

# A fast response cadmium-selective polymeric membrane electrode based on *N,N'*-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide as a new neutral carrier

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## Abstract

A new polyvinylchloride membrane sensor for  $\text{Cd}^{2+}$  ions based on *N,N'*-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide (Mebqb) as a new and excellent neutral ionophore has been prepared. The sensor shows a Nernstian response for cadmium ions over a wide concentration range ( $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M) with the determination coefficient of 0.9964 and slope of  $29.9 \pm 0.5$  mV decade $^{-1}$ . The limit of detection is  $8 \times 10^{-7}$  M. It has a fast response time of 3–8 s and can be used for at least 8 weeks without any divergence in potential. The electrode can be used in the pH range from 4.0 to 9.0. The proposed sensor shows a very good discriminating ability towards  $\text{Cd}^{2+}$  ion in comparison to some alkali, alkaline earth, transition and heavy metal ions. It was successfully applied for the direct determination of  $\text{Cd}^{2+}$  in standard and real sample solutions.

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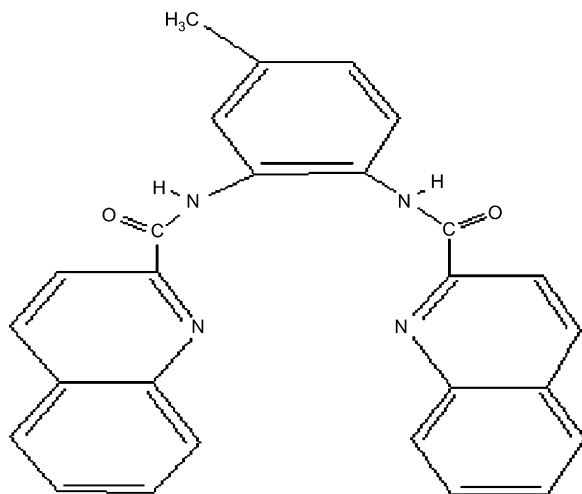
**Keywords:** Cadmium ion-selective electrode; PVC membrane; Mebqb; Potentiometry; Polyvinylchloride

## 1. Introduction

There is a challenge for analytical chemists to develop new sensors for the fast, accurate, reproducible, and selective determination of various species in the fields of environmental, agricultural and medicinal analysis. During the past two decades, many efforts has been done in the synthesis and characterization of neutral ionophore with high selectivity for specific metal ions to develop new potentiometric and optical sensors for the determination of the respective metal ions in real samples [1–3]. In modern world, the pollution of heavy metal ions is becoming more and more severe. Cadmium is a toxic heavy metal that appears in the environment mainly due to industrial processes. Besides natural exposure from soils or earth crust with high content of cadmium, anthropogenic processes like combustion of coal and mineral oil, smelting, mining, alloy processing, paint industries, etc. are the major sources of lead and cadmium to the people in the vicinity of the industrial areas.

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Cadmium strongly adsorbs to organic matter in soils. United States Environmental Protection Agency (EPA) has found cadmium to potentially cause the following health effects when people are exposed to it at levels above the minimum concentration level (MCL) for relatively short periods of time: nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure and in long-term cadmium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: kidney, liver, bone and blood damage [4]. Recently, several techniques including; flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICP-MS) and atomic fluorescence spectrometry (AFS) [5–12] have been used for the determination of trace elements in different samples, but the wide utilization of these methods is limited by the expensive equipment. At the same

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Scheme 1. The Mebqb structure.

time, numerous voltammetric methods especially using chemically modified electrodes (CME) have been developed [13,14]. Because of some imperfectness of these methods for application to routine analysis, considerable efforts have been directed towards the design and synthesis of highly selective ionophore [15]. Since less than three decades ago the solid-state ISE based on a mixed CdS/Ag<sub>2</sub>S membrane has been commercially available [16]. Polymeric carrier-based ion-selective electrodes (ISEs) for determining the alkali metal cations such as sodium [17,18], potassium and lithium [19] have been studied numerously. The efforts are needed to make ion-selective electrodes for heavy metal ions in very low concentration [20,21], so we were interested in preparation of a new solvent polymeric membrane electrode for selective and fast monitoring of cadmium ion in solutions. The most important advantages of proposed polymeric carrier-based ISE over solid-state ISE based on a mixed CdS/Ag<sub>2</sub>S membrane are their required fine conditioning, near-Nernstian slope and short response time [16]. In the present work, we use Mebqb, synthesized recently in our laboratories, as an excellent neutral ion carrier in construction of novel cadmium(II)-PVC membrane electrode [22]. The ionophore is shown in Scheme 1.

## 2. Materials and methods

### 2.1. Reagents

Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) were purchased from Merck and polyvinylchloride (PVC) with high molecular weight from Fluka were used as received.

A 0.1 M stock solution of cadmium nitrate was prepared by dissolving an appropriate, accurate amount of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Merck). A 1.0 × 10<sup>-6</sup> to 1.0 × 10<sup>-1</sup> M solution of cadmium ion was prepared daily by sequential dilution of the appropriate stock solution with doubly distilled water. Nitrate salts of cations (all from Merck) were of the high-

est purity available. All other reagents used were of analytical reagent grade, and doubly distilled water was used throughout. Mebqb as an ionophore was synthesized recently in our laboratories.

### 2.2. Construction and calibration of electrodes

Membranes with different PVC/plasticizer ratios were studied for finding the most suitable membrane composition. The optimum composition was 31% of powdered PVC, 59% of a plasticizer (DOP), 4% of an additive (NaTPB) and 6% of the corresponding ionophore. These were mixed in 5 mL THF. The resulting clear mixture was evaporated at room temperature slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d.) was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0 × 10<sup>-3</sup> M Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O). The electrode was finally conditioned by soaking for 24 h in a 0.01 M solution of cadmium nitrate. An SCE electrode was used as the reference internal electrode. The compositions of the membrane electrode are summarized in Table 1.

### 2.3. Apparatus and emf measurements

A cadmium-selective PVC electrode and a saturated calomel electrode (SCE) were used as an indicating electrode and a reference electrode, respectively. The emf measurements were carried out at room temperature with a Fanavary Tajhizat Sanjesh pH meter Model 162, a double junction SCE reference electrode. The electrode cell assembly of the following type was used: (SCE) internal solution (1.0 × 10<sup>-3</sup> M Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) sensor membrane (sample solution) (SCE).

The potential reading of each solution was recorded when it became stable, and then plotted as a logarithmic function of Cd(II) cation activity. The activities of metal ions were based on the activity coefficient *g*, data calculated from the modified form of the Eq. (1) (Debye–Huckel Eq.), which is applicable to any ion:

$$\text{Log } \gamma = -0.511Z^2[\mu^{1/2}/(1 + 1.5\mu^{1/2}) - 0.2\mu] \quad (1)$$

where  $\mu$  is the ionic strength and *Z* is the valency. All measurements were carried out at 25 ± 0.1 °C.

### 2.4. Procedure for the determination of Cd Ion in the real samples

Spiked and real water and waste water samples containing different cadmium concentrations for standard addition method were prepared by adding known amounts of cadmium to the samples. The cadmium selective and reference electrodes were immersed in the samples and the cadmium concentrations were determined by direct potentiometry and using the standard addition technique.

Table 1  
Composition and optimization of membranes ingredients

No.	PVC (%)	Plasticizer (%)	Ionophore (%)	NaTPB (%)	Slope (mV decade <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )	R <sup>2</sup>
1	29.7	DOP, 61.3	5	4	-27.6	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	0.9999
2	29	DOP, 62	5	4	-20.7	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	0.9963
3	28.5	DOP, 62.5	5	4	-19.3	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	0.9752
4	30.7	DOP, 61.7	5	3	-26	5.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	0.9979
5	30	DOP, 61	6	3	-28.7	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	0.9956
6	30	DOP, 59	7	4	-36.2	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-2</sup>	0.9959
7	30	DOP, 31 DBP, 31	5	3	-21.3	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	0.9743
8	31	DBP, 59	6	4	-29.9	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	0.9964
9	30	DOP, 60	6	4	-28.6	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	0.9991
10	29	DOP, 60	7	4	-32.7	1.0 × 10 <sup>-6</sup> to 5.0 × 10 <sup>-2</sup>	0.9944
11	33	64	–	3	-10.5	1.0 × 10 <sup>-4</sup> to 1.0 × 10 <sup>-1</sup>	0.8153
12	32	DOP, 63	5	–	-13.2	1.0 × 10 <sup>-4</sup> to 1.0 × 10 <sup>-1</sup>	0.8327

### 3. Results and discussion

#### 3.1. Preliminary potentiometric studies

In preliminary experiments, the proposed ligand was used, in the preliminary experiments, as a neutral carrier to prepare polymeric membrane electrodes for a variety of metal ions. As it can be seen from Fig. 1, among different tested cation, Cd<sup>2+</sup> with the most sensitive response seems to be suitably determined with the PVC membrane based on the proposed ligand and the emf responses obtained for all other cation-selective electrodes are much lower than the predicted by the Nernst equation. The results might indicate that the selectivity towards these ions is masked by the low detection limit of the electrode, which is most probably due to the transport of Cd<sup>2+</sup> ions from the measuring solution to the boundary between membrane and the solution as discussed by Bakker and co-workers [23,24]. Among the properties of the zinc group metal ions is their unique ability to adopt various coordination geometries and to form different chelates ring size with chelating ligands bearing strong δ-donor atoms [25,26]. The interaction between the metal ion and the donor atoms of the ligand is in part electrostatic leading to the complexes that can participate in reversible reactions. Mebqb is N<sub>4</sub> tetradentate ligand that provides the optimum structure for selective interaction with Cd<sup>2+</sup>.

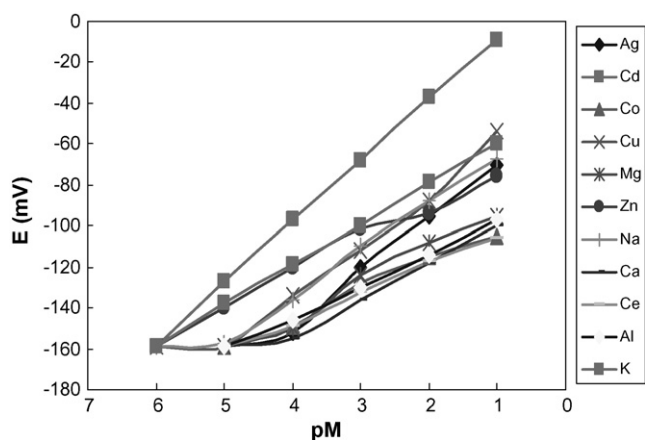


Fig. 1. Potential response of various ion-selective electrodes based on Mebqb.

#### 3.2. Influence of membrane composition

Besides the critical role of the nature of ion carriers in preparing membrane-selective sensors, some other important features of the PVC membrane are known to significantly influence the sensitivity, linearity range and selectivity of ion-selective electrodes. These include the amount of ionophore, the nature of solvent mediators, the plasticizer/PVC ratio, and especially the amount and nature of the additives used [27]. Thus, different aspects of membrane preparation based on Mebqb for Cd<sup>2+</sup> ions were optimized and the results are summarized in Table 1. Ligands used as ionophore in a Cd(II) ion-selective electrode should be selective for Cd<sup>2+</sup> ion over other metal cations due to its ring structure size and distance between electron donor group, and be sufficiently lipophilic to prevent leaching of the ligand into the aqueous solution surrounding the membrane electrode and have fast exchange capabilities [28,29]. Due to its sufficient insolubility in water and the presence of two oxygen and several nitrogen-donating atoms in its structure, this ligand was expected to act as a suitable ion carrier in the PVC membrane-based sensors. For the proposed membrane the presence of the ionophore has highly considerable effect on the slope and electrode response, as demonstrated on membrane No. 11.

By increasing the amount of the additives the electrode represents acceptable response and slope is getting close to Nernstian slope. So the polymeric membranes were investigated to measure the ability of the ionophore to act as an ion carrier in the absence and presence of the lipophilic additive. The response of the membrane without additive gave poor sensitivity and resulted in diminished slope (membrane No. 12).

If the plasticizer percentage arises in mixture, the hydrophilic characteristics and so the electrode response increase to a specific limit and after that the interfering ions have negative effects on membrane selectivity and sensitivity (membrane No. 3).

The results obtained with different membrane compositions show that membrane number 8 with composition of DOP:PVC:Mbqb:NaTPB and the percent ratio of 59:31:6:4 has the optimum composition, slope and dynamic range for detecting cadmium ions, so it was selected for preparation of the polymeric membrane electrode.

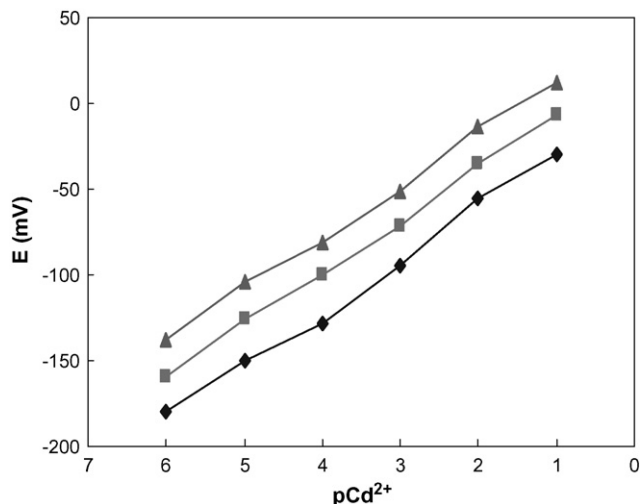


Fig. 2. Effect of the concentration of an internal reference solution on electrode response at various concentrations of  $1.0 \times 10^{-1}$  M (◆),  $1.0 \times 10^{-3}$  M (■), and  $1.0 \times 10^{-5}$  M (▲).

### 3.3. Effect of internal reference solution

Effect of the internal standard solution concentration ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) of the membrane-selective electrode on the emf- $p(\text{Cd}^{2+})$  signal was studied in concentrations  $1.0 \times 10^{-1}$ ,  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-5}$  M of  $\text{Cd}^{2+}$  (Fig. 2). The results showed that the variation of the internal  $\text{Cd}(\text{NO}_3)_2$  concentration did not cause any significant difference in potential response. In fact, the main factor for not changing of potential slope and response is the membrane enough thickness and decrease of trans-membrane flux [30]. Thus, the  $\text{Cd}(\text{NO}_3)_2$  concentration of  $1.0 \times 10^{-3}$  M, that was quite appropriate for smooth functioning of the electrode system, was selected for the internal standard solution.

### 3.4. Influence of pH

The effect of pH on the electrode potential at various cadmium concentrations was studied by adding diluted solutions of HCl (0.1 M) or NaOH (0.1 M) and adjusting the pH by a pH meter in the range of 1.0–11.0. The pH dependence of the electrode potential was listed over the range of 1–11 for  $1.0 \times 10^{-3}$  M Cd(II) ions. The results showed that the useful range is 4.0–9.0 because the potential remain almost constant in this range (Fig. 3). The sharp change in potential at higher pH values may be due to the formation of some hydroxy complexes of  $\text{Cd}^{2+}$ , while at lower pH values  $\text{H}_3\text{O}^+$  ions start to contribute to the charge transport process by the membrane, thereby causing interference.

### 3.5. Response characteristics

ISE characterization performed with a mathematical and computational program has been shown to be very useful for determination of detection limits and selectivity constants among others [31]. Linear curve fitting using IUPAC method has been used for the determination of ISE characteristics. The

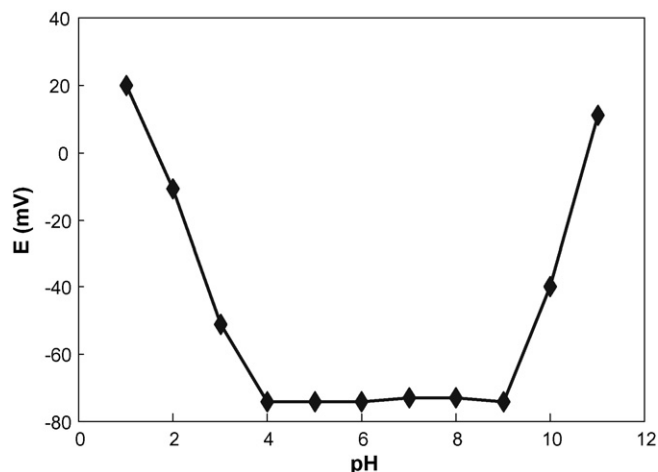


Fig. 3. Influence of pH on the potential response of the cadmium-selective electrode to  $1.0 \times 10^{-3}$  M  $\text{Cd}^{2+}$ .

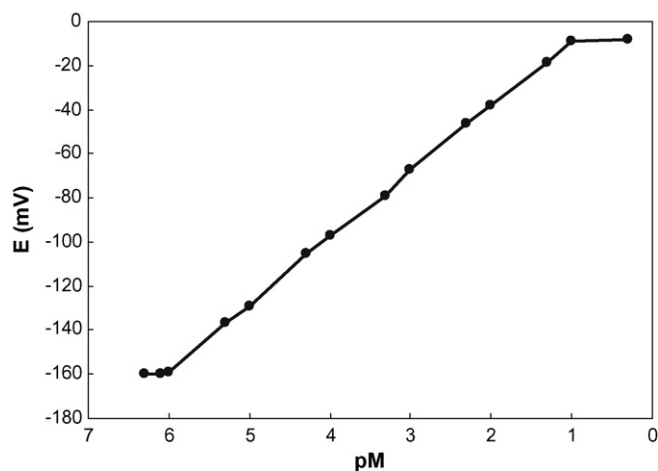


Fig. 4. Calibration graph for the proposed  $\text{Cd}^{2+}$  ion-selective electrode.

electrode shows a linear response ( $R^2 = 0.9964$ ) to the activity of  $\text{Cd}^{2+}$  ion in the range about  $1.0 \times 10^{-1}$  to  $1.0 \times 10^{-6}$  M (Fig. 4). The calibration parameters obtained are included in Table 2.

It is evident that the lifetime of electrodes depends on the components of the working solution and the measured specimens with electrodes. The lifetime of the electrodes was found out by performing calibrations periodically with standard solutions and calculating the response, slope over the range  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  M cadmium nitrate solution. The experimental results show that the lifetime of the present electrode was over 2 months. During this period, the electrode was

Table 2  
Response characteristics of the proposed cadmium-selective electrode

Slope (mV decade <sup>-1</sup> )	$-29.9 \pm 0.5$
Linear range (mol L <sup>-1</sup> )	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$
Detection limit (mol L <sup>-1</sup> )	$8 \times 10^{-7}$
Response time (s) $1 \times 10^{-6}$ to $1.0 \times 10^{-1}$ mol L <sup>-1</sup>	<8 s
Working pH range	4–9
Life time (months)	2

Table 3  
Conditioning time of optimized Cd<sup>-</sup> ISE

Time (day)	Slope (mV decade <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )
1	-29.9 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
2	-29.9 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
5	-29.9 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
9	-29.9 ± 0.5	1.0 × 10 <sup>-6</sup> –1.0 × 10 <sup>-1</sup>
15	-29.9 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
23	-29.5 ± 0.5	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
35	-29.5 ± 0.5	5.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
45	-29.5 ± 0.5	5.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>
60	-29.5 ± 0.5	5.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>

in a cadmium nitrate solution and the detection limit and the slope of the electrode remained almost constant. Subsequently the electrochemical behavior of the electrode gradually deteriorated which may be due to ageing of the polymer (PVC), plasticizers and ionophore (Table 3).

The response time of the electrode was tested by measuring the time required to achieve a steady potential within 1 mV fluctuation by increasing in the Cd(II) ion concentration. The response time of the electrode based on the proposed ligand yielded a steady potential within 8 s (Fig. 5). (The response time for lower concentrations range elevates fairly compare to the higher concentrations range.)

In Table 4, the response characteristics of the proposed electrode are compared with those of several recently reported selective electrodes for Cd<sup>2+</sup> ions [16,32–46]. As it shows, the proposed electrode represents wider dynamic range compare to most of the sensors (except for [36,40]) and near-Nernstian

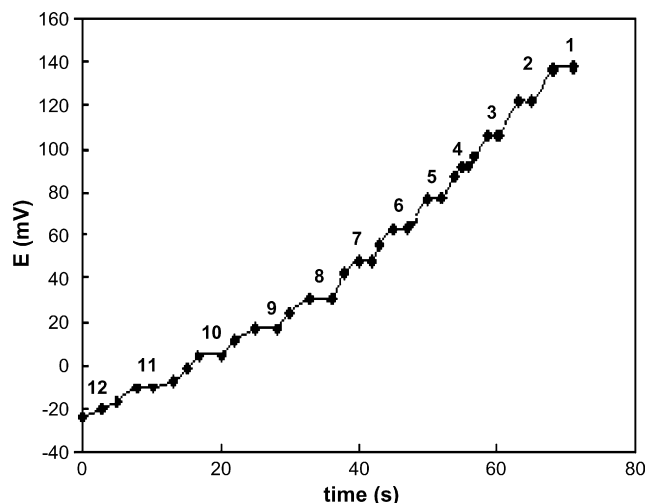


Fig. 5. The response time of the cadmium-selective electrode during step by step changing of cadmium ions concentration of: (1) 1.0 × 10<sup>-1</sup> M, (2) 5.0 × 10<sup>-2</sup> M, (3) 1.0 × 10<sup>-2</sup> M, (4) 5.0 × 10<sup>-3</sup> M, (5) 1.0 × 10<sup>-3</sup> M, (6) 5.0 × 10<sup>-4</sup> M, (7) 1.0 × 10<sup>-4</sup> M, (8) 5.0 × 10<sup>-5</sup> M, (9) 1.0 × 10<sup>-5</sup> M, (10) 5.0 × 10<sup>-6</sup> M, (11) 1.0 × 10<sup>-6</sup> M, and (12) 5.0 × 10<sup>-7</sup> M.

slope compare to sensors referred as [32,43]; also it has a very short response time in comparison to some of them (except for [35,41]).

### 3.6. Selectivity

The most important characteristics of membrane sensors are the selectivity behavior confirming whether a reliable mea-

Table 4  
Comparison of some characteristics of the proposed electrode with previous Cd<sup>2+</sup> ISEs

Interfering ion with K <sub>pot</sub> ≥ 1.0 × 10 <sup>-2</sup>	DL (mol L <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )	Working pH range	Slope (mV decade <sup>-1</sup> )	Response time (s)	Ref.
Na <sup>+</sup> , K <sup>+</sup> , Pb <sup>2+</sup> , Fe <sup>3+</sup> , Tl <sup>+</sup> , Ag <sup>+</sup> , Zn <sup>2+</sup> , Cu <sup>2+</sup>	8 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	4.0–9.0	-29.9	<8	Proposed electrode
None	1.0 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-1</sup>	1.0–7.0	-28.0	NM	[16]
None	9.0 × 10 <sup>-6</sup>	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	4.0–7.0	-27.8	<15	[32]
Most of the cations	NM	3.9 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	3.2–7.5	-30.0	<25	[33]
Most of the cations	NM	3.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	2.0–5.4	-30.0	<23	[34]
Co <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup> , Fe <sup>2+</sup> , Cu <sup>2+</sup>	5.9 × 10 <sup>-6</sup>	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	4.3–8.5	-28.5	<5	[35]
Most of the cations	NM	2.1 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	1.9–7.0	-29.0	<17	[36]
NM	9.9 × 10 <sup>-6</sup>	1.0 × 10 <sup>-5</sup> to 1.0 × 10 <sup>-1</sup>	5.0–7.7	-29.0	<10	[37]
NM	NM	1.0 × 10 <sup>-6</sup> to 1.0 × 10 <sup>-2</sup>	3.0–7.0	-29.8	<60	[38]
NH <sub>4</sub> <sup>+</sup>	5.0 × 10 <sup>-8</sup>	7.9 × 10 <sup>-8</sup> to 1.0 × 10 <sup>-1</sup>	2.0–8.0	-30.0	10	[39]
Pb <sup>2+</sup> , Cu <sup>2+</sup> , Ag <sup>+</sup> , Tl <sup>+</sup>	1.0 × 10 <sup>-7</sup>	4.0 × 10 <sup>-7</sup> to 1.0 × 10 <sup>-1</sup>	2.5–8.5	-29.0	<10	[40]
Pb <sup>2+</sup> , Cu <sup>2+</sup> , Ag <sup>+</sup> , Hg <sup>2+</sup> , Fe <sup>3+</sup>	6 × 10 <sup>-7</sup>	1.5 × 10 <sup>-6</sup> to 1 × 10 <sup>-1</sup>	2.0–8.0	-29.0	3	[41]
Hg <sup>2+</sup>	8 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> to 1 × 10 <sup>-1</sup>	2.0–8.0	-25.1	7	[41]
Cu <sup>2+</sup> , Et <sub>4</sub> N <sup>+</sup>	10 <sup>-10</sup> , 10 <sup>-8</sup>	10 <sup>-5</sup> to 10 <sup>-9</sup>	5.7–6.8	-32.0	NM	[42]
Pb <sup>2+</sup> , Cu <sup>2+</sup> , Ag <sup>+</sup> , Mg <sup>2+</sup> , Ni <sup>2+</sup>	5.0 × 10 <sup>-6</sup>	4.4 × 10 <sup>-4</sup> to 1.0 × 10 <sup>-1</sup>	2.5–6.5	-29.0	12	[43]
NM	NM	2.0 × 10 <sup>-5</sup> to 5.0 × 10 <sup>-2</sup>	2.5–7.0	-29.0	<20	[44]
None	7.3 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup> to 1 × 10 <sup>-1</sup>	2.8–8.6	-29.4	<10	[45]
None	1.5 × 10 <sup>-10</sup>	5.0 × 10 <sup>-10</sup> to 1 × 10 <sup>-5</sup>	Just 7	NM	NM	[46]

NM, not mentioned.



Table 5  
Potentiometric selectivity coefficient values for various interfering ions at concentration of  $1.0 \times 10^{-2}$  M

$M^{n+}$	$K_{Cd,M}^{pot}$	$M^{n+}$	$K_{Cd,M}^{pot}$
$Fe^{3+}$	$6.92 \times 10^{-2}$	$Cr^{3+}$	$3.91 \times 10^{-4}$
$Ce^{4+}$	$3.16 \times 10^{-4}$	$Tl^{+}$	$8.3 \times 10^{-2}$
$Mg^{2+}$	$4.46 \times 10^{-3}$	$Ag^{+}$	$9.1 \times 10^{-2}$
$Ni^{2+}$	$3.16 \times 10^{-3}$	$Zn^{2+}$	$1.58 \times 10^{-2}$
$Co^{2+}$	$2.69 \times 10^{-3}$	$Cu^{2+}$	$2.11 \times 10^{-1}$
$Mn^{2+}$	$1.65 \times 10^{-3}$	$Zr^{4+}$	$4.7 \times 10^{-3}$
$Pb^{2+}$	$2.34 \times 10^{-2}$	$Al^{3+}$	$7.08 \times 10^{-4}$

surement in the target sample is possible. In order to assess the selectivity of the proposed cadmium ion-selective electrode over other cations ( $M^{n+}$ ), the method of fixed interference was employed [47]. According to this method, the potentiometric selectivity coefficients,  $K_{Cd,M}^{pot}$ , can be evaluated from the potential measurements of solutions containing a fixed concentration of interfering ion,  $M^{n+}$  ( $aM^{n+}$ , 0.01 M) and titration with  $Cd^{2+}$  solution. The potential values obtained were then plotted against the activity of the cadmium ion. The intersection of the extrapolated linear portions of this curve will indicate the activity of  $Cd^{2+}$  ( $a_{Cd}$ ), which is to be used to calculate  $K_{Cd,M}^{pot}$  values from the equation:

$$K_{Cd,M}^{pot} = \frac{a_{Cd}(DL)}{a_M^{2/n}}$$

The resulting  $K_{Cd,M}^{pot}$  values are summarized in Table 5. For most of the polyvalent cations used, the selectivity coefficients show low values, indicating negligible interference in the performance of the membrane electrode assembly. On the other hand, in the case of univalent cations used, the selectivity coefficients seem to be somehow large. It is noteworthy that such deceptively larger  $K_{Cd,M}^{pot}$  values arise from the term  $a^{2/n}$  in Eq. (2); the smaller the charge of interfering ion,  $n$ , the larger the selectivity coefficient,  $K_{Cd,M}^{pot}$ .

#### 4. Applications of method

The new cadmium-selective electrode was applied to obtain recoveries of cadmium in tap water, river water, an electroplating factory and mobarekeh steel complex waste water samples by proposed electrode with satisfactory results. The analysis was performed by using the standard addition technique. The results are summarized in Table 6. Good recoveries were obtained in all samples. The electrode was also successfully applied to the direct determination of cadmium in waste water samples from a near Isfahan Electroplating Factory. The cadmium content obtained from three replicate measurements in two different samples was  $2.8 \pm 0.1$  and  $4.3 \pm 0.1 \mu\text{g mL}^{-1}$  which was found to be in agreement with that obtained by atomic absorption spectrometry ( $2.9$  and  $4.5 \mu\text{g mL}^{-1}$ , respectively) which the results are represented in Table 7.

Table 6  
Determination of Cd(II) recovery by the proposed electrode in the real samples

Sample	Added cadmium ( $\mu\text{g mL}^{-1}$ )	Found cadmium ( $\mu\text{g mL}^{-1}$ )	Recovery (%)
Tap water	2.19	$2.17 \pm 0.01$	99.0
	3.51	$3.48 \pm 0.02$	99.1
	5.60	$5.57 \pm 0.04$	99.5
River water	2.65	$2.62 \pm 0.02$	98.9
	3.65	$3.59 \pm 0.03$	98.9
	5.64	$5.56 \pm 0.04$	98.6
Waste water	2.26	$2.21 \pm 0.03$	97.7
	4.49	$4.56 \pm 0.05$	101.5
	5.68	$5.56 \pm 0.06$	97.8

Table 7  
Determination of Cd(II) by the proposed electrode in the real samples

Sample	Added cadmium ( $\mu\text{g mL}^{-1}$ )	Found cadmium by proposed method ( $\mu\text{g mL}^{-1}$ )	Found cadmium by AAS method ( $\mu\text{g mL}^{-1}$ )
Electroplating waste water (1)	0.0	$2.8 \pm 0.1$	2.9
	11.2	$13.7 \pm 0.4$	14.2
	22.5	$24.7 \pm 0.5$	25.1
Electroplating waste water (2)	0.0	$4.3 \pm 0.1$	4.5
	11.2	$15.1 \pm 0.3$	15.3
	22.5	$26.4 \pm 0.3$	26.6
	33.7	$37.7 \pm 0.4$	38.3

#### 5. Conclusions

The proposed ionophore demonstrates good results as a neutral carrier in developing a new cadmium-selective electrode. The electrode shows better selectivity and response time than most of the previous cadmium determining techniques. A major advantage of the present electrode concerns its direct measurement of cadmium in real samples without prior separation steps, thus considerably simplifying the determination procedure compared with other analytical methods.

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#### References

- [1] G.J. Moody, B.B. Saad, J.D.R. Thomas, The development of polymer matrix membranes for ion-selective electrodes, *Sel. Electrode Rev.* 10 (1988) 71.
- [2] D. Ammann, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch, W. Simon, *Ion-Sel. Electrode Rev.* 5 (1983) 3.
- [3] M.A. Arnold, M.E. Meyerhoff, Recent advances in the development and analytical applications of biosensing probes, *Crit. Rev. Anal. Chem.* 20 (1988) 149–196.
- [4] <http://www.epa.gov/safewater/dwh;t-ioc;cadmium.html>.

- [5] Y. Li, Y. Jiang, X.P. Yan, W.J. Peng, Y.Y. Wu, A flow injection on-line multiplexed sorption preconcentration procedure coupled with flame atomic absorption spectrometry for determination of trace lead in water, tea, and herb medicines, *Anal. Chem.* 74 (2002) 1075–1080.
- [6] Q. Ye, Y. Li, Y. Jiang, X. Yan, Determination of trace cadmium in rice by flow injection on-line filterless precipitation-dissolution preconcentration coupled with flame atomic absorption spectrometry, *J. Agric. Food Chem.* 51 (2003) 2111–2114.
- [7] M. Yaman, *Anal. Biochem.* 339 (2005) 1–8.
- [8] Z.R. Xu, H.Y. Pan, S.K. Xu, Z.L. Fang, A sequential injection on-line column preconcentration system for determination of cadmium by electrothermal atomic absorption spectrometry, *Spectrochim. Acta B* 55 (2000) 213–219.
- [9] D.L. Tsalev, L. Lampugnani, R. Georgieva, K.K. Chakarova, I.I. Petrov, Electrothermal atomic absorption spectrometric determination of cadmium and lead with stabilized phosphate deposited on permanently modified platforms, *Talanta* 58 (2002) 331–340.
- [10] S.P. Dolan, D.A. Nortrup, P.M. Bolger, S.G. Caper, Analysis of dietary supplements for arsenic, cadmium, mercury, and lead using inductively coupled plasma mass spectrometry, *J. Agric. Food Chem.* 51 (2003) 1307–1312.
- [11] L.F. Dias, G.R. Miranda, T.D. Saint-Pierre, S.M. Maia, V.L.A. Frescura, A.J. Curtius, Method development for the determination of cadmium, copper, lead, selenium and thallium in sediments by slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry and isotopic dilution calibration, *Spectrochim. Acta B* 60 (2005) 117–124.
- [12] Y.K. Lu, H.W. Sun, C.G. Yuan, X.P. Yan, Simultaneous determination of trace cadmium and arsenic in biological samples by hydride generation-double channel atomic fluorescence spectrometry, *Anal. Chem.* 74 (2002) 1525–1529.
- [13] K. Wu, S. Hu, J. Fei, W. Bai, Mercury-free simultaneous determination of cadmium and lead at a glassy carbon electrode modified with multi-wall carbon nanotubes, *Anal. Chim. Acta* 489 (2003) 215–221.
- [14] G. Marino, M.F. Bergamini, M.F.S. Teixeira, E.T.G. Cavalheiro, Evaluation of a carbon paste electrode modified with organofunctionalized amorphous silica in the cadmium determination in a differential pulse anodic stripping voltammetric procedure, *Talanta* 59 (2003) 1021–1028.
- [15] H. Zheng, Z. Yan, H. Dong, B. Ye, Simultaneous determination of lead and cadmium at a glassy carbon electrode modified with Langmuir–Blodgett film of p-tert-butylthiacalix[4]arene, *Sens. Actuators B* 120 (2007) 603–609.
- [16] Y.G. Vlasov, New solid-state ion-selective electrodes Sensors for chemical analysis of solutions Fresenius Z, *Anal. Chem.* 335 (1989) 92–99.
- [17] M. Careri, A. Casnati, A. Guarinoni, A. Mangia, G. Mori, A. Pochini, R. Ungaro, Study of the behavior of calix[4]arene-based sodium-selective electrodes by means of ANOVA, *Anal. Chem.* 65 (1993) 3156–3160.
- [18] W.H. Chan, A.W.M. Lee, K.W. Lee, K.W. Wang, Design and characterization of sodium-selective optode membranes based on the lipophilic tetraester of calix[4]arene, *Analyst* 120 (1995) 1963–1967.
- [19] A. Cadogan, D. Diamond, S. Cremin, M.A. Mckervey, S.J. Harris, *Anal. Proc.* 28 (1991) 13–14.
- [20] V.K. Gupta, S. Chandra, H. Lang, A highly selective mercury electrode based on a diamine donor ligand, *Talanta* 66 (2005) 575–580.
- [21] H. Oh, E.M. Choi, H. Jeong, K.C. Nam, S. Jeon, Poly(vinyl chloride) membrane cesium ion-selective electrodes based on lipophilic calix[6]arene tetraester derivatives, *Talanta* 53 (2000) 535–542.
- [22] S. Megdadi, M. Amirnasr, V. Langer, A. Zamanpour, Synthesis and characterization of  $[M^{II}(\text{bqb})]$  ( $M = \text{Co}, \text{Ni}, \text{Cu}$ ),  $[N(n\text{-Bu})_4][\text{Co}^{III}(\text{bqb})(\text{CN})_2]$ , and  $[N(n\text{-Bu})_4][\text{Co}^{III}(\text{bqb})(\text{N}_3)_2]$  containing deprotonated  $N,N'$ -bis(2-quinolinecarboxamide)-1,2-benzene (bqb) – X-ray crystal structures of  $[\text{Ni}^{II}(\text{bqb})]$  and  $[N(n\text{-Bu})_4][\text{Co}^{III}(\text{bqb})(\text{N}_3)_2]$ , *Can. J. Chem.* 84 (2006) 971–978.
- [23] E. Bakker, Determination of unbiased selectivity coefficients of neutral carrier-based cation-selective electrodes, *Anal. Chem.* 69 (1997) 1061–1069.
- [24] T. Sokalaski, A. Ceresa, M. Fibboli, T. Zwiell, E. Bakker, E. Pretsch, Lowering the detection limit of solvent polymeric ion-selective membrane electrodes. 2. Influence of composition of sample and internal electrolyte solution, *Anal. Chem.* 71 (1999) 1210–1214.
- [25] M.A. Ali, A.H. Mirza, W.B. Ejau, P.V. Bernhardt, Preparation and characterization of pentagonal-bipyramidal zinc(II) and cadmium(II) complexes of a neutral  $\text{N}_3\text{S}_2$  thiosemicarbazone derived from 2-N-methylthiosemicarbazide and the X-ray crystal and molecular structures of the free ligand and its cadmium(II) complex,  $\text{Cd}(\text{dap-}^2\text{NMtsc})(\text{NO}_3)_2$ , *Polyhedron* 25 (2006) 3337–3342.
- [26] S.H. Rahaman, R. Ghosh, T.H. Lu, B.K. Ghosh, Chelating  $N,N'$ -(bis(pyridin-2-yl)alkylidene)propane-1,3-diamine pseudohalide copper(II) and cadmium(II) coordination compounds: Synthesis, structure and luminescence properties of  $[\text{M}(\text{bpap})(\text{X})]\text{ClO}_4$  and  $[\text{M}(\text{bpap})(\text{X})_2]$  [ $M = \text{Cu}, \text{Cd}; \text{X} = \text{N}_3^-, \text{NCS}^-$ ], *Polyhedron* 24 (2006) 1525–1532.
- [27] M. Arvand-Barmchi, M.F. Mousavi, M.A. Zanjanchi, M. Shamsipur, A PTEV-based zeolite membrane potentiometric sensor for cesium ion, *Sens. Actuators B* 96 (2003) 560–564.
- [28] K.C. Gupta, M.J. D'Arc, Performance evaluation of copper ion selective electrode based on cyanocopolymers, *Sens. Actuators B* 62 (2000) 171–176.
- [29] K.C. Gupta, M.J. D'Arc, Effect of concentration of ion exchanger, plasticizer and molecular weight of cyanocopolymers on selectivity and sensitivity of Cu(II) ion selective electrodes, *Anal. Chim. Acta* 437 (2001) 199–215.
- [30] A. Ceresa, T. Sokalski, E. Pretsch, Influence of key parameters on the lower detection limit and response function of solvent polymeric membrane ion-selective electrodes, *J. Electroanal. Chem.* 501 (2001) 70–76.
- [31] E. Bakker, R.K. Mervura, E. Pretsch, M.E. Meyerhoff, Selectivity of polymer membrane-based ion-selective electrodes: self-consistent model describing the potentiometric response in mixed ion solutions of different charge, *Anal. Chem.* 66 (1994) 3021–3030.
- [32] M. Javanbakht, A. Shabani-Kia, M.R. Darvich, M.R. Ganjali, M. Shamsipur, Cadmium(II)-selective membrane electrode based on a synthesized tetrol compound, *Anal. Chim. Acta* 408 (2000) 75–81.
- [33] V.K. Gupta, P. Kumar, Cadmium(II)-selective sensors based on dibenzo-24-crown-8 in PVC matrix, *Anal. Chim. Acta* 389 (1999) 205–212.
- [34] V.K. Gupta, A.K. Jain, P. Kumar, PVC-based membranes of dicyclohexano-24-crown-8 as Cd(II) selective sensor, *Electrochim. Acta* 52 (2006) 736–741.
- [35] C. Wardak, B. Marczewska, J. Lenik, An ion-selective electrode with a polymeric membrane containing an active chelating substance, *Desalination* 163 (2004) 69–75.
- [36] V.K. Gupta, S. Chandra, R. Mangla, Dicyclohexano-18-crown-6 as active material in PVC matrix membrane for the fabrication of cadmium selective potentiometric sensor, *Electrochim. Acta* 47 (2002) 1579–1586.
- [37] V.K. Gupta, P. Kumar, R. Mangla, PVC based Monoaza-18-crown-6 membrane potentiometric sensors for cadmium, *Electroanalysis* 12 (2000) 752–756.
- [38] R.D. Tsingarelli, I.P. Nikolenko, A.F. Radchenko, S.P. Chukov, *Zh. Anal. Khim.* 41 (1986) 449.
- [39] V.K. Gupta, A.K. Singh, B. Gupta, Schiff bases as cadmium(II) selective ionophore in polymeric membrane electrodes, *Anal. Chim. Acta* 583 (2007) 340–348.
- [40] M. Shamsipur, M.H. Mashhadizadeh, Cadmium ion-selective electrode based on Tetrathia-12-crown-4, *Talanta* 53 (2001) 1065–1071.
- [41] M.N. Abbas, E. Zahran, Novel solid-state cadmium ion-selective electrodes based on its tetraiodo- and tetrabromo-ion pairs with cetylpyridinium, *J. Electroanal. Chem.* 576 (2005) 205–213.
- [42] S. Plaza, Z. Szigeti, M. Geisler, E. Martinoia, Aeschlimann B potentiometric sensor for determination of Cd(2+) transport in yeast and plants, *Beit Aeschlimann*. 347 (2005) 6–10.
- [43] K.C. Gupta, M.J. D'Arc, Effect of concentration of ion exchanger, plasticizer and molecular weight of cyanocopolymers on selectivity and sensitivity of Cd(II) ion selective electrode, *Talanta* 52 (2000) 1087–1103.

- [44] S.K. Sindhu, D.S. Siddhu, A. Himanshu, C. Sulekh, Cadmium(II) ion selective electrode based on pyridine-3-carboxyaldehyde thiosemicarbazone, *J. Indian Chem. Soc.* 82 (2005) 472–474.
- [45] H.A. Zamani, M.R. Ganjali, M. Adib, Cd(II) PVC-based membrane sensor based on *N'*-[1-(2-furyl) methylidene]-2-furohydrazide, *Sens. Lett.* 4 (2006) 345–350 (6).
- [46] A.C. Ion, E. Bakker, E. Pretsch, Potentiometric Cd<sup>2+</sup>-selective electrode with a detection limit in the low ppt range, *Anal. Chim. Acta* 440 (2001) 71–79.
- [47] Y. Umezawa, K. Umezawa, H. Sato, Electrochemical science and technology information resource (ESTIR), *Pure Appl. Chem.* 67 (1995) 5.