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*Original Research Article*

# PVC Membrane Electrode Modified by Lawson as Synthetic Derivative Ionophore for Determination of Cadmium in Alloy and Wastewater

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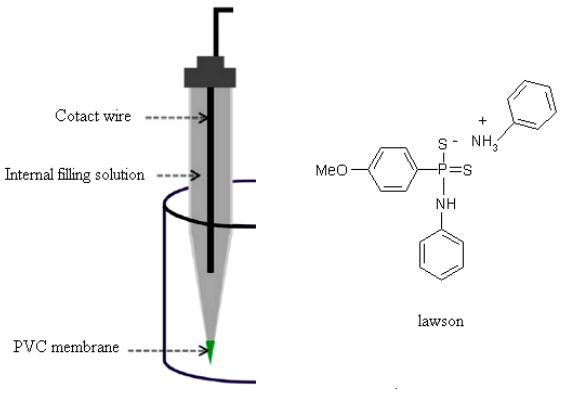
**ABSTRACT**

In this study, a PVC membrane electrode was modified by a derivative of lawason that is a neutral ionophore for Cd (II) determination in alloy and wastewater as real samples. The modified electrode showed a linear electrochemical response to Cd (II) concentration between 5.0×10−8 to 1.5×10−1 molL-1 (LOD = 2.51×10−8 molL-1). In selecting and determining the level of an effective composite of the membrane, the highest results were achieved in the membrane composition 33% PVC, 64.0% TEHP, 1.5% NaTPB, and 1.5% ionophore. The time it takes for the response to reach its maximum and remain stable at this electrode is very favorable (response time < 12 s). The responses of the electrode in consecutive uses for two months did not deviate significantly. In investigating the disturbance of other ions and compounds in the measurement of cadmium, the designed electrode had a very good selectivity for cadmium. The best conditions for measuring cadmium with this electrode are in an acidic environment (pH range of 2.8–6.5). In this research, potentiometric titration with the use of chromate as titrant was used in water and alloy samples.

**GRAPHICAL ABSTRACT**

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## Introduction

In the biological systems of animals and plants, heavy metals play important roles. Many biological problems occur due to the absence or deficiency of these microelements. It should be noted that the presence of excessive amounts of these substances will also cause harmful problems. Heavy metals are non-degradable and remain in wastewater and the environment and can be absorbed by plants into the food cycle of living organisms and cause serious pollution and health hazards. In addition to the loss of heavy metals to health, the presence of these elements in the soil and dissolution in groundwater cause severe damage to agriculture and economy. One of these heavy metals that play an important role in life and danger of living organisms is cadmium. Therefore, the determination of this toxic metal is important in various fields such as food control, occupational medicine, toxicology, and hygiene [1-4]. The entry of toxic heavy metals into the environment through industrial products and wastewater leads to the accumulation of these indestructible metals in the human body and other organisms [5-8]. Therefore, some new analytical methods which can measure cadmium contents in its trace level will be of great significance to report. Different analytical methods are used to determine cadmium such as flame atomic absorption spectrometry [9], electrochemical flame atomic absorption spectrometry [10, 11], stripping chronopotentiometry [12], flow injection analysis [13], and anodic square wave voltammetry [14].

Among different instrumental methods, electrochemical methods, especially ion-selective electrodes (ISEs), have advantages due to fast response, low cost, portability, non-destruction, etc., are widely used [15-20]. One of the most important points about electrodes is their high sensitivity and selectivity to ions. A good ion-selective electrode should be able to measure the desired element with excellent selection and acceptable response time in different samples and environments. Carbon paste electrodes are a good choice for ion-selective electrodes due to their ability to accumulate a large number of measured ions on the electrode surface and ease of fabrication. These electrodes with different modifiers and compounds can be specified for different ions [21, 22].

In this study, a PVC ion-sensitive electrode for cadmium determination was successfully designed and used as a working electrode in a potentiometric titration using chromate titrant. Also, it is used in real samples with optimal accuracy and sensitivity.

## Material and methods

*Reagents*

Many pure chemical reagents such as 1, 3-diphenyltriazen (DPTA), high relative molecular weight PVC, dioctylphethalate (DOP), tris(2-ethylhexyl) phosphate (TEHP), tetrahydrofuran (THF), dioctylsebasate (DOS), 2-nitrophenyloctylether (O-NPOE), oleic acid (OA), sodium tetraphenylborate (NaTPB), and dibutylphethalate (DBP), were purchased from Merck for fabrication of modified PVC membrane electrode and used as received. A 0.1 $molL^{-1}$ acetic acid/sodium acetate solution as a buffer was used to adjust the pH (at pH 4.7). NKK No. 916 Aluminum and NKK No. 920 Aluminum Alloy as real samples were used and from Nippon Keikinzoku Kogyo (NKK). All aqueous solutions were made by doubly distilled de-ionized water.

*Synthesis of the new lawson derivate reagent*

The ligand used as the ionophore (Figure 1) was synthesized by the following method: 5.0 ml mol of lawson reagent was dissolved in 50.0 ml of acetonitrile solution. Then, 10.0 ml of aniline was added to the solution. The resulting mixture was refluxed at 70.0 °C for three hours. After cooling the solution, the resulting output was formed and separated by suitable filter paper for future characterization. The yield was approximately 75-80%. Elemental analysis of Lawson ($C_{19}H_{23}N_2S_2OP$) was performed using the Heraeus CHN elemental analysis system. Anal. Calc.: C: 58.47, H: 5.89, N: 7.17%. Fund: C: 57.30, H: 5.63, N: 6.82%. Infrared spectra were recorded on a Shimadzu IR-470 instrument. IR spectra confirmed ligand structure. IR (KBr): 2320(m), 2800(m), 3000(m), 1600, 1568, 1497, 1284, 1262, 1140, 1024(s), 934, 688 $cm^{-1}$.

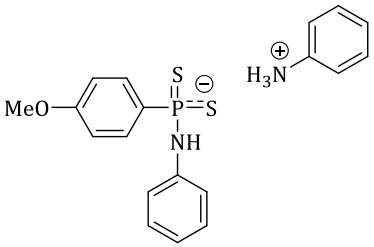

**Figure 1:** Structures of Lawson synthetic derivate used as ionophore in the membrane matrix

*Alloy samples preparation*

In order to dissolve the prepared alloy samples (916 Aluminum and NKK No. 920 Aluminum Alloy), the following method was performed: A 1.0 g of each alloy sample measured and transferred into a suitable container and dissolved in 5.0 ml concentration nitric acid by heating. After dissolving the alloy, the solution was allowed to cool at room temperature. Then, the resulting solution was diluted and filtered. The filtrated solutions were diluted (100 mL) and the pH of them was kept at 4.7.

*Electrode preparation*

To prepare the PVC membrane, 33.0 mg of powdered PVC, 64.0 mg of plasticizer (TEHP), 1.5 mg of additive (NaTPB), and 1.5 mg of 1, 3- lawson synthetic derivate ionophores were mixed in 3.0 ml of THF and it was transferred into a glass dish of 2.0 cm diameter. An oily concentrated mixture was obtained by evaporation of the solvent at room temperature. The modified PVC membranes were made by dipping a Pyrex or Teflon tube (3-5 mm i.d. on top) into the mixture and held inside it for about 10 s. Finally, a transparent membrane with about 0.3 mm thickness was obtained. To obtain a smooth surface, the fabricated electrode was polished and kept at room temperature for 1 h. Then, it was filled up with $1.0\times10^{-4}$ molL$^{1}$ of cadmium nitrate solution as an internal solution. To balance the electrode surface, it was placed in solution $1.0\times10^{-4}$ mol L$^{-1}$ of $Cd(NO_3)_2$ for 24 hours.

*Apparatus and potential measurements*

The cell assembly in this study included:
Ag/AgCl, KCl (3.0 mol L-1)│internal solution: Cd(NO3)2 (1.0×10-4 molL-1) │PVC membrane │test solution│ Hg2Cl2-Hg, KCl (satd.).

All measurements were carried out at room temperature (25.0±0.1 °C) by using a digital pH-ion meter (Model HANA 302). In calculations, the activity coefficients (γ) of Cd (II) that was calculated by a modified form of the Debye–Huckel equation was used [23].

*Complexation study*

Lawson derivative formed a stable complex with cadmium, a conductometric method was used to measure its stability and stoichiometry. In this way, a $1.0\times10^{-5}$ mol L$^{-1}$ solution of the cadmium ion at the acetonitrile solution was titrated with different volumes of $1.0\times10^{-3}$ mol L$^{-1}$ of lawson derivate (acetonitrile solution), and the curve of conduction changes was plotted against the molar ratio ([L]/[M]), as shown in Figure 2. The plot at [L]/[Cd (II)] mole ratio of about 1.0 showed an inflection point, emphasizing the formation of a 1:1 (metal-to-ligand) complex in the solution. KINFIT as a non-linear least-squares program was used to calculate the complex formation constant of the lawson-Cd complex. In this calculation, the molar conductance was fitted, at various mole ratios against the previously derived equations $\Lambda_{obs}$ as a function of the free and complexed metal ions [24]. The logarithm of formation constant was obtained as 5.97±0.03 for Cd (II)-lawson derivate complex. A thermostatic bath (Huber polyester cc1) was used in all measurements to keep constant the temperature (25.0±0.1 °C).

**Result and Dissection**

*Effect of membrane composition on the potential response characteristics of Cd(II) sensor*

In the primary experiments, the conductometric measurement proved that there was a good tendency to form a stable complex formation between Cd(II) metal ion and lawson derivate used ionophore (Figure 2). Thus, we are motivated to use the lawson derivate used ionophore to construct a PVC membrane sensor as a potential ionophore. After confirming that Lawson could be used as an ionophore to measure cadmium ions, the different ratios of the membrane electrode components such as ionophore, PVC, plasticizer, and additive materials were investigated (Table 1). As it is obvious from Table 2, the highest electrochemical signal was

obtained with electrode composition No. 9, (64.0% TEHP, 33% PVC, 1.5% ionophore, and 1.5% NaTPB). Also, it has an excellent Nernstian slope 29.9±0.2 mV and a linear response signal between $5.0\times10^{-8}$ to $1.5\times10^{-1}$ molL$^{-1}$ with detection of limit (LOD) $2.51\times10^{-8}$ molL$^{-1}$.

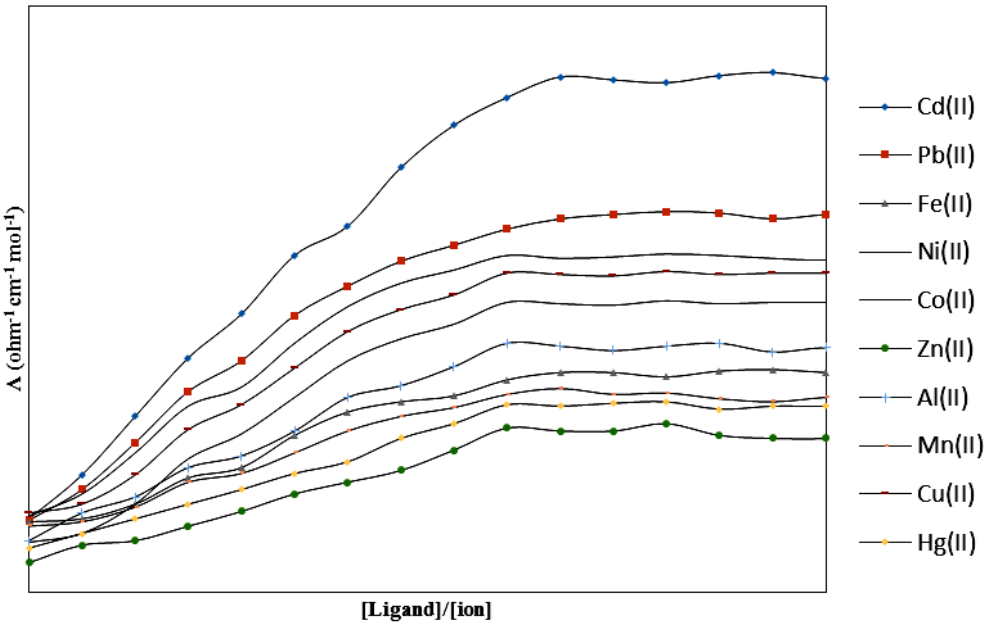


**Figure 2:** Conductance Vs [ligand]/[Cd(II)] mole ratio plot for lawson synthetic derivate used ionophore in acetonitrile at 25 °C

**Table 1:** ISE membrane optimization for the Cd (II)-sensor (n=5)

| Membrane number | Composition (%) | | | | Slope (mV/decade$^{-1}$) | Linear range (mol L$^{-1}$) |
|---|---|---|---|---|---|---|
| | PVC | Plasticizer | Ligand | Additive | | |
| 1 | 33.0 | 66.0 (NPOE) | 1.0 | 0.0 | 33.5 ± 0.4 | $2.0\times10^{-3}$-$1.0\times10^{-1}$ |
| 2 | 33.0 | 66.0 (DOS) | 1.0 | 0.0 | 8.5 ± 0.3 | $2.0\times10^{-3}$–$1.5\times10^{-1}$ |
| 3 | 33.0 | 66.0 (DBP) | 1.0 | 0.0 | 11.3 ± 0.4 | $1.5\times10^{-4}$-$1.0\times10^{-1}$ |
| 4 | 33.0 | 66.0 (DOP) | 1.0 | 0.0 | 12.3 ± 0.4 | $2.0\times10^{-5}$-$1.3\times10^{-3}$ |
| 5 | 33.0 | 66.0 (TEHP) | 1.0 | 0.0 | 14.7 ± 0.3 | $1.0\times10^{-6}$-$1.2\times10^{-2}$ |
| 6 | 33.0 | 65.0 (TEHP) | 1.0 | 1.0 (OA) | 17.5 ± 0.3 | $2.0\times10^{-6}$-$1.3\times10^{-1}$ |
| 7 | 33.0 | 65.0 (TEHP) | 1.0 | 1.0 (NaTPB) | 23.3 ± 0.3 | $1.7\times10^{-7}$-$2.5\times10^{-1}$ |
| 8 | 33.0 | 65.0 (TEHP) | 1.5 | 1.0 (NaTPB) | 25.7 ± 0.2 | $8\times10^{-8}$-$2.0\times10^{-1}$ |
| 9 | 33.0 | 64.0 (TEHP) | 1.5 | 1.5 (NaTPB) | 29.9± 0.2 | $5.0\times10^{-8}$-$1.5\times10^{-1}$ |
| 10 | 33.0 | 64.0 (TEHP) | 2.0 | 1.5 (NaTPB) | 27.3± 0.3 | $5.0\times10^{-8}$-$3\times10^{-1}$ |
| 11 | 33.5 | 63.0 (TEHP) | 1.5 | 2.0 (NaTPB) | 28.2 ± 0.3 | $1.2\times10^{-6}$-$2.3\times10^{-1}$ |
| 12 | 34.5 | 66.0 (TEHP) | 0.0 | 0.0 (NaTPB) | 3.6 ± 0.4 | $1\times10^{-3}$-$1.6\times10^{-1}$ |

**Table 2:** Various interfering ions' selectivity coefficients calculated by the FIM method (n=3)

| Interfering ion | $-logK^{pot}_{Cd,M}(a)$ | Interfering ion | $-logK^{pot}_{Cd,M}(a)$ |
|---|---|---|---|
| $Cu^{2+}$ | 3.53 ± 0.23 | $Hg^{2+}$ | 3.94 ± 0.20 |
| $Ni^{+}$ | 3.43 ± 0.32 | $La^{3+}$ | 4.31 ± 0.25 |
| $Pb^{2+}$ | 3.33 ± 0.31 | $Ce^{3+}$ | 4.73 ± 0.26 |
| $Co^{2+}$ | 3.65 ± 0.34 | $Al^{3+}$ | 4.47 ± 0.27 |
| $Zn^{2+}$ | 3.74 ± 0.25 | $Cr^{3+}$ | 4.57 ± 0.32 |
| $Fe^{2+}$ | 3.94 ± 0.23 | $Ca^{2+}$ | 3.99 ± 0.33 |
| $Mn^{2+}$ | 3.99 ± 0.32 | $Sr^{2+}$ | 4.09 ± 0.25 |
| $Ba^{2+}$ | 3.87 ± 0.24 | $K^{+}$ | 5.53 ± 0.20 |
| $Na^{+}$ | 5.74 ± 0.33 | $Mg^{2+}$ | 3.84 ± 0.24 |
| $Li^{+}$ | 4.82 ± 0.24 | $Fe^{3+}$ | 4.63 ± 0.31 |
| $H^{+}$ | 4.27 ± 0.22 | | |

The optimal membrane electrode response to other metal ions was investigated. This study aimed to investigate the disturbance of these ions in the measurement of cadmium ions and to study

the selectivity of the optimized electrode for the measurement of cadmium ions. As shown in Figure 3, unlike cadmium ion, in which the response of the electrode is Nernstian, the intensity of the electrode response to other ions is much less and their curve is non-Nernstian. The optimal electrode has a strong tendency to Cd (II) due to non-dissolution of lawson in water and reaction with very rapid kinetics of Cd (II) ion exchange and also very high metal-binding properties of Cd (II).

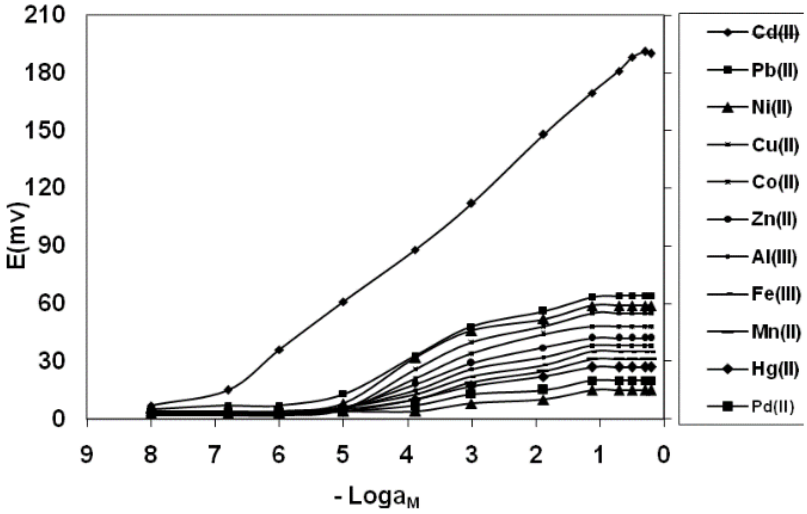


**Figure 3:** Potential response of ISEs based on lawson derivate ionophore towards various metal ions. Composition: PVC (33 mg), TEHP (64.0mg), ionophore (1.5mg) and NaTPB (1.5 mg)

Table 1 shows the effect of the absence and different concentrations of ionic additives on the response of PVC membrane electrodes. In the absence of ionic additive (No. 1-5), the electrode has a sub-Nernstian response with a low slope, but the presence of anionic additive (NaTPB) (membranes No. 7-12) increases the slope of the curve and makes it Nernstian.

Sodium tetraphenyl borate (NaTPB) as a lipophilic anionic salt reduces ohmic resistance, response time, anionic perturbations, and improves the selectivity of the cationic ion electrode. In addition, it increases the sensitivity of the electrode if the electrode acceptance capacity is low or the ionophore content is insufficient [20, 25-26].

In addition to the benefits listed above for the presence of ionic additives in the membrane, these materials can increase their synthetic rate and improve membrane selectivity by catalyzing ion-exchange reactions performed on the membrane surface [27]. In addition to ionic additives, the type and amount of plasticizer used in the membrane affect the behavior and response of the ion-selective electrode. As a solvent mediator, these materials affect and improve the physical properties of membranes such as dielectric constant, polarity, viscosity, and ion mobility [23, 24].

*The effect of pH*

One of the effective parameters in ion-selective electrodes is the pH of the solution that is measured. Ion-selective PVC membrane electrodes optimized for measuring Cd (II) at a concentration of $1.0\times10^{-3}$ mol $L^{-1}$ were examined. As shown in Figure 4, in the acidic pH range 2.8-6.5, the pH potential of the electrode is independent.

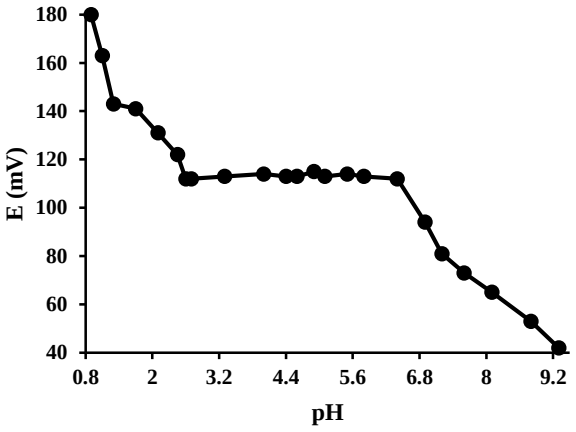


**Figure 4:** pH effect on the response of the cadmium ISE based on lawson derivate ionophore (composition No. 8)

The decreased potential response of the proposed electrode, at pH lower than 2.8, pertains to protonation of the ionic part of the lawson reagent and at pH higher than 6.5, it may be due to the formation of some of cadmium hydroxide species. Therefore, the pH range of 2.8-6.5 was selected as the range for other studies and the acetic acid/sodium acetate buffer solution (0.1 mol $L^{-1}$) with a pH of 4.7 in this range was used.

*Response time, reproducibility and life time*

In the study of the optimized membrane electrode response time, five solutions in the concentration range of $1.0\times10^{-5}$ and $1.0\times10^{-1}$ mol $L^{-1}$ were used. The time it took for the response of the electrode to reach the maximum value was measured with a range of about 0.5 mV. In all solutions, after less than 12 seconds, the electrode response reached a maximum and remained constant for 5 minutes.

Two very important parameters in the design and construction of electrochemical sensors that should be considered are lifetime and reproducibility. To evaluate the lifetime of the designed electrode, an electrode was made and used at regular intervals to measure cadmium ion. The electrodes provided suitable responses at equal concentrations of cadmium ions over a period of 2 months.

Also, to evaluate the reproducibility of the designed electrode, five different sensors were made in equal conditions and used to measure cadmium ion in two solutions $2.0\times10^{-3}$ and $3.0\times10^{-5}$ mol $L^{-1}$. The results showed that the manufactured electrodes produce close results ($RSD_s\%$ <6.2%).

*Selectivity coefficients of cadmium selective electrode*

Any ioni-selective electrode can be sensitive to other ions in addition to the analyte ion. To investigate the interfering effect of other ions, the parameter of potentiometric selectivity coefficient k ($k_{Cd,M}^{pot}$) for analyte ion and each of the disturbing ions is calculated using the fixed interference method (FIM) method and using the Nikolsky/Eisenman equation [28]. In this method, the electrode response is recorded at different concentrations of interfering ions and constant concentrations of analyte ions ($1.0\times10^{-2}$ mol $L^{-1}$). The $E_{ISE}$ diagram is plotted against log $a_{Cd}$ and the selectivity coefficient is calculated using Equation 1:

$$k_{Cd,M}^{Pot} = \ln a_A / a_B^{2/Z_B} \quad (1)$$

In this equation, $a_A$ is proportional to the activity of the cadmium ion which the linear and rising portion of the graph deviates by 2.303RT log Z/F mV from the curved part [29] and $a_B$ and $Z_B$ are the activity and charge of interfering ion, respectively. The results of calculating the selectivity the coefficient for different disturbing ions are shown in Table 2. As can be seen, the small values of these coefficients indicate that these ions, even at high concentrations, cannot interfere with the measurement of cadmium ions.

*Analytical Application*

In order to investigate the application of the optimized membrane electrode in real samples, two opposing methods were used. In the first experiment, under optimal conditions and pH equal to 4.7, the detector electrode was designed to find the endpoint of the titration of 20 ml of cadmium ion solution ($1.0\times10^{-3}$ mol $L^{-1}$) by $2.0\times10^{-3}$ mol $L^{-1}$ of $CrO_4^{2-}$ . The electrode expressed an endpoint of 10.2 mL, which was calculated in very good agreement with the equivalence point (10 mL).

In the second experiment, the proposed Cd (II) sensor was used to measure the amount of cadmium ion in the wastewater, tap water, and alloy samples. The results obtained with this electrode showed satisfactory agreement with the results of other methods such as atomic absorption spectroscopy (AAS) (Table 3-4). Accurate, precise, and quantitative results were obtained by the new modified and optimized ISE sensor.

**Table 3:** The cadmium content measurement in tape and waste water samples (n=5)

| Sample | Cadmium ion added (mol $L^{-1}$) | Found (mol $L^{-1}$) | |
|---|---|---|---|
| | | Proposed electrode (mol $L^{-1}$) | AAS (mol $L^{-1}$) |
| | $5.0 \times 10^{-4}$ | $(5.24\pm 0.25 \times 10^{-4})$ | $(5.19\pm 0.23 \times 10^{-4})$ |
| Waste water | $1.50 \times 10^{-3}$ | $(1.43 \pm 0.05\times 10^{-3})$ | $(1.53 \pm 0.06\times 10^{-3})$ |
| | $4.50 \times 10^{-3}$ | $(4.65 \pm 0.17\times 10^{-3})$ | $(.64 \pm 0.16\times 10^{-3})$ |
| Tape water | $3.0 \times 10^{-6}$ | $(3.24 \pm 0.21\times 10^{-6})$ | $(3.21 \pm 0.21\times 10^{-6})$ |
| | $6.50 \times 10^{-5}$ | $(6.11 \pm 0.34\times 10^{-5})$ | $(6.87 \pm 0.39\times 10^{-5})$ |
| | $5.0 \times 10^{-4}$ | $(5.20 \pm 0.24\times 10^{-4})$ | $(5.20 \pm 0.25\times 10^{-4})$ |
| | $7.5 \times 10^{-3}$ | $(7.73 \pm 0.27\times 10^{-3})$ | $(7.27 \pm 0.22\times 10^{-3})$ |

**Table 4:** The cadmium content measurement in alloy samples (n=5)

| Sample | Composition (%) | Certified value (%) | Found by ISE (%) |
|---|---|---|---|
| NKK No. 916 Aluminum Alloy | Si; 0.41, Mg; 0.10, Cr;0.05, Fe; 0.54, Ni; 0.06, Ti;0.10, Sn; 0.05, Cu; 0.27, V; 0.02, Sb; 0.01, B; 0006, Bi; 0.03, Co; 0.03, Mn; 0.11, Zr; 0.05 | 0.040 | 0.042 ± 0.003 |
| NKK No. 920 Aluminum Alloy | Sn; 0.20, Sb; 0.10, Mg; 0.46, Cr; 0.27, Ni; 0.29, Bi; 0.06, Ga;0.05; Ca; 0.03; Zn; 0.8, Co; 0.1, Mn; 0.2, Cu; 0.71, V; 0.15, Si; 0.78, TiO; 0.15 | 0.10 | 0.092 ± 0.05 |

## Conclusion

Modified PVC membrane with Lawson derivative was used for selective measurement of cadmium ion. The results showed that this electrode has a selective response, fast, with appropriate linear amplitude, low detection limit, very short response time, reproducibility, and effective in the appropriate pH area. This electrode was used in real samples including alloy, wastewater, and tap water in an acceptable way.

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## Authors' contributions

All authors contributed toward data analysis, drafting and revising the paper and agreed to be responsible for all the aspects of this work.

## Conflict of Interest

We have no conflicts of interest to disclose.

## References

[1]. Gholivand M.B., Bahrami S., Abbasi S., Sohrabid A., *Electroanalysis* 2008, **20**:1367 [Crossref], [Google Scholar], [Publisher]

[2]. Kashanian S., Khodaei M.M., Roshanfekr H., Peyman H., *Spectrochim. Acta A Mol. Biomol. Spectrosc.,* 2013, **114**:642 [Crossref], [Google Scholar], [Publisher]

[3]. Pyman H., Roshanfekr H., Ansari S., *Eur. Chem. Commun.,* 2020, **2**:213 [Crossref], [Google Scholar], [Publisher]

[4]. Heydarzadeh S., Roshanfekr H., Peyman H., Kashanian S., *Colloids Surf. A Physicochem. Eng. Asp.,* 2020, **587**:124219 [Crossref], [Google Scholar], [Publisher]

[5]. Vernet J.P., *Impact of Heavy Metals on the Environment,* Elsevier. New York. 1992 [Google Scholar]

[6]. Rahmati Farmani M., Peyman H., Roshanfekr H., *Spectrochim. Acta A Mol. Biomol. Spectrosc.,* 2020, **229**:117960 [Crossref], [Google Scholar], [Publisher]

[7]. Rahimi F., Roshanfekr H., Peyman H., *Food Chem.,* 2021, **343**:128436 [Crossref], [Google Scholar], [Publisher]

[8]. Ghasemi J., Peyman H., Niazi A., *J. Chin. Chem. Soc.,* 2013, **54**:1093 [Crossref], [Google Scholar], [Publisher]

[9]. Prasad K., Gopikrishna P., Kala R., Prasada Rao T., Naidu G.R.K. , *Talanta*, 2006, **69**:938 [Crossref], [Google Scholar], [Publisher]

[10]. Paz de Mattos J.C., Nunes A.M., Martins A.F., Dressler V.L., de Moraes Flores É.M., *Spect.*

*Chimica. Acta. Part B*, 2005, **60**:687 [Crossref], [Google Scholar], [Publisher]
[11]. García J.C.R., García J.B., Latorre C.H., Martín S.G., Pena Crecente R.M., *Food Chem.,* 2005, **91**:435 [Crossref], [Google Scholar], [Publisher]
[12]. Coco F.L., Monotti P., Cozzi F. , Adami G., *Food Control,* 2006, **17**:966 [Crossref], [Google Scholar], [Publisher]
[13]. Nezio M.S.D., Palomeque M.E., Band B.S.F. , *Talanta*, 2004, **63**:405 [Crossref], [Google Scholar], [Publisher]
[14]. Li G., Ji Z., Wu K., *Anal. Chim. Acta,* 2006, **577**:178 [Crossref], [Google Scholar], [Publisher]
[15]. Meyerhoff M.E., Opdyche M.N., *Adv. Clin. Chem.*, 1986, **25**:1 [Crossref], [Google Scholar], [Publisher]
[16]. Moody G.J., Saad B.B., Thomas J.D.R., *Sel. Electrode Rev.*, 1988, **10**:71 [Google Scholar]
[17]. Inoue Y.H., by Macrocycles T.I.C.B., Inoue Y., Gokel G.W., *Cation Binding by Macrocycles*. Marcel Dekker: New York. 1990 [Google Scholar]
[18]. Bakker E. , Buhlmann P., Pretsch E., *Chem. Rev.,* 1997, **97**:3083 [Crossref], [Google Scholar], [Publisher]
[19]. Buhlmann P., Pretsch E., Bakker E., *Chem. Rev.,* 1998, **98**: 1593 [Crossref], [Google Scholar], [Publisher]
[20]. Gholivand M.B., Babakhanian A., Joshaghani M., *Anal. Chim. Acta,* 2007, **584**:302 [Crossref], [Google Scholar], [Publisher]
[21]. Gholivand M.B., Peyman H., Gholivand K., Roshanfekr H., Taherpour A., Yaghobi R., *Appl. Biochem. Biotechnol.,* 2007, **182**:925 [Crossref], [Google Scholar], [Publisher]
[22]. Alidadykhoh M., Pyman H., Roshanfekr H., *Chem. Methodol.,* 2021, **5**:96 [Crossref], [Google Scholar], [Publisher]
[23]. Dye J.L., Nicely V.A., *J. Chem. Educ.,* 1971, **48**:443 [Crossref], [Google Scholar], [Publisher]
[24].Ganjali M.R., Rouhollahi A., Mardan A.R., Shamsipur M., *J. Chem. Soc. Faraday Trans.* 1998, **94**:1959 [Crossref], [Google Scholar], [Publisher]
[25]. Gholivand M.B., Ahmadi F., Rafiei E., *Electroanalysis*, 2006, **18**:1620 [Crossref], [Google Scholar], [Publisher]
[26]. Michalska A., Konopka A., Maj-Zurawska M., *Anal. Chem.,* 2003, **75**:141 [Crossref], [Google Scholar], [Publisher]
[27]. Kamata S., Kubo Y., Murata H., Bhale A., *Analyst*, 1989, **114**:1029 [Crossref], [Google Scholar], [Publisher]
[28]. Yuan R., Wu H.L., Yu R.Q., *Sci. Chin*., 1993, 36:140 [Crossref], [Google Scholar], [Publisher]
[29]. Kane P., Diamond D., *Talanta*, 1997, **44**:1847 [Crossref], [Google Scholar], [Publisher]

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