

Assembly and Application of New Calcium Ion –Selective Electrode for Determination of Calcium Ions .

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Abstract:

A new calcium ion- selective electrode was prepared from calcium glyoxalate complex doped with PVC and plasticizer .The electrode was characterized by its stable Nernstian response 59.9 mV/decade . with a linear range of $(10^{-5} - 10^{-1})\text{ M}$, detection limit of 10^{-5} M and response time of $(20 - 60\text{ sec.})$ within the electrode lifetime which lasted four months. Suitable pH range for electrode response was $(5 - 9)$ and little temperature effect was found on the efficiency of the electrode. High selectivity of the electrode to calcium ions in the presence of many cation was found which clarified from the lower potentiometric selectivity coefficients . Most of the anions are severely interfered as a result of precipitation or stable complex formations with calcium ions and these interferents were exploited in the determination of the anions or the calcium ions. Encouraging and promising results were obtained using this new calcium ISE in the determination of calcium in drinking water and human blood serum coincidental with the spectrophotometric methods.

Keywords: Calcium Ion-Selective Electrode (Ca- ISE) , Glyoxal bis (2-Hydroxyanil) (GBHA), Poly Vinylchloride (PVC) , Tetrahydro Furan(THF) , Plasticizer , Ca-BiSTMBPP ion-exchanger.

Introduction :

The first calcium ion-selective electrode was fabricated by Ross (1) in 1967 for clinical purposes . The assembly of the electrode was based on liquid ion-exchanger and neutral carrier (2) .The best development of calcium ISEs was the incorporation of ion exchanger or neutral carrier in PVC matrix (3,4) . These PVC matrices membrane ISEs were simply designed , considerably economic in sensor materials and offer longer life times which led to more and wide applications (5) especially in clinical analysis (6-8).

Recently , a new calcium ISEs was fabricated from calcium complex with zincon in PVC instead of ion-exchangers or neutral carriers (9) . The electrode found wide applications in the determination of calcium ions using different techniques . After the success of using calcium complex with zincon doped in PVC to prepare an electroactive membrane for calcium determination , the present work is concentrated on the homemade of new calcium ion-selective electrode from the complex with Glyoxal bis (2 - hydroxyanil , GBHA) doped in PVC with certain plasticiser and solvent .

Experimental:

All chemicals used in this investigation are of analytical-reagent grade . Double distilled water was used for the preparation of solutions. Most measurements were carried out at room temperature .

Preparation of calcium glyoxalate complex (10) :

100 ml of 0.01 M of alcoholic solution of glyoxal (GBHA) was added to 200 ml of 0.02 M of alcoholic solution of NaOH with continuous stirring at room temp. until pale yellow colour was observed. The whole mixture was gradually added with stirring to 300 ml of 0.01 M CaCl_2 in a waterbath at 60°C . The mixture got red colour which was an indication of complex formation. The mixture was left at this temperature until smooth red precipitate occurred , then kept at 80°C for two hours until complete coagulation of the precipitate. The precipitate was filtered , washed and dried at 110°C and then reserved in a desiccator containing silica gel .

Identification of Ca-GBHA Complex:

IR Identification :

IR spectra of GBHA and Ca-GBHA complex were measured in KBr discs using Philips PU 9706 IR

spectrophometer in the range of ($4000-600$) cm^{-1} on the same chart .

UV-Vis analysis of glyoxal and its complex with Ca :

Small amounts of GBHA and Ca-GBHA complex were dissolved in ethanol to form 10^{-4}M for each and the UV-Vis spectra were taken using 760 JENWAY UV-Vis spectrophotometer in a range of ($200-800$) nm against ethanol as a blank. Absorption bands spectrum were obtained for GBHA at certain wavelength which were shifted into longer wavelengths for Ca-GBHA complex.

Determination of the percentage of calcium in Ca-GBHA complex :

0.2 g of Ca-GBHA was ashed in a Muffle furnace at 500°C for one hour. The residue was dissolved in sufficient volume of HNO_3 (1:1) and completed to 50 ml with distilled water. A flame emission photometer (Jenway, UK) was calibrated by series calcium standard solutions and the concentration of calcium in the Ca-GBHA complex was picked up from the calibration curve.

Preparation of the master membranes of Ca-ISEs:

The master membrane of the Ion-Selective electrode was prepared according to the technique of Craggs et al (11), which involved mixing 0.4 g of Ca-GBHA with 0.36 g of Tributylphosphate (as plasticiser) with stirring until homogeneous mixture was observed. A mixture of 0.1 g of PVC (BreonIII EP, BP Chemicals International Ltd.) was dissolved in 5 ml of THF and added to the above mixture with continuous stirring. The whole mixture was transferred into a cylindrical glass casting fixed on a smooth glass plate. The glass cylinder was covered with filter paper pad and held by a suitable weights and left for 24 hours for gradual evaporation of the solvent. The membrane was prised out from inside edges of the ring, wrapped with tissue paper and stored in a plastic container and kept in a refrigerator at 4°C .

By the same technique, three other master membranes were prepared using calcium bis[$(1,1,3,3\text{-tetra methylbutyl})\text{phenyl}]$ phosphate (Ca-Bis TMBPP) ion exchanger for comparison, Ca-GBHA with Iodine in ratio of (1:1) and Ca-GBHA with calcium Bis TMBPP in ratio of (1:1) as shown in table (1) hoping to improve the selectivity and sensitivity of Ca-ISE No(1).

1	0.4 g Ca-GBHA complex	Tributylphosphate
2	0.4 g Ca-Bis TMBPP ion exchanger	Tributylphosphate
3	0.4 g Ca-GBHA + 0.4 g Ca-Bis TMBPP	Tributylphosphate
4	0.4 g Ca-GBHA + 0.4 g I ₂	Tributylphosphate

Assembly of Ca-ISEs:

A disc of 1 mm diameter and 0.5 mm thickness from each master membrane was cut by suitable porer and held to polythane tube by adhesive of PVC in THF. The polythane tube was filled with a mixture of 0.1M CaCl_2 and 0.1M KCl saturated with AgCl to form the internal reference solution. Ag/AgCl electrode was inserted inside the internal solution and connected to a convenient cable to the ion-meter. The electrode was put in 0.1M calcium ion solution for 24 hours before application.

Calibrations of the assembled Ca-ISE:

A series of standard solutions ranged from $10^{-6} - 10^{-1}\text{M}$ were prepared from calcium chloride di-hydrated salt.

The calibrations were performed for all the prepared electrodes and the recorded potentials were plot versus $\log [\text{Ca}^{2+}]$ and from the calibration curves many important informations were obtained like slopes, linear ranges, detection limits which illustrate the efficiencies of the electrodes. Calibrations were also accomplished at different periods to find out the active lifetimes of the electrodes.

pH effect on the responses of the electrodes:

Tris-Buffer (Tris (Hydroxy methylamino methane)) was used to prepare buffer solutions with pHs in the range of $7.3 - 11.7$ applying hydrochloric acid (10% and 20%) to lower pH and concentrated ammonia to raise it. The potentials of the prepared solutions were measured by Ca-ISEs relative to saturated calomel reference electrode and plotted VS. pH values.

Effect of temp. on the response of Ca-ISEs No. 1 :

The effect of temperature on the response of Ca-ISE number (1) was studied by potential measurements for a series of calcium standard solutions at different temperatures (20°C , 30°C and 40°C). The slopes determined by Ca-ISE No. (1) were not mostly affected by temperature changes. But the electrode membrane were intensively affected by high temperatures (above 60°C) at which the membranes decomposed and solubility of the components

Table(1) : The master membranes for Ca-ISEs.

No. of the membra-ne	Electroactive material	Plasticier 0.36 g
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especially the Ca-GBHA complex and the plasticizer(١٢) .

Interference studies of cations on calcium ion determination by Ca-ISE No. (١) :

Mixed solution method(١٣) was used to study the effect of a number of cations on the response and selectivity of the new Ca-ISE number (١) .The method involved constant activity of the interferent ion while variation the calcium ion activity in the range of $10^{-5} - 10^{-1}$ M. The following ions ; Na^+ , K^+ , NH_4^+ , Ag^+ , Ba^{2+} , Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Al^{3+} , Cr^{3+} and Fe^{3+} were examined as interferents in the determination of calcium ions

put
and selectivity coefficient , $K_{Ca,M}$.

The potentiometric selectivity coefficients were calculated from the following relation :

$$a_{Ca^{2+}} = K_{Pot,Ca,M} \times a_M^{Z_{Ca}/Z_M}$$

Where $a_{Ca^{2+}}$ = the activity of calcium ions which were practically determined from the calibration curve , a_M = the activity of the interferent cation and Z_{Ca} and Z_M are charges of Ca^{2+} and interferent cation respectively .

Applications of the Ca-ISE No.(١) :

Determination of Calcium in drinking water:

Direct potentiometric method , calibration curve method and potentiometric titration method were applied for the determination of calcium ion in drinking water using the new Ca-ISE No.(١) relative to reference calomel electrode.

The classical titration method of calcium ions with EDTA in the presence of murexide metal -ion indicator was used to determine calcium ions for comparison at pH = ١٢ (١M NaOH) .

Flame atomic emission method was also used to determine calcium ions in drinking water for comparison which was considered the reference method.

Potentiometric titration determination of some anions with calcium ions:

Since most of anions are severely interfered in the determination of calcium ions as a result of precipitations and complex formations , this technique was utilized in the determination of oxalate , sulphate , carbonate , phosphate and fluoride ions , using different concentrations . A clear , suitable and practical potential shifts were observed at equivalence points. Chloride and Nitrate ions don't interfere , thus , calcium

chloride and calcium nitrate solutions were used as standards for calibration of Ca-ISEs.

Determination of calcium in human blood serum:

Three samples each of ٥ ml of blood were taken from three persons and transferred into centrifuge tubes and left for half an hour at room temperature . The tubes were transferred into a centrifuge and switched on in a speed of ٣٠٠ rpm for ten minutes to get blood serum.

The blood serum was transferred into clean and dry tubes and firmly tied up and kept at $-٢٠^{\circ}C$ until biochemical tests. The calibration curve method was set up to determine calcium concentration in blood serum using the new Ca-ISE No(١).

A spectrophotometric method(١٤) was also used for comparison depending on the complex formation of ortho- cresolphthaline with calcium at pH ١٠,٧ and at wavelength of ٥٧٠ nm.

Results and Discussions :

(١) Identification of the glyoxal and its complex with calcium ion:

IR Spectra of glyoxal and its complex with calcium ions :

Table(٢) depicts IR spectra of the functional groups of glyoxal and its calcium complex. It is clear from the table the absorption band at 1604 cm^{-1} of C=N group in glyoxal has shifted into lower wave number 1590 cm^{-1} in the complex due to participations of the imine group C=N in the coordination sites with calcium ion.

The disappearance of the absorption band at 3379 cm^{-1} due to OH phenol groups in the complex is an indication of engagements of both OH groups in the formation of the complex , after displacement of acidic hydrogen ion(١٥). The appearance of broad peak at 3417 cm^{-1} in the complex represents the absorption band of water molecules only in the complex which offers it octahedral form(١٦).

Table(٢) : IR spectra of functional groups in glyoxal and its complex with calcium.

Group	Glyoxal cm^{-1}	Glyoxal complex cm^{-1}
HC=N	١٦٠٤	١٥٩٠
O-H	٣٣٧٩	OH, ٣٤١٧
C – N	١٣٤٢	١٣١٩
C – H	٣٠٦٨	٣٠٦٢
C– H aromatic	٣٠٤٠	٣٠٠٨
O – H bending	١٤٤٢	١٣٧٣
C=C aromatic	١٥٠٦	١٤٥٠

UV-Vis Spectral analysis of glyoxal and its complex:

Three absorption bands were obtained in glyoxal at 216, 298 and 360 nm which were shifted into longer wavelengths in the complex at 203, 320 and 310 nm table (3).

These shiftings were due to the engagement of imine and hydroxyl groups in coordination with calcium ions(17). Therefore, the opportunities of formation of inter and intra molecular hydrogen bondings in glyoxal were lowered or diminished in the complex which assist the transferring of electrons at lower energies and higher wavelengths which is another indication of complex formation.

Table (3) UV-Vis absorption bands of glyoxal and its calcium complex in ethamal.

Glyoxal		Calcium Glyoxalate Complex	
Absorban-ce	Wavelength (nm)	Absorban-ce	Wavelength (nm)
3,000	216	3,180	203
1,049	298	1,143	320
0,663	360	1,816	310

Percentage of calcium in calcium glyoxalate complex.

Flame atomic emission technique was applied to determine calcium in calcium glyoxalate complex using calibration curve method. The percentage was found to be 12,63% with a standard deviation of $\pm 0,22$. The theoretical percentage of calcium was calculated and found 12,73% which insured the combination of two water molecules with complex to form the octahedral structure (16) of the complex in order to approach this percentage. Fig(1) exhibits the proposed structures of glyoxal and its complex with calcium.

(2) :Calibration of the four calcium Ion-selective electrodes:

The electrodes were calibrated using a series of standard calcium solutions in concentrations ranged (10-6 -10-1) M, relative to calomel reference electrode. Table(4) includes information obtained from the calibration curves of these electrodes.

Table (4) : Slopes and lifetimes of the fabricated calcium ISEs.

No	Component of the electrode membrane		Slopes in beginning	Lifetime of the electrode	Slop-es in the end
	Active Material	Plastici-ser	mV/De-cade		mV/De c-ade
1	Ca-GBHA Compl-ex	Tributyl phosph-ate	29,97	4 months	23,0

2	Ca-Bis-TMBPP	Tributyl Phosph-ate	29,96	3 months	23,7
3	Ca-GBHA + Calcium Bis-TMBPP	Tributyl Phosph-ate	28,60	2 Months	23,9
4	Ca-GBHA + Iodine	Tributyl Phosph-ate	29,17	0 weeks	23,3

The linear range of the response of the electrodes were (10-5 - 10-1) M with a detection limit of 10-5 M and response time in the range of (20-60) sec.(Fig. 2).

The response time became longer for dilute solutions and multi use of the electrodes(18). The calibrations of the electrodes were carried out at different periods. The electrode lifetime approached its end when its slope became very low and far from Nernstian and its linear range has been shortened to (10-3 - 10-1) M.

The response mechanism of the electrodes depend on the ionic conductivity of calcium ions within the membrane and their exchange with the corresponding calcium ions in the external solutions that generates a potential directly proportional to the log activity or concentration of the calcium ions (19).

It is clear from table(4) that the Ca-GHBA, Ca-ISE No.(1) is superior to the electrode No.2 assembled from Ca Bis -TMBPP ion exchanger from the higher slopes values and longer lifetime. It was anticipated that improvement may be attained to ISE No.(1) by addition either the ion exchanger or Iodine, but shorter lifetimes and lower slopes were obtained (Table 4). Therefore, there is no advantages from addition ion exchanger or iodine to Ca-GHBA complex and most of the research was confined on Ca-ISE No.(1).

(3) : pH effect on the response of the new Ca-ISE No. (1).

The best pH for the linear response of the new Ca-ISEs No.(1) was found in the range of (0-9) where the electrode response was suitable and steady for most calcium ion concentrations, (Fig. 3).

The range was diverged with more dilutions of concentrations where the response was affected by the extreme acidic and basic media At pH above 9, the

decrease in electrode response was due to formation of $\text{Ca}(\text{OH})^+$ which is not responded by the electrode and the formation of $\text{Ca}(\text{OH})_2$ precipitate ($\text{pH} > 10$).

At pH less than 10, the elevation in electrode response was due to increase in hydrogen ions which penetrate inside the membrane causing positive increase in potential as a result of response of the electrode to hydrogen ions in addition to calcium ions ($\text{pH} < 10$).

This range of pH is near to the pH range of Ca-ISEs fabricated from calcium and zincom complex ($\text{pH} \approx 10$) ($\text{pH} \approx 10$).

(4) : Interference studies of cations on the response of the new Ca-ISE No(1) :

It was found in this research that there is no interference of the cations: Na^+ , K^+ , Mg^{2+} , Ba^{2+} , NH_4^+ , Ni^{2+} , Co^{2+} and Fe^{3+} on the response of the new Ca-ISE No.(1) at low concentrations (10^{-5} - 10^{-3}) M. The electrode has recorded rather little effect of these cations (Table 6). However, the selectivity of the electrode was relatively high which was proved from the very low values of selectivity coefficients in the range of (10^{-5} x 10^{-3} - 10^{-5} x 10^{-2}) (table 6). The lower interferences exhibited in the presence of sodium, potassium and magnesium ions would enable the electrode to be used in the biological researches and studies(7).

Table (6) selectivity coefficient of the new Ca-ISE No. (1) in the presence of various activities of some cations.

Interference	Activity of interferent (aM) M	aCa ²⁺ from the graph	Selectivity coefficient
Na^+	10^{-5} 10^{-1}	10^{-5} $2, 5 \times 10^{-5}$	10^{-5} $2, 5 \times 10^{-5}$
K^+	10^{-5} 10^{-1}	10^{-5} $2, 5 \times 10^{-5}$	10^{-5} $2, 5 \times 10^{-5}$
Mg^{2+}	10^{-5} 10^{-1}	10^{-5} $1, 5 \times 10^{-5}$	10^{-5} $1, 5 \times 10^{-5}$
Ba^{2+}	10^{-5} 10^{-1}	10^{-5} 10^{-5}	10^{-5} 10^{-5}
NH_4^+	10^{-5} 10^{-1}	----- $5, 9 \times 10^{-5}$	----- $5, 9 \times 10^{-5}$
Ni^{2+}	10^{-5} 10^{-1}	10^{-5} 5×10^{-5}	10^{-5} 5×10^{-5}
Co^{2+}	10^{-5} 10^{-1}	10^{-5} 5×10^{-5}	10^{-5} 5×10^{-5}
Fe^{3+}	10^{-5} 10^{-2}	10^{-5} $1, 5 \times 10^{-5}$	10^{-5} $1, 5 \times 10^{-5}$
Ag^+ , Zn^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+}	10^{-5} - 10^{-1}	No interferences	

(5) Applications of the new Ca-ISE No(1) :

Determination of calcium ion concentration in drinking water (tap water) :

Table(7) shows a summary of the calcium ion concentration found in drinking water by the new Ca-ISE No. (1) compared with other techniques. The results were in good agreement about $118,0$ ppm and matching the results obtained by flame atomic emission photometry. The relative errors were due to experimental errors.

The calcium concentration levels found in drinking water were within the acceptable World Health Organization specialists(8).

Therefore, the new Ca-ISE assembled from calcium glyoxalate complex offered high efficiency in determination of calcium in aqueous solutions.

Table (7): Calcium ion concentration in drinking water (tap water) (in ppm)

Method of analysis	Ca concentration (ppm)	Relative error %
Flame emission photometry	117,6	Reference Value
Direct potentiometry	117,2	-0,34
Calibration curve	118,0	0,34
Potentiometric titration with EDTA	117,2	-0,34
Classical titration with EDTA in presence of murexide indicator	117,3	-0,20

Determination of some anions by Potentiometric titration with standard calcium ion solutions:

Since most anions showed an intense interferences with calcium ions, these reactions were utilized in the determination. The concentrations of these anions by potentiometric titration with standard calcium solutions using the new ISE. No.(1) (Fig 4). Different concentrations of anions solutions were used and the results were compiled in table(8).

A sudden shift in potentials at equivalence points have been found for oxalate, carbonate, phosphate, sulphate and fluorides. However, there was no clear precipitate of calcium sulphate because of the high solubility of CaSO_4 (22) ($0,10\text{g/l} = 100\text{ mg/l}$) and $\text{KSP CaSO}_4 = 2,3 \times 10^{-5}$ at 25°C . Therefore, there was a suitable opportunity to form ion pairs Ca^{2+} , SO_4^{2-} instead of precipitate. Table(8) exhibits the results of potentiometric titrations of these anions with their relative errors which were attributed to experimental errors.

Table (V) Concentrations in (ppm) for five anions determined by titration with standard calcium ion solutions .

Anion	Added Concentration (ppm)	Recovery (ppm)	Relative error%
CrO_4^{2-}	٤٤٠	٤٤٥	+١,١٤
	٤٤	٤٣,٥	-١,١٤
	٤,٤	٤,٣	-٢,٢٧
SO_4^{2-}	٤٨٨	٤٨٦	-٠,٤١
	٤٩	٤٧,٨	-٢,٤٥
	٥,٥٦	٥,٤٣	-٢,٣٤
CO_3^{2-}	٣٣٠	٣٣٣	+٠,٩١
	٣٦	٣٤,٩	-٣,٠٥
	٣,٨	٣,٦٨	-٣,١٦
H_2PO_4^-	٤٨٥	٤٨٧	+٠,٦٥
	٤٧,٥٨	٤٧,٢٧	-٢,٨٦
	٤,٨٩	٤,٧٥	-٢,٨٦
F^-	٤٧٥	٤٧٨	+٠,٦٣
	٤٧,٥٥	٤٧,٣١	-٠,٥١
	٤,٨٦	٤,٧٥	-٢,٢٦

Determination of free calcium ion in human blood serum:

Table(٨) contains the concentrations of free calcium ions in three samples of human blood serum determined by Ca-ISE No.١ using calibration curve technique which were matching the results obtained by spectrophotometric method(١٤) . The first and third samples showed normal average levels of calcium concentrations in human body while the second sample showed shortage in calcium levels which should be cured(١٤).

Table (٨) : Results of calcium ion concentration determined by Ca-ISE No.(١) and spectrophotometric methods in human blood serum.

Sample No.	Sex and age(y)	Conc. By ISEs mg/l	Conc.by spectro mg/l	Normal average of calcium ٨٥-١٠٤ mg/l
(١)	Male , ٣٥	٩١,٤	٩٠,٤	Within the average
(٢)	Female , ٥٥	٧٩,٦	٧٥,٨	Less than the average
(٣)	Male , ٣٠	٩٥,٩	٩١,٧	Within the average

The little increase found by Ca-ISE No.(١) may be due to the little interferences of cations in the blood that should be characterized by a special blank.

Conclusion:

A new Ca-ISEs assembled from calcium glyoxalate complex offered high efficiency in determination of calcium ions in drinking water and blood serum . Little

interferences were found by many cations but most of anions were severely interfered which were exploited for determination either the anions or calcium ions.

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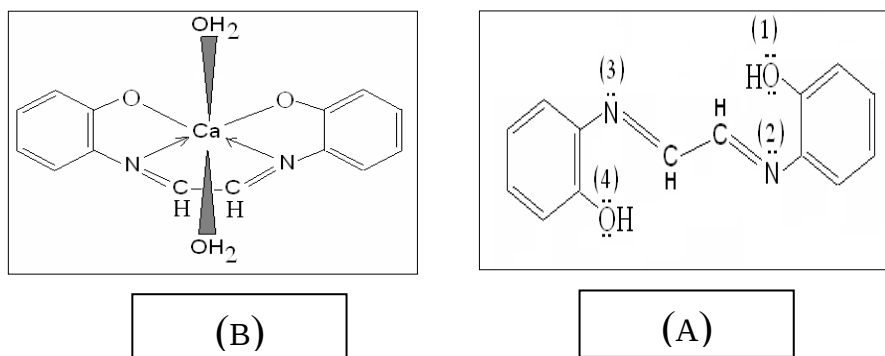


Fig (١) :A : Structure of formula of Glyoxal .

B : Octahedral form of Ca – Glyoxal

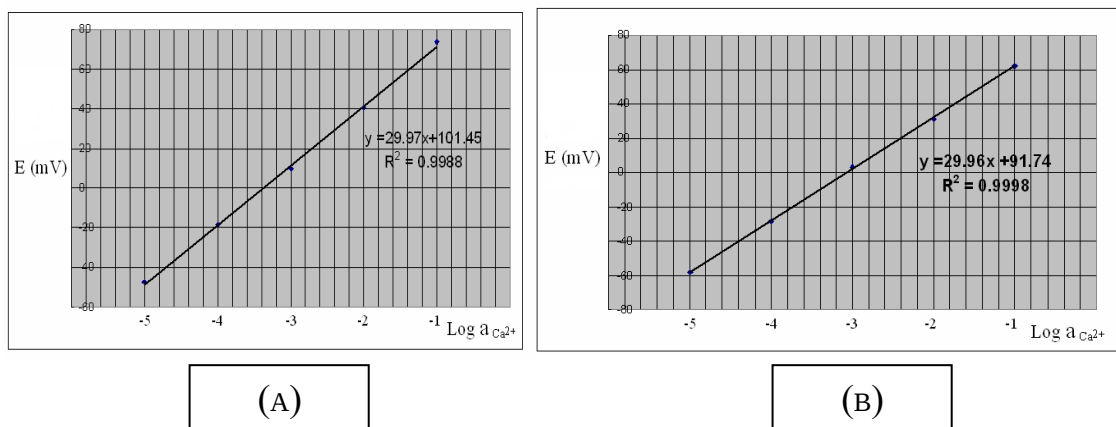


Fig (٢) :A : Calibration curve of new Ca-ISE No.١ in the first week of its use .

B : Calibration curve of CaBiSTMBPP electrode in the first week of its use .

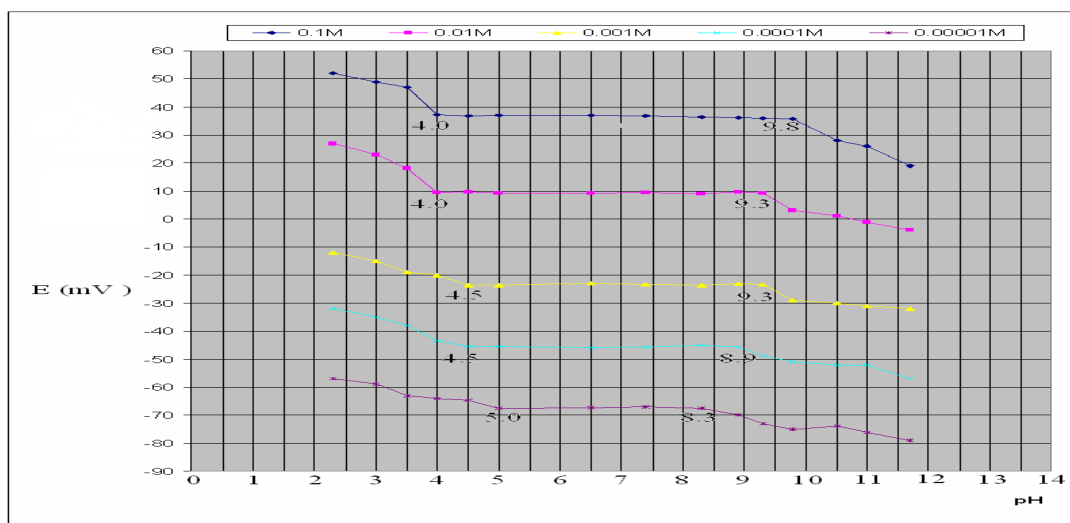


Fig (٣) : Effect of pH on the linear range of the new Ca – ISE No.١.

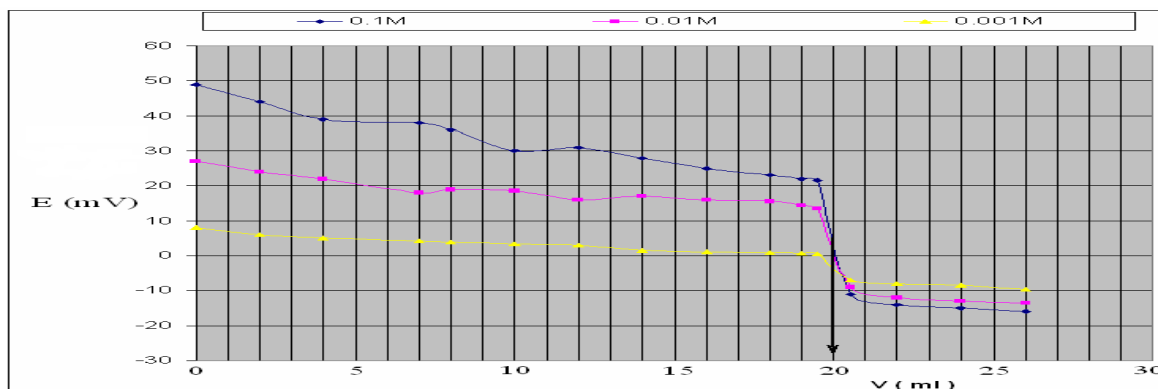


Fig (٤):Potentiometric titration curves of Calcium Chloride solutions with Sodium fluoride solutions at different concentrations using Ca-ISE No. ١

تحضير وتطبيق قطب جديد للكالسيوم الانتقائي لتقدير ايونات الكالسيوم .

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الخلاصة: حضر قطب جديد انتقائي لايونات الكالسيوم من معقد كلايوكسولات الكالسيوم المدمج في متعدد كلوريد الفيناييل (PVC) ومادة ملدنة . وقد تميز القطب باستجابته النيرنستية المستقرة (29.97 mV/decade) مع استجابة خطية في المدى ($10^{-5} - 10^{-1}$) مولاري وحد كشف يساوي 10^{-5} مولاري وزمن استجابة في المدى ($20-60$) ثانية بعمر للقطب يساوي أربعة أشهر . وكان مدى الـ pH الذي يعمل فيه القطب بدون تداخل H^+ , OH^- يساوي ($5 - 9$) وكان تأثير درجة الحرارة قليلا على كفاءة القطب . وقد أثبتت الانتقائية العالية لقطب الكالسيوم الجديد بوجود عدد كبير من الايونات الموجبة والتي تظهر جلوية من القيم الواطنة لمعاملات الانتقائية الجهدية في حين أن الايونات السالبة تتداخل بشدة نتيجة ترسيبها لايونات الكالسيوم أو تكوينها معقدات ثابتة معه . وقد استثمرت هذه التداخلات في تقدير تلك الايونات بتسحيحها مع ايونات الكالسيوم القياسية أو تقدير ايونات الكالسيوم بتسحيحها مع محلول إحدى تلك الايونات السالبة . وقد تم الحصول على نتائج مشجعة وطموحة باستعمال قطب الكالسيوم الانتقائي لتقدير ايونات الكالسيوم في مياه الشرب وتقدير الكالسيوم في مصل دم الإنسان مقارنة بالطرائق الطيفية المعتمدة في التحليلات المرضية.