

The Construction and Performance Characteristics of Carbon Paste Electrodes for Oxomemazine Hydrochloride

Yousry M. Issa¹, Sayed A. Ahmed^{2,*}, Nabila S. Mohamed³, Naglaa M. Mohamed³

¹Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

²Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

³Department of Environmental Sciences and Industrial Development, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, Beni-Suef, Egypt

Email address:

sayed.hassan@science.bsu.edu.eg (S. A. Ahmed)

*Corresponding author

To cite this article:

Yousry M. Issa, Sayed A. Ahmed, Nabila S. Mohamed, Naglaa M. Mohamed. The Construction and Performance Characteristics of Carbon Paste Electrodes for Oxomemazine Hydrochloride. *American Journal of Applied and Industrial Chemistry*. Vol. 1, No. 1, 2017, pp. 14-21. doi: 10.11648/j.ajaic.20170101.14

Received: September 21, 2016; **Accepted:** September 26, 2016; **Published:** April 1, 2017

Abstract: The construction and performance characteristics of carbon paste electrodes for Oxomemazine Hydrochloride (OXCl) are described. Different methods for electrode fabrication (modified with the ion-pair, ion pairing agent or soaking the plain electrode in the ion-pair suspension) have been used. Matrix compositions were optimized on the basis of effects of type and content of the modifier as well as influence of the plasticizers. The fabricated electrodes worked satisfactorily in the concentration range from 1×10^{-6} to 0.001 M with Nernstian cationic slopes, depending on the method of electrode fabrication. The ion-pair modified electrode showed the best performance (slope 57.7 ± 2.1 mV decade⁻¹) compared with the plain electrodes or modified with sodium tetraphenylborate (NaTPB) and fast response time of about 15 s and adequate lifetime (6 weeks). The developed electrodes have been successfully applied as well as end point indicator electrode for the potentiometric titration of OXCl with high accuracy and precision.

Keywords: Oxomemazine HCl, Pharmaceutical Analysis, Ion-Selective Electrodes, Carbon Paste Electrodes, Potentiometry Titration

1. Introduction

Oxomemazine, a phenothiazine derivative, is an antihistamine used for the symptomatic relief of hypersensitivity reaction. It is also an ingredient of compound preparations for the symptomatic treatment of cough and the common cold. It is given orally in doses equivalent to 10 to 40 mg of oxomemazine daily. Oxomemazine may also be administered rectally in form of suppositories. Oxomemazine hydrochloride (OXCl) has been used similarly by mouth. It is chemically known as [3-(5, 5-dioxodo-10H-phenothiazin-10-yl)-N, N, 2-trimethylpropan-1-amine] (Scheme [1]) Jacob (1961). The assay of the drug in pure and dosage forms is, as far as we know, not official in any pharmacopoeia, and therefore requires much more investigation. The different analytical techniques that have

been reported for its determination including spectrophotometry Zivanov, and Akram (2005) and HPLC Hoogewijs (1984). Regarding the quality control, it is used in pharmaceutical industry to analyze starting materials, intermediates, and finished products.

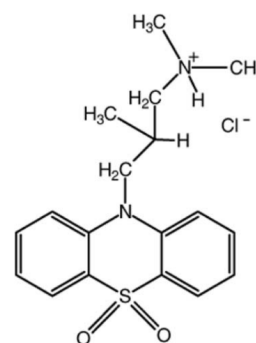


Fig. 1. The chemical structure of OMCl.

Ion-selective electrode (ISEs) are electrochemical sensors based on a thin selective membrane or a film, allowing the potentiometric determination of the activity of certain ions in the presence of other ions in the sample solution. In recent years, ISEs have been used for the determination of solubility products of different sparingly soluble salts. In spite of the successful progress in the design of highly selective electrodes for various ions, there has not been any report on the development of selective and sensitive sensors for oxomemazine Buck (1994).

The present study is concerned with preparation, characterization and application of simple potentiometric sensors for rapid determination of OX. Electrodes were fabricated in plain and modified forms and then subjected to a series of tests to select sensor possessing the most favorable analytical characteristics. The developed sensors were also applied as indicator electrode in the potentiometric titration of OX Vytras (1985), and Issa (2001),

2. Materials

2.1. General

All reagents used throughout the work were of analytical reagent grade. Bidistilled water was used throughout all experiments. Oxomemazine hydrochloride (OMCl, Mwt = 366.91) and its pharmaceutical preparation were provided by (EUROPEAN EGYPTIAN Pharmaceutical INDUSTRIES Company) (ALEXANDRIA-EGYPT).

Sodium tetraphenylborate (NaTPB) $\text{Na}[\text{C}_{24}\text{H}_{20}\text{B}]$ (Fluka), Sun flower oil, Corn oil, Olive oil, as natural plasticizers, poly vinyl chloride (PVC) of relatively high molecular weight (Aldrich), Tetrahydrofuran (THF) (Aldrich), Graphite powder 1-2 micron from Aldrich, Sodium chloride (NaCl), Potassium chloride (KCl), Ammonium chloride (NH_4Cl), Calcium chloride (CaCl_2), Magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), Ferric chloride (FeCl_3), Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Zinc sulphate (ZnSO_4), Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), Strontium chloride (SrCl_2), Cobalt chloride (CoCl_2) were obtained from Riedel de Haen Chemical Company, Glucose, Lactose, Maltose, Fructose, Sucrose, D-alanine, Glycine, Thiamine hydrochloride (vitamin B_1), pyridoxine hydrochloride (vitamin B_6) were obtained from Aldrich chemical company.

2.2. Methods

All potential measurements were performed using a 3510

Jenway pH meter with PC interface, equipped with silver-silver chloride double junction reference electrode in conjugation with the sensing drug ISE. A combined pH glass electrode was used for all pH measurements.

In carbon paste membrane electrodes, the amount of lipophilic salt should be sufficient to obtain reasonable ionic exchange at the gel layer-test solution interface, which is responsible for the membrane potential. Also, the amount of the plasticizer should be to the extent that produces a membrane of good physical properties and at the same time plays efficiently its role as a solvent mediator for the ion-exchanger(s) lipophilic salts.

In the present investigation, (carbon paste electrodes) membranes plasticized with corn oil and containing the lipophilic salt, OM-TPB were prepared. corn oil used has a significant influence on the response of the electrode.

Ion-selective electrodes containing different membranes compositions were prepared to select the optimum composition exhibiting the best performance characteristics, e.g. slope, linear range, different compositions of the membranes and the slope (mV/concentration decade) of the obtained calibration graphs. Each membrane was prepared three times and the calculated relative standard deviations of the slope value were always very small showing the reproducibility of the preparation process. Freshly prepared electrodes must be soaked in drug solution to form an infinitesimal thin gel layer at which ion exchange occurs. This preconditioning process requires different soaking times depending on diffusion and equilibration at the interface, fast establishment of equilibrium is certainly a sufficient condition for fast response Antropov (1977), Abdel-Ghani (2002), Khaled (2007) and Eisenman (1968). The soaking time differ according to the electrode types. Study of the soaking time showed that 15 minutes were satisfactorily for all the electrodes.

3. Results and Discussion

3.1. Effect of Composition

Comparing the slope values of the calibration graphs obtained using the different compositions and parameters we found that the optimum compositions exhibiting the best performance, for OM-TPB attained up on 5% ion associate, 47.5% of graphite and 47.5% of corn oil).

Table 1. Composition of oxomemazine carbon paste membrane electrodes and slopes of their corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 30 min of soaking in $10^{-3} \text{ mol L}^{-1}$ OMCl.

OM-TPB electrodes	Composition % (w/w)				
Parameters	Ion associate 3	Ion associate 5	Ion associate 7	Ion associate 9	Ion associate 12
Graphite	48.5	47.5	46.5	45.5	44.0
Corn oil	48.5	47.5	46.5	45.5	44.0
Slope mV/decade	52.2	57.7	56.1	54.8	49.9
RSD%	1.28	1.75	0.72	0.86	1.22
Linearity range (mol L^{-1})	1.5×10^{-5} - 1.0×10^{-2}	3.1×10^{-5} - 1.0×10^{-2}	1.5×10^{-5} - 1.0×10^{-2}	3.1×10^{-5} - 1.0×10^{-2}	1.9×10^{-5} - 1.0×10^{-2}
LOD (mol L^{-1})	1.2×10^{-5}	2.5×10^{-5}	1.0×10^{-5}	2.5×10^{-5}	1.5×10^{-5}
LOQ (mol L^{-1})	3.99×10^{-5}	8.32×10^{-5}	3.33×10^{-5}	8.32×10^{-5}	4.99×10^{-5}
Response time (s)	10	10	10	10	10

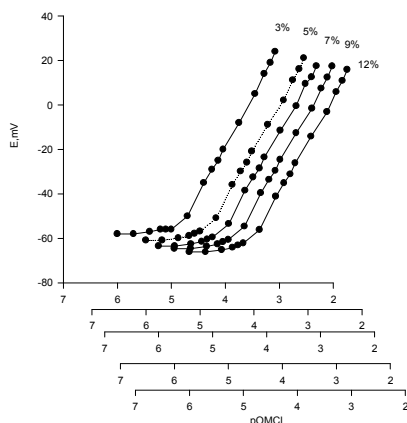


Fig. 2. Calibration graphs using OM-TPB Carbon paste electrode corn oil at different ion associate percentage.

3.2. Effect of Plasticizer

Table 2. Effect of plasticizers on oxomemazine carbon paste membrane electrodes and slopes of their corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 30 min soaking in 10^{-3} mol L $^{-1}$ of OMCl.

OM-TPB electrodes	Plasticizer (5%)			
Parameters	Without plasticizer	Corn oil	Sun flower oil	Olive oil
Slope mV/decade	56.1	57.7	50.6	59.8
RSD%	0.79	1.68	1.98	1.22
Linearity range (mol L $^{-1}$)	1.5×10^{-5} - 1.0×10^{-2}	3.1×10^{-5} - 1.0×10^{-2}	5×10^{-5} - 1.0×10^{-2}	3.9×10^{-5} - 1.0×10^{-2}
LOD (mol L $^{-1}$)	1.2×10^{-5}	2.5×10^{-5}	3.9×10^{-5}	3.1×10^{-5}
LOQ (mol L $^{-1}$)	3.99×10^{-5}	8.32×10^{-5}	12.98×10^{-4}	12.98×10^{-4}
Response time (s)	10	10	10	10

3.3. Effect of Buffer

Using of different buffers is shown in table (3) note that phthalate buffer gives the highest slope with lower difference in slope value with phosphate and acetate. This indicate that the electrode condition stable and the change by adding buffer solutions is low.

Table 3. Effect of buffer on oxomemazine carbon paste membrane electrodes and slopes of their corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 30 min soaking in 10^{-3} mol L $^{-1}$ of OMCl.

OM-TPB electrodes	Buffer		
Parameters	Phosphate	Acetate	Phthalate
Slope mV/decade	57.7	59.4	59.7
RSD%	0.89	0.79	1.68
Linearity range (mol L $^{-1}$)	3.1×10^{-5} - 1.0×10^{-2}	1.5×10^{-5} - 1.0×10^{-2}	3.9×10^{-5} - 1.0×10^{-2}
LOD (mol L $^{-1}$)	2.5×10^{-5}	1.2×10^{-5}	3.1×10^{-5}
LOQ (mol L $^{-1}$)	8.32×10^{-5}	3.99×10^{-5}	10.32×10^{-4}
Response time (s)	10	10	10

3.4. Effect of Soaking on Life-Span of the Carbon Paste Membrane Electrodes

Freshly prepared electrodes must be placed in soaking solutions to activate the surface of the membrane by forming an infinitesimal thin gel layer at which ion-exchange process occurs. This preconditioning requires different soaking intervals depending on diffusion and equilibrium at the interface; fast establishment of equilibrium is certainly a sufficient condition for fast response. The performance characteristics of the investigated electrodes were studied as a function of soaking times. For this purpose, the electrodes

The plasticizers used seem to have a significant influence on the response of the electrodes. three plasticizers with different polarities including corn oil, sunflower oil, and olive oil were examined as solvent mediator (Table 2, and Figure 2). Different plasticizer /PVC (w/w) ratios were studied; the 1:1 plasticizer/PVC ratio produce maximum sensitivity for all the plasticizers. The results reveal that olive oil is the best of the plasticizers tested in case of OM-TPB and corn oil, respectively. Poor sensitivities for the electrodes plasticized by other plasticizers are due to low solubilities or low distributions of OM-TPB ion exchangers in these solvents. The electrodes using olive oil, as a plasticizer provided not only higher Nernstian slope but also a wider response, more stable potential reading and a lower limit of detection.

were soaked in 10^{-3} M solution of OMCl for different time intervals (starting from 30 minutes reaching about 30 days) and then the effect of soaking on the calibration graph slope, concentration range and the response time was studied for each electrode independently. The results indicate that in case of (OM-TPB) electrode corn oil, the slope of the calibration graph was $59.7 \text{ mV decade}^{-1}$ after 30 min and remains constant till 24 hours, then decreased reaching nearly 58.8, 58.5, 58.4, and 56.1 mV decade^{-1} after 2, 8, 21, and 30 days of soaking.

The life span of the electrode is closely related to the nature of ion-exchanger, and its rate of leaching to the bathing

solution. Continuous soaking of the electrodes for elongated intervals of time affected negatively their response to the drug cation. This negative effect of soaking is attributed to the

leaching of the ion-exchanger and plasticizer to the bathing solution. This is related to the distribution equilibria and diffusion rates Armstrong (1990) and Buck (1994).

Table 4. Effect of soaking on corn oil carbon paste membrane electrodes at $25.0 \pm 1.0^\circ\text{C}$.

OM-TPB electrodes	Soaking time				
Parameters	0.5-24 h	2 days	8 days	21 days	30 days
Slope mV/decade	59.7	58.8	58.5	58.4	56.1
RSD%	0.78	2.64	0.86	1.45	1.22
Linearity range (mol L ⁻¹)	2.5×10^{-5} - 1.0×10^{-2}	1.5×10^{-5} - 1.0×10^{-2}	2.5×10^{-5} - 1.0×10^{-2}	1.5×10^{-5} - 1.0×10^{-2}	1.2×10^{-5} - 1.0×10^{-2}
LOD (mol L ⁻¹)	1.9×10^{-5}	1.2×10^{-5}	1.9×10^{-5}	1.2×10^{-5}	1.0×10^{-5}
LOQ (mol L ⁻¹)	6.32×10^{-5}	3.99×10^{-5}	6.32×10^{-5}	3.99×10^{-5}	3.33×10^{-5}
Response time (s)	10	10	10	10	10

3.5. Effect of Internal Filling Solution Concentration

Using a series of different concentrations of filling solutions in order to choose the best conditions of electrodes in case of corn oil the best concentration of filling solution is 10^{-3} OMCl + 10^{-1} NaCl.

Table 5. Effect of internal filling solution on oxomemazine carbon paste corn oil electrodes and slopes. of their corresponding calibration graphs at $25 \pm 1^\circ\text{C}$ and 30 min soaking in 10^{-3} mol L⁻¹ of OMCl.

OM-TPB electrodes	Filling solution mol L ⁻¹				
Parameters	10^{-2} OMCl	10^{-3} OMCl	10^{-4} OMCl	10^{-2} OMCl + 10^{-1} NaCl	10^{-3} OMCl + 10^{-1} NaCl
Slope mV/decade	51.6	49.5	56.3	49.5	59.6
RSD%	2.89	3.76	1.51	3.45	3.98
Linearity range (mol L ⁻¹)	1.5×10^{-5} - 1.0×10^{-2}	1.9×10^{-5} - 1.0×10^{-2}	2.5×10^{-5} - 1.0×10^{-2}	3.1×10^{-5} - 1.0×10^{-2}	3.1×10^{-5} - 1.0×10^{-2}
LOD (mol L ⁻¹)	1.2×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	1.9×10^{-5}	1.9×10^{-5}
LOQ (mol L ⁻¹)	3.99×10^{-5}	4.99×10^{-5}	4.99×10^{-5}	6.32×10^{-5}	6.32×10^{-5}
Response time (s)	10	10	10	10	10

3.6. Response Time of the Ion Selective Electrodes

The response time is the time which elapses between the instant when an ion-selective electrode and a reference electrode (ISE cell) are brought into contact with a sample solution (or at which the activity of the ion of interest in a solution is changed) and the instant at which the emf /time slope ($\Delta E/\Delta t$) becomes equal to a limiting value selected on the basis of the experimental conditions and on some requirements concerning the accuracy. The response time of the investigated electrodes was calculated according to this definition.

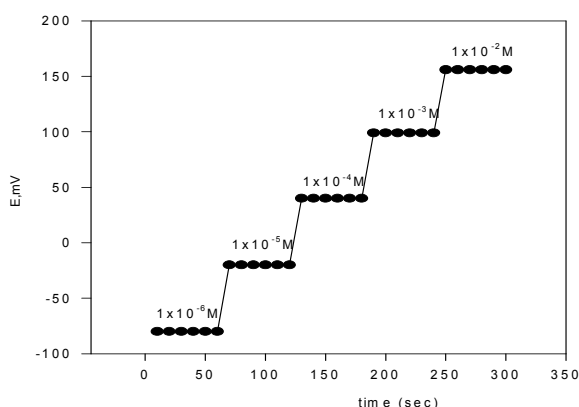


Fig. 3. Potential-time plot for OM-TPB corn oil carbon paste electrode.

3.7. Effect of pH

The effect of pH of the test solution on the potential

readings of the developed electrodes was studied. The variation in potential with change in pH was followed from pH 2.0 to pH 12.0 by the addition of small volumes of hydrochloric acid and sodium hydroxide (each 0.1-1.0 M) to 10^{-2} , 10^{-3} and 10^{-4} M solution of OMCl. The results indicated that the electrode did not respond to the pH change in the range 2.0-9.8 for OM-TPB corn oil. Figure (3). The decrease in potential occurring at higher pH values is most probably attributed to formation of the free oxomemazine base in solution, leading to a decrease in concentration of oxomemazine cation: a $pK_a = 10.6$ (Vytras (1990), Vytras (1997), Elmonem (2014) and Meloum (2004).

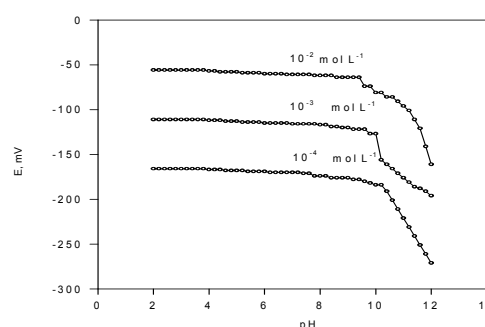


Fig. 4. Effect of pH of the test solution on the potential response using OM-TPB corn oil carbon paste electrode.

3.8. Effect of Temperature

3.8.1. Thermal Stability of the Electrodes

To study the thermal stability of the electrodes, calibration

graphs (E_{elect} vs p_{drug}) were constructed at different test solution temperature covering the range 30-70°C. The slope and usable concentration range of the electrode at different test solution temperature are given in Table (6) for OM-TPB corn oil and sun flower oil electrodes. The results indicate that the slopes of the calibration graphs slightly increase, however, still in the Nernstian range in spite of the increase of the temperature of the test solutions up to 70°C.

3.8.2. Determination of the Isothermal Coefficient of the Electrodes

The potential of ion-selective electrodes is usually affected by the temperature of the test solution. A thermally stable electrode is characterized by low thermal coefficient. This means the successful applicability of the electrode over a wide range of temperature. To calculate the thermal coefficient (dE°/dt) of the cell, the standard cell potentials, E°_{cell} , were determined at different temperatures from the respective calibration plots as the intercept of these plots at $p_{\text{drug}} = 0$, knowing that E°_{cell} is related to (dE°/dt) by the

equation (Reda Ammar (2012), Ali TA (2013), and oeschv (1986).

$$E^\circ_{\text{cell}} = E^\circ_{25^\circ\text{C}} + (dE^\circ/dt)(t-25) \quad (1)$$

Plot of (E°_{cell}) versus ($t-25$) produced a straight line; the slope of this line is taken as the thermal coefficient of the cell.

The value of the standard potentials of electrodes (E°_{elec}) were calculated after the subtraction of the standard electrodes potential of the calomel electrode at different temperatures.

Plots of (E°_{elec}) versus ($t-25$) for each electrode gave a straight line, The slope of the line was taken as the thermal coefficient of the electrode. The values of (dE°/dt)_{cell} are 1.00×10^{-3} and the value of (dE°/dt)_{electrode} are 1.666×10^{-3} for OM-TPB corn oil respectively. Revealing the high thermal stability of the studied electrodes within the investigated temperature range and show no deviation from the theoretical Nernstian behaviour.

Table 6. Performance characteristics of oxomemazine carbon paste membrane Corn oil electrodes at different temperatures.

OM-TPB electrodes	Temperature °C.				
Parameters	30	40	50	60	70
Slope mV/decade	56.1	57.1	58.4	59.4	59.7
RSD%	1.45	1.87	0.64	0.78	1.76
Linearity range (mol L ⁻¹)	1.5×10^{-5} - 1.0×10^{-2}	1.2×10^{-6} - 1.0×10^{-2}	3.9×10^{-5} - 1.0×10^{-2}	3.9×10^{-5} - 1.0×10^{-2}	5.0×10^{-5} - 1.0×10^{-2}
LOD (mol L ⁻¹)	1.2×10^{-5}	1.0×10^{-5}	3.1×10^{-5}	3.1×10^{-5}	3.9×10^{-5}
LOQ (mol L ⁻¹)	3.99×10^{-5}	3.33×10^{-5}	10.32×10^{-4}	10.32×10^{-4}	12.98×10^{-4}
E°_{cell} Mv	170	180	190	200	210
Response time (s)	10	10	10	10	10

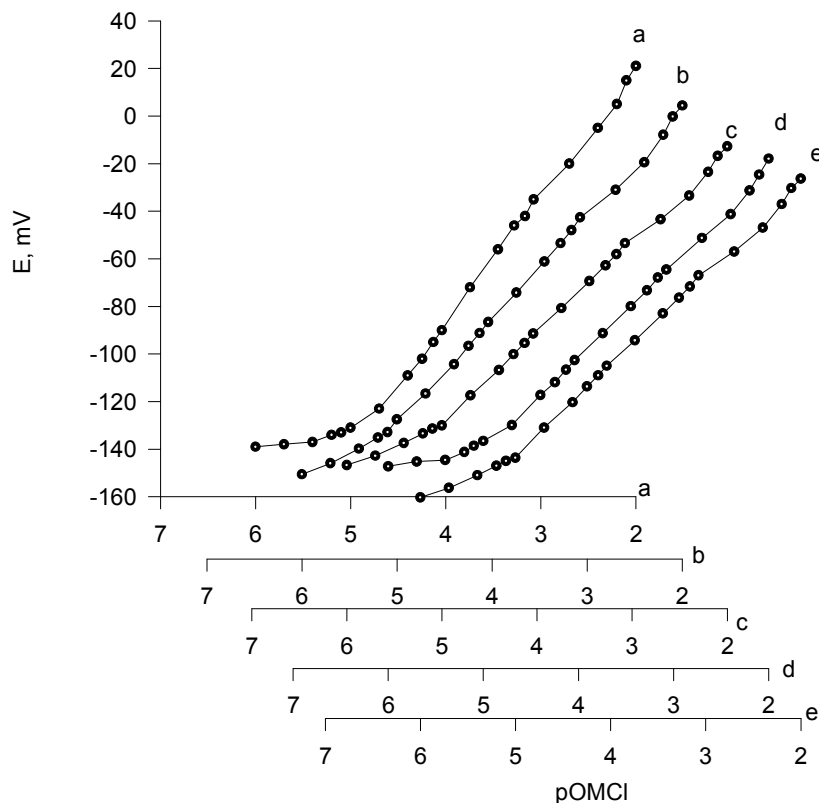


Fig. 5. Calibration curves using OM-TPB carbon paste electrode corn oil at test solution. temperatures of 30 (a), 40 (b), 50 (c), 60 (d), and 70°C (e).

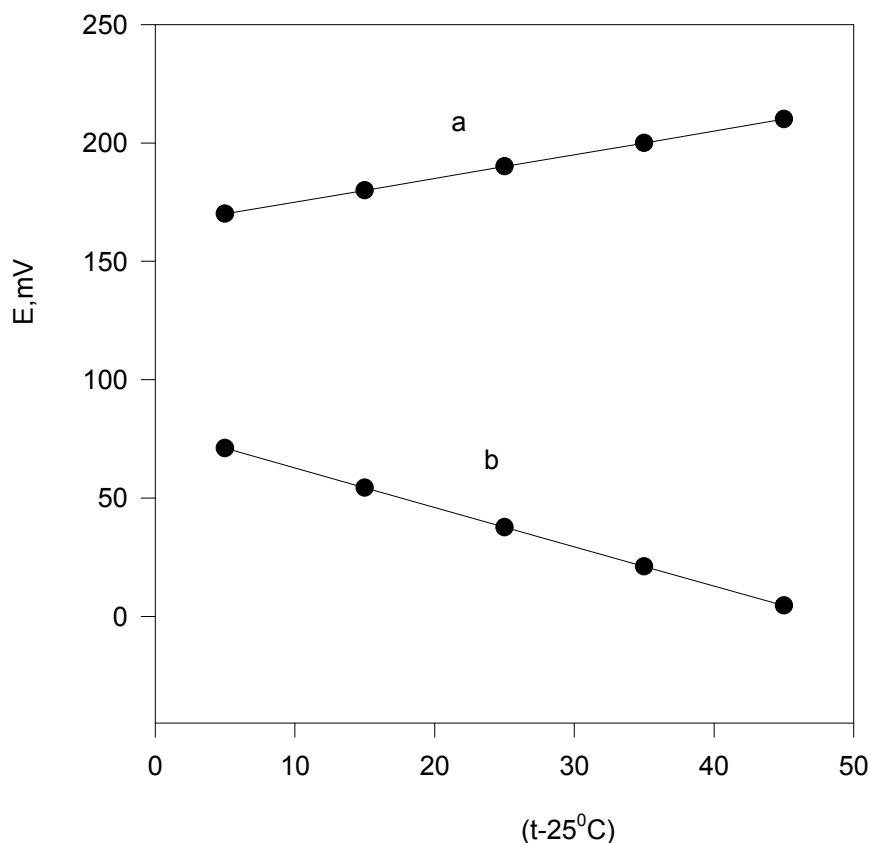


Fig. 6. Variation of the cell e.m.f (a) and standard electrode potential (b) with temperature for OM-TPB electrode. (e).

3.9. Selectivity of the Electrodes

The selectivity coefficient $K_{OMJ^{Z+}}^{pot}$ is the main source of information concerning interference on the electrode response. In analytical applications, the selectivity for the analyte must be as high as possible, i.e. the selectivity for foreign substances must be very small, so that the electrode exhibits a Nernstian dependence on the primary ion over a wide concentration range. The selectivity of the ion-exchanger of the sensor depends on the selectivity of the ion exchange process at the sensor-test solution interface and the mobilities of the respective ions in the matrix of the sensor. The hydrophobic interactions between the primary ions and the sensor are reflected by the values of the Gibb's energy of transfer for ions between aqueous and sensor phase.

The response of the electrodes towards different substances and ionic species such as inorganic cations, amino acids, sugars, vitamins was checked. The values of selectivity coefficients $-\log K_{OMJ^{Z+}}^{pot}$, shown in Table (7), were used to evaluate their degree of interference.

Since many years, the method of determination of selectivity coefficients of electrodes in potentiometric measurements was a subject of discussion in the literature Nagele (1686) and Yoshida (1998). Two specialized IUPAC committees were held concerning the determination of potentiometric selectivity coefficients Guilbault (1971). In the first IUPAC committee held in 1 (Abdel Ghani (2000). the separate solution method (SSM) was recommended only

if the electrode exhibits Nernstian response, but it was considered less desirable compared to fixed interference method (FIM), because it does not represent as well the actual conditions under which the electrodes are used. In 1995, the second IUPAC committee on methods for reporting selectivity coefficients, recommended the matched potential method (MPM) which is independent of Nicolsky Eisenman equation (Umezawa 1851).

In batch measurements of the present study, selectivity coefficients were determined by separate solution method (SSM) for ionic species and in case of neutral species the selectivity coefficients were determined by matched potential method (MPM). The selectivity coefficients value $-\log K_{OMJ^{Z+}}^{pot}$ of the electrodes listed in Table (7.) reflect a high selectivity of these electrodes towards oxomemazine cation.

The mechanism of selectivity is mainly based on the stereospecificity and electrostatic environment and it is dependent on how much fitting is present between the locations of the lipophilicity sites in the two competing species in the bathing solution side and those present in the receptor of the ion exchanger Abdel Ghani (2000). Inorganic cations do not interfere because of differences in ionic size, mobility and permeability. In cases of sugars, amino acids and vitamins, the high selectivity is mainly attributed to the difference in polarity and to the lipophilic nature of their molecules relative to OMCl.

Table 7. Selectivity coefficients – $\log K_{OM, J^{z+}}^{\text{pot}}$ for the OM corn oil electrodes.

Interferent	OM-TPB	
	SSM	MPM
Na ⁺	2.65	3.45
K ⁺	2.22	2.68
NH ₄ ⁺	1.65	1.90
Ca ²⁺	3.59	4.76
Mg ²⁺	2.77	3.56
Co ²⁺	3.59	4.30
Zn ²⁺	3.48	4.45
Ni ²⁺	3.26	3.98
Sr ²⁺	2.91	2.88
Ba ²⁺	4.26	4.65
Fe ³⁺	3.55	4.40
Cu ⁺²	3.22	3.76
Cd ⁺²	4.25	4.55
Glucose	-	2.40
Fructose	-	2.18
Maltose	-	2.25
Lactose	-	2.36
Alanine	-	2.29
Glycine	-	2.28
Urea	-	2.18
Ascorbic acid	-	2.19

3.10. Analytical Applications.

Several methods are applied for quantitative analysis using ion-selective electrodes. These comprise: (i) Direct calculation of the concentration applying Nernst equation. This method is subjected to several sources of errors, e.g. 1mV shift in electrode potential reading leads to 4n% errors where n is the change of the ion. (ii) potentiometric titration involving the use of counter ion as titrant ion which is more accurate depending essentially on the use of ISE as end point detector. (iii) The standard addition method, which is frequently applied in using ISE.

3.10.1. Potentiometric Determinations Applying the Standard Addition Method

The standard addition method, described in the experimental part, was proved to be successful for the determination of oxomemazine in pure solutions and in pharmaceutical formulations, using the prepared electrodes as sensors.

3.10.2. Determination of the Drug in Bulk and Pharmaceutical Formulation

The standard addition method, described in the experimental part, was proved to be successful for the determination of OM-TPB corn oil in pure solutions by using the respective electrode as sensor. This is clear from with small RSD values in ranges (2.65- 2.91%) (3.67 - 5.06%) and 0.85 -0.38) for OM-TPB carbon paste electrode membrane with corn oil, which reflects the high accuracy and precision of the electrodes.

3.10.3. Potentiometric Titrations

Though, the determination of concentration using potentiometric titration is time consuming, offers the advantage of high accuracy and precision, the end point can

be easily determined by a sharp potential break, also, the use of partially exhausted electrode is possible and the actual potential value at the end point is of secondary interest Ilcheva (1993).

The main idea of this type of titration depends on ion-associates formation. The feasibility of such titration depends on degree of completeness of the reaction. Since the equilibrium constant of precipitation titration is inversely proportional to the solubility product, it is natural that the smaller the solubility product of the formed ion-exchanger, the sharper is the end point. So, the determination of the solubility product of the precipitate is of prime importance if a titration, leading to the formation of this precipitate is under investigation. The reciprocal of the solubility product is approximately equal to the equilibrium constant of the precipitation reaction employed in the titration. Moreover, it has been shown (Vytras 1989, and Meites 1964) that in a precipitation titration curve, the point with maximum slope may slightly precede the equivalence point if the solubility product of the precipitate formed is relatively high.

The OM-TPB electrodes were proved to be useful for the determination in pure solutions by potentiometric titration against standard solution of sodium tetraphenyl borate. Representative titration curves are shown in at which, it is noticed that as the concentration of the drug increases, the inflection of the break point becomes more sharper than low drug concentration. The relative standard deviation (RSD) and the recovery values are listed in table (8, 9).

Table 8. Determination of OMCl in pure solution and pharmaceutical preparations applying the standard addition method on 5% corn oil. Carbon paste membrane electrodes.

Sample	Taken mg	Found mg	Mean Recover %	RSD %
OM-TPB pure solution	10.80	10.80	99.5	2.65
	21.60	22.40	97.3	2.66
	32.40	32.72	100	2.44
	43.20	42.72	98.9	2.91
Toplexile syrup	32.72	32.06	98	3.67
	65.44	65.44	99.3	4.66
	98.16	97.17	99	5.06
Rectoplexile suppositotry	3.30	3.29	99.5	0.85
	6.60	6.81	96.4	0.63
	9.90	10.16	102.7	0.38

Table 9. Determination of OMCl in pure solution applying potentiometric titrations method on 5% corn oil. (Carbon paste membrane electrodes potentiometric titrations)

Sample	Taken ml	Found ml	Mean Recover %	RSD %
OM-TPB	3	3.01	99.5	2.65
pure solution	9	9.2	97.3	2.66

4. Conclusion

The present work has successfully demonstrated the fabrication of OX-CPE electrode utilizing different preparation methods. The fabricated electrodes showed Nernstian slopes in the concentration range 10^{-6} - 10^{-2} mol L⁻¹ with fast response time (15 s), and long operational life time (4 weeks). The fabricated electrodes were successfully

applied as end point indicator electrode for potentiometric titration of OX with NaTPB in the concentration range 10^{-6} - 10^{-2} mol L⁻¹ with good accuracy and sensitivity. fabricated electrode possessed shorter response time (10 s) compared with drug electrode.

References

- [1] L. L. Antropov. Theoretical Electrochemistry, Mir, Mosco, 1977.
- [2] A. M. El-Didamony. Arch Pharm Chem Life Sci 338 (2005) 190.
- [3] R. D. Armstrong, G. Horvai. Electrochem. Acta, 35 (1990) 1.
- [4] N. T. Abdel-Ghani, A. F. Shoukry, S. H. Hussein (2002) J Pharm. Biomed Anal 30 (2002) 601.
- [5] T. A. Ali, G. G. Mohamed, M. M. I. El-Dessouky, S. M. A. ElElla, R. T. F. Mohamed (2013) Int. J. Electrochem. Sci., 8 (2013) 1469.
- [6] N. T. Abdel Ghani, M. S. RizK, R. M. RizK, R. M. El-Nashar. analyte 125 (2000) 1129.
- [7] R. P. Buck, E. Lindner. Pure Appl. Chem 66 (1994) 2527.
- [8] M. A. Elmonem, S. A. Abdulla. Res. J. Pharm. Bio. Chem. Sci., 5 (2014) 1113.
- [9] G. G. Guilbault, pure Appl. Chem., 25 (1971) 727.
- [10] G. Hoogewijs, D. L. Massart. J Pharm Biomed Anal 2 (1984) 449.
- [11] Y. M. Issa, A. F. Shoukry, and R. M. El-Nashar. J Pharm Biomed Anal 26 (2001) 379.
- [12] L. Ilcheva, M. Trojanowicz, and T. K. Velkrawczyk, Fresenius Z (1993).
- [13] J. isoe, E. kaneko, S. hoshi, K. Akatsuka. Bunseki Kagaku 51 (2002) 657.
- [14] E. Khaled, H. N. A. Hassan, M. S. Kamel, B. N. Barssoum. Curr Pharm Anal 3 (2007) 262.
- [15] M. Meloum, T. Syrový, A. Vrana, Talanta 62 (2004) 522.
- [16] L. Meites. J. A. Goldman, Anal. Chem. Acta, (1964) 30:200.
- [17] A. F. Shoukry, N. T. Abdel-Ghani, Y. M. Issa, and H. M. Ahmed Electroanalysis (1999) 11: 443- 446.
- [18] M. Nagele, E. Bakker, E. pretsch, Anal. Chem (1999) 71: 1041.
- [19] V. Oesch, W. Simon. Clin. chem, 32 (1986) 1148.
- [20] A. Reda Ammar, Haleemaotaif, and Abdulrhman Al-warthan. Int. J. Electrochemsci 7 (2012) 2531.
- [21] A. F. Shoukry, N. T. Abdel-Ghani, Y. M. Issa, and H. M. Ahmed. (1999) Electroanalysis 11 (1999) 443.
- [22] Y. Umezawa, K. Umezawa, K. Buhlmann, K. Tohda, S. Amemiya. (2000) pure Appl Chem., 72 (2000) 1851.
- [23] Vytras K. (1985) Electrode Rev 7: 77
- [24] K. Vytras. J. pharm.Biomed. Anal., 7 (1989) 789.
- [25] K. Vytras. Czech Chem. Commun 55 (1990) 941.
- [26] K. Vytras, J. Kalous, J. Jezkova. J. Anal. Chem., 6 (1997) 107.
- [27] M. Yoshida, K. Matsui, K. Maeda, S. Kihara, Anal. Chem. Acta, 374 (1998) 269.
- [28] D. Zivanov-Stakic, L. Deric. Arch Farm 29 (1979) 21.