

## A Novel Terpolymer Membrane-Based Electrode Sensor for Selective Determination of Cd(II) Ions

GEETU GAMBHIR<sup>1,✉</sup>, DRASHYA GAUTAM<sup>1,✉</sup>, LAISHRAM SAYA<sup>1,2,3</sup>, AMIT KUMAR<sup>1</sup>, SUBODH KUMAR<sup>1</sup>,  
AARUSHI SINGH<sup>4</sup>, SNIGDHA SINGH<sup>4</sup>, RAMESH CHANDRA<sup>4,\*</sup> and SUNITA HOODA<sup>1,\*✉</sup>

<sup>1</sup>Polymer Research Laboratory, Department of Chemistry, Acharya Narendra Dev College (University of Delhi), Govindpuri, Kalkaji, New Delhi-110019, India

<sup>2</sup>Department of Chemistry, Sri Venkateswara College (University of Delhi), Dhaula Kuan, New Delhi-110021, India

<sup>3</sup>Department of Chemistry, Manipur University, Canchipur, Imphal-795003, India

<sup>4</sup>Drug Discovery and Development Laboratory, Department of Chemistry, University of Delhi, Delhi-110007, India

\*Corresponding authors: acbrdu@hotmail.com; sunitahooda@andc.du.ac.in

Received: 29 December 2021;

Accepted: 5 February 2022;

Published online: 14 February 2022;

AJC-20714

A new polymeric membrane sensor for Cd(II) ion based on methyl acrylate-acrylonitrile-methyl methacrylate terpolymer as membrane carrier has been synthesized *via* atom transfer radical polymerization (ATRP) method at 60 °C. Preliminary investigation with the membrane exhibited promising selectivity for Cd(II) ion with a slope of 32.02 mV/decade and the same could be estimated in the concentration range of  $1 \times 10^{-6} - 1 \times 10^{-1}$  M in the working pH range of 4-6 for up to 90 days. The potentials generated across the membrane were reproducible and the response time was less than one minute. The electrode works well even in a partially non-aqueous media. The effect of surfactant and detergent on the working of Cd(II) selective electrode was also studied. A decrease in potential was observed in the presence of appreciable amount of surfactant and detergent. Addition of plasticisers was found to greatly improve the performance of membrane, best results being obtained with the membrane ratio (NaTPB:TP:TBP::1:100:06), exhibiting a working concentration range of  $1 \times 10^{-6} - 1 \times 10^{-1}$  mol L<sup>-1</sup> with a short response time of 10 s. The proposed sensor shows significantly good selectivity toward Cd(II) ion in comparison with some alkali, alkaline earth, transition and heavy metal ions. It was successfully employed as an indicator electrode in potentiometric titration of cadmium(II) ions against EDTA solution.

**Keywords:** Methyl methacrylate, Terpolymer, Sensor, Cadmium(II), Ion selective electrode, Membrane.

### INTRODUCTION

In recent times, there has been an unwanted accumulation of heavy metal ions in the environment due to their utilization on a wide scale in various activities such as agricultural, technological and industrial applications, *etc.* This has posed a serious threat to the eco-system, particularly human beings [1,2]. Amongst all heavy metals, cadmium is attracting much concerning attention as it is one of the most toxic metals associated with serious health effects. Cadmium is present in its inorganic form in phosphate rocks. However, huge amount of cadmium is introduced into the environment due to widespread use of phosphate fertilizers as well as from the waste effluents of industries like electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [3-5].

Chronic exposure to cadmium can cause adverse health problems such as destruction of the red blood cells, high blood pressure, damage to kidney, lungs and liver, *etc.* [6,7]. Cadmium is also known to cause severe joint and spine pain due to osteomalacia, osteoporosis and itai-itai disease as cadmium potentially interferes with mineralization of bone [8,9]. Cadmium is even declared a carcinogen [10]. The daily permissible limit for cadmium intake from various sources is 1.0-1.2 µg/g of human body weight as recommended by food scientists. According to the guidelines of United States Environmental Protection Agency (USEPA), the maximum cadmium content in drinking water is 5 ppb [11]. In this scenario, detection of cadmium content in water sources has become very important so that subsequent actions can be implemented for its removal or reducing to the minimal permissible level.

This is an open access journal, and articles are distributed under the terms of the Attribution 4.0 International (CC BY 4.0) License. This license lets others distribute, remix, tweak, and build upon your work, even commercially, as long as they credit the author for the original creation. You must give appropriate credit, provide a link to the license, and indicate if changes were made.

Some of the analytical techniques currently being adopted for the detection of cadmium ions include high-performance liquid chromatography (HPLC), Inductively coupled plasma mass spectrometry (ICP-MS) [12], isotope dilution, electrothermal atomic absorption spectrometry (ETAAS) [13], mass spectroscopy, differential pulse polarography [14], neutron activation analysis, X-ray fluorescence, flame atomic absorption spectrometry (FAAS) [15,16], fluorescence spectroscopy [17], *etc.* These methods are both high energy and time consuming, involving multiple analysis or too expensive for most of the analytical laboratories and has requirement of trained personnel, *etc.* [18-20]. In view of these drawbacks, development of simple, cost-effective and more environment friendly methods for cadmium detection is of primary importance. Potentiometric sensing method that makes use of ion-selective electrodes as sensors offers a good alternative convenient method for the analysis of heavy metal ions in solutions. Besides, these sensors have certain other advantages such as ease of preparation and operation, low cost, small size, quick response, diverse laboratory applications with acceptable sensitivity and selectivity [21,22].

The development of a good and efficient sensor for the detection of cadmium ions has long been of interest for analytical chemists and tremendous efforts have been made in this field in the last four decades. Moreover, the increasing momentum in the application of ion-selective electrode sensors in the field of environmental, agricultural and medicinal analysis is encouraging analytical chemists to develop new and superior sensor materials for fast, accurate, reproducible and selective determination of ions [23]. Several types of membranes fabricated from diverse materials have been reported, which can act as efficient ion-selective electrode (ISEs). Polymeric ISEs are also one of the widely used type of sensors particularly for the detection of Cd(II) ions. Sugiyasu & Swager [24] reported the use of conducting organic which showed promising efficient as sensing materials for the detection of various analytes. New liquor contact polymer acrylonitrile-butadiene linked to tetraphenylborate ion exchanger functionalized with allylic moieties as also successfully applied as a polymeric membrane ISE by Giannetto *et al.* [25]. Other researchers also fabricated numerous polymer-based sensors for the detection of a wide range of heavy metal ions [26-28]. Overviews on electrochemical sensors have also been reported by several researchers [29,30] as promising sensors for various metal ions especially heavy metal ions in water samples [31-35]. Studies with inorganic exchange resins have also been reported by various researchers [36-38]. There have also been reports on the use of Schiff bases as Cd(II) selective ionophores in polymeric membrane electrodes [39,40].

This work reports the fabrication of novel methyl acrylate-acrylonitrile-methyl methacrylate terpolymer membrane, which was subsequently used in the establishment of a Cd(II) ion selective membrane sensor. The new terpolymer membrane not only acts a good sensor for Cd(II) but also exhibits better selectivity for Cd(II) ions in comparison to other heavy metals ions. This membrane was observed to work well over a wide concentration range, *i.e.* from  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  M concentration of Cd(II) ions with a super Nernstian slope of 32.02

mV/decade. To the best of our knowledge, this particular type of terpolymer membrane sensor has not been studied so far for the potentiometric detection of Cd(II) ions.

## EXPERIMENTAL

Acrylonitrile (AN, 99%; Merck), methyl methacrylate (MMA, 99%; Merck) and methyl acrylate (MA, 99%; Merck) dried over CaH<sub>2</sub>, vacuum distilled, and kept below 5 °C before use. Methyl 2-bromopropionate (MBP, 98%), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, 97%) and CuBr (98%) were purchased from Aldrich and used as received.

**Synthesis of methylacrylate-acrylonitrile-methyl methacrylate terpolymer:** Methyl acrylate, methyl methacrylate and acrylonitrile monomers were purified by vacuum distillation, dried over CaH<sub>2</sub> and kept below 5 °C to prevent them from polymerization. All the reactants and the required solvents were purified before use. Terpolymerization of acrylonitrile (A), methyl methacrylate (B) and methyl acrylate (M) was carried out using ATRP conditions in an atmosphere of nitrogen [41]. For the process, optimized ATRP conditions were followed starting with different in-feed ratios of monomers, taking MBP as an initiator, CuBr as a catalyst and dNbpy as a ligand in molar ratios of 100:1:0.5:0.5 for monomer:MBP:CuBr:dNbpy. Calculated amount of CuBr, dNbpy and monomers were added in different in-feed ratios were added to a round-bottomed flask and degassed by three vacuum/nitrogen cycles, followed by addition of a specific amount of initiator MBP with the help of a syringe. The solution was again purged with nitrogen. Finally, the round bottom flask was placed in an oil bath maintained at 60 °C as shown in Fig. 1. The solution showing a gradual increase in viscosity was a sign of initiation of the polymerization process. The polymerization was quenched by adding tetrahydrofuran so as to limit the conversion percentage upto less than 10%. Excess methanol was added to obtain precipitates of the terpolymers. The catalyst was removed by passing the dried samples diluted with THF over alumina. Finally, the clean and pure samples were dried overnight in vacuum.

**Preparation of terpolymer membrane and electrode:** The ingredients *viz.* terpolymer, PVC and ionophore were thoroughly mixed in tetrahydrofuran (THF) [42]. The mixture was then stirred at 25 °C till the formation of a viscous solution, which was then casted into a cyclic ring fixed on a glass plate. Slow evaporation of the solvent formed an oily concentrated mixture, which was left undisturbed overnight at room temperature for the formation of a stable membrane. A uniform, flexible, transparent, and homogeneous membrane of about 1 mm thickness was obtained. The casted membrane was removed from the glass plate and the circular cast to be further set for the formation of the electrode.

The electrode preparation was carried out by neatly fixing the membrane prepared on to a pyrex tube with the help of araldite and left for drying. Cadmium nitrate (0.1 M) was taken as reference solution in the pyrex tube fixed with the stable prepared membrane while Hg/HgCl<sub>2</sub> electrode (saturated calomel electrode) was used as the inner reference electrode. The

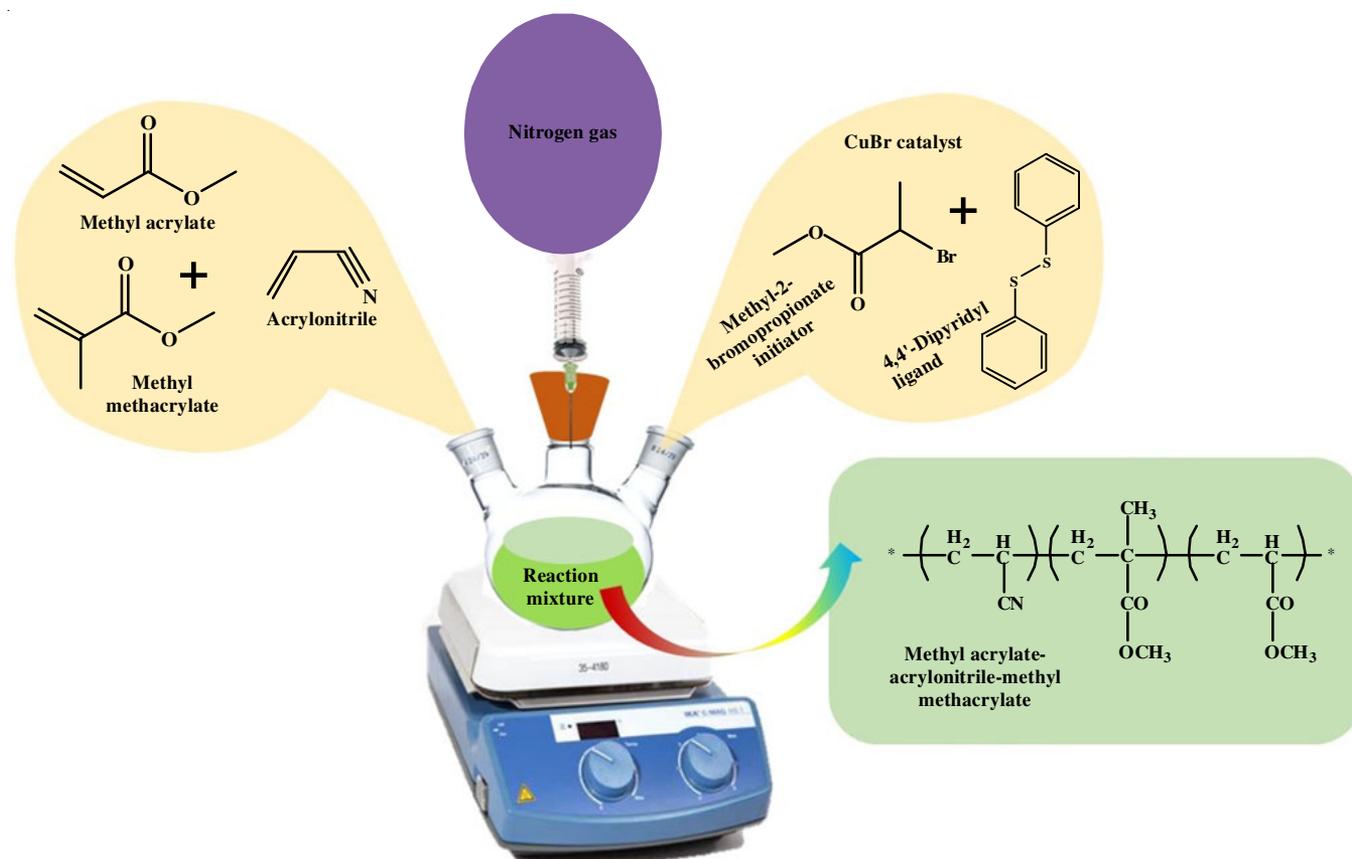


Fig. 1. Schematic representation of synthesis of terpolymer

electrodes were then conditioned in 0.1M  $\text{Cd}(\text{NO}_3)_2$  solution for 2-3 days.

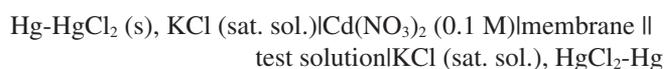
**Determination of functional properties of terpolymer membrane:** The behaviour of membrane is closely linked to its structure. The membrane shows ion selective character due to the diffusion of ions. The first pre-requisite for understanding the performance of an ion exchange membrane is its complete physico-chemical characterization. The process involves the determination of those parameters which affect the electrochemical properties of the membrane *i.e.* water content, porosity and electrolyte absorption. The functional properties of the terpolymer membrane are compiled in Table-1.

## RESULTS AND DISCUSSION

Methyl acrylate-acrylonitrile-methyl methacrylate terpolymer was prepared *via* atom transfer radical polymerization and its chemical composition was determined previously using quantitative  $^{13}\text{C}$  [ $^1\text{H}$ ] NMR spectrum [41]. The analytical characteristics of the as-synthesized terpolymer as a membrane in the electrochemical detection of ions such as slope of the calibration plot, detection limit, lifetime, response time, selectivity

for cadmium(II) ions in presence of zinc, nickel, cobalt, calcium, mercury, copper, barium, magnesium, manganese, potassium and sodium ions, as well as the pH-dependence of the electrode potential have been investigated in this work.

**Potential measurement:** The following electrochemical assembly setup has been established and connected to a potentiometer for the accurate examination of all response potentials for the fabricated terpolymer membrane electrode:



Saturated calomel electrodes (SCE) were employed both as the outer and inner reference electrodes. The cell EMFs (potential) of various test solutions of Cd(II) ions were measured for concentrations varying in the range of  $1.00 \times 10^{-6}$  to  $1.00 \times 10^{-1}$  M. The cell potential was obtained within  $\pm 2.0$  mV accuracy in all the measurements. The potential response curves were obtained as a logarithmic function of Cd(II) ionic activity (Fig. 2).

**Effect of internal solution:** The internal solution may start affecting the sensing performance of the membrane when the internal diffusion potential of the membrane becomes

TABLE-1  
FUNCTIONAL PROPERTIES OF TERPOLYMERIC MEMBRANE

Membrane	Water content per g wet membrane (g)	Porosity	Amount of KCl absorbed per g of membrane
Methyl acrylate – Acrylonitrile -Methyl methacrylate Terpolymer	0.22	0.051	$3.5 \times 10^{-2}$

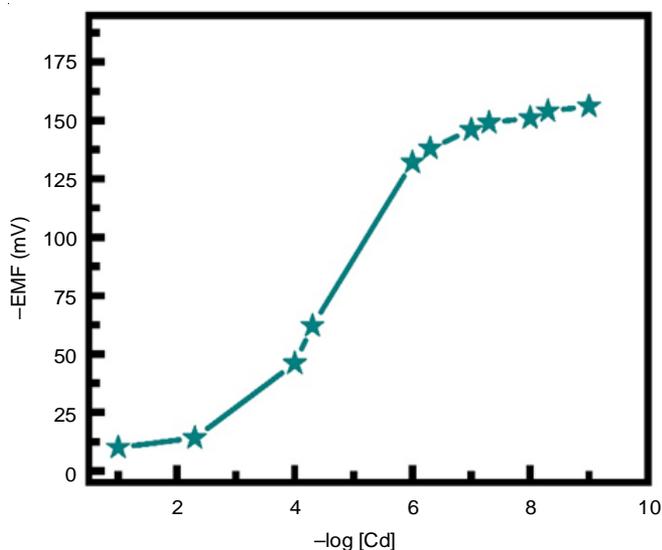


Fig. 2. Variation of EMF with  $-\log [Cd]$  for cadmium ion selective electrode

appreciable. In order to investigate the effect of the internal solution on the sensor response of the membrane, the cell potentials were measured at varying activity of internal solution, *i.e.* at  $1.0 \times 10^{-1}$ ,  $5.0 \times 10^{-2}$  and  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of Cd<sup>2+</sup> ions. Results showed that internal solution of activity  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> showed the best performance in terms of slope and working concentration range. Thus, an optimized activity of  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> of the internal solution was maintained for all further studies.

**Calibration curve and estimation of cadmium ions:** For obtaining a calibration curve, cell potentials were measured for varying concentrations of Cd(II) ions. Experiments were repeated three to four times to ensure the reproducibility of the electrode system. The EMFs were then plotted against logarithm of concentration of Cd(II) ions. The calibration curve is shown in Fig. 3, which clearly implicates that the membrane nearly exhibits Nernstian response to Cd(II) ions with a slope of 32.02 mV/decade in a wide range of concentrations ( $1 \times 10^{-1} - 1 \times 10^{-6}$  M), which is considered as an effective and narrow working concentration range for an electrode. Hence, the fabricated membrane electrode can be employed for the estimation of Cd(II) ions in the above-mentioned range of concentrations.

For achieving maximum selectivity toward a specific ion, it is necessary to prevent counter ions from entering the mem-

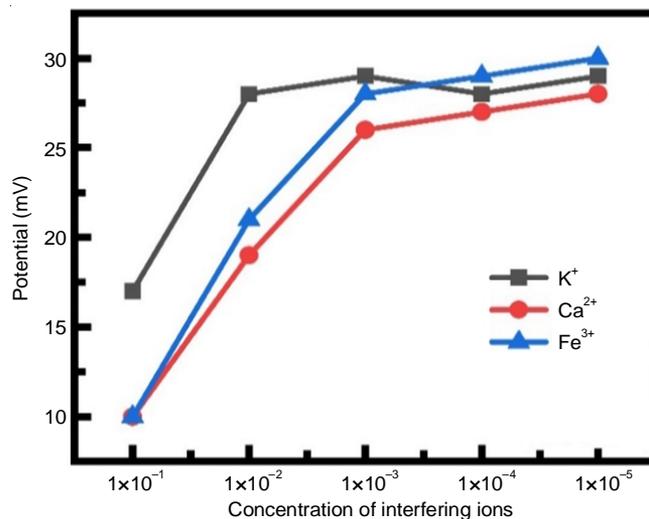


Fig. 3. Effect of concentration of interfering ions on potential of Cd(II) ion selective electrode

brane phase. Thus, for reducing the interference from anions and bulk membrane impedance as well for optimizing the sensing selectivity all prepared membranes were treated with sodium tetra phenyl borate (NaTPB) [37].

#### Response time and lifetime of terpolymer membrane:

The response time of the electrode has been measured at various concentrations of salt solutions as the elapse time between the instant at which the activity of Cd(II) ions in the test solution showed a change after the membrane electrode and the reference electrode were brought into contact and the same was found to be 20 s at all dilutions. Along with this the potentials stays constant for more than 5 min. The Nernstian slope as well as the response time obtained for the ISE using MMA terpolymer membrane is considerably good as compared to those of already reported membranes as listed in Table-2.

The lifetime of an ISE is an important parameter for judging its sustainable utility in the long run. It depends upon various factors such as the components with which the membrane sensor is made up of as well as the species which are being detected. For determining the lifetime of the terpolymer membrane sensor, calibrations were performed with standard solutions at regular intervals of 10 days time for more than 3 months. The Nernstian slope obtained for each calibration curve in the chosen working concentration range of Cd(II) ions *i.e.*,  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-6}$  mol L<sup>-1</sup> was found to be almost in a

TABLE-2  
COMPARISON OF ELECTROCHEMICAL PERFORMANCE OF MMA TERPOLYMER MEMBRANE SENSOR WITH OTHERS

Carrier	Linear range (mol dm <sup>-3</sup> )	Slope (mV per decade)	Response time (s)	Ref.
Benzo-15-crown-S	$3.16 \times 10^{-5} - 1.0 \times 10^{-1}$	20	< 30	[43]
Dibenzo-24-crown-8	$3.9 \times 10^{-5} - 1.0 \times 10^{-1}$	$30.0 \pm 1.0$	25	[44]
<i>p-tert</i> -Butylcalix[6]arene	$9.7 \times 10^{-5} - 1 \times 10^{-1}$	$29.0 \pm 1$	35	[45]
Dicyclohexano-24-crown-8	$3.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$30.0 \pm 1.0$	23	[46]
Carbon paste electrode	$8 \times 10^{-8} - 1 \times 10^{-1}$	$29.4 \pm 0.12$	~ 5	[47]
Polyaniline Sn(IV) silicate composite	$1 \times 10^{-1} - 1 \times 10^{-7}$	28.53	10	[48]
Tetrathia-12-crown-4	$4.0 \times 10^{-7} - 1.0 \times 10^{-1}$	$29 \pm 1$	< 10	[49]
[1,1'-bicyclohexyl]-1,1',2,2'-tetrol	$1.0 \times 10^{-1} - 1.0 \times 10^{-5}$	27.8	< 15	[50]
Methyl acrylate-acrylonitrile-methyl methacrylate terpolymer	$1 \times 10^{-6} - 1 \times 10^{-1}$	32.02	10	This study

close range for up to 90 days. After this, a gradual deterioration in the potentiometric response of the ISE was observed which may be attributed to deterioration of the membrane.

**Selectivity:** Selectivity coefficients of cadmium membrane electrode were evaluated by fixed interference method (FIM) [51] at  $1 \times 10^{-4}$  M interfering ions concentrations. The EMFs were plotted against the logarithm of the determinant activity. The intercept of the asymptotes to this curve gives the  $a_i$  values that are used for the determination of  $K_{ij}$  from the following relation:

$$K_{ij} = \frac{a_i}{a_j^{z_i/z_j}}$$

It can be seen that Cd(II) ISE has a great selectivity for Cd(II) ions in presence of other ions. The ions intervene in the detection of Cd(II) ions. It is observed that monovalent cations cause significant interference, whereas bivalent and polyvalent cations do not interfere. The selectivity coefficient values for monovalent cations in case of cadmium selective electrodes are of the order of 0.1- 0.5, whereas bivalent and polyvalent cations values are  $10^{-2}$  and  $10^{-3}$ , respectively. The low values of selectivity coefficient indicate the poor interference of bivalent and polyvalent cations even if present in equivalent amounts. The selectivity coefficient values of other ions in Table-3 are such that they would cause some interference at concentrations equal or greater than Cd(II) ion concentration. However, in small amounts (10 time less) than Cd(II) ions, their interference would be practically negligible. To confirm this conclusion based on selectivity constant values, potential of mixtures containing various concentrations of alkali metal ions were investigated. Alkali metal ion show practically no interference when their concentration is ten times less than Cd(II) ion concentration (Fig. 3). This study was carried out with  $1 \times 10^{-2}$  M concentration of Cd(II) ions in solution.

TABLE-3  
SELECTIVITY COEFFICIENT VALUES FOR Cd(II)  
SELECTIVE ELECTRODE AS CALCULATED  
BY FIXED INTERFERENCE METHOD

Interfering ion	Selectivity coefficient ( $K_{ij}$ )	Interfering ion	Selectivity coefficient ( $K_{ij}$ )
$K^+$	$6.8 \times 10^{-3}$	$Ni^{2+}$	$1.1 \times 10^{-3}$
$Li^+$	$1.2 \times 10^{-3}$	$Pb^{2+}$	$1.8 \times 10^{-3}$
$Ca^{2+}$	$3.1 \times 10^{-4}$	$Fe^{3+}$	$2.3 \times 10^{-5}$
$Sr^{2+}$	$2.7 \times 10^{-4}$	$Al^{3+}$	$1.2 \times 10^{-4}$
$Cu^{2+}$	$2.1 \times 10^{-4}$		

**Effect of pH:** The pH range, in which the terpolymer membrane sensor can be used, has also been determined. It is observed that the potential increases in the low pH region and remains almost constant in the pH range of 4-6 (Fig. 4) beyond which the EMF shows a decline. Hence the pH range 4-6 may be considered as the working pH range of this membrane.

**Effect of solvent:** Nature of the solvent also plays an important role in the performance of the membrane as a sensor. Hence, various solvents (e.g., acetone, ethanol and acetonitrile) are examined to check the efficacy of the membrane. It is observed that the electrode assembly can also be used to determine Cd(II) ion concentration in partially non-aqueous media,

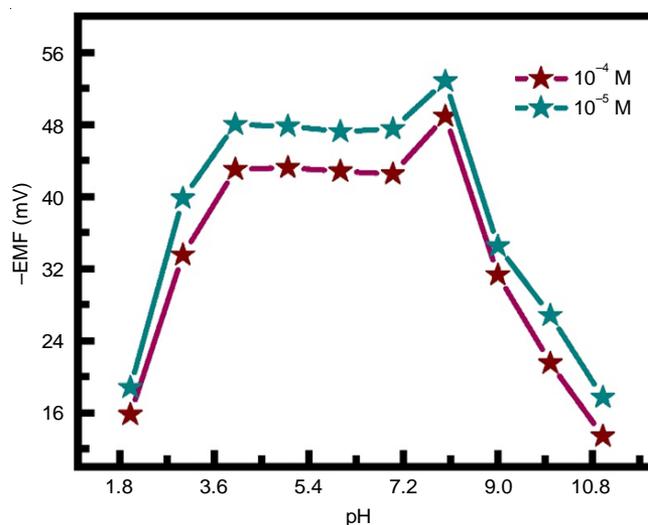


Fig. 4. Effect of pH of solution on the potential of Cd(II) ion selective electrode

like alcohol, up to a maximum of 50% non-aqueous content. When potentiometry experiments were performed using the above mentioned partially non-aqueous solvents in varying concentrations, the working concentration range for Cd(II) ions is found to be the same as observed in that of pure aqueous medium. Moreover, the Nernstian slopes obtained were also observed to be almost same for all the solvents in spite of the change in the %content of the non-aqueous component. This implicates the possible applicability of the fabricated membrane sensor in aqueous as well as partially non-aqueous media. To illustrate the effect of these partially non-aqueous media on the working of Cd(II) ion selective electrode, plots of EMF versus log of Cd(II) ions concentration in various partially non-aqueous media (25% non-aqueous content) are shown in Fig. 5.

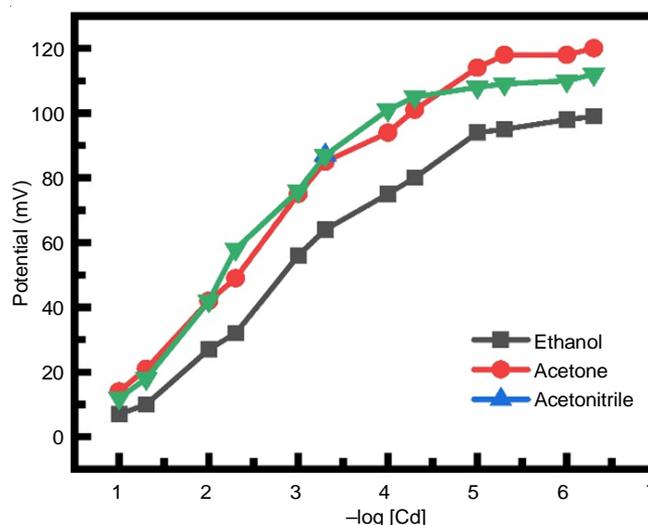


Fig. 5. Plots of EMF versus  $-\log [Cd(II)]$  ions for partially non-aqueous media

**Effect of surfactant and detergent:** The presence of surface active substances like surfactants and detergents usually

affect the functioning of the ISE. To investigate this, a comparative study of the electrode performance with and without surfactants has been carried out, which is shown in Fig. 6. Interestingly, it can be seen that the addition of the surfactant (sodium lauryl sulphate) and detergents greatly decreases the EMF values over a wide range of Cd(II) concentrations. Apart from this, experiments were performed with various commercially available detergents in order to study their effect on the EMF response of the ISE results of which are enumerated in Table-4. It is observed that with the increase in the concentration of detergent, the cell EMF progressively decreases.

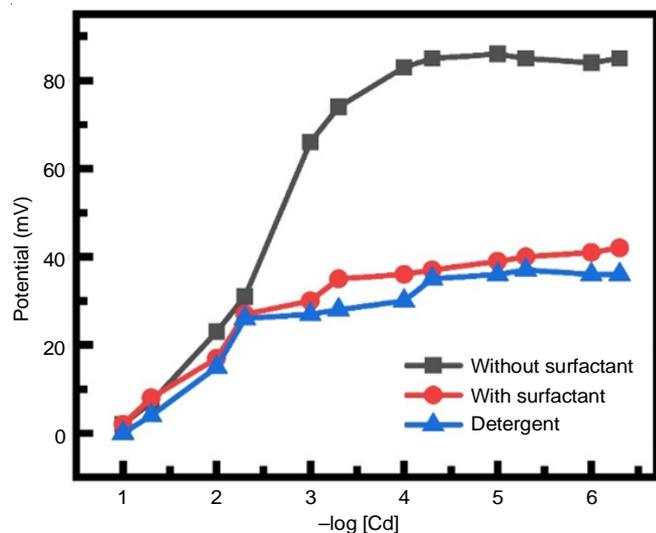


Fig. 6. Effect of detergent and surfactant on potential of Cd(II) solution

TABLE-4  
EFFECT OF DIFFERENT DETERGENTS ON WORKING OF Cd(II) SELECTIVE ELECTRODE

Conc. of solution (M) $1 \times 10^{-5}$	Potential (mV)		
	Surf excel	Ariel	Wheel
20 + 5 mL 1% detergent	53	24	29
20 + 5 mL 2% detergent	42	21	23
20 + 5 mL 3% detergent	25	19	19
20 + 5 mL 4% detergent	19	17	17
20 + 5 mL 5% detergent	16	16	16

**Effect of plasticisers:** It can be seen from Fig. 2 that the sensor having the membrane without plasticizer gives linear response over a working concentration of  $1.0 \times 10^{-6} - 1.0 \times 10^{-1} \text{ mol L}^{-1}$  with a slope of 32.02 mV/decade of activity. Further

attempts have been made to improve the performance of the membrane by the addition of optimized amount of plasticizer. Plasticizers, when added in the correct proportion, are known not only to improve the workability of the membrane but also enhance the detection limit, increase stability and shelf life of the sensor [38]. In the present work, five plasticizers namely DOP, DBP, TBP, CN and DBBS have been tried in order to enhance the functioning of the membrane sensors. The performance characteristics of the sensors are compiled in Table-5.

It is observed from Table-5 that not all plasticizers have the property to improve the overall performance of the MMA terpolymer membranes (sensor no. 1-8), which is evident from the values of the slope, working concentration range and response time of the various membranes. Of all the membrane sensors with varying ratios of plasticizers, improved performance is observed only in sensors 6 and 7; the best result being obtained for sensor 7 synthesized with the membrane ratio (NaTPB:TP:TBP::1:100:06). It was found to exhibit a working concentration range of  $1 \times 10^{-6} - 1 \times 10^{-1} \text{ mol L}^{-1}$  with a super Nernstian slope of 42.3 mV/decade of Cd(II) ions and a short response time of 10 s.

**Potentiometric titrations:** The electrochemical set up was also analyzed for its applicability in the direct determination of Cd(II) ion in solution through potentiometric titration of Cd(II) ions against a standard EDTA solution. The fabricated terpolymeric membrane was employed as an indicator electrode combined with an external standard calomel electrode (SCE) reference. The two electrodes were connected through a salt bridge made up of KCl in agar-agar gel. Potentiometric titration was performed taking 20 mL of  $10^{-3} \text{ M Cd(NO}_3)_2$  solution against  $10^{-2} \text{ M EDTA}$  using the proposed ISE (Fig. 7). Cell EMF was noted for every addition of a known volume of EDTA in small amounts. The inflexion points in the titration curve as shown in Fig. 7 indicates to the stoichiometric amount of EDTA which is required to completely remove all the Cd(II) ions in the solution taken. These results suggest that the terpolymer membrane electrode assembly can be successfully used as an indicator electrode for quantitative determination of Cd(II) ions in solution.

**Mechanism:** Fig. 8 demonstrates the suggested coordination scheme with cadmium centre in terpolymer. The selectivity was mainly controlled by specific interactions between metal centre and anions present in the structure of ionophore (CN, CO and  $\text{OCH}_3$ ). Terpolymer structure has an influence upon the interaction of metal centre with anions [52,53].

TABLE-5  
EMF RESPONSE OF MEMBRANE SENSORS AFTER THE ADDITION OF PLASTICIZERS IN VARYING RATIOS

NaTPB	Percentage (w/w) of component in membrane					Terpolymer (TP)	Working conc. range (M)	Slope (mV/decade)	Response time (s)
	DOP	TBP	DBP	CN	DBBP				
1	40					100	$1 \times 10^{-1} - 1 \times 10^{-6}$	14.9	50
1		40				100	$1 \times 10^{-1} - 1 \times 10^{-6}$	15.3	20
1			40			100	$1 \times 10^{-1} - 1 \times 10^{-6}$	6.6	30
1				40		100	$1 \times 10^{-1} - 1 \times 10^{-6}$	19.9	60
1					40	100	$1 \times 10^{-1} - 1 \times 10^{-6}$	9.9	40
1	6					100	$1 \times 10^{-1} - 1 \times 10^{-6}$	35.5	30
1		6				100	$1 \times 10^{-1} - 1 \times 10^{-6}$	42.3	20
1			6			100	$1 \times 10^{-1} - 1 \times 10^{-6}$	28.0	20

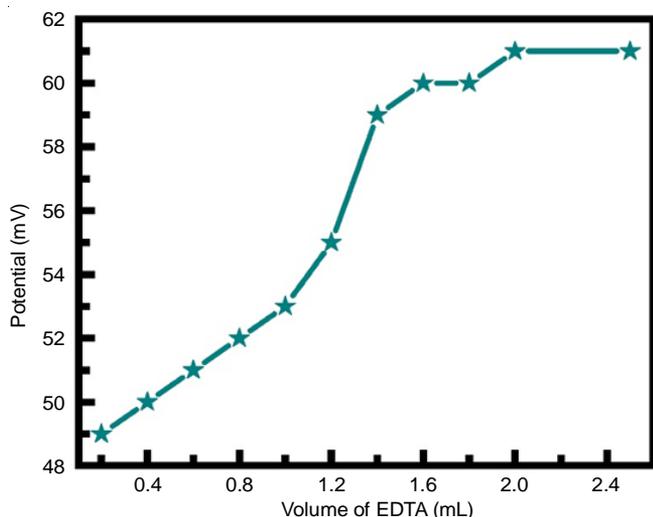


Fig. 7. Titration curve for potentiometric titration of  $10^{-3}$  M Cd(II) solution with  $10^{-2}$  M EDTA solution

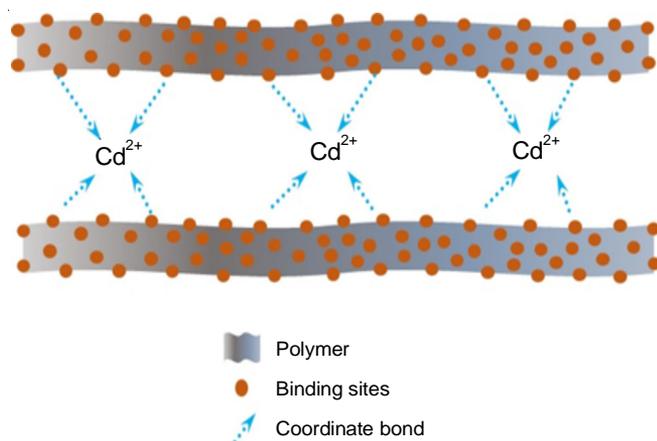


Fig. 8. Mechanism of sensing cadmium ion through terpolymer membrane

## Conclusion

The present work illustrates the development of terpolymer membrane sensor for cadmium(II) ions. Calibration experiments performed on the sensor in various time intervals show that the sensor can be used effectively up to 90 days without any significant alteration in the electrochemical response toward Cd(II) ions. This indicates a considerably good lifetime of the fabricated ISE. Addition of plasticizers was found to greatly improve the performance of membrane, best results being obtained with the membrane ratio (NaTPB:TP:TBP::1:100:06), exhibiting a working concentration range of  $1 \times 10^{-6} - 1 \times 10^{-1}$  mol L<sup>-1</sup> with a super Nernstian slope of 42.3 mV/decade of Cd(II) ions and a short response time of 10 s. The cell response was found to show a consistent response in terms of EMF in the pH range 4-6, which infers this range as the working pH range of the membrane sensor. Experimented with various solvents such as acetone, ethanol, acetonitrile, the concentration range for Cd(II) ions was also found to be almost same as observed in pure aqueous medium. The membrane electrode assembly was also successfully employed as an indicator electrode in the potentiometric titration of Cd(II) ion with EDTA.

## ACKNOWLEDGEMENTS

The authors are thankful to UGC, New Delhi, India for providing financial assistance and (Late) Dr. Vandana Uberoi, Principal Investigator to carry out this work. The authors are grateful to the Principals of Acharya Narendra Dev College and Sri Venkateswara College, for their valuable encouragement and guidance.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## REFERENCES

- J. Briffa, E. Sinagra and R. Blundell, *Heliyon*, **6**, 04691 (2020); <https://doi.org/10.1016/j.heliyon.2020.e04691>
- M. Zaynab, R. Al-Yahyai, A. Ameen, Y. Sharif, L. Ali, M. Fatima, K.A. Khan and S. Li, *J. King Saud Univ. Sci.*, **34**, 101653 (2022); <https://doi.org/10.1016/j.jksus.2021.101653>
- Z.R. Holan, B. Volesky and I. Prasetyo, *Biotechnol. Bioeng.*, **41**, 819 (1993); <https://doi.org/10.1002/bit.260410808>
- B. Volesky, H. May and Z. Holan, *Biotechnol. Bioeng.*, **41**, 826 (1993); <https://doi.org/10.1002/bit.260410809>
- K.H. Chong and B. Volesky, *Biotechnol. Bioeng.*, **49**, 629 (1996); [https://doi.org/10.1002/\(SICI\)1097-0290\(19960320\)49:6<629::AID-BIT4>3.0.CO;2-Q](https://doi.org/10.1002/(SICI)1097-0290(19960320)49:6<629::AID-BIT4>3.0.CO;2-Q)
- M. Hutton and C. Symon, *Sci. Total Environ.*, **57**, 129 (1986); [https://doi.org/10.1016/0048-9697\(86\)90018-5](https://doi.org/10.1016/0048-9697(86)90018-5)
- J.O. Nriagu, *Environ. Pollut.*, **50**, 139 (1988); [https://doi.org/10.1016/0269-7491\(88\)90189-3](https://doi.org/10.1016/0269-7491(88)90189-3)
- G. Genchi, M.S. Sinicropi, G. Lauria, A. Carocci and A. Catalano, *Int. J. Environ. Res. Public Health*, **17**, 3782 (2020); <https://doi.org/10.3390/ijerph17113782>
- Z.S. Fu and S.H. Xi, *Toxicol. Mech. Methods*, **30**, 167 (2020); <https://doi.org/10.1080/15376516.2019.1701594>
- A.A. Tinkov, T. Filippini, O.P. Ajsuvakova, M.G. Skalnaya, J. Aaseth, G. Björklund, E.R. Gatiatulina, E.V. Popova, O.N. Nemereshina, P.-T. Huang, M. Vinceti and A.V. Skalny, *Environ. Res.*, **162**, 240 (2018); <https://doi.org/10.1016/j.envres.2018.01.008>
- H. Sharma, N. Rawal and B.B. Mathew, *Int. J. Nanotechnol. Nanosci.*, **3**, 1 (2015).
- Z. Shao, M. Xue, Q. Liu, P. Li, Y. Fang and Q. Hu, *J. Consum. Prot. Food Saf.*, **15**, 193 (2020); <https://doi.org/10.1007/s00003-020-01275-0>
- I. López-García, Y. Vicente-Martínez and M. Hernández-Córdoba, *Talanta*, **110**, 46 (2013); <https://doi.org/10.1016/j.talanta.2013.02.015>
- M.A. Taher, *Turk. J. Chem.*, **27**, 529 (2003).
- Y. Tu, S. Ju and P. Wang, *Spectrosc. Lett.*, **49**, 249 (2016); <https://doi.org/10.1080/00387010.2015.1134578>
- G. Yang, Q. Hu, Z. Huang and J. Yin, *J. Braz. Chem. Soc.*, **16**, 1154 (2005); <https://doi.org/10.1590/S0103-50532005000700011>
- S. Charles, F. Dubois, S. Yunus and E.V. Donckt, *J. Fluoresc.*, **10**, 99 (2000); <https://doi.org/10.1023/A:1009430723152>
- A. Shirzadmeh, M. Rezaei, H. Bagheri and H. Khoshsafar, *Int. J. Environ. Anal. Chem.*, **96**, 929 (2016); <https://doi.org/10.1080/03067319.2016.1210608>
- A. Afkhami, T. Madrakian, A. Shirzadmeh, M. Tabatabaee and H. Bagheri, *Sens. Actuators B Chem.*, **174**, 237 (2012); <https://doi.org/10.1016/j.snb.2012.07.116>
- A. Afkhami, H. Bagheri, A. Shirzadmeh, H. Khoshsafar and P. Hashemi, *Electroanalysis*, **24**, 2176 (2012); <https://doi.org/10.1002/elan.201200246>

21. Ö. Isildak, O. Özbek and K.M. Yigit, *Int. J. Environ. Anal. Chem.*, **101**, 2035 (2020);  
<https://doi.org/10.1080/03067319.2019.1691542>
22. H. Bagheri, A. Shirzadmehr, M. Rezaei and H. Khoshsafar, *Ionics*, **24**, 833 (2018);  
<https://doi.org/10.1007/s11581-017-2252-1>
23. J. Habes and D. Messadi, *Environ. Res. J.*, **2**, 1 (2008).
24. K. Sugiyasu and T.M. Swager, *Bull. Chem. Soc. Japan*, **80**, 2074 (2007);  
<https://doi.org/10.1246/bcsj.80.2074>
25. M. Giannetto, A. Bello, M. Gennari, L. Marchio and G. Mori, *Sens. Actuators B Chem.*, **133**, 235 (2008);  
<https://doi.org/10.1016/j.snb.2008.02.040>
26. K. Sugiyasu and T.M. Swager, *Bull. Chem. Soc. Jpn.*, **80**, 2074 (2007);  
<https://doi.org/10.1246/bcsj.80.2074>
27. C. Wardak and B. Marczewska, *J. Chem. Anal.*, **49**, 497 (2004).
28. J.R. Stetter, W.R. Penrose and S. Yao, *J. Electrochem. Soc.*, **150**, S11 (2003);  
<https://doi.org/10.1149/1.1539051>
29. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Water Res.*, **33**, 2469 (1999);  
[https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8)
30. C.K. Ho, A. Robinson, D.R. Miller and M.J. Davis, *Sensors*, **5**, 4 (2005);  
<https://doi.org/10.3390/s5010004>
31. V. Adam, J. Zehnalek, J. Petrlova, D. Potesil, B. Sures, L. Trnkova, F. Jelen, J. Vitecek and R. Kizek, *Sensors*, **5**, 70 (2005);  
<https://doi.org/10.3390/s5010070>
32. S.K. Mittal, H.K. Sharma and A.S. Kumar, *Sensors*, **4**, 125 (2004);  
<https://doi.org/10.3390/s40800125>
33. M. Naushad, *Ion Exchange Lett.*, **2**, 1 (2009);  
<https://doi.org/10.3260/iel.2009.03.001>
34. H.K. Lee, K. Song, H.R. Seo, Y.K. Choi and S. Jeon, *Sens. Actuators B Chem.*, **99**, 323 (2004);  
<https://doi.org/10.1016/j.snb.2003.11.029>
35. D. Vlascici, E. Fagadar-Cosma, E. Pica, V. Cosma, O. Bizerea, G. Mihailescu and L. Olenic, *Sensors*, **8**, 4995 (2008);  
<https://doi.org/10.3390/s8084995>
36. J. Yin and H.W. Blanch, *Biotechnol. Bioeng.*, **34**, 180 (1989);  
<https://doi.org/10.1002/bit.260340206>
37. S.K. Srivastava, V. Sahgal and H. Vardhan, *Sens. Actuators B Chem.*, **13**, 391 (1993);  
[https://doi.org/10.1016/0925-4005\(93\)85409-4](https://doi.org/10.1016/0925-4005(93)85409-4)
38. Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, **67**, 507 (1995);  
<https://doi.org/10.1351/pac199567030507>
39. V.K. Gupta, M. Al Khayat, A.K. Singh and M.K. Pal, *Anal. Chim. Acta*, **634**, 36 (2009);  
<https://doi.org/10.1016/j.aca.2008.11.065>
40. V.K. Gupta, A.K. Singh and N. Mergu, *Electrochim. Acta*, **117**, 405 (2014);  
<https://doi.org/10.1016/j.electacta.2013.11.143>
41. A.S. Brar, A.K. Goyal, S. Hooda and R. Shankar, *J. Polym. Sci.*, **47**, 25 (2009);  
<https://doi.org/10.1002/pola.23096>
42. S. Lal, S. Hooda, A. Kumar, S. Kumar, A. Singh, S. Singh, R. Chandra, V. Kumar, V. Uberoi and G. Gambhir, *Int. J. Adv. Educ. Res.*, **3**, 107 (2018).
43. S.K. Srivastava, V.K. Gupta and S. Jain, *Electroanalysis*, **8**, 938 (1996);  
<https://doi.org/10.1002/elan.1140081017>
44. V.K. Gupta and P. Kumar, *Anal. Chim. Acta*, **389**, 205 (1999);  
[https://doi.org/10.1016/S0003-2670\(99\)00154-3](https://doi.org/10.1016/S0003-2670(99)00154-3)
45. V.K. Gupta, S. Kumar, R. Singh, L.P. Singh, S.K. Shoorra and B. Sethi, *J. Mol. Liq.*, **195**, 65 (2014);  
<https://doi.org/10.1016/j.molliq.2014.02.001>
46. V.K. Gupta, A.K. Jain and P. Kumar, *Electrochim. Acta*, **52**, 736 (2006);  
<https://doi.org/10.1016/j.electacta.2006.06.009>
47. R.F. Aglan, M.M. Hamed and H.M. Saleh, *J. Anal. Sci. Technol.*, **10**, 7 (2019);  
<https://doi.org/10.1186/s40543-019-0166-4>
48. M. Naushad, Inamuddin and T.A. Rangrez, *Desalin. Water Treat.*, **55**, 463 (2015);  
<https://doi.org/10.1080/19443994.2014.915389>
49. M. Shamsipur and M.H. Mashhadizadeh, *Talanta*, **53**, 1065 (2001);  
[https://doi.org/10.1016/S0039-9140\(00\)00602-0](https://doi.org/10.1016/S0039-9140(00)00602-0)
50. M. Javanbakht, A. Shabani-Kia, M.R. Darvich, M.R. Ganjali and M. Shamsipur, *Anal. Chim. Acta*, **408**, 75 (2000);  
[https://doi.org/10.1016/S0003-2670\(99\)00771-0](https://doi.org/10.1016/S0003-2670(99)00771-0)
51. R.P. Buck and E. Lindner, *Pure Appl. Chem.*, **66**, 2527 (1994);  
<https://doi.org/10.1351/pac199466122527>
52. M.-R. Huang, Y.-B. Ding, X.-G. Li, Y.J. Liu, K. Xi, C.-L. Gao and R.V. Kumar, *Appl. Mater. Interfaces*, **6**, 22096 (2014);  
<https://doi.org/10.1021/am505463f>
53. F. Criscuolo, M.I.N. Hanitra, I. Taurino, S. Carrara and G. De Micheli, *IEEE Sens. J.*, **21**, 22143 (2021);  
<https://doi.org/10.1109/JSEN.2021.3099209>