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A NEW SELECTIVE ELECTRODE FOR ANALYSIS CERIUM (IV) IONS BY USING CARBON PASTE ELECTRODE (CPE) $_{CERIUM}$ MODIFIED

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ABSTRACT

In that work , we Adopt Preparation anew Carbon Paste electrode for Cerium ions based on complex (1,3-di phenyl-5- para nitro phenyl Formazan) With Cerium Ions As electroactive material The best component for Carbon paste electrode – Cerium (IV) ions :(4% Ionophore ,49,8% Graphite powder ,46% Plasticizers (Paraffin oil) ,0.2%NaTBPH)**.**The electrode exhibited a Nernstain slope of (14.76±1) mv per decade of Cerium Ions over concentration range of ($0.75{\times}10^{-7-}$ $0.50{\times}10^{-1}$) M in The PH range (3 - 6.8).By using (MPM) Matched Potential Method This electrode revealed good Selectivity for Cerium Ions over wide variety of other metal ions with (R= 0.999).The detection limit was (3.5^{x} 10^{-8}) M and The response time was about (20) s. The Electrode can be used for at least 3 months without a considerable divergence in potential response .the proposed electrode was used for determination of Cerium in a standard solutions and was successfully applied as an indicator electrode for potentiometric titration of Cerium Ions with EDTA.

INTRODUCTION

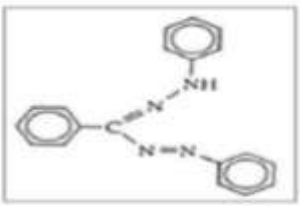
The world first know the rare earth elements (REE) 233 years ago¸ in 1788 [1] ,these elements were similar in their physical and chemical properties this allowed participation in the development of chemistry and industrial sciences. REE have a special importance in progress at the Nano Scale, technical, military, medicine and industries [2] .cerium was discovered in 1803 after the asteroid ceres in 1801. Cerium is the most abundant of the rare earth elements, Applications of cerium are abundant, they include various medical,technical, catalysis, permanent magnets [3] As well as to render glass opaque to nearultraviolet radiation , Cerium is used as component of some diesel fuel additives , and it may be added to residual diesel fuel additives [4]

The Current techniques existed in the Litreature for determain of Cerium(IV) include : Inductivity coupled plasma –atomic emission spectroscopy (ICP-AES) [5],Inductivity coupled plasma- Mass spectroscopy (ICP-MS) [6],Flame atomic absorption spectrometry [7],X-ray Flourecence (XRF) [8] , High Performance Liquid Chromatography [9], Stripping Voltametry [10-11] ,and Neutron Activation analysis (NAA) [12] Are various instrumental methods used for determination Cerium (IV) ions.However, These methods are time consuming,multi steps and require large infrastructure and are too expensive for many analytical laboratories .Thus ,the development of covenient and direct method to assay of cerium ions in different samples is urgently needed .Among the various classes of chemical sensors , ion-Selective electrodes were described (1906) and offered great advantages such as wide linear working range,low detection limits ,low-energy consumption,short response time hight selectivity and sensevity, lowcost [13] precisely , Carbon paste modified electrodes have appeared as a model of modified models for ion selective electrodes [14-15] , The ion selective Carbon paste electrode (ISCPE) and potentiometry method have some advantages over other membrane electrodes: such as "renewability , stable response, low ohmic resistance ,no need for internal solution ".[16]They are the most frequent use of Potantiometric sensors in analytical chemistry also in biochemical and biophysical fields [17] In this paper ,we aim to provide an overview of the current advancees in the cerium (IV) – selective potentiometric electrodes and its applications.

EXPERIMENTAL DETAILS

2.1. Reagent and materials:

Formazan pigment was purshacied from MERCK.The graphite powder (MERCK) with the paraffin oil, silicon oil , DBP,DOP,DOS (Aldrich) was high purity, cerium (IV) sulphate GR pro analysis and Nitrate salts of cations were purchased from MERCK. Deionized water was used for preparing all of the Solutions.



Formazan pigment

2.2. Construction of the modified electrodes:

Carbon paste electrode preparation desired of Formazan pigment , graphite powder , paraffin oil and tetra phenyl borate sodium as material to good Response Nernstain, These components were thoroughly mixed and then transferred into (syringe ,glass tube),of i.d.5 mm and a high of 3cm[18] . After the mixture was uniformed as well as possible, to avoid the formation of air gaps, the paste was packed carefully into the syringe (tube). This can prevent the increase of the resistance of the electrode. Then the electrical contact was made by inserting silver wire in to the opposite end. The working surface of the electrode was polished by using soft abrasive paper, then; the electrode was conditioned for 24 **h** by being soaked in a ($1.0^{x}\ 10^{-3}$) $mol.l^{-1}$ of Ce $(so4)_2$.4H2o solution [19]. Then the electrode was used for potentiometric measurements of this metal cation in solution. The type and the amount of the Carbon paste electrode (CPE)-$ce_{(IV)}$ ingredients graphite powder , ionophore , plastizers and additive) are important factors affecting the sensitivity ,selectivity and stability of the ion selective electrode [20] .therefore, it is essential to optimize their values to construct a selective electrode [21]with suitable electrochemical characteristics .in order to choose a suitable plasticizer , several tests were performed using **PARAFFIN OIL,DOS,DOP,DBP** and **silicon oil** and the experimental results showed that a good Nernstain behaviour is observed in the presence of PARRAFFIN Oil . Therefore, we use this plasticizer in in the construction of the proposed electrode. The ranges of the amounts of the ingredients of the selective (carbon paste electrode) Cerium which were studied shown in table (1).

2.3. Apparatus and Potantiometric measurements:

All potential measurement were carried out by the Following the electrochemical cell, where the electrochemical cell contained: a silver – silver chloride double – junction reference electrode REF361 (one 274-F01) as a reference electrode and the Cerium (IV) sensor as an indicator electrode [22]. The schematic figure (2) is as follows:

Ag- Agcl (Saturated) ‖ Sample Solution ‖Carbon paste electrode.

After EMF is Calculated, Calibration curve is drawn by plotting potential, versus, the logarithm of the cerium ions concentration**s.** We notice increase E (mv) for cell with increase the cerium ions concentrations.

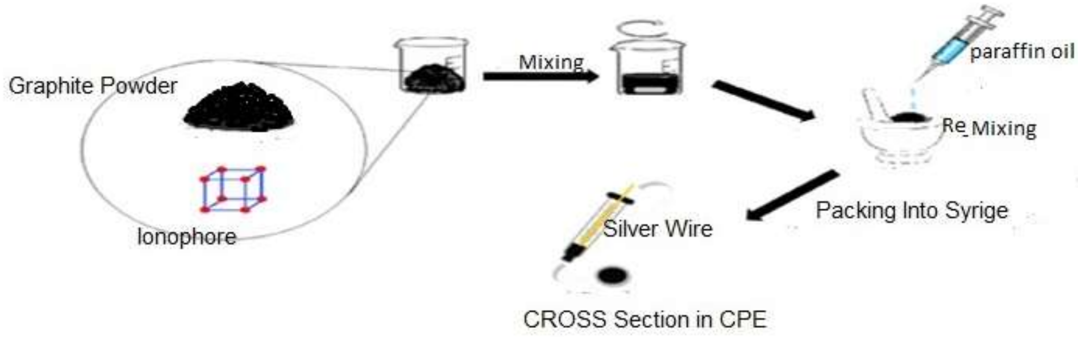


Figure (1): ingredients and preparing carbon paste electrode

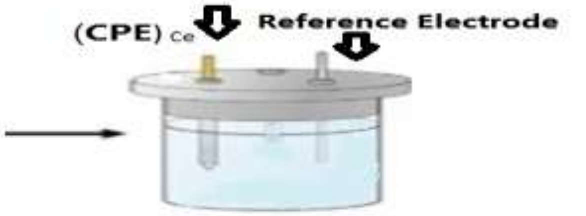


Figure (2): electroc ... posed as an indicator

Table (1): ... –Ce (IV) ion

Ionophore%			NaTPHB%
4.00%	49.80%	46.00%	0.20%

RESULTS AND DISCUSSION

3.1. Influence of nature and amount of plasticizers on electrochemical response of the electrode:

The response of an ion selective electrode depends on the amount and the nature of the ingredients of the carbon paste electrode . Since plastizers plays an important role in performance ion-selective electrodes[23], and the nature of plasticizers influences the dielectric constant of the carbon paste phase ,the mobility of the ionophore molecules in the carbon paste and also the state of ionophore [24], therefore, we preferred to choose the type of plasticizers .thus , several carbon paste electrode with similar composition of graphite powder ,ionophore and additive ,but five different composition of plasticizers with different dielectric constant were prepared and tested.

The result and summarized in table (2). The best electrochemical response was obtained in presence of (paraffin oil). Since the carbon, paste has a high lipophilicity, high molecular weight, low vapor pressure, and low tendency for exudation from the polymer matrix and high capacity to dissolve the substrate and the other additives present in carbon paste and also they should possess an adequate dielectric constant [25].Paraffin oil with high dielectric constant and good polarity can be affected the characteristics of the carbon paste and ionophore.

3.2. Determination of optimum effects of carbon paste electrode ingredients:

In the next step, for determination the optimum amount of carbon paste electrode ingredients. Ionophore, graphite powder, plasticizers and additive were chosen as the variables towards the electrochemical response of the constructed electrode .the amount of. Ionophore, graphite powder, plasticizers and additive [20] that were selected and listed in table (3) .these components represent 100 weight- percent of the total formulation that is:

A+B+C+D = 100%

A: Ion-exchanger
B: Graphite pow
C: Plasticizer
D: NaTBPH

3.3. Effect of pH :

On one of the important characteristics of an ion selective electrode is the pH range of the solution at which the pH does not affect the response of the electrode to the target ion .the effect of pH on the potential response of the constructed electrode was investigated over the pH range (2.0-13.0)in solution of (1.0×10^{-3})M and (1.0×10^{-4}) M of Ce(IV)ions .the pH of the solutions was adjusted with dilute solutions of HNO3 and NaoH .As is shown in figure (4), the potential remains constant over the pH range of 4.0 to 6.5.the change in potential at low pH values, may be attributed to the response of the electrode to the H_3O^+ ions I solution .At higher pH values than 6.5, the Ce(IV) ions may interact with OH^- ions in solution [25].

3. 4. Response time and lifetime of the electrodes

The response time of the carbon paste electrode is an important parameter for their analytical application. After successive immersion of the electrode in a series of its respective ion solutions, each concentration has 10-fold increase than in concentration previous (1.0×10^{-7}M to 1.0×10^{-3}M) of Ce (IV) ions solutions. The response of the electrode is stabilized after 20 S compared with before concentration, as is shown in figure (5).

The lifetime of an electrochemical sensor based on carbon paste electrode matrix, depended on the distribution coefficient of the ionophore and plasticizer between carbon paste electrode and aqueous phases and also depended on how to use the electrode [26].the experimental results were shown that the constructed could be used for at least (10) weeks without any change in the Nernstain slope and detection limit Figure (6).

Table (2): Effect polarity of plasticizers on the Nernstain slope

Paraffin oil	DOPH	DOS	DBPH	Silicon OIL
Slope(mv/decade)	Slope(mv/decade)	Slope(mv/decade)	Slope(mv/decade)	Slope(mv/decade)
14.76 mv/decade	19.39 mv/decade	15.80 mv/decade	21.71 mv/decade	**17.80** mv/decade

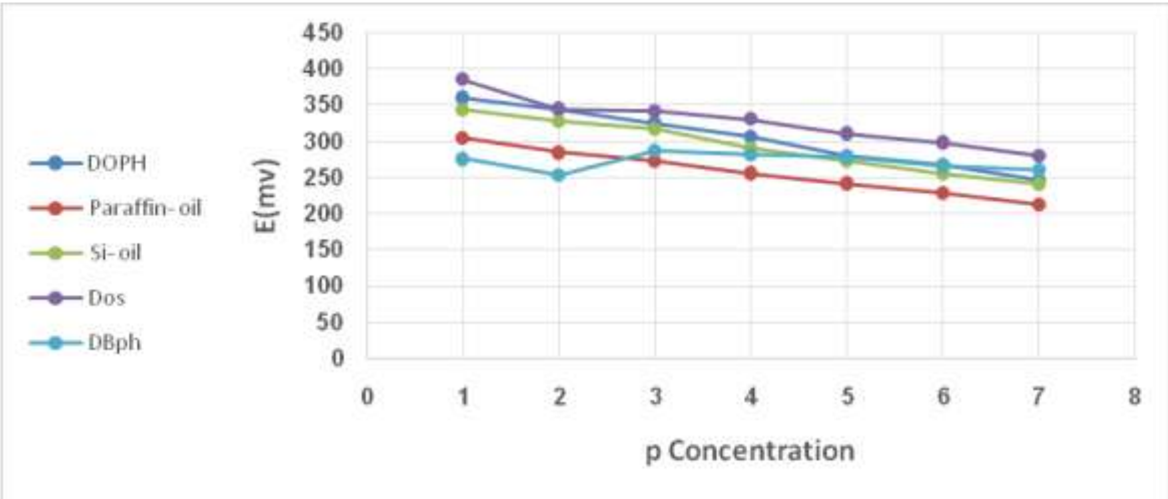


Figure (3) Effect of plasticizes on the proposed electrode

Table (3): The precentage of composition of the carbon paste electrode and its response characteristics

A%	B%	C%	D%	Slope (mv/decade)	Linear range (mol.l^{-1})	Detection Limit (mol.l^{-1})
1	49.50	49.50	-	3.60	0.50×10^{-3}-0.50×10^{-1} M	1.00×10^{-5}

2	49.00	49.00	-	3.30	$1.00{\times}10^{-5}$- $0.50{\times}10^{-3}$ M	$4.00{\times}10^{-5}$
3	48.50	48.50	-	3.50	$0.25{\times}10^{-4}$- $0.50{\times}10^{-1}$ M	$9.00{\times}10^{-6}$
4	48.00	48.00	-	6.50	$0.50{\times}10^{-5}$- $1.00{\times}10^{-2}$ M	$5.00{\times}10^{-8}$
5	47.50	47.50	-	6.20	$0.75{\times}10^{-4}$- $0.25{\times}10^{-2}$ M	$1.00{\times}10^{-5}$
4	49.90	46.00	0.1	11.20	$0.75{\times}10^{-5}$- $0.25{\times}10^{-3}$ M	$8.00{\times}10^{-7.}$
4	49.80	46.00	0.2	14.76	$0.75{\times}10^{-7-}0.50{\times}10^{-1}$M	$8.00{\times}10^{-8}$
4	49.70	46.00	0.3	17.80	$0.25{\times}10^{-5}$-$0.50{\times}10^{-3}$ M	$3.50{\times}10^{-8}$
4	49.60	45.00	0.4	18.75	$0.75{\times}10^{-4}$-$1.00{\times}10^{-1}$ M	$3.00{\times}10^{-5}$
4	49.00	46.00	1.0	16.80	$0.75{\times}10^{-5}$-$0.25{\times}10^{-1}$ M	$3.25{\times}10^{-6}$
4	49.80	46.00 Si Oil	0.2	17.80	$0.25{\times}10^{-4}$-$0.25{\times}10^{-1}$ M	$9.50{\times}10^{-6}$
4	49.80	46.00 Di octyle sbekate	0.2	15.80	$0.50{\times}10^{-4}$-$1.00{\times}10^{-1}$ M	$7.00{\times}10^{-6}$
4	49.80	46.00 Paraffin Oil	0.2	14.76	$0.75{\times}10^{-7}$-$0.50{\times}10^{-1}$M	$3.50{\times}10^{-8}$
4	49.80	46.00 DiOctyl Phthalate	0.2	19.39	$0.25{\times}10^{-4}$-$0.75{\times}10^{-2}$M	$1.50{\times}10^{-5}$
4	49.80	46.00 Di Butyle Phthalate	0.2	21.71	$0.50{\times}10^{-5}$-$1.00{\times}10^{-1}$M	$4.00{\times}10^{-6}$

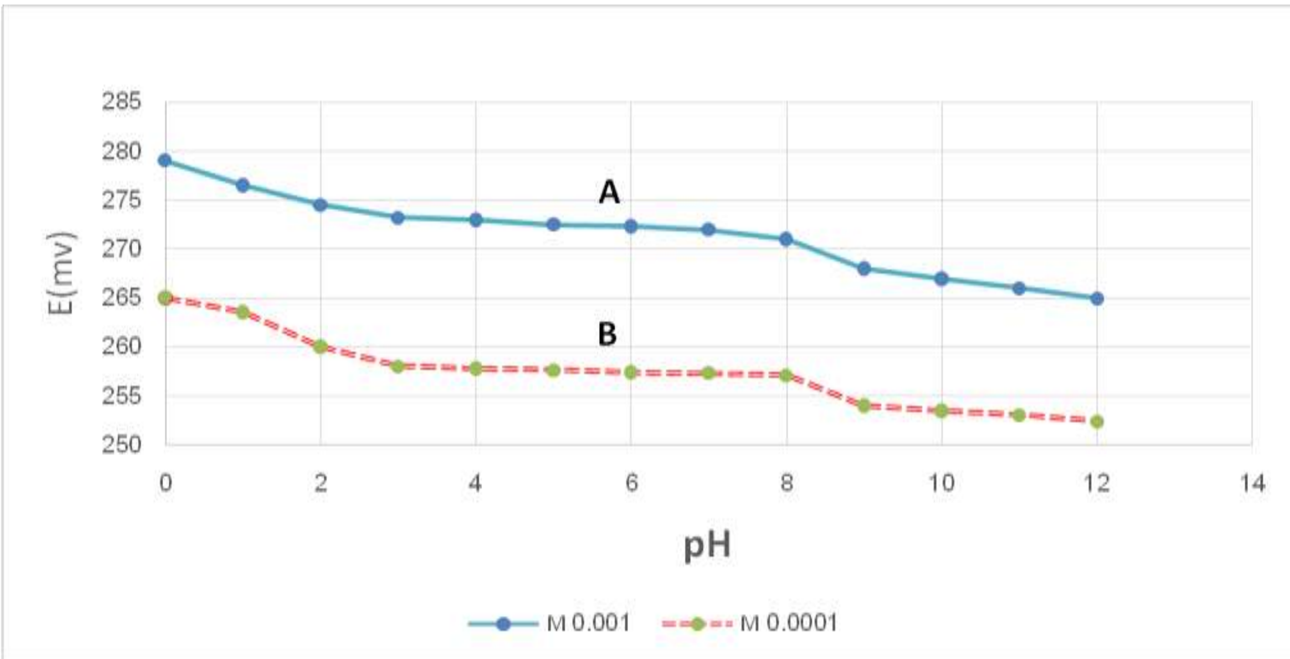
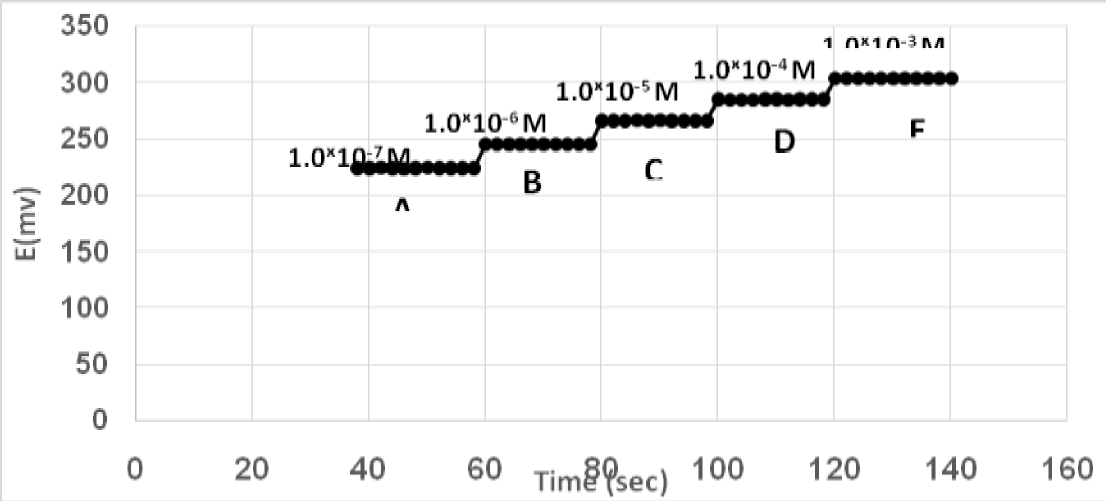


Figure (4): effect of pH on potential response of Ce (IV) ions selective carbon paste electrode based on (1, 3-di phenyl-5- paranitrophenyl Formazan) with ce (IV) ions as an ionophore .A{Ce(IV) =10^{-3} M},B{(Ce(IV)=10^{-4}M} CPE ingredients,(4% Ionophore,49.8% Graphite powder ,46% Plasticizers ,0.2% NATBPH).



Figure(5):Static potential –Time plots for different concentrations of cerium (IV) ions (A)$1.0{\times}10^{-7}$M, (B)$1.0{\times}10^{-6}$ M,(C)$1.0{\times}10^{-5}$ M,(D)$1.0{\times}10^{-4}$M,(E)$1.0{\times}10^{-3}$ M .CPE ingredients,(4% Ionophore ,49.8% Graphite powder ,46% Plasticizers ,0.2% NATBPH).

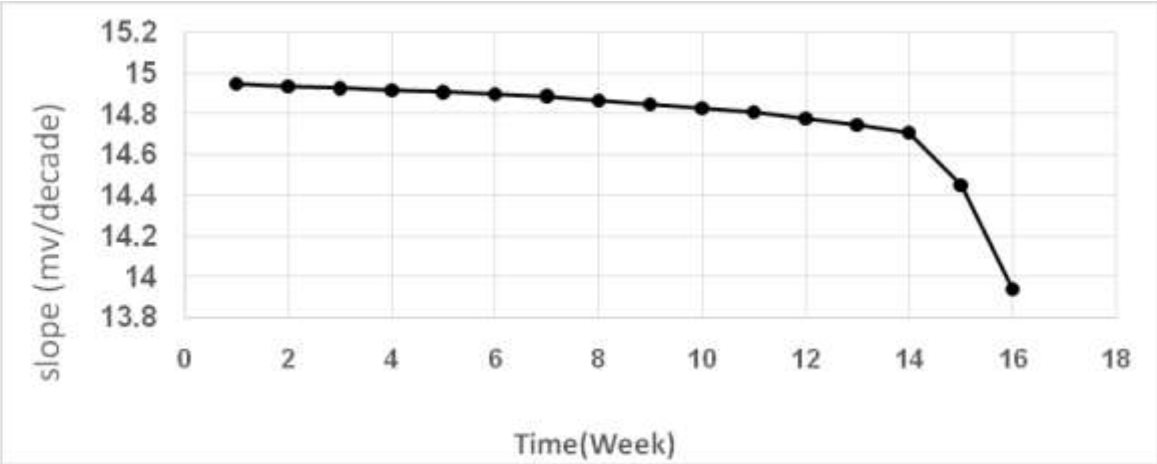


Figure (6): Lifetime of the Ce (IV) ions Carbon Paste Electrode, CPE ingredients, (4% Ionophore, 49.8% Graphite powder, 46% Plasticizers, and 0.2% NATBPH)

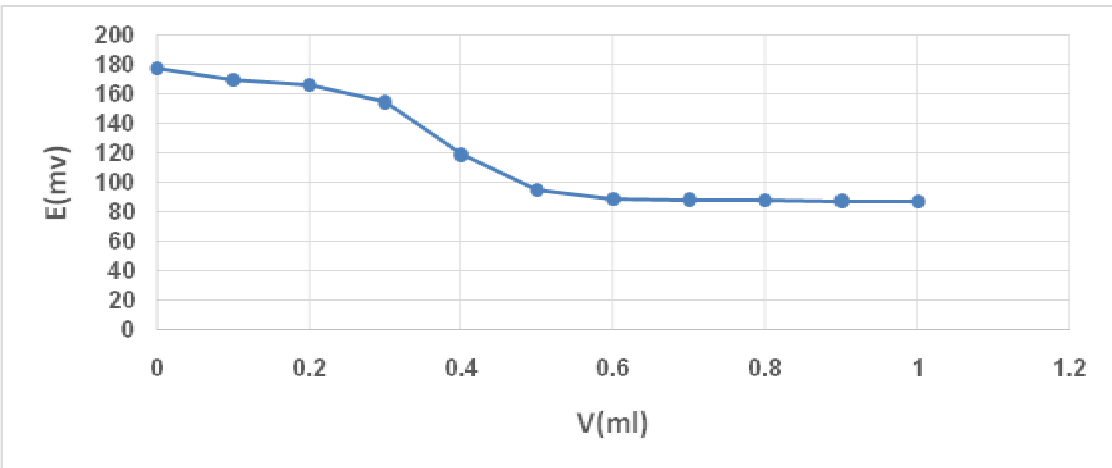


Figure (7): Potentiometric titration curve of 25 ml of Ce (IV) ions (2.0×10^{-4}M) with standard solution of EDTA (1.0×10^{-2} M), using the proposed CPE, CPE ingredients, (4% Ionophore, 49.8% Graphite powder, 46 % Plasticizers, and 0.2% NATBPH).

Analytical applications of the constructed electrode

The fabricated electrode was used as an indicator electrode in successful titration of 25 ml of Ce (IV) ions (2×10^{-4}M) with standard solution of EDTA (1×10^{-2} M) at pH (7.0) The resulting titration curve for titration of Ce (IV) ions solution with the solution of EDTA, which is presented in figure (7), shows that amount of Ce (IV) ions in solution can be accurately determined with the fabricated selected electrode.

Potentiometric Selectivity:

Selectivity coefficient explains the effect of interfering ions on response of ion- selective electrode. In this work ,we measured selectivity coefficient by matched potential method, ∂specified activity (concentration) of primary ions is added to a reference solution , and the potential is measured .In other experiment, interfering ions(B) are added to an identical reference solution until the measured potential matches that obtained before the addition of primary ions.

In this method selectivity coefficient, $K_{A,B}^{MPM}$ is then given by the resulting primary ion to interfering ion activity (concentration) ratio:

$$K_{ce^{+4},M^{+n}}^{MPM}=\frac{(a_A{'}-a_A)}{a_B}$$

∂_A is primary ion activity (concentration) and ∂_B is interfering ion activity (concentration) [27]. the resulting selectivity coefficients of Cerium-CPE in the presence of various interfering ions is in the order of (1×10^{-2}) M or less .As a result, there is a good performance of the fabricated CPE towards the Ce (IV) and interaction between Ce (IV) Ions and complex is effective

Table (4): Selectivity Coefficients ($K_{ce4+,M+}^{MPM}$) of various interfering metal ions

Interfering ion	$K_{ce4+,M+}^{MPM}$	Interfering ion	$K_{ce4+,M+}^{MPM}$
Ca^{2+}	3.3×10^{-4}	Cr^{3+}	1.8×10^{-4}
Mg^{2+}	4.9×10^{-4}	Cd^{2+}	5.8×10^{-3}
Fe^{3+}	3.2×10^{-5}	Al^{3+}	2.5×10^{-4}
Co^{2+}	8.2×10^{-4}	$NH4^{+}$	2.6×10^{-4}
Na^{+}	2.6×10^{-4}	K^{+}	4.2×10^{-4}
Pb^{2+}	8.6×10^{-3}	La^{3+}	7.0×10^{-3}

CONCLUSION:

In this research work, an ion selective electrode was fabricated based on using Formazan –Ce(IV) ion as an Ionophore for Determination the Concentration of Ce(IV)ions in Solutions.

The main advantages of the constructed electrode are simplicity of its preparation, short conducting time , fast response time a wide dynamic range , low detection limit, low cost long lifetime with a Nernstain response . The proposed electrode reveals an excellent selectivity towards Ce (IV) ions in present of some of alkali, alkaline earth and some heavy metal ion, in aqueous medium .the proposed Ce (IV) ion- selective electrode was used successfully for potentiometric titration of this metal ion with EDTA.

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