

Scientific paper

Flow Injection Potentiometric Determination of Cd²⁺ Ions Using a Coated Graphite Plasticized PVC-Membrane Electrode Based on 1,3-Bis(2-cyanobenzene)triazene

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Abstract

1,3-Bis(2-cyanobenzene)triazene, **L**, was used as a suitable ionophore for the fabrication of a new PVC-based polymeric membrane coated graphite electrode for selective sensing of Cd²⁺ ion. The electrode exhibited a selective linear Nernstian response to Cd²⁺ ion at an optimal pH range of 6–9 with a limit of detection of 8.0×10^{-6} M and a fast response time of about 2 s. The electrode was used as a proper detection system in flow-injection potentiometry of cadmium ion and resulted in well defined peaks for cadmium ions with stable baseline, excellent reproducibility and high sampling rates of over 100 injections per hour. It showed good stability, reproducibility and fast response time. The practical utility of the proposed system has also been reported.

Keywords: Flow injection potentiometry; coated graphite electrode; 1,3-bis(2-cyanobenzene)triazene; cadmium ion determination

1. Introduction

The advantages of flow injection potentiometry (FIP) by ion-selective electrodes, including low cost, simple instrumentation, rapid response, wide linear response, high selectivity and high sampling rate, have been well established during the past two decades.^{1–8} In addition, the transient nature of the signals in FIA may help to overcome the effects of interfering ions if the electrode's response to these ions is slower than that to the target analyte,² and the lifetime of electrodes may be extended as the surface is predominantly exposed to carrier solution. However, fabrication/packaging and selectivity are still remaining as two of the key aspects in the design of potentiometric sensors.³

While there is no report definitely indicating Cd²⁺ ion as an essential trace element in biological processes, it

is well known that this element is highly toxic to a wide variety of living organisms, including man.⁹ Thus, in recent years, a number of ion-selective electrodes for cadmium assay have been reported in the literature,^{10–19} while none of which is used in flow injection potentiometric determination of cadmium ion. Thus, in this work, we used 1,3-bis(2-cyanobenzene)triazene (**L**, Fig. 1) as a suitable lipophilic neutral ionophore for the preparation of PVC-membrane coated graphite (CGE) electrode for selective determination of cadmium ion in solution under batch and flow injection modes.

Although a number of recent articles describing the application of 1,3-bis(2-cyanobenzene)triazene as sorbent for Hg²⁺²⁰ and Ag⁺²¹ ions is reported in the literature, to the best of our knowledge, this ligand has not been tested as an ionophore in preparation of PVC-membrane Cd²⁺ sensor.

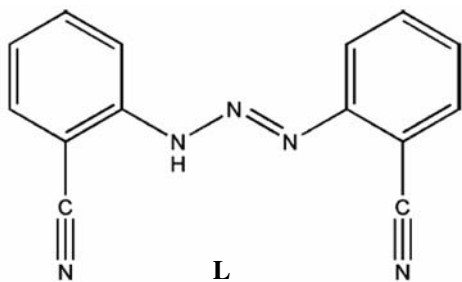


Figure 1. Structure of 1,3-bis(2-cyanobenzene)triazene (L).

2. Experimental

2.1. Reagents

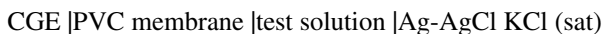
High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(4-chlorophenyl)borate (KTPClPB), sodium tetraphenylborate (NaTPB) *o*-nitrophenyl octyl ether (NPOE), dioctyl phthalate (DOP), benzyl acetate (BA), diethyl sebacate (DES), dibutyl phthalate (DBP), acetonitrile (AN) and tetrahydrofuran (THF) were obtained from Fluka chemical company. The nitrate or chloride salts of all cations used (from Merck or Aldrich) were of the highest purity available and used as received. Doubly distilled water was used throughout. The standard stock aqueous solutions of Cd^{2+} and other cations were prepared in slightly acidified doubly distilled water for the sake of preservation and avoiding their adsorption on the container walls prior to analysis.

The ligand 1,3-bis(2-cyanobenzene)triazene (L) was prepared by the following method. A 1 liter flask was charged with 100 g of ice and 150 mL of doubly distilled water and then cooled to 0 °C in an ice-bath. To this was added 11.80 g (0.10 mol) of *o*-cyanoaniline and 13 g (0.13 mol) of hydrochloric acid ($d = 1.18 \text{ g mL}^{-1}$). To this solution was added a solution containing 4.10 g (0.06 mol) NaNO_2 in 25 mL of water during a 15-min period. After mixing for 15 min, a solution containing 14.76 g (0.18 mol) of sodium acetate in 45 mL of water was added and mixed for 45 min. Then, the resulting yellow precipitate was filtered and dissolved in Et_2O . After evaporation of Et_2O , a purified sharp yellow powder of L was obtained (yield, 62%, 7.66 g, M.P. 128–130 °C). IR and ^1H NMR spectra confirmed the CBT structure, as: IR (KBr): 3222, 3104, 3029, 2233, 1800–1600, 1604, 1588–1486, 1300–1000, 1064, 900–600, 759 cm^{-1} ; ^1H NMR (dimethylsulfoxide, DMSO): 7.2–7.8 (phenyl protons); 13.4 (NH proton); 3.3–2.4 (solvent).

2.2. Apparatus

All UV-Visible Spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10-mm quartz cells.

All electromotive force (emf) measurements were carried out with the following cell assembly:



A Metrohm analyzer was used for potential measurements at 25.1 ± 0.1 °C. The emf observations were made relative to a silver-silver chloride (Metrohm). Activity coefficients were calculated according to the Debye-Huckel procedure.^{7,8}

A schematic representation of manifold of the flow injection potentiometric analysis system employed is shown in Fig. 2. A home-made polyacrylamide 70- μL flow cell was used. The cell contained a coated graphite cadmium ion selective electrode (ISE) with effective surface area of 4.90 mm^2 and a commercial Ag/AgCl reference electrode (Metrohm) with a double junction having a terminal tube diameter of 2.5 mm. A 12-channel peristaltic pump (Desaga) was used to continuously draw solution through the cell. A low-pressure rotary injection valve (model 5020 Rheodyne four way rotary valve, USA) was used in the flow system.

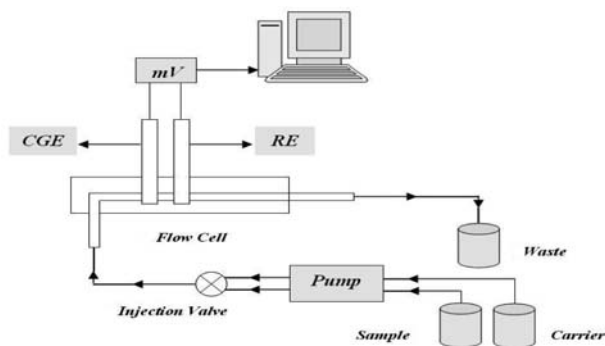


Figure 2. Manifold of the FIP system.

2.3. Electrode Preparation

The PVC membrane solution was prepared by thoroughly mixing of 32 mg of powdered PVC, 58 mg of plasticizer BA and 5 mg of additive KTPClPB in 2 mL of THF. To this mixture was added 5 mg of ionophore L and the solution was mixed well. The solvent was evaporated slowly until an oily concentrated mixture was obtained. To prepare the coated graphite electrode, spectroscopic grade graphite rods of 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end of the graphite rod, and the electrode was sealed into the end of a PVC tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air. The polished graphite electrode was then dipped into the PVC membrane solu-

tion mentioned above for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The electrode was then pulled out from the mixture and was allowed to stabilize for 12 h. The electrode was finally conditioned by soaking in a 1.0×10^{-3} M solution of cadmium nitrate for 24 h.

3. Results and Discussion

3.1. Preliminary Studies

In preliminary experiments, the complexation of **L** with some potential transition metal ions including Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} and Cd^{2+} ions was investigated spectrophotometrically in AN solution, in order to obtain a clue about the stoichiometry, stability and selectivity of the resulting complexes. The electronic absorption spectra of a 5.8×10^{-5} M solution of the ligand **L** in the presence of increasing concentration of Cd^{2+} ion in AN solution at 25.0 ± 0.1 °C are shown in Fig. 3A. As seen, the strong absorption of ligand at 360 nm decreases with increasing concentration of the metal ion in the expense of developing of a new broad band at 420 nm.

The resulting absorbances of the ligand (at 360 nm) and its cadmium complex (at 420 nm) against the $[\text{Cd}^{2+}]/[\text{L}]$ mole ratio plots shown in Fig. 3B revealed a distinct inflection point a metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution. The stoichiometry of the resulting complex was further determined by the continuous variation method,²² and also found to be 1:1.

For evaluation of the conditional formation constants, the mole ratio data obtained at the two wavelengths (Fig. 3B) were fitted to a previously reported equation using a non-linear least-squares curve fitting program KINFIT.²³ The conditional formation constants of the complex was evaluated as $\log K_f = 8.62 \pm 0.02$ at 340 nm and $\log K_f = 8.57 \pm 0.03$ at 420 nm, which are actually the same within the corresponding experimental errors. It was found that the stability of **L** complexes with other tested metal ions including Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+} is much less than that with Cd^{2+} ion (i.e., about 2 to 3 orders of magnitude).

In order to obtain more information about the conformational change of **L** upon complexation with Cd^{2+} ion, the molecular structures of the uncomplexed ligand and its 1:1 Cd^{2+} complex were built with the Hyperchem program version 7.²⁴ The structure of free ligand was optimized using the 6-31G* basis set at the restricted Hartree-Fock (RHF) level of theory. The optimized structure of the ligand was then used to find out the initial structure of its 1:1 cadmium complex. Finally, the structure of the resulting 1:1 complex was optimized using the Lan12mb basis set at the RHF level of theory. No molecular symmetry constraint was applied; rather, full optimization and frequency option of all bond lengths, bond angles and torsion

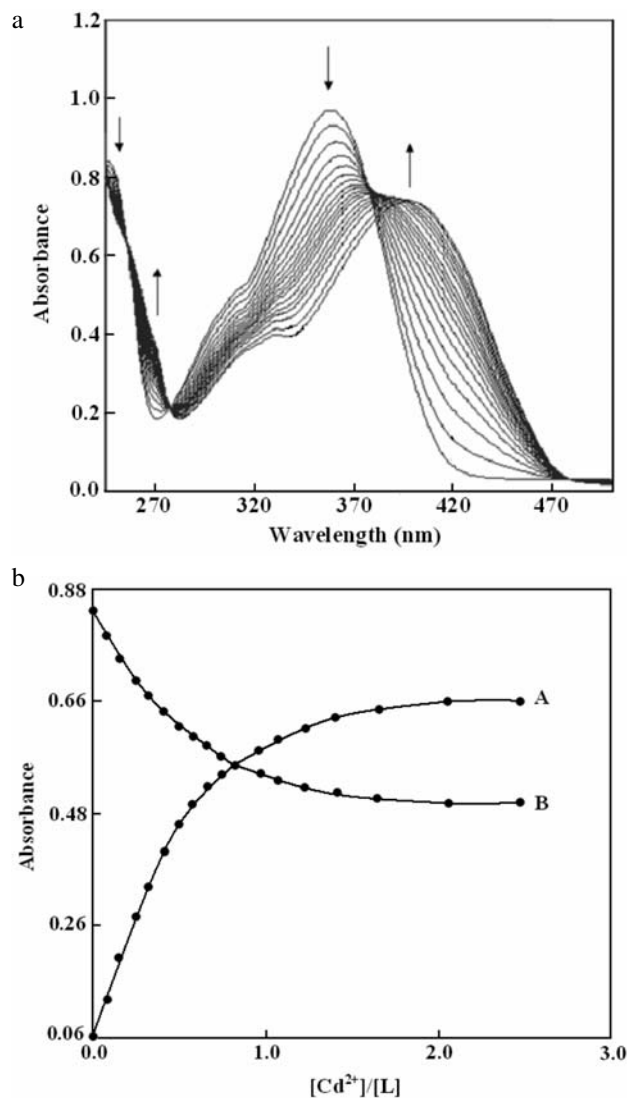


Figure 3. (a) UV-Vis spectra of 5.8×10^{-5} M of **L** in AN in the presence of increasing concentration of Cd^{2+} ion, (b) mole ratio plots for the titration of 5.8×10^{-5} M of **L** with a $\text{Cd}(\text{OAc})_2$ solution in AN at 420 nm (A) and 380 nm (B).

angles were carried out using the Gaussian 98 program.²⁵

The optimized structures of **L** and $(\text{CdL})^{2+}$ species are shown in Fig. 4. It should be noted that, only real frequency values were observed, indicating that the structural geometries shown in Fig. 5 are quite acceptable.²⁶ As it is obvious from Fig. 4A, the ligand forms a more or less planar structure which is quite symmetrical around the plane passing through the central triazine nitrogen atom. However, in the case of the cadmium complex (Fig. 4B), one of the two 2-cyanobenzene groups in the optimized complex structure is twisted by about 45° so that the two cyano nitrogens together with the two side nitrogen atoms of the triazine base have found the opportunity to participate in bond formation with the central cadmium ion to form a slightly distorted tetrahedral geometry, such as that re-

cently reported in the literature for some Cd^{2+} complexes.^{27,28}

Thus, based on the results obtained from selective complexation of cadmium ion with the ligand as well as its high lipophilic character, the ligand **L** was expected to act as a potential ionophore in the preparation of PVC-based ion-selective electrodes for Cd^{2+} ion.

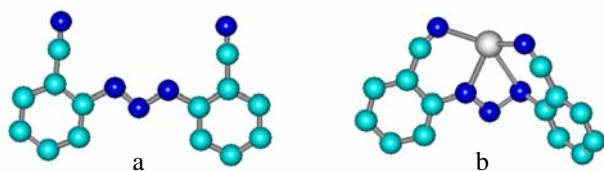


Figure 4. Optimized structures of **L** (a) and its 1:1 complex with cadmium (b).

In preliminary experiments, it was found that while the use of an ionophore free PVC-membrane revealed no measurable response with respect to Cd^{2+} ion, the addition of **L** resulted in a Nernstian response for the cation in the range of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ M (Fig. 5). Meanwhile, **L** was also used as a neutral carrier to prepare PVC membrane coated graphite electrodes for a variety of bivalent transition and heavy metal ions, and the resulting potential responses are also shown in Fig. 5. As seen, except for the Cd^{2+} ion sensor, in all other cases, the slope of the corresponding potential pM plots was much lower than the expected Nernstian slope of 29.5 mV per decade for these bivalent cations although over a limited linear range. The results clearly indicated that the Cd^{2+} ions are more easily

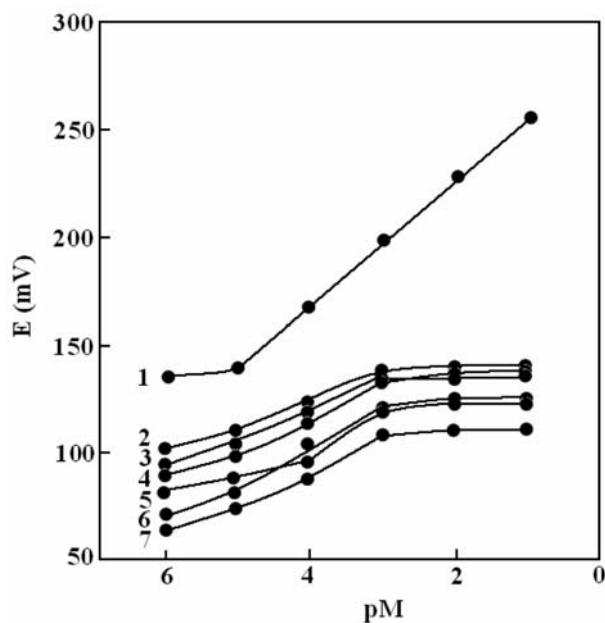


Figure 5. Potential responses of various ISEs based on **L**: (1) Cd^{2+} , (2) Zn^{2+} , (3) Pb^{2+} , (4) Ni^{2+} , (5) Ca^{2+} , (6) Co^{2+} , (7) Mg^{2+} .

attracted to the PVC-**L** membrane, resulting in a Nernstian potential-concentration response over a wide concentration range.

Thus, several parameters were studied in order to evaluate the performance of the resulting Cd^{2+} ion-selective coated graphite electrodes based on **L** in terms of PVC membrane composition, calibration slope, linear range, limit of detection, reproducibility, response time, selectivity and applications.

3. 2. Optimization of Potentiometric Response of the Coated Graphite Electrode

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition.^{7,8,10–19} Thus, different compositions of the PVC-membrane were examined in order to obtain the optimized membrane composition (Table 1). It is reported that the response characteristics of ISEs are largely affected by the nature and amount of plasticizer used, due to the influence of plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands.^{29,30} As it is seen from Table 1, among the six different plasticizers used, BA results in the best sensitivity.

Moreover, 5.0% of **L** was chosen as the optimum amount of ionophore in the PVC-membrane. Meanwhile, it is well known that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance and improving the response behavior and selectivity, but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode.^{29–32} Moreover, additives may catalyze the exchange kinetics at the sample-membrane interface.³³ From Table 1, it is seen that the addition of KTpCIPB will increase the sensitivity of the electrode response considerably. The use of 5% KTpCIPB resulted in a Nernstian behavior of the electrode (no. 10). As is obvious from Table 1, membrane number 10 with a PVC:BA:L: KTpCIPB percent ratio of 32.0:58.0:5.0:5.0 resulted in the Nernstian behavior of the membrane electrode over a wide concentration range. Thus, this membrane composition was used for the preparation the Cd^{2+} -selective electrodes for further studies. The electrode prepared under optimized membrane ingredients found to generate stable potentials when placed in contact with Cd^{2+} solutions.

The effect of pH of test solution in the range of 2 to 12 on the response of the electrode in a 1.0×10^{-3} M solution of Cd^{2+} was studied. The pH of solution was adjusted using a 0.1 M solution of either HCl or NaOH. The resulting emf-pH plot, shown in Fig. 6, revealed that there is no significant variation in the values of potential when the pH of solution varies from 6 to 9. For

Table 1. Optimization of membrane components

No.	Components (wt %)			Additive	Slope (mV decade ⁻¹)	Linear range (M)
	Plasticizer	PVC	L			
1	59.7 (BA)	35.7	4.6	–	25.0	1×10^{-5} – 1×10^{-2}
2	60.0 (NPOE)	32.0	5.0	3.0 (NaTPB)	10.0	1×10^{-5} – 1×10^{-3}
3	60.0 (DOP)	31.0	4.8	4.2 (NaTPB)	7.0	1×10^{-5} – 1×10^{-2}
4	60.5 (AP)	32.5	4.0	3.0 (NaTPB)	17.5	1×10^{-4} – 1×10^{-2}
5	56.5 (DBP)	32.5	5.0	6.0 (NaTPB)	21.4	1×10^{-5} – 1×10^{-2}
6	55.7 (DES)	32.8	5.3	6.2 (NaTPB)	17.0	1×10^{-4} – 1×10^{-2}
7	60.8 (BA)	29.5	4.0	5.7 (NaTPB)	23.5	1×10^{-5} – 1×10^{-3}
8	53.5 (NPOE)	26.8	3.2	16.0 (OA)	20.0	1×10^{-4} – 1×10^{-2}
9	55.1 (BA)	29.6	5.0	10.3 (OA)	11.5	1×10^{-5} – 1×10^{-3}
10	58.0 (BA)	32.0	5.0	5.0 (KTPCIPB)	29.1	1×10^{-5} – 1×10^{-1}
11	57.5 (BA)	31.5	5.0	6.0 (KTPCIPB)	38.0	1×10^{-5} – 1×10^{-1}

pH values lower than 6, there is a decrease in the electrode potential, indicating that the ionophore in the membrane can be protonated at lower pH values. The observed decrease in potential at pH > 9 could be due to the formation of some hydroxyl complexes of Cd²⁺ in solution.

The average time required for the membrane electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of Cd²⁺ ion solutions, each having a 10-fold difference in concentration, was investigated. The static response time of the membrane obtained was about 2 s for concentration

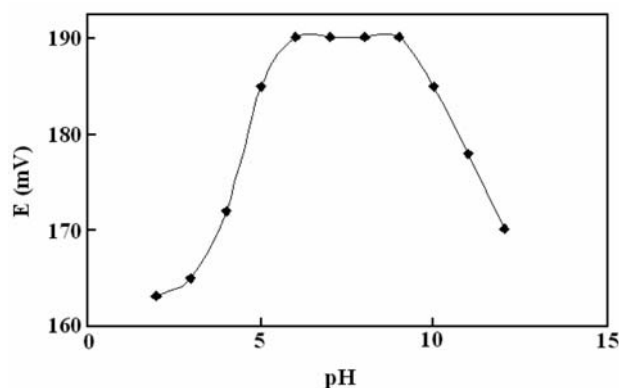


Figure 6. Effect of pH on the potential response of the electrode to a 1.0×10^{-3} M solution of Cd²⁺.

$\leq 1.0 \times 10^{-4}$ M, after which the equilibrium potentials essentially remained constant for more than 5 min. The electrodes prepared can be used under-stretch conditions for at least 3 months without any measurable divergence.

Under the optimized composition, the linear response to the activity of Cd²⁺ ion was investigated for the proposed electrode and the resulting plot is shown in Fig. 7. As is obvious from Fig. 7A, a Nernstian response (slope of 29.2 mV decade⁻¹) is obtained. The resulting limit of

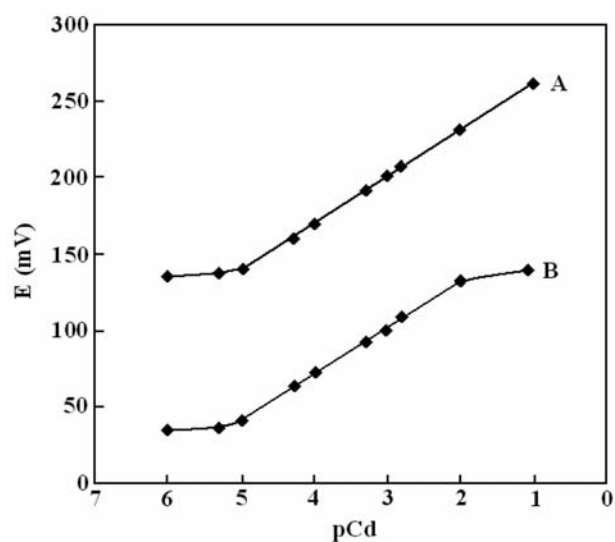


Figure 7. Calibration curves for the CGE (A) and FIP (B).

detection (LOD), obtained from the intersection of the two linear parts of the calibration plots, was found to be 8.0×10^{-6} M.

The selectivity behavior is well known as one of the most important characteristics of a selective electrode, determining whether a reliable measurement in the target sample is possible.^{29,34} Thus, the influence of several common cationic species on the potential response of the proposed Cd²⁺-selective electrode was tested by determining the potentiometric selectivity coefficient of the electrodes by using the separate solution method, SSM.^{29,34,35} The SSM involves the measurement of two separate solutions, one containing the ion of interest I at the activity a_I (but no J) and the other containing the interfering ion J at the same activity $a_J = a_I$ (but no I). Then, the selectivity coefficient can be derived from the following equation:

$$\log K_{IJ}^{pot} = \frac{z_I F \{E(J) - E(I)\}}{2.303 RT} + \log \left[\frac{a_I(I)}{a_J(J)^{z_I/z_J}} \right]$$

Table 2. Selectivity coefficients ($K_{I,J}^{Pot}$) of various interfering ions (M^{n+})

M^{n+}	$K_{I,J}^{Pot}$	M^{n+}	$K_{I,J}^{Pot}$
Tl ⁺	4.9×10^{-3}	Fe ²⁺	3.5×10^{-2}
Na ⁺	7.4×10^{-3}	Ni ²⁺	7.5×10^{-2}
K ⁺	4.0×10^{-2}	Cu ²⁺	4.9×10^{-2}
Li ⁺	1.5×10^{-2}	Sr ²⁺	1.3×10^{-2}
NH ₄ ⁺	4.6×10^{-2}	Zn ²⁺	4.9×10^{-2}
Cs ⁺	1.5×10^{-2}	Pb ²⁺	1.2×10^{-3}
Ca ²⁺	1.8×10^{-2}	Co ²⁺	4.0×10^{-2}
Mg ²⁺	1.1×10^{-1}	Hg ²⁺	1.6×10^{-1}

where a_i and a_j are the activities of I and J, z_i and z_j are charges of I and J, and E (I) and E (J) are the emf response of I and J ions, respectively. The resulting selectivity coefficient ($K_{I,J}^{Pot}$) values at 1.0×10^{-3} M of the primary and interfering ions are listed in Table 2. It is seen that, except for the cases of Mg²⁺ and Hg²⁺ ions, the selectivity coefficients are in the order of 10^{-2} and lower, indicating negligible interference in the performance of the membrane sensor assembly.

3. 3. Flow-Injection Potentiometry with the Proposed Coated Graphite Electrode

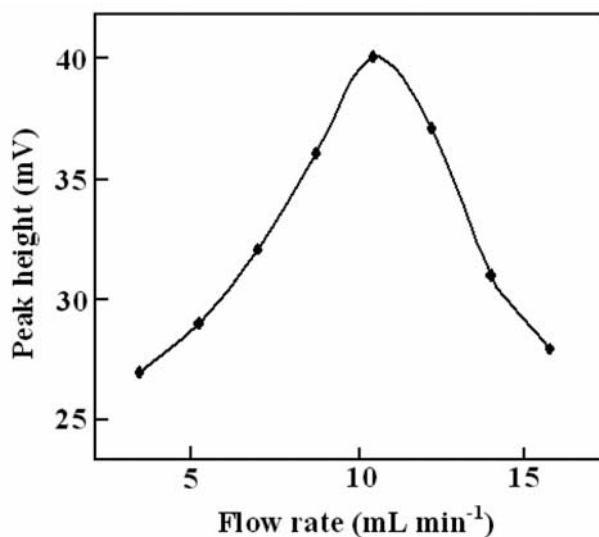
In the next step, the proposed Cd²⁺-selective electrode was used successfully as a suitable indicator electrode in the flow-injection system (Fig. 2) and the best FIP response of different flow injection parameters were investigated as follows.

The length of tubing from injection valve port to the flow cell was kept small, as practically possible, to achieve minimum dispersion and dilution. For the proposed electrode, a 5-cm length was selected for tubing.

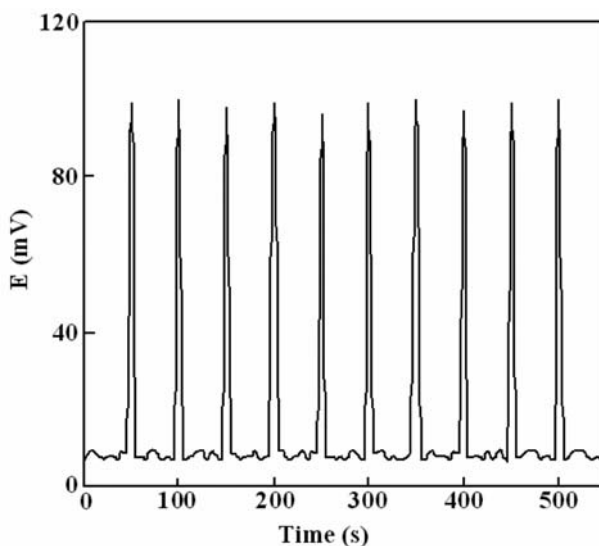
The dependency of the peak heights and width (and time to recover the base line) with flow rate was studied using the electrode response to 1.0×10^{-3} M solution of Cd²⁺ (Fig. 8). As seen, as the flow rate increased, the peaks become narrower and increased in height to a nearly plateau at a flow rate 10 mL min^{-1} . However, the peak width increased considerably at flow rates higher than 10 mL min^{-1} . Thus a flow rate of 10 mL min^{-1} was selected for further studies.

In general, peak heights increased with the increasing sample volume, although the effect was less marked at higher concentrations.^{7,8} For the proposed electrode, different sample volumes from 100 to 600 μL were studied, and the results revealed that the peak height reached nearly 100% of steady state at a sample volume of 500 μL . Thus, this sample volume was selected as an optimum value for further studies.

Generally, the composition of the carrier solution also affects the response behavior of ion selective electrode in term of the base line stability.⁴ In this work, we found that the use of doubly distilled water as carrier resulted in a nice stable base line when samples were injected in the concentration range of 1.0×10^{-5} – 1.0×10^{-2} M.

**Figure 8.** Effect of flow rate on the response of a 1.0×10^{-3} M solution.

Under the optimized experimental conditions, the repeatability of the proposed CGE in the flow injection system was examined by ten repetitive injection of a 1.0×10^{-2} M solution of Cd²⁺ ion and the results are shown in Fig 9. As seen, excellent response repeatability with a peak height relative standard deviation (%RSD) of <1.0% is obtained

**Figure 9.** Reproducibility of the flow injection signals for ten repetitive injections of a 1.0×10^{-3} M solution of Cd²⁺ ion.

In Fig. 10 are also shown the peaks from the proposed FIP system for varying concentrations of Cd²⁺ solutions in the range of 1.0×10^{-6} to 1.0×10^{-1} M concentrations, from low-to-high and high-to-low concentrations. A corresponding calibration graph is also included in Fig. 7B. As is obvious from Fig. 7B, the calibration curve is

quite linear over a wide concentration range of 1.0×10^{-5} M to 1.0×10^{-2} M with a slope of $28.3 \text{ mV decade}^{-1}$ and low LOD of 8.0×10^{-6} M. The proposed potentiometric FIA system revealed sampling rates higher than 100 injections per hour.

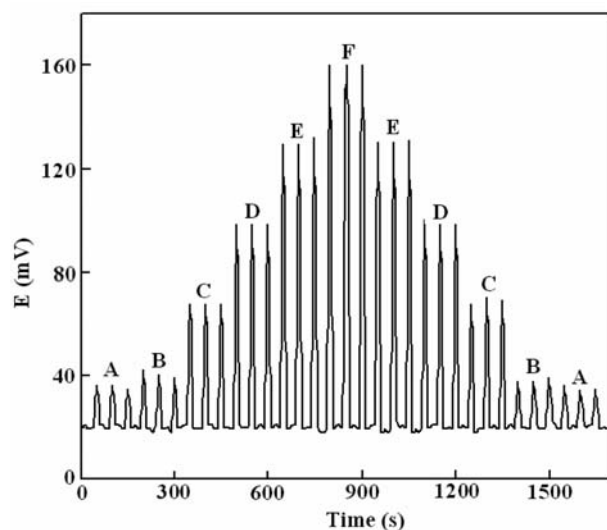


Figure 10. Triplicate potentiometric peaks for measurement of different Cd^{2+} ion concentrations: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M, (F) 1.0×10^{-1} M.

3. 4. Analytical Applications

The proposed PVC membrane coated graphite Cd^{2+} ion-selective sensor was found to work well under laboratory conditions. It was applied to the titration of Cd^{2+} ion

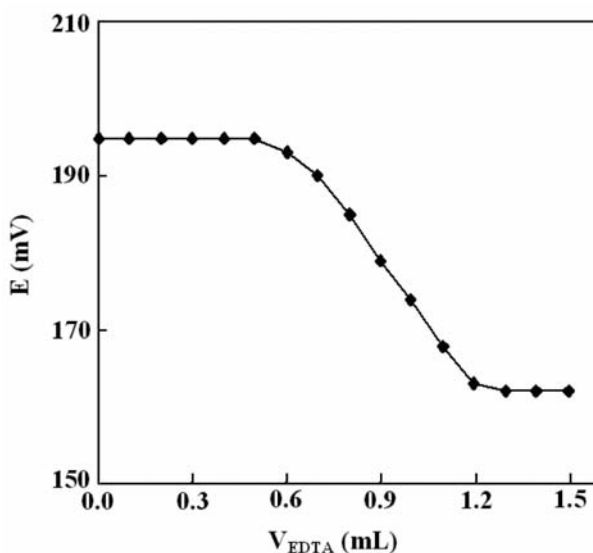


Figure 11. Potentiometric titration curve of 10.0 mL of 1.0×10^{-3} M $\text{Cd}(\text{II})$ solution with 0.011 M EDTA at pH 7, using the proposed sensor as an indicator electrode.

with an EDTA solution at pH 7, and the resulting titration curve is shown in Fig 11. As shown, the amount of Cd^{2+} ions solution can be accurately determined with the electrode.

The proposed FIP system was also successfully applied to the direct determination of varying amounts of cadmium ion spiked to tap water samples (at 1.0×10^{-4} M and 4.5×10^{-5} M levels), with very good recoveries. There were satisfactory agreements between the cadmium contents evaluated by the FIP system, at respective $(9.6 \pm 0.5) \times 10^{-5}$ M and $(4.8 \pm 0.4) \times 10^{-5}$ M levels, and the corresponding spiked values.

4. Acknowledgement

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5. References

1. E. Pungor (Ed.), Modern Trends in Analytical Chemistry. Part A. Electrochemical Detection in Flow Analysis, Akademiai Kiado, Budapest, Hungary, **1984**.
2. K. Cammann, *Fresenius J. Anal. Chem.* **1988**, 329, 691–697.
3. A. Izquierdo, M. D. Luque de Castro, *Electroanalysis* **1995**, 7, 505–519.
4. X. Yang, D. B. Hibbert, P. W. Alexander, *Anal. Chim. Acta* **1998**, 372, 387–398.
5. H. Karami, M. F. Mousavi, M. Shamsipur, *Talanta* **2003**, 60, 775–786.
6. H. Karami, M. F. Mousavi, M. Shamsipur, in Encyclopedia of Sensors, Volume X Edited by C. A. Grimes, E. C. Dickey, M.V. Pishko, American Scientific Publishers, New York, **2006**, pp 1–35.
7. M. Shamsipur, F. Mizani, M. F. Mousavi, N. Alizadeh, K. Alizadeh, H. Eshghi, H. Karami, *Anal. Chim. Acta* **2007**, 589, 22–32.
8. M. Shamsipur, F. Mizani, K. Alizadeh, M. F. Mousavi, V. Lippolis, A. Garau, C. Caltagirone, *Sens. Actuators B* **2008**, 130, 300–309.
9. B. G. Katzung, Basic and Clinical Pharmacology, 3rd edn., Appleton and Lange, Norwalk, CT, **1987**.
10. M. Javanbakht, A. Shabani-Kia, M. R. Darvich, M. R. Ganjali, M. Shamsipur, *Anal. Chim. Acta* **2000**, 408, 75–81.
11. V. K. Gupta, R. Mangla, P. Kumar, *Electroanalysis* **2000** 12, 752–756.
12. M. Shamsipur, M. H. Mashhadizadeh, *Talanta* **2001**, 53, 1065–1071.
13. V. K. Gupta, S. Chandra, S. R. Mangla, *Electrochim. Acta* **2002**, 47, 1579–1586.
14. S. Plaza Z. Szigeti, M. Geisler, E. Martinoia, B. Aeschlimann, D. Gunther, E. Pretsch, *Anal. Biochem.* **2005**, 347, 10–16.

15. V. K. Gupta, A. K. Singh, B. Gupta, *Anal. Chim. Acta* **2007**, *583*, 340–347.
16. V. K. Gupta, A. K. Jain, R. Ludwig, G. Maheshwari, *Electrochimica Acta*, **2008**, *53*, 2362–2368.
17. M. H. Mashhadizadeh, K. Eskandari, A. Foroumadi, A. Shafiee, *Electroanalysis* **2008**, *20*, 1891–1896.
18. B. Rezaei, S. Meghdadi, R. F. Zarandi, *Hazard. Mat.* **2008**, *153*, 179–186.
19. V. K. Gupta, M. Al Khayat, A. K. Singh, M. K. Pal, *Anal. Chim. Acta* **2009**, *634*, 36–43.
20. T. Hashempur, M. K. Rofouei, A. Rajabi Khorrami, *Microchem. J.* **2008**, *89*, 131–136.
21. M. K. Rofouei, M. Payehghadr, M. Shamsipur, A. Ahmadalinezhad, *J. Hazard. Mat.* **2009**, *168*, 1184–1187.
22. W. Likussar, D. F. Boltz, *Anal. Chem.* **1971**, *43*, 1265–1272.
23. N. Alizadeh, S. Ershad, H. Naeimi, H. Sharghi, M. Shamsipur, *Polish J. Chem.* **1999**, *73*, 915–926.
24. Hyperchem, Release 7.0. Hypercube, Inc., Gainesville, 2002.
25. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, K. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1998**.
26. S. K. Sahoo, M. Baral, B. K. Kanungo, *Polyhedron* **2006**, *25*, 722–736.
27. Q. Gao, C. Y. Zhang, Y. Cui, Y. B. Xie, *Acta Crystallogr.* **2009**, *E 65*, m838–m839.
28. F. Jalilevand, B. O. Leung, V. Mah, *Inorg. Chem.* **2009**, *48*, 5758–5771.
29. E. Bakker, P. Buhlmann, E. Pretsch *Chem. Rev.* **1997**, *97*, 3083–3132.
30. M. R. Ganjali, A. Rouhollahi, A. R. Mardan, M. Hamzeloo, A. Moghimi, M. Shamsipur, *Microchem. J.* **1998**, *60*, 122–133.
31. E. Eugster, P. M. Gehrig, W. E. Morf, U. Spichiger, W. Simon, *Anal. Chem.* **1991**, *63*, 2285–2289.
32. T. Rostazin, E. Bakker, K. Suzuki, W. Simon. *Anal. Chim. Acta* **1993**, *280*, 197–208.
33. P. M. Gehrig, W. E. Morf, M. Welti, E. Pretsch, W. Simon., *Helv. Chim. Acta* **1990**, *73*: 203.
34. E. Bakker, *Electroanalysis* **1997**, *9*, 7–12.
35. K. Y. Umezawa, Umezawa, H. Sato, *Pure Appl. Chem.* **1995**, *67*, 507–518.

Povzetek

1,3-Bis(2-cianobenzen)triazen, L je bil uporabljen kot primeren ionofor za pripravo grafitne elektrode prevlečene s PVC polimerno membrano za selektivno določanje Cd^{2+} ionov. Elektroda ima Nernstov naklon v pH območju med 6 in 9, mejo zaznave 8.0×10^{-6} M in odzivni čas približno 2 s. Elektroda je bila uporabljena v pretočni injekcijski potenciometriji za določanje kadmijevih ionov, pri kateri daje dobro oblikovane vrhove, stabilno osnovno linijo, dobro ponovljivost in omogoča preko 100 injeciranj v eni uri. Odlikuje jo dobra stabilnost, ponovljivost in kratek odzivni čas. Prikazana je tudi praktična uporabnost predlaganega analiznega sistema.