Раси. С.

Доктор универсаитета , Альбаас университет, факультет

«Естественных наук»

Фаяд. К.

Студент

2 курс, магистратура, Альбаас университет, факультет

«Естественных наук»

Россия, г. Москва

CHARACTERIZATION SELECTIVE ELECTRODE FOR DETERMINATION OF CADMIUM ION (II) BY POTENTIOMETRIEC

Annotation: *A chemically modified carbon paste electrode with 1-(2-pyridylazo)-2-naphthol (PAN) the potentiometric determination of Cd(II) is demonstrated. The electrode exhibits linear response to Cd(II) over a wide concentration range (3.00×10^{-7}-3.34×10^{-4}M) with Nernstian slope of 29.775 mV per decade. It has a response time of about 50 s and can be used for a period of two months with good reproducibility.*

Keywords: *Cadmium, Potentiometric method validation.*

Аннотация: *На химически модифицированном углеродном пастообразном электроде с 1- (2-пиридилазо) -2-нафтолом (PAN) продемонстрировано потенциометрическое определение Cd (II). Электрод демонстрирует линейный отклик на Cd (II) в широком диапазоне концентраций ($3,00 \times 10$–7–$3,34 \times 10$–4 М) с наклоном Нернста 29,775 мВ за десятилетие. Он имеет время отклика около 50 с и может использоваться в течение двух месяцев с хорошей воспроизводимостью.*

Ключевые слова: *Кадмий, Потенциометрический метод валидации.*

1. Introduction:

In potentiometry we measure the potential of an electrochemical cell under static conditions. Because no current—or only a negligible current—flows through the electrochemical cell, its composition remains unchanged. For this reason, potentiometry is a useful quantitative method. The first quantitative potentiometric applications appeared soon after the formulation of the Nernst equation, which relates an electrochemical cell's potential to the concentration of electroactive species in the cell [1,c.344]. Many sensitive techniques such as spectrophotometric [2,c.], Spectrofluorimetry [3,c.89], electrochemical methods [4,c.699] Voltammetry [5,c.62] , X-ray fluorescence [6,c.266], Neutron Activation Analysis (NAA) [7,c.193], Grafite furnace atomic absorption spectroscopy (GF-AAS) [8,c.7], Inductively coupled plasma-mass spectrometry (ICP-MS) [9,c.85], Inductively coupled plasma-optical emission spectroscopy (ICP-OES) [10,c.276], High Performance Liquid Chromatography (HPLC), and Pulse polarography [12,c.9] have been widely applied to the determination of cadmium. These methods are disadvantageous in terms of cost and the instruments used in routine analysis.

2. Experimental Section

2.1. Reagents

All chemicals used were of analytical grade. Double distilled water was used throughout all experiments. 1-(2-pyridylazo)-2-naphthol (PAN) was from BDH. $Cd(NO_3)_2.4H_2O$ and Sodium tetraphenylborate (Na–TPB) was from Merck, while dibutyl phthalate (DBP), dioctyl phthalate (DOP) and paraffin oil (p.Oil) were from BDH. Graphite powder was obtained from Aldrich.

2.2. Apparatus

Potentiometric and pH measurements was carried out using a digital Shott Gerate pH meter (Consort C 830, Belgium) with combined glass pH electrode. A water bath shaker (Grant instruments, Cambridge Ltd, England) was used to control the temperature of the test solutions. A saturated calomel electrode (SEC) was used as the

external reference (Mettler, Switzerland). The electrochemical system may be represented as follows:

carbon paste electrode/test solution/saturated calomel electrode

FT-IR 4100 (Fourier transform infrared spectrometer) Jasco.

2.3. Preparation of Standard solutions

Standard stock solution of 1.0×10^{-2} M Cd^{+2} was prepared daily by dissolving the appropriate amount of $Cd(NO_3)_2 \cdot 4H_2O$ in double distilled water. Standard working solutions 1.0×10^{-2}, 1.0×10^{-3} and 1.0×10^{-4} M were freshly prepared by suitable dilutions of the stock solution with double distilled water.

Table 1. IR data for PAN and Complex between PAN and Cd.
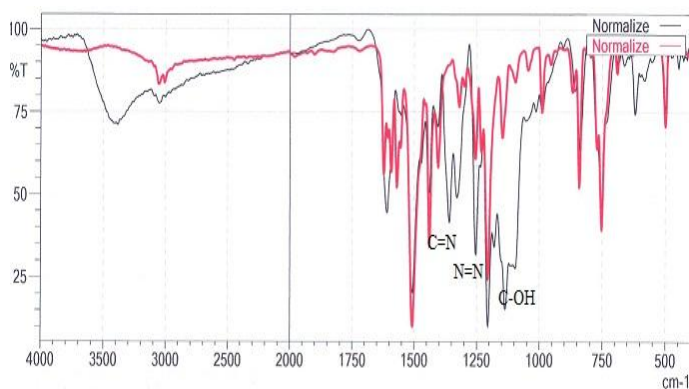
Figure of light Cd- PAN (black Spectrum)

	IR/cm^{-1}	
	PAN	**Cd –PAN**
N=N	1506	1383
C=N	1591	1348
C-O	1469	1252

1. IR spectrum PAN (red spectrum),

2.4. Preparation of Complex (Cd -PAN)

Complex (Cd-PAN) was prepared by mixing equal volumes of 10^{-2}M solution of Cd^{2+} with hot methanolic solution of PAN with stirring, then we evaporate methanol gradually to obtain a precipitate. IR data (Fig 1.) of Cd -PAN shown in (Table 1).

2.5. Preparation of CMCPE and Construction of Cd electrode.

MCPEs were prepared by thoroughly mixing various amounts of ion pairing agents with carbon powder and plasticizer in the mortar, until homogenization of this mixture was achieved. The resulting paste was then packed firmly into the hole of the electrode body. Electrical contact to the carbon paste was made with a copper wire. Fresh surface was obtained by applying manual pressure to the carbon paste and polished on a filter paper to a shiny surface

The electrical connection was made with a copper. Electrode potential was measured against the SCE as the reference electrode.

2.6 Selectivity of sensors

Potentiometric selectivity coefficient $K_{A,B}^{pot}$ of an ion-selective electrode (ISE) was commonly used as quantitative expression of the ability of the electrode to respond primarily to the analyze ion in the presence of interfering ions. The effect of the presence of some different species on the response of Cd^{2+}electrode was investigated, and the selectivity coefficient $K_{A,B}^{pot}$ of the proposed electrode was calculated in the presence of related organic and inorganic substances using matched potential method (MPM). The selectivity coefficient $K_{A,B}^{pot}$ which was measured by matched potential method was calculated according to the following equation: (1)

$$K_{A,B}^{MPM} = \frac{(a'_A - a_A)}{a_B}$$

Where a'_A is the known activity of primary ion, a_A is the fixed activity of primary ion, and a_B is the activity of interfering ions .

2.7 General procedure

The performance of the electrode prepared was investigated by measuring e.m.f. values of 5.0×10^{-7}–5.5×10^{-2} M of $Cd^{2+.}$ The electrode was calibrated by added volumes of 50 mM stock solution of Cd^{2+} successively in 50 ml of water to generate a total concentration ranging from 5.0×10^{-7}–5.5×10^{-2} M Cd^{2+}, followed by immersing the Cd^{2+} electrode, together with a calomel reference electrode in the solution. The potential reading was recorded after stabilization, and the e.m.f was plotted as a function of the logarithm of the Cd^{2+} concentration. The concentration graph was used for subsequent determinations of unknown Cd^{2+} concentrations.

3. Results and Discussion

3.1 Optimization of the amount of modifier in the electrode

For this purpose seven electrodes were prepared. The amounts of carbon powder and dioctyl phthalate (DOP) were constant in each electrode. The resulting Nernstian

slopes and Linear range are shown in (Table 2). These results show that by increasing the percentages of modifier up to 2-4.0% the slopes decrease sharply, but within 5.0–6.0 % the slopes are becoming more Nernstian and slopes of the electrode are only slightly changed. Electrodes with 5.0% of modifier show super Nernstian slopes, since in these compositions electrodes behave mostly as a pure carbon paste electrode. Since electrode with 5% of ionophore has a good slope and the amount of the ionophore was less than the other Nernstian electrode this percentage was chosen as the optimum amount for the cadmium electrode.

Table 2. The paste compositions and the electrode characteristics of Cd(II) sensor**.**.

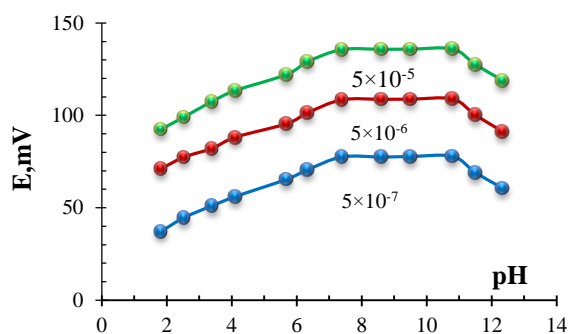|	Composition,%(w/w)				
Electrodes	ionophore	G	P	Slope, mV decade-1	Linear range M
I	2	49.0	49.0	46.362	1.25×10^{-5}-3.34×10^{-4}
II	3	48.5	48.5	37.473	3.09×10^{-6}-3.34×10^{-4}
III	4	48.0	48.	33.062	1.50×10^{-6}-3.34×10^{-4}
IV	**5**	**47.5**	**47.5**	**29.775**	$\mathbf{3.00\times10^{-7}}$-$\mathbf{3.34\times10^{-4}}$
V	6	47.0	47.0	26.853	7.00×10^{-7}-3.34×10^{-4}
VI	7	46.5	46.5	24.189	1.50×10^{-6}-3.34×10^{-4}
VII	8	46.0	46.0	20.787	1.50×10^{-6}-3.34×10^{-4}

G: graphite powder, P: paraffin oil

3.2. Response of electrode to various cations.

The potential responses of various chemically modified CPEs based on PAN The Cadmium selective electrode exhibited linear response to the logarithm of the activity of Cd^{2+} ions within the concentration range of $(3.00\times10^{-7}$-$3.34\times10^{-4})$M of Cd^{+2} with Nernstian slope of 29±775 mV per decade and correlation coefficient of 0.9994.

3.3 Optimization of pH

The behavior of the Cadmium electrode in relation to the variation of pH (1–12) was studied. The composition of the electrode were kept constant during all experiments. The results showed that the potential remained constant despite pH change in the range of 7.5-10.5 indicating applicability of this electrode in the specified pH range (Fig. 2).

Figure 2. Effect of the pH on the response of the electrode

3.4 Calibration graphs

Using the optimized composition and conditions described above, the potentiometric response of the electrode was studied based on the Cd concentration in the range of 5.0×10^{-7}–5.5×10^{-2} M. The calibration curves for the electrodes containing 5% of ionophore gave an excellent linear response from (3.00×10^{-7}-3.34×10^{-4}M), as shown in (Fig 3.). The results given in (Tab 3.) show the characteristics performance of the electrode.

Table 3. Response characteristics of electrodes

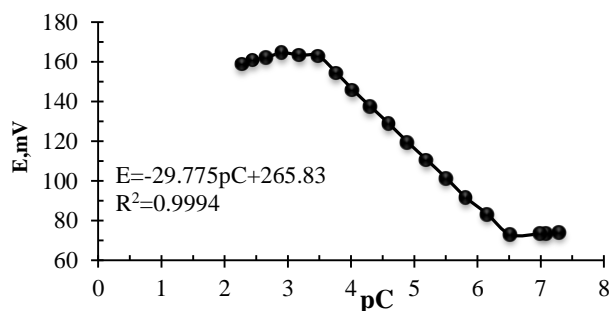| Electrode	5% -ionophore
Plasticizer	**DOPH**
Parameter	
Slope mV.decad^{-1}	29.775
Correlation cofficient	0.9994
Linearity range (M)	(3.00×10-7-3.34×10-4
Lower detection limit(M)	8.82×10-8
Response time(s)	t $\leq$50
Working pH range	7.5-10.5
Temperature°C	25
Life time(day)	31

Figure 3. Calibration graph of Cu electrode.

3.5 Response characteristics of modified and unmodified carbon paste electrodes

The unmodified electrode shows no response under the optimum condition. The response time of the modified electrode is measured according to IUPAC recommendation. The response time in variation of concentration from 3.00×10^{-7}-3.34×10^{-4}M Cd^{+2} is shown in (Fig 4.); the measured response time was 50 s.
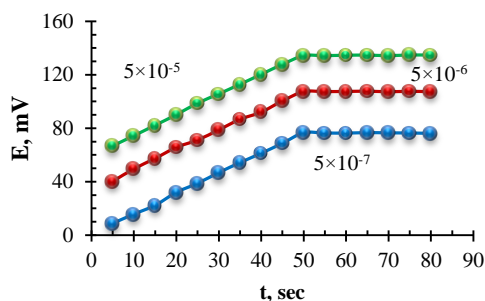

Figure 4. Response time of electrode

3.6 Lifetime

The electrode lifetime was investigated by performing the calibration curve and the periodic testing of standard solutions (3.00×10^{-7}-3.34×10^{-4}M) and calculating the response slope. It was observed that the electrode exhibit good stability in terms of slope in the linear domain of concentration and the electrode can be used continuously for about 31 days without considerable decrease in its slope value.

3.7 Selectivity of electrode

The influence of some inorganic cations such as of Li^+, Na^+, K^+, $Ca^{2+,}$ Zn^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, NH_4^+, pb^{2+}, CO^{2+}, Fe^{3+}, Al^{3+}, Cr^3 on the electrode response was investigated. The selectivity of the electrode was measured by applying the matched

potential method (MPM). According to this method, the activity of Cd^{+2} was increased from $a_A = 1$ mM (reference solution) to $a'_A = 1.1$ mM, and the changes in potential (ΔE) corresponding to this increase were measured. Then a solution of an interfering ion of concentration a_B is added to a new 1mM reference solution until the same potential change (ΔE) was recorded. The selectivity factor, $K_{A,B}^{MPM}$ for each interference was calculated using equation (1). The results are given in (Table 4). Results revealed reasonable selectivity for Cd^{+2} in presence of many related substances. The selectivity coefficient obtained by this method showed that there were no significant interferences from the cations, this reflected a very high selectivity of the investigated electrode towards Cd.

Table 4. Selectivity coefficients for of the Cd-PAN responsive electrode

Interferent	$K_{A,B}^{MPM}$	Interferent	$K_{A,B}^{MPM}$
Ni^{2+}	1.06×10^{-2}	K^+	1.41×10^{-4}
Cu^{2+}	5.87×10^{-3}	Na^+	5.67×10^{-5}
Fe^{2+}	2.92×10^{-2}	NH_4^+	2.31×10^{-3}
Fe^{3+}	3.39×10^{-3}	Ca^{2+}	7.21×10^{-5}
Al^{3+}	6.41×10^{-3}	Mg^{2+}	4.77×10^{-4}
Cl^-	-	Mn^{2+}	5.98×10^{-4}
SO_4^{2-}	-	Pb^{2+}	6.69×10^{-3}
CO_3^{2-}	-	Zn^{2+}	2.41×10^{-3}
PO_4^{3-}	-	Co^{2+}	4.21×10^{-2}

3.8. Effect of plasticizer on the potential response

In this study, three plasticizers, di-octylphthalate (DOP), di-butylphthalate (DBP) and paraffin oil (p. Oil) were used to examine possible optimization of the paste. Contents of examined plasticizers were 47.5 w %, contents of graphite powder were 47.5 w % and contents of electroactive compound 5 w %, respectively. The sum of percentages of all three components was always adjusted to 100 %. The results obtained showed that response performances of prepared pastes are rather different, depending on the kind of plasticizer, proportion of the plasticizer towards graphite and

amount of electroactive compound (Table 5). Typical potential responses of electrodes constructed with three plasticizers, the DOP-graphite electrodes were superior to DBP-graphite and p.Oil-graphite electrodes in both the response slope and linear concentration range. So, DOP was selected as the plasticizer of the carbon paste. The best paste composition of the DOP-graphite electrode was 47.5 % graphite, 47.5 % DOP and 5 % IP.

Table 5. General characteristic of different plasticizers of Cd-PAN electrode.

Composition of the plasticizer, %	IP, %	$S / mV\ dec^{-1}$	Linear range, M	LOD, M	Response time, s
DOP (47.5)	5	29.775	3.00×10^{-7}-3.34×10^{-4}	8.82×10^{-8}	50
DBP (47.5)	5	40.158	1.50×10^{-6}-3.34×10^{-4}	6.90×10^{-7}	55
p. Oil (47.5)	5	24.164	6.26×10^{-6}-3.34×10^{-4}	1.45×10^{-6}	50

3.9. Validity of the proposed method

The precision and accuracy of the method were also evaluated. The standard deviation, relative standard deviation and recovery of different Cd amounts were determined and recorded in (Table 6). The accuracy of the method is indicated by excellent recovery (98.44-102.24 %) and precision is supported by low standard deviation.

Table 6. Accuracy and precision for the determination of Cd-ISE in pure solution.

R%	RSD%	SD*, M	C **Found**, M	C **Taken**, M
102.24	2.21	1.132×10^{-8}	5.112×10^{-7}	5×10^{-7}
98.44	2.01	9.91×10^{-8}	4.922×10^{-6}	5×10^{-6}
99.32	1.46	7.232×10^{-7}	4.966×10^{-5}	5×10^{-5}
99.54	1.06	1.06×10^{-6}	9.954×10^{-5}	1×10^{-1}

*:Average of five determinations

3.10. Determination of cadmium ions in various water samples

The proposed Cd-electrode was found to work well under laboratory conditions. It was successfully applied to the determination of cadmium ions in tap water and well water using the Direct method The analysis of samples does not required pretreatment for poteniometric determination using the present electrode (Table 7).

Table 7. Determination of Cd (II) in various water samples.

	Cd^{2+}found M	SD, M	RSD%
Tap water	5.24×10^{-6}	1.41×10^{-7}	2.69
Well water	9.49×10^{-6}	1.43×10^{-7}	1.51
Inindustrial waste water	7.67×10^{-5}	1.75×10^{-6}	2.28

Five independent analyses.

4. Conclusions

The proposed chemically modified carbon paste electrode (MCPE) demonstrated advanced performance with fast response time and long stability, and shows high sensitivity, reasonable selectivity, and applicability over wide concentration range without sample pretreatment. The proposed potentiometric method offers the advantages of simplicity, accuracy and applicability to turbid and sample solutions.

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