal bleeding, liver and kidney failure and death. The toxicity is generally attributed to the aquo-complexed "free" copper(II) ion rather than its organic or inorganic complex. Copper is an essential element and adverse health effects are related to deficiency (Menkes disease) as well as excess (Wilson disease), hypoglycemia, dyslexia, gastrointestinal cattarch. In view of such toxic effects of copper, its determination in environmental samples is very important.

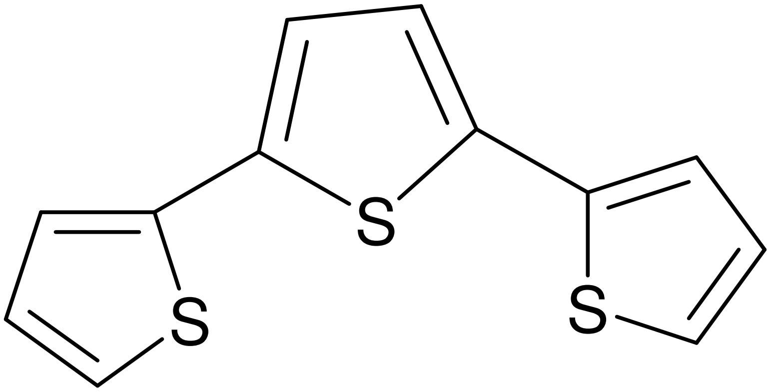

Figure 1. Structure of ionophore (I) 2,2': 5',2''-Terthiophene used in the preparation of copper(II) ion-selective electrode (E1)

Potentiometric ion sensors such as neutral-carrier-type ion-selective electrodes (ISEs) are very useful [1]. The ion-selectivities are generally determined by the ion-exchange equilibrium at the interface between the membrane and the aqueous sample phases, which is in turn the metal-ion extraction equilibrium between the two immiscible phases. They offer several advantages as small size, simplicity of operation and low cost per sample. Besides, they are ideally suited for on-site analysis and nowadays they find several applications in the analysis of some biologically relevant ions, process control and environmental analysis [2]. Nevertheless, the application of ISEs in process analytical chemistry is often restricted because of the lack of measurement protocols and insufficient properties of the electrodes. Since the response mechanisms of the soft-metal ISEs such as silver, thallium were based on the d-orbital coordination of neutral carriers to analyte ion in most cases, the strong interaction often causes slow ionic exchanges at the membrane interface of resulting ISEs, thus leading to their slow EMF response and thereby to their poor sensitivity. On the other hand, the interaction between the transition metal ion like copper(II) and the neutral carrier bearing sulfur- or nitrogen- atom as the coordinating atoms have been well known to be not very powerful but selective for transition metal ion. Some Cu(II) selective sensors based on macrocyclic, non-macrocyclic carriers such as thioethers, dithiocarbamates, thiohydrazone, thiosemicarbazone, calixarenes and Schiff bases have been described [3-16]. However, all of these copper sensors may have either of problems such as high detection limit or narrow working concentration range or serious interfering effect of cations such as Fe^{3+}, Na^{+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cs^{+}, Hg^{2+}, Ag^{+} and K^{+}.

Sulfur containing ligands like thiophenes and thiosemicarbazones etc. have been found to show antitumour [17], antibacterial, antifungal [18] properties and many of their other physiochemical effects [19] are reported. Oligothiophenes [20,21] find application in the field of electronic, photonic and sensing techniques. Since the sulfur donor atoms are well known to coordinate strongly with transition and heavy metal ions, in this paper we employed 2,2’: 5’,2’’-Terthiophene (figure 1) as a suitable ion-carrier to construct a PVC-based membrane electrode which exhibits significantly high selectivity to Cu(II) ions over alkali, alkaline-earth and several transition metal ions.

2. EXPERIMENTAL PART

2.1. Reagents and materials

High molecular weight poly(vinyl chloride) (PVC), ortho-Nitrophenyloctylether (o-NPOE), Dioctylsebacate (DOS), Benzylacetate (BA), Dibutylphthalate (DBP), Tributylphosphate (TBP) were purchased from Fluka. The ionophore 2,2’: 5’,2’’-Terthiophene, Oleic acid (OA), Sodium tetraphenylborate (NaTPB) were used as received from Aldrich. Especially dried tetrahydrofuran (THF) was purchased from Lancaster. 0.1M stock solutions were prepared by dissolving AR grade metal nitrates in double distilled water and standardized wherever necessary. The working solutions of different concentration were prepared by diluting the stock solutions. Double distilled water was used throughout.

2.2. Procedure

The membranes were prepared by the method reported earlier [22]. The membranes were prepared by dissolving appropriate amount of PVC, plasticizer, ionophore (2,2’: 5’,2’’-Terthiophene) and ion-exchanger in about 5 ml of tetrahydrofuran. To obtain membranes with reproducible characteristics, the viscosity of the solution and the solvent evaporation were carefully controlled otherwise morphology and thickness of the membranes has shown a drastic variation, which ultimately affected the sensor response. Before their first use, the membranes thus prepared were equilibrated for 2-3 days in $1.0x10^{-2}M$ $Cu(NO_3)_2$ solution and stored in the same solution when not in use. A blank membrane was prepared in the same way but without the carrier. Membranes of different compositions were prepared and investigated. Those that gave reproducible results and best performance characteristics were selected for detailed studies. The optimum composition of membranes for best performance is given in table 1. Each solution was stirred and the potential reading was recorded. When it became stable, graph of E(mV) versus $\log[Cu^{2+}]$ was plotted. All the measurements were carried out at room temperature.

Table 1. The composition and electrode characteristics of copper(II) ion-selective electrodes based on ionophore (I)

ISE	PVC	Plasticizer	Ionophore	Additive	Slope (mV/dec)	Linear range (M)	Detection limit (M)	Time response (s)
E1	100.0	200.0 (o-NPOE)	5.0	1.6 (OA)	29.88	$5.0x10^{-6}$-$1.0x10^{-1}$	$2.34x10^{-6}$	10
E2	99.6	200.3 (DOS)	5.0	1.5 (OA)	34.03	$1.0x10^{-5}$-$1.0x10^{-2}$	$6.60x10^{-6}$	15
E3	99.9	200.1 (BA)	5.0	1.3 (OA)	52.17	$5.0x10^{-5}$-$1.0x10^{-2}$	$3.23x10^{-5}$	25
E4	99.8	200.2 (DBP)	5.0	1.5 (OA)	28.28	$1.0x10^{-5}$-$1.0x10^{-1}$	$6.16x10^{-6}$	15
E5	99.7	200.3 (TBP)	5.0	1.4 (OA)	32.83	$5.0x10^{-5}$-$1.0x10^{-1}$	$2.95x10^{-5}$	10
E6	100.0	0.0	5.0	1.5 (OA)	33.00	$1.0x10^{-3}$-$1.0x10^{-1}$	$6.30x10^{-4}$	30
E7	101.0	199.9 (o-NPOE)	5.0	1.2 (NaTPB)	11.59	$5.0x10^{-5}$-$1.0x10^{-1}$	$1.62x10^{-5}$	35
E8	100.0	200.0 (o-NPOE)	5.0	1.6 (NaTPB)	14.92	$1.0x10^{-4}$-$1.0x10^{-1}$	$2.18x10^{-5}$	30
E9	100.1	200.3 (o-NPOE)	0.0	0.0	3.0	$5.0x10^{-5}$-$1.0x10^{-1}$	$5.12x10^{-5}$	35
E10	100.0	200.2 (o-NPOE)	0.0	1.6 (OA)	8.68	$5.0x10^{-5}$-$1.0x10^{-1}$	$1.17x10^{-5}$	30
E11	100.0	200.0 (o-NPOE)	7.0	1.6 (OA)	28.82	$5.0x10^{-5}$-$1.0x10^{-1}$	$2.69x10^{-5}$	15
E12	100.0	200.0 (o-NPOE)	10.0	1.6 (OA)	27.34	$5.0x10^{-5}$-$1.0x10^{-1}$	$3.31x10^{-5}$	15
E13	100.0	200.0 (o-NPOE)	13.0	1.6 (OA)	22.83	$5.0x10^{-5}$-$1.0x10^{-1}$	$2.88x10^{-5}$	20
E14	100.0	200.0 (o-NPOE)	5.0	-	7.84	$1.0x10^{-4}$-$1.0x10^{-1}$	$1.41x10^{-5}$	30
E15	100.1	200.2 (o-NPOE)	5.0	0.6 (OA)	22.80	$1.0x10^{-3}$-$1.0x10^{-1}$	$1.99x10^{-4}$	15
E16	100.2	200.1 (o-NPOE)	5.0	2.6 (OA)	30.12	$5.0x10^{-5}$-$1.0x10^{-1}$	$2.69x10^{-5}$	15

2.3. Instrumentation

All of the measurements of the electrode potentials were made with an Equip-tronics model EQ-602 potentiometer. The pH measurements were made using an Elico LI-model-120 pH meter. The electrochemical cell assembly used for this study was as follows:

Ag-AgCl / KCl (3.0M) / 1.0×10^{-2} M $Cu(NO_3)_2$ (internal reference solution) / PVC membrane / test solution / 3M KCl / Hg-Hg_2Cl_2 (saturated)

Standard solutions of cupric nitrate were obtained by diluting 0.1M $Cu(NO_3)_2$ solution.

3. RESULTS AND DISCUSSION

3.1. Potentiometric Response

The plasticized PVC-based membrane electrode containing (I) as the neutral ion-carrier, generated stable potential responses in solutions containing copper. Therefore, we studied in detail the performance of the membrane electrodes based on this carrier (I) for copper(II) ion in aqueous solutions. In preliminary experiment, membranes with and without carriers were constructed. The membranes with no carrier displayed insignificant selectivity toward copper(II) ion and its response was not reliable, whereas, in the presence of the proposed carrier, the optimized membranes demonstrated Nernstian response and remarkable selectivity for copper(II) ion over a wide variety of metal ions, including alkali (Li^+, Na^+, K^+, Cs^+), alkaline-earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), transition and heavy metal ions (Co^{2+}, Ni^{2+}, Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+}). The potentiometric response curves obtained for individual metal ions with ionophore (I) under identical conditions are given in figure 2. Among these ions, except for Cu(II) ion, for all other ions the slope of the corresponding potential vs. log $[M^{n+}]$ plots is much lower than the expected Nernstian slopes of 59.0, 29.5 mV per decade for the univalent and divalent cations, respectively with very narrow linear ranges of concentration. This is likely due to the high selectivity of the ionophore for copper ions over other metal ions and rapid exchange kinetics of the resulting Cu(II)-ionophore (I) complex. Thus, the electrode (E1) was conditioned in a solution of 10^{-2}M $Cu(NO_3)_2$. The selectivity observed for copper(II) ion over other ions is most probably related to participation of the three sulfur atoms in copper ion binding. Moreover, the suitable size of copper ion may provide a proper fitting condition for stable and selective complex formation. Thus, we decided to examine its capability as a suitable ionophore in preparing new cation-selective membrane electrode. The copper(II) ion-selective electrode (E1) exhibits a wide linear concentration range of 5.0×10^{-6}-1.0×10^{-1}M with a Nernstian slope of 29.88 mV per decade. The most suitable internal reference solution was found to be 1.0×10^{-2}M cupric nitrate $Cu(NO_3)_2$. The detection limit of the electrode (E1) was found to be 2.34×10^{-6}M.

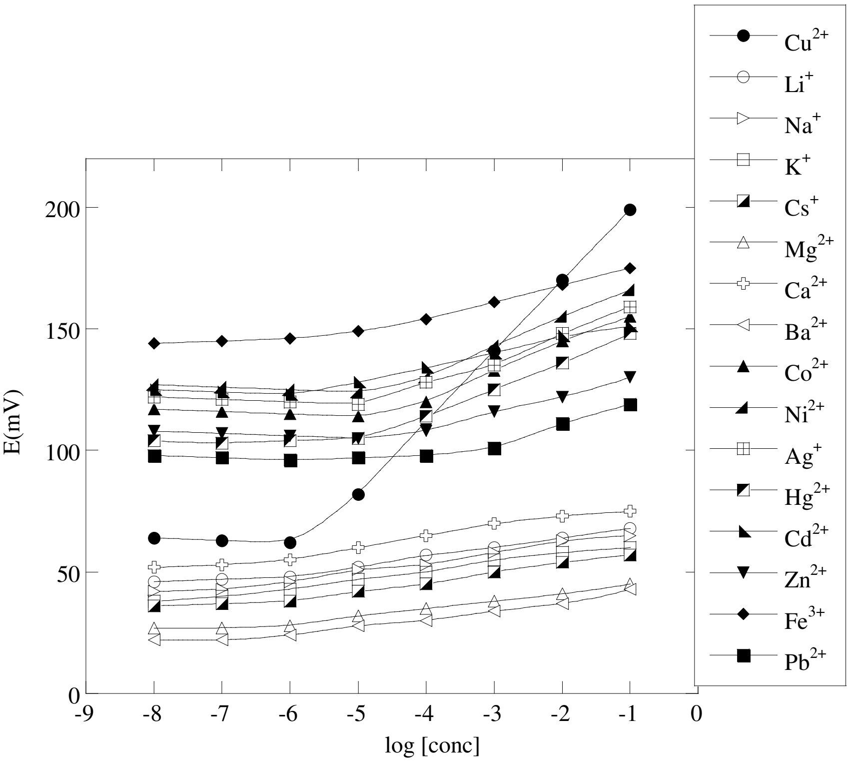

Figure 2. The potentiometric response curves of ion-selective electrodes for various metal ions on ionophore (I) as an ion-carrier

3.2. Composition of copper(II)-selective electrode

The influence of membrane composition on the potential response of the Cu(II) ion-selective electrode was also investigated in this study. It is well known that the electrode response such as sensitivity, working concentration range, selectivity and potential stability depends on the amount and the nature of the electrode's components [23]. A large number of membranes containing varying amount of ionophore (I) and an appropriate proportion of poly(vinyl chloride) (PVC) and ortho-nitrophenyloctyl ether (o-NPOE) as the plasticizer were prepared and subjected to preliminary investigations. The compositions and the electrode characteristics of the membranes prepared are given in table 1. The prepared electrode (E1) based on ionophore (I) was equilibrated in $1.0\text{x}10^{-2}$M cupric nitrate solution for 2-3 days until it generated stable and reproducible potentials. To check the reproducibility of the electrode response, ten potential measurements of the primary ion solution of concentration $1.0\text{x}10^{-1}$M or $1.0\text{x}10^{-2}$M were made and the standard deviation observed for the slope was ±1mV, which shows good reproducibility. The electrode was stored in the conditioning solution of $1.0\text{x}10^{-2}$M cupric nitrate and re-equilibrated with internal filling solution whenever any drift in the potentiometric response was observed.

The electrode response not only depends upon the concentration gradient of Cu(II) ions across the membrane but also depends on the properties of the polymer matrix, amount of the carrier and plasticizer. In order to optimize the composition of the membrane, various factors such as: (a) Effect of ionophore content (b) plasticizer/PVC ratio (c) Effect of nature of plasticizers and (d) Effect of lipophilic additive, which greatly influence [23] the sensitivity of an ion-selective were examined. Membranes of different compositions were prepared and investigated. Those that gave reproducible results and best performance characteristics were selected for detailed studies. These are discussed in the following sections.

3.2.(a) Effect of ionophore content

The effect of ionophore content in the PVC membrane with a diameter of 5 cm for Cu(II) ion sensor based on ionophore (I) was investigated. For that, the membrane E1, E10-E13 containing varying percentages (by weight) of ionophore (I) that is 1.6% (E1), 0% (E10), 2.3% (E11), 3.2% (E12), 4.1% (E13) were prepared and their electrode characteristics were studied (table 1). With the increase in ionophore content from E10 (0%) to E1 (1.6%) the slope has increased, linear concentration range has increased and the detection limit has gone lower. The performance of the membrane without ionophore (dummy membrane) was also investigated and negligible potential was generated. With further increase in the ionophore content from E1 (1.6%) to E11 (2.3%) to E12 (3.2) to E13 (4.1%), the slope, linear range has decreased and detection limit has become of the order of 10^{-5}M. Variation in potential response with different amounts of carrier was observed. The amount of carrier in the membrane was varied with plasticizer concentration, thus the water uptake capacity of the membrane changes that in turn affects the behavior of the electrode. Without any carrier, the sensitivity of the electrode (E10) was decreased. This clearly demonstrated a need of carrier in the fabrication of the electrode. The sensitivity of the electrode response increases with the increasing ionophore content until a value of 1.6% is reached. Further, addition of ionophore will, however, result in diminished and sluggish response of the electrode. This is most probably due to some inhomogenities and possible saturation of the membrane. The data in table 1 clearly indicates with the further increase of the ionophore's amount, the electrode response in higher concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ion-selective electrodes [23,24]. Thus 1.6% of the ionophore (I) was chosen as the optimum amount of ionophore in the PVC membrane. Moreover, the most appropriate results are obtained with E1 so it is this electrode with which further studies were done.

3.2.(b) Effect of plasticizer/ PVC ratio

The three different plasticizer/ PVC ratios that is 2.0, 1.6 and 1.3 using o-NPOE as plasticizer while keeping the amount of ionophore constant (i.e. 1.6%) were examined while optimizing the membrane composition. The membrane with plasticizer/ PVC ratio of 2.0 was found to give the best reproducibility and sensitivity of 29.88 mV per decade over the widest linear concentration range of $5.0\text{x}10^{-6}$-$1.0\text{x}10^{-1}$M in comparison to the other two ratios tested. Therefore, the plasticizer/ PVC ratio of 2.0 was used in the preparation of Cu(II) ion-selective electrode (E1) based on ionophore (I). In general, the thickness of the membrane depends on the membrane content of PVC and a good correlation between the membrane thickness and the PVC content of the membrane is found. The detection limit of the sensor increases with a decrease in the PVC content. However, if the membrane is too thin, it losses its mechanical strength and is easily broken as previously explained [25]. Furthermore, the mobility of the sodium ions (NaTPB) decreases with increasing PVC content mainly due to an increasing membrane viscosity.

3.2.(c) Effect of nature of plasticizers

Plasticizer is an important constituent of the electrode and influences the detection limit [24], sensitivity, selectivity of the electrodes and mobility of the electroactive cation in the membrane. The improvement in the performance was attempted by the addition of plasticizers to the membranes. The addition of plasticizers not only improves the workability of the membranes, but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [26]. However, the selectivity remains usually unaffected and mainly depends on the metal-ionophore interaction. The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate [27]. In the present study, the effect of five plasticizers of different polarities such as ortho-nitrophenyloctylether (o-NPOE), dioctylsebacate (DOS), benzylacetate (BA), dibutylpthalate (DBP), tri-n-butylphosphate (TBP) was investigated on copper(II) ion-selective electrode based on ionophore (I). o-NPOE is more effective solvent mediator than DBP or DOS for copper(II) ion-selective electrode due to its large dielectric constant. From the data in table 1, it is clear that o-NPOE proved to be the most suitable plasticizer as it gives a Nernstian slope of 29.88 mV per decade and a detection limit of $2.34\text{x}10^{-6}$M. It showed high sensitivity, reasonable selectivity and wide linear concentration range of $5.0\text{x}10^{-6}$M to $1.0\text{x}10^{-1}$M (E1). Electrodes (E2, E3, E5) with DOS, BA, TBP as plasticizers respectively were found to give super-Nernstian slopes in narrow linear concentration ranges ($1.0\text{x}10^{-5}$-$1.0\text{x}10^{-2}$M, $5.0\text{x}10^{-5}$-$1.0\text{x}10^{-2}$M, $5.0\text{x}10^{-5}$-$1.0\text{x}10^{-1}$M) whereas electrode (E4) with DBP was found to give sub-Nernstian slope with $1.0\text{x}10^{-5}$-$1.0\text{x}10^{-1}$M as the concentration range. Thus, the membrane (E6) even without a plasticizer performs well and the addition of plasticizers DOS, BA shows no improvement in the performance. Only o-NPOE improves the performance. The plasticizing nature of the ionophore thus explains the better detection limit of the membrane without plasticizer than the membranes with plasticizers DOS, BA. Repeated monitoring of potentials (15 measurements) at the same concentration ($1.0\text{x}10^{-2}$M) gave a standard deviation of ±1mV. This shows that ionophore (I) in the PVC membrane gave good response towards Cu(II) ion with o-NPOE as the plasticizer.

3.2.(d) Effect of lipophilic additive

The effect of an additive on the performance characteristics of the membrane electrode was also investigated. In general, in neutral-carrier-based liquid membrane electrodes, incorporated anionic sites, example sodium tetraphenylborate or oleic acid were introduced in order to reduce interference of lipid-soluble sample anions (Donnan exclusion). The presence of mobile cation-exchange sites in cation-selective membranes based on neutral carriers has also proved to be beneficial in many other respects. For example, the additive lowers the electric membrane resistance as well as the activation barrier for the cation-exchange reaction at the membrane-solution interface, reduces the response time after activation step, gives rise to significant changes in selectivity and reduces the bulk membrane impedance [28]. With the increase in additive content from E14 (0%) to E15 (0.2%) to E1 (0.5%) to E16 (0.8%) the slope has increased with the increase in the linear range. Detection limit has changed from the order of 10^{-4}M to 10^{-6}M. Addition of 0.5% oleic acid as a suitable additive increases the slope of the potential response of the sensor from a poor value of 7.84 mV per decade (E14) to a Nernstian value of 29.88 mV per decade (E1). It was expected to contribute to the dielectric constant of the membrane in addition to the plasticizer. It may act as cooperative carrier in the transport of copper ion to the membrane. It also enhances the sensitivity of the membrane electrode in cases where the extraction capability of the ionophore is poor. The most appropriate results are obtained with E1 so it is this electrode with which further studies were done. The first use of oleic acid as a very suitable lipophilic additive in inducing permselectivity to some PVC-based ion-selective electrodes has been reported and discussed its specific features in details [29].

On the basis of the above discussion, it was concluded that the ionophore content of 1.6% (w/w) and plasticizer/ PVC ratio of 2.0 with o-NPOE as plasticizer is the most suitable composition for the preparation of copper(II) ion-selective electrode (E1) based on ionophore (I). As can be seen from table 1, electrode (E1) with a PVC: o-NPOE: ionophore (I): OA percent ratio of 32.6 : 65.3 : 1.6 : 0.5

shows a Nernstian behavior over a very wide concentration range. This electrode (E1) was further studied for selectivity and other performance characteristics.

3.3. Response Time

The dynamic response time is an important factor for all of the ion-selective electrodes. The average time required for the Cu(II) ion-selective electrode to reach a potential within ±1mV of the final equilibrium value after successive immersion of a series of copper ion solutions, each having a ten-fold difference in concentrations, was measured. The dynamic response time was recorded at different concentrations of cupric nitrate in the sample solution. The response times, thus obtained for copper(II) ion sensors based on ionophore(I) are tabulated in table 1. In this study, the practical response time was recorded by changing the Cu(II) concentration in solution over a concentration range of $1.0\text{x}10^{-5}$M to $1.0\text{x}10^{-1}$M. The actual potential versus time traces is shown in figure 3. As can be seen, over the whole concentration range the electrode (E1) reaches its equilibrium response in a very short time(10s). This is most probably due to the fast exchange kinetics of complexation-decomplexation of the Cu(II) ion with the ionophore at the test solution-membrane interface [30]. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations (figure 4). It was found that the potentiometric response of the sensor is reversible, although the time needed to reach the equilibrium values was longer than that for the low-to-high sample concentration procedure. It is well documented that, in the case of high-to-low concentrations, the time needed to attain a stable potential is some 100-times larger than that required for the case of low-to-high concentrations (for a

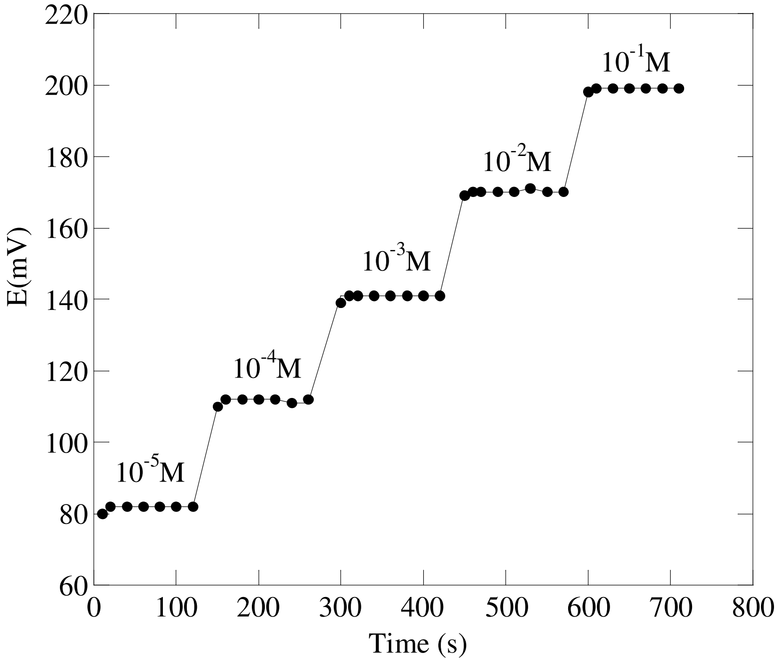

Figure 3. Dynamic time response of copper(II) electrode (E1) for step changes in concentration of copper ion: (A) $1.0\text{x}10^{-5}$M , (B) $1.0\text{x}10^{-4}$M, (C) $1.0\text{x}10^{-3}$M, (D) $1.0\text{x}10^{-2}$M, (E) $1.0\text{x}10^{-1}$M

10-times change in the cation concentration) [23]. The electrode potential remained constant for more than five minutes, after which a very slow divergence was observed. It can be seen that the response time ($t_{95\%}$) for all sensors was reasonably short and the stability of potentiometric signal was also found to be quite satisfactory. The electrode potentials were reproducible and the standard deviation of ten identical measurements was ±1mV at various concentrations of Cu(II) ions. Electrode (E6) having membranes without plasticizer gave a steady response in 30s (Table 1). Of all the plasticizers used, o-NPOE improved the response time to the maximum extent (i.e. 10s for E1). The main factor responsible for the limited lifetime of a sensor is believed to be the loss of one or more of its components while contacting with aqueous solutions. Sufficient lipophilicity of ionophores and plasticizers ensures stable potentials and long lifetimes [27,28].

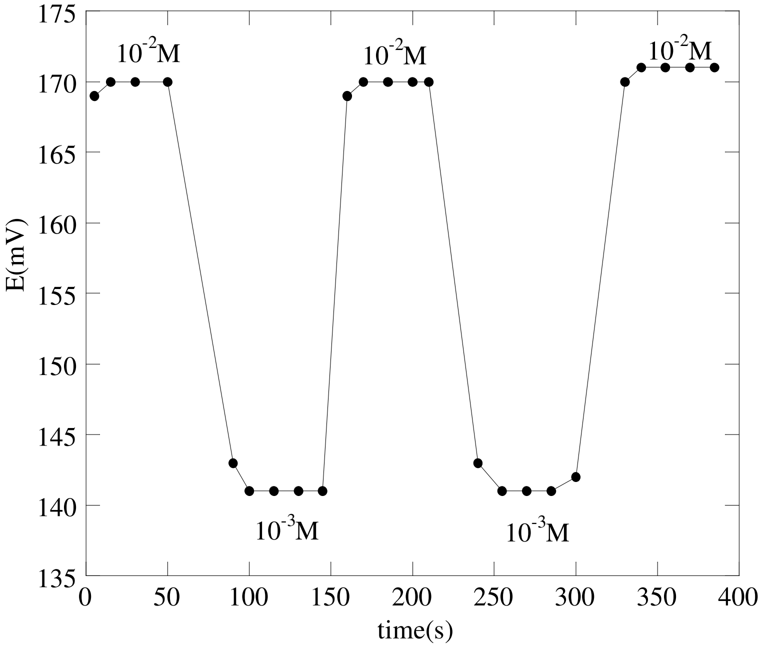

Figure 4. Dynamic response characteristics of the copper(II) electrode (E1) for several high-to-low sample cycles

3.4. Lifetime of Copper(II) sensors

The response of copper(II) ion-selective electrode (E1) was examined at regular intervals to check the reproducibility and lifetime of the sensor (table 2). It was observed that during the long time period of four months, the slope of the sensor drifts only by 2.57 mV per decade from 29.88 to 27.31 mV per decade and detection limit is increased by a small factor. But after four months, the electrode characteristics significantly drifted away from the Nernstian behavior. This may be attributed to the decrease in the quantity of ionophore and the plasticizer in the membrane due to migration of these components from the PVC membrane into the PVC tube. Therefore, copper(II) ion-selective electrode (E1) can be used over a period of four months without any considerable change in the value of the slope, working concentration range and detection limit.

Table 2. Lifetime behavior of copper(II) ion-selective electrode (E1)

Time	Linear Range (M)	Slope (mV/dec)	Detection limit (M)
1 day	$5.0x10^{-6}$-$1.0x10^{-1}$	29.88	$2.34x10^{-6}$
7 days	$5.0x10^{-6}$-$1.0x10^{-1}$	29.88	$2.34x10^{-6}$
3 weeks	$5.0x10^{-6}$-$1.0x10^{-1}$	29.88	$2.34x10^{-6}$
1 month	$5.0x10^{-6}$-$1.0x10^{-1}$	29.88	$2.34x10^{-6}$
2 months	$5.0x10^{-6}$-$1.0x10^{-1}$	29.21	$2.52x10^{-6}$
3 months	$5.0x10^{-6}$-$1.0x10^{-1}$	28.93	$3.65x10^{-6}$
4 months	$5.0x10^{-6}$-$1.0x10^{-1}$	27.31	$4.89x10^{-6}$

3.5. Effect of concentration of internal reference solution

The influence of the concentration of the internal solution on the potential response of the polymeric membrane electrode was investigated. The working of the electrode (E1) in relation to the variation in concentration of internal reference solution was observed at four different concentrations of copper(II) ion such as $5.0x10^{-2}$M, $1.0x10^{-2}$M, $5.0x10^{-3}$M and $1.0x10^{-3}$M. It was found that with the change in the concentration of internal reference solution from $5.0x10^{-2}$M to $1.0x10^{-2}$M to $5.0x10^{-3}$M to $1.0x10^{-3}$M, the slope of the electrode (E1) has decreased from 36.73 to 19.30 mV per decade with the accompanied change in the detection limit from 10^{-6}M to 10^{-5}M. But there was an increase in the linear concentration range of ($1.0x10^{-5}$-$1.0x10^{-1}$ to $5.0x10^{-6}$-$1.0x10^{-1}$M) as the concentration of the internal reference solution is changed from $5.0x10^{-2}$M to $1.0x10^{-2}$M. When the concentration of the internal reference solution was changed from $1.0x10^{-2}$M to $5.0x10^{-3}$M to$1.0x10^{-3}$M, linear concentration range of electrode (E1) decreased [$5.0x10^{-6}$-$1.0x10^{-1}$ to $5.0x10^{-5}$-$1.0x10^{-1}$M]. But the most appropriate results are obtained with $1.0x10^{-2}$M cupric nitrate as the internal reference solution as it was most suitable for the smooth functioning of this sensor.

3.6. Effect of pH

The pH dependence of response of the electrode E1 has been tested in the range of 1.0 to 12.0 at two Cu(II) concentrations of $1.0x10^{-2}$M and $1.0x10^{-3}$M Cu(II) ions. The pH was adjusted with dilute nitric acid and sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results are shown in figure 5. The potential remains constant over the pH range of 2.8-7.5, which may be taken as the working pH range of the sensor assembly. At pH lower than 2.8, the interference of H^+ ions is more which is due to the high rate of diffusion of H^+ ions from sample solution to membrane matrix (extract H^+ ion) where they interact with carrier and its protonation takes place resulting in decreased selectivity of Cu(II) ions. In this case, the membrane sensor then responds to hydrogen ions. At pH higher than 7.5, the deviation in the electrode response is due to the formation of some hydroxyl complexes of Cu(II) ion in solution [24,27,30].

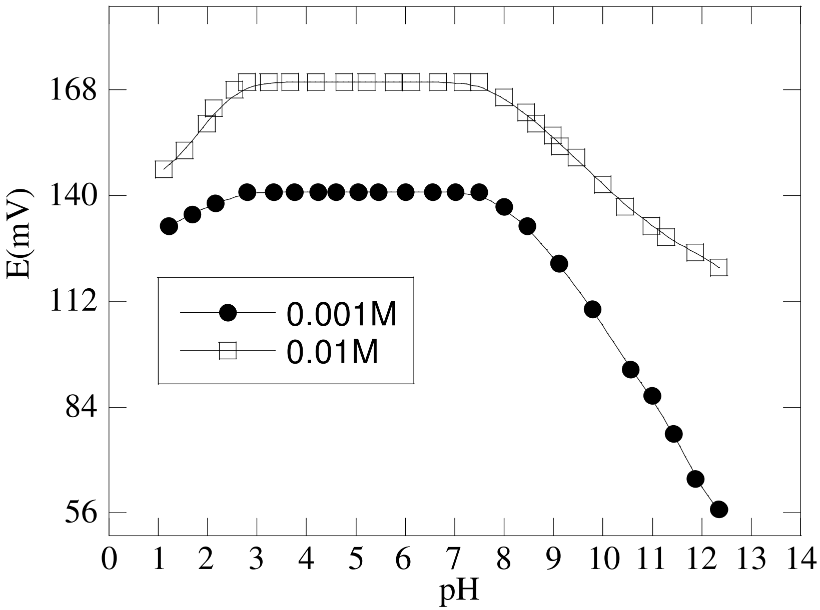

Figure 5. Effect of pH on cell potential; $[Cu^{2+}] = 1.0x10^{-2}$M (a) and $1.0x10^{-3}$M (b) for electrode E1

3.7. Selectivity

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations. So the design and development of Cu(II) electrode and the evaluation of degree of interference from other ions would be of great importance [31]. This is measured in terms of the potentiometric selectivity coefficient [32] ($K^{Pot}_{A,B}$), which has been evaluated by the fixed interference method [33] that is based on the semi empirical Nikolsky-Eisenman equation

$$E_{ISE} = E^o \pm [RT / (Z_A F)] \ln [a_A + \sum K^{Pot}_{A,B} (a_B)^{Z_A/Z_B}]$$

Where E_{ISE} is the measured potential, E^o is the standard cell potential, a_A and a_B are the activities of primary and interfering ions and all other symbols have their usual meanings. In this fixed interference method, the concentration of the copper ion is varied while that of the interfering ions is 0.01 mol l^{-1}. From the plots of E_{ISE} vs. log a_{Cu} and using the expression

$$\ln K^{Pot}_{A,B} = \ln [a_A / (a_B)^{Z_A/Z_B}]$$

the selectivity coefficient was determined. The value of is a_A is estimated by determining the Cu(II) activity for which the linear and rising portion of the graph deviates by 2.303RT log [2 / (F)] mV from the curved part [33] and the value of $(a_B)^{2/Z_B}$ that was used to calculate the potentiometric selectivity coefficient. The resulting selectivity coefficients are summarized in table 3. As can be seen, $K^{Pot}_{Cu,B}$ are in the order of 10^{-3} or smaller, indicating that all diverse ions would not significantly disturb the functioning of the Cu(II) ion-selective membrane. It is possible to determine Cu(II) in the presence of

Table 3. Selectivity data (log $K^{Pot}_{Cu,B}$) of Cu^{2+} ion-selective electrodes based on ionophore(I)

Diverse ions	E1	E2	E4	E5	E11	E12	E15
Li^+	-3.15	-3.00	-3.10	-3.00	-3.12	-3.00	-3.08
Na^+	-3.42	-3.15	-3.38	-3.25	-3.33	-3.15	-3.21
K^+	-3.81	-3.45	-3.77	-3.16	-3.61	-3.28	-3.49
Cs^+	-3.25	-3.21	-3.19	-3.11	-3.04	-3.00	-3.20
NH_4^+	-3.00	-2.75	-2.71	-2.88	-3.09	-3.11	-3.13
Ag^+	-3.34	-3.27	-3.27	-3.21	-3.13	-3.13	-3.29
Mg^{2+}	-3.15	-3.11	-3.00	-3.08	-3.24	-3.19	-3.13
Ca^{2+}	-3.11	-3.08	-3.05	-3.00	-3.39	-3.00	-3.02
Sr^{2+}	-3.42	-3.37	-3.31	-3.25	-3.15	-3.16	-3.35
Ba^{2+}	-3.65	-3.48	-3.49	-3.38	-3.74	-3.23	-3.41
Co^{2+}	-2.21	-2.18	-2.35	-2.37	-2.15	-2.30	-2.14
Ni^{2+}	-2.10	-2.05	-2.19	-2.51	-2.00	-2.19	-2.09
Zn^{2+}	-3.88	-3.14	-3.75	-3.45	-3.21	-3.14	-3.23
Cd^{2+}	-2.98	-2.88	-2.54	-2.94	-2.44	-2.87	-2.77
Hg^{2+}	-2.18	-2.00	-2.21	-2.25	-2.12	-2.12	-2.13
Pb^{2+}	-2.10	-2.04	-2.15	-2.13	-2.17	-2.05	-2.06
UO_2^{2+}	-2.75	-2.61	-2.89	-2.44	-2.32	-2.64	-2.58
Fe^{3+}	-2.50	-2.39	-2.48	-2.26	-2.16	-2.38	-2.31

Table 4. Comparison of the proposed Cu^{2+} sensor (E1) with the reported Cu^{2+} ion-selective electrodes

Ref.	Potentiometric Selectivity Coefficients Log $K^{Pot}_{Cu,B}$							Slope mV/dec	Linear range (M)	Detection limit (M)	Method of select.	pH range	Resp. time (s)	*
	K^+	Ag^+	Ca^{2+}	Sr^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}							
[9]	-3.30	-	-1.00	-	-	-	-	29.50	$1.0x10^{-6}$ to $1.0x10^{-2}$	$5.62x10^{-7}$	FIM	3.5 to 6.0	14	1
[29]	-1.20	-1.35	-1.49	-1.20	-1.72	-1.20	-1.39	30.6	$1.0x10^{-5}$ to $1.0x10^{-1}$	-	FIM	2.8 to 7.9	12	~4
[30]	-2.44	-2.10	-3.23	-3.33	-1.49	-2.27	-1.37	27.3	$1.0x10^{-5}$ to $1.0x10^{-1}$	$8.00x10^{-6}$	MSM	3.0 to 6.0	<20	1
[31]	-3.13	-0.83	-2.46	-2.04	-2.24	-2.28	-0.40	30.0	$7.5x10^{-6}$ to $1.0x10^{-1}$	$3.00x10^{-6}$	FIM	3.0 to 6.5	15	3
This work	-3.81	-3.34	-3.11	-3.42	-3.88	-2.98	-2.10	29.88	$5.0x10^{-6}$ to $1.0x10^{-1}$	$2.34x10^{-6}$	FIM	2.8 to 7.5	10	~4

* Life time (months)

interfering ions at a concentration level smaller or slightly higher than the Cu(II) concentration. It is important to point out that the concentration level of the interfering ion, which the electrode can tolerate, depends on the numerical value of selectivity coefficient. The smaller the value of the selectivity coefficient, the higher is the concentration of interfering ion(s), which can be tolerated by the sensor. The above results clearly demonstrate that the electrode (E1) has shown the best selectivity for Cu(II) ion. In table 4 the selectivity coefficients for the proposed sensor are compared with selectivity coefficients of previously reported PVC-membrane Cu(II)-selective electrodes based on different neutral carriers [34-36]. As seen, the proposed electrode shows somewhat similar values in some cases and superior in most cases.

3.8. Application

The Cu(II) ion-selective electrode (E1) was found to work well under the laboratory conditions. The proposed sensor was also used as an indicator electrode in titration of 40 ml of $1.0\text{x}10^{-3}$M cupric nitrate with $1.0\text{x}10^{-1}$M EDTA. The resulting sigmoid titration curve is shown in figure 6. As can be seen, the amount of Cu(II) ions in solution could be determined with the electrode. The electrode (E1) was successfully applied to the recovery of copper from wastewater samples. The copper contents were determined with the proposed-electrodes and atomic absorption spectrometry (AAS). The results of the recovery test of copper added to a wastewater sample using both the proposed electrode and AAS are summarized in table 5. It can be seen that the electrode (E1) resulted in acceptable recoveries of Cu(II) ion, which are also in satisfactory agreement with those obtained by AAS.

Table 5. Recovery of copper(II) from waste water

No.	Copper Added (M)	Copper Found (M)	
		ISE	AAS
1	$5.0\text{x}10^{-6}$	$5.2\text{x}10^{-6}$	$5.1\text{x}10^{-6}$
2	$3.0\text{x}10^{-6}$	$3.1\text{x}10^{-6}$	$2.9\text{x}10^{-6}$
3	$1.0\text{x}10^{-5}$	$1.1\text{x}10^{-5}$	$1.0\text{x}10^{-5}$
4	$2.5\text{x}10^{-5}$	$2.5\text{x}10^{-5}$	$2.6\text{x}10^{-5}$

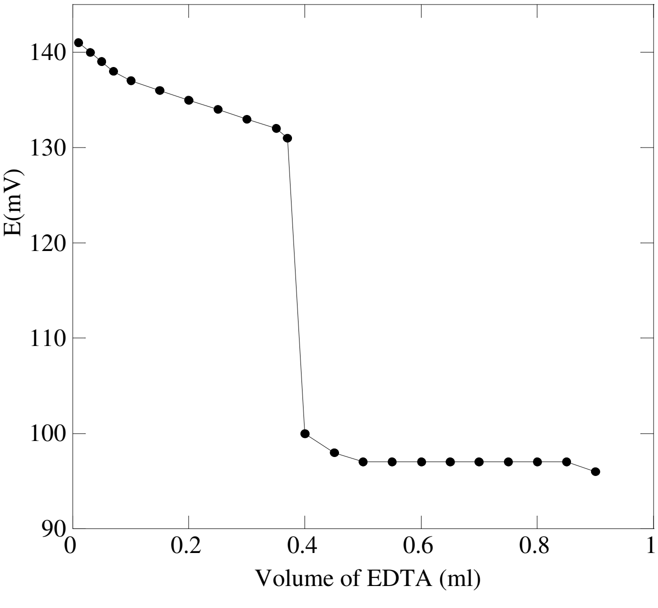

Figure 6. Potentiometric titration of 40 ml of $1.0\text{x}10^{-3}$M $Cu(NO_3)_2$ with $1.0\text{x}10^{-1}$M EDTA solution by using the proposed membrane electrode as an indicator electrode

4. CONCLUSIONS

The proposed Cu(II) selective membrane electrode based on 2,2': 5',2''-Terthiophene displays a Nernstian response in a wide concentration range with a detection limit of 2.34×10^{-6}M. It has a very short response time. The copper(II) electrode (E1) shows very good selectivity with respect to common cations. It can be used to determine copper(II) in industrial samples.

ACKNOWLEDGEMENTS
One of us (Pallavi Sood) is thankful to University Grants Commission, New Delhi, India for providing Junior Research fellowship.

References

1. P. Bühlmann, E. Pretsch and E. Bakker, *Chem. Rev.*, 98 (1998) 1593
2. C. C. Young, *J. Chem. Edu.*, 74 (1997) 177
3. D. C. Jeong, H. K. Lee and S. Jeon, *Bulletin of the Korean Chemical Society*, 27 (2006) 1593
4. M. M. Ardakani, S. H. Mirhoseini, and M. Salavati-Niasari, *Acta Chimica Slovenica*, 53 (2006) 197
5. V. K. Gupta, R. N. Goyal, N. Bachheti, L. P. Singh and S. Agarwal, *Talanta*, 68 (2005) 193
6. A. K. Jain, V. K. Gupta, L. P. Singh and J. R. Raisoni, *Talanta*, 66 (2005) 1355
7. V. K. Gupta, R. Prasasd and A. Kumar, *J. of Applied Electrochemistry*, 33 (2003) 381
8. V. K. Gupta, R. Prasasd and A. Kumar, *Talanta,* 60 (2003) 149
9. I. A. Marques de Oliveira, M. Pla-Roca, Ll. Escrich, J. Casabo, N. Zine, J. Bausells, F. Teixidor, E. Crespo, A. Errachid and J. Samitier, *Electrochimica Acta*, 51 (2006) 5070
10. Z. Yan, Y. Hou, Z. Zhou, C. Du, and Y. Wu, *Fenxi Ceshi Xuebao,* 24 (2005) 104
11. A. K. Singh, P. Saxena, and A.Panwar, *J. of InclusionPhenomena and Macrocyclic Chemistry*, 54 (2006) 299
12. I. A. Marques de Oliveira, M. Pla-Roca, Ll. Escrich, J. Casabo, N. Zine, J. Bausells, J. Samitier, and A. Errachid, *Materials Science & Engineering, C: Biomimetic and Supramolecular Systems,* 26 (2006) 394
13. M. Ocypa, A. Michalska, and K. Maksymiuk, *Electrochimica Acta*, 51 (2006) 2298
14. H. A. Zamani, G. Rajabzadeh, A. Firouz, and A. A. Ariaii-Rad, *J. of the Brazilian Chemical Society*, 26 (2005) 1061
15. M. Akhond and M. Ghaedi, *J. Bulletin of the Korean Chemical Society*, 26 (2005) 882
16. A. R. Fakhari, T. A. Raji and H. Naeimi, *Sensors and Actuators B: Chemical*, B104 (2005) 317
17. J. R. Miller, N. Kourkoumelis, S. K. Demertzis, Z. Afrasiabi, E. Sinn, J. Chem, et. al, *Inorganica Chimica Acta*, 357 (2004) 271
18. R. K. Agarwal, L. Singh and D. K. Sharma, *Bioinorganic Chemistry and Applications*, 2006 (2006) Article ID 59509
19. E. Labisal, K. D. Haslow, A. Sousa-Pedrares, J. Valdes-Martiniz, S. Hernandez-Ortege and D. X. – West, *Polyhedron*, 22 (2003) 2831
20. D. Fichou , *Handbook of oligo- and polythiophenes*, , Wiley-VCH, Weinheim, Germany (1999)
21. T. A. Skothei, R. L. Elsenbaumer and J. R. Reynolds, *Handbook of Conducting Polymers*, Dekker, New York (1997)
22. R. K. Mahajan, R. Kaur, I. Kaur, V. Sharma and M. Kumar, *Anal. Sci.*, 20 (2004) 811
23. E. Bakker, E. Buhlmann and E. Pretsch, *Chem. Rev., 97* (1997) 3083
24. K. C. Gupta and M. J. D' Arc, *Anal. Chim. Acta*, 437 (2001) 199

25. R. D. Armstrong, A. K. Covington and W. G. Proud, *J. Electroanal. Chem.*, 257 (1988) 155
26. W. Zhang, L. U. Jenny and E. Spichiger, *Anal. Sci.*, 16 (2000) 11
27. M. De los A, A. Perez, L. P. Martin, J. C. Quintana and M. Yazdani-Pedran, *Sens. Actuators B*, 89 (2003) 262
28. M. Telting-Diaz, and E. Bakker, *Anal. Chem.*, 73 (2001) 5582
29. M. Shamsipur, M. Yousefi, and M. R. Ganjali, *Anal. Chem.*, 72 (2000) 2391
30. M. R. Ganjali, T. Poursaberi, L. H. –A. S. Babaei, Rouhani, M. Yousefi, M. Kargar-Razi, A. Moghimi, H. Aghabozorg and M. Shamsipur, *Anal. Chim. Acta*, 440 (2001) 81
31. K. M. O' Connor, D. Arrigan and G. Svehla, *Electroanalysis*, 7 (1995) 205
32. Y. Umezawa, K. Umezawa and K. Sato, *Pure Appl. Chem.*, 67 (1995) 507
33. P. Kane and D. Diamond, *Talanta*, 44 (1997) 1847
34. V. K. Gupta, A. K. Jain, G. Maheshwari, H. Lang and Z. Ishtaiwi, *Sensors and Actuators B*, 117 (2006) 99
35. M. Shamsipur, A. Avanes, M. Javanbakht, M. R. Ganjali, and H. Sharghi, *Anal. Sci.*, 18 (2002) 875
36. S. Sadeghi, M. Eslahi, M. A. Naseri, H. Naeimi, H. Sharghi, and A. Shameli, *Electroanalysis*, 15 (2003) 1327