

Full Paper

Development of a Polymeric Membrane Electrode for Determination of Citrate Ions by Potentiometric Technique

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Abstract- This paper reports a new citrate-selective electrode based on mono- and di-nuclear copper (II) complexes that bear a salicylaldehyde-semi-carbazone tridentate Schiff bases ligand. The electrode serves as a membrane carrier for citrate anions. The performance of the electrode is investigated using potentiometric technique. The results of potentiometry indicate that the developed electrode has a Nernstian slope of 19.7 ± 0.3 mV in a linear concentration range of 1.0×10^{-7} - 1.0×10^{-1} M, a detection limit of 6.3×10^{-8} M, an applied pH range of 8.0-12.0, and a response time of less than 15 seconds. It can also be used for 21 days without any considerable divergence of potentials.

Keywords- Citrate-selective electrode, Ionophore, Polyvinyl chloride membrane, Potentiometry

1. INTRODUCTION

As an additive, citric acid (CA) is used as a flavoring and preservative in food and beverages, especially fruit juices [1]. It is extensively used upon food industries. It is also utilized within the pharmaceutical field because of its anticoagulant and antacid properties,

and for preventing kidney calculi as well [2]. Citric acid presents an antibacterial effect and well as a pH controlling property [3]. They are generally used for inhibiting yeast and mold growth, being also effective against a wide range of bacteria. These compounds are most active in foods with low pH values and essentially ineffective in foods at neutral pH [4].

The standard methods for citric acid determination are detected. For example, chromatographic [5], high performance liquid chromatography [6,7], gas chromatography [8], Electrochemical [9], spectrophotometric [10], polarography [11], spectrometry [12–14] capillary electrophoresis [15] and enzymatic [16] methods are applied. So far, its complex with Cu (II) has been the subject of several proposals in the literature.

A membrane is a phase, finite in space, which separates two other phases and exhibits individual resistance to the permeation of different species. Polymer membrane gives a unique opportunity to obtain a variety of electrodes selective towards particular ions by doping the membrane with certain ionophore. Polymer matrix provides mechanical stability of the membrane, chemical stability, clean surface of the resulting membrane, chemical inertness, and can be adjusted to extra requirements, i.e., physiological fluids sample, biocompatibility, adhesion, etc [17].

At present, the areas of analytical chemistry associated with design of chemical sensors of various types are being intensively developed. A particular place is occupied by studies concerned with such sensors as ion-selective electrodes (ISE), which are very convenient in measurements, do not require any complex and expensive apparatus, and can be used in field conditions [18]. ISEs are frequently used in research, mainly to measure ionic activities in the study of electrolyte equilibria [19]. Conventional ion-selective electrodes (ISEs) have been extensively used for the analysis of pharmaceutical [20,21] and environmental samples [22]. They have the capability of performing direct measurements in turbid and colored samples [23]. Such electrodes are based on hydrophobic ion-selective membranes (ISM) most often comprising a plasticized polymer that forms an organic membrane phase immiscible with the aqueous sample. This membrane incorporates an ionophore and a lipophilic ion-exchanger that confer ion selectivity and permselectivity, respectively, to the ISMs. The ion-exchange equilibrium at the organic|aqueous phase boundaries generates a membrane potential that enables ultimately the potentiometric determination of the sample ion activity [24].

The ion-selective electrode for the citrate anion was made by Ribeiro, Delerue Matos, Goreti, Sales, Carmo, and Vaz (2002) [25]. Othmana, Rizk, and El-Shahawi (2004) prepared polymer membrane sensors for sildenafil citrate (Viagra) determination in pharmaceutical products [26].

In 2008, Broncová, Shishkanova, Krondak, Volf, and Král prepared citrate-selective electropolymerized poly (neutral red) electrodes [27]. Also, Araujo, Melo, and Coelho (2011) had the development, evaluation and application of a simple and low-cost graphite carbon electrode for the direct determination of citrate [1]. Finally, a citrate selective electrode based

on surfactant modified nano-clinoptilolite was made by Nezamzadeh-Ejhih and Hasheminejad (2015) [28]. Sawsen, Hirak, Mounir, Mohammed, Cherif, Abdelhamid, and Anthony (2016) prepared Citrate-selective electrochemical μ -sensor for early stage detection of prostate cancer [29]. Finally, a Molecularly imprinted polymers based biomimetic sensors for mosapride citrate detection in biological fluids was made by Mohamed El Nashar, Abdel Ghani, A. El Gohary, Barhoum, Madbouly (2017) [30].

A selective PVC electrode based on mono- and di-nuclear copper (II) complexes bearing a salicylaldehydesemicarbazone tridentate Schiff base ligand (CuLBr) is described in this paper. Also, its application is presented for citrate determination in juices.

2. EXPERIMENTAL

2.1. Reagents

The ionophores of mono- and di-nuclear copper (II) complexes with salicylaldehydesemicarbazone tridentates Schiff-base ligands (CuLBr) (Fig. 1) were synthesized and used after purification.

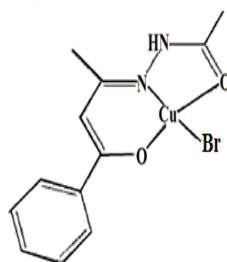


Fig. 1. Structure of mono- and di-nuclear copper (II) complexes bearing salicylaldehydesemicarbazone tridentate schiff bases ligand (CuLBr)

Triethylmethyl ammonium chloride (MTOAC), tetrahydrofuran (THF), dioctyl phthalate (DOP), dimethyl phthalate (DMF), sulfuric acid, sodium hydroxide, and salts of all the anions were purchased from Merck. Solutions of different concentrations were made by gradual dilution of stock solutions that were prepared by dissolving an appropriate amount of sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), or other anions, in an adequate volume of water. Adjustments were made of pH with hydrochloric acid and sodium hydroxide solutions as required.

2.1.1. Syntheses of Schiff base ligand, HL

The benzoylacetoneacetohydrazid tridentate Schiff base, HL, was prepared by condensation of an equimolar amount of benzoylacetone (20 mmol, 3.24 g) and acetohydrazid (20 mmol, 1.48 g) in methanol (30 mL). The mixture was refluxed for two

hours during which a light yellow precipitate was formed. The reaction mixture was then cooled to room temperature, and the formed solid compound was filtered. The compound was recrystallized from warm acetone. The specifications of the reaction included yield of 67%, IR (KBr, cm^{-1}): $\bar{\nu}$ C=N=1610, $\bar{\nu}$ C=O=1650. The electronic spectra in acetone were characterized as λ_{max} (nm), ($\log \epsilon$): 333 (2.66), 232 (4.29).

2.1.2. Syntheses of complexe CuLBr

A CuBr_2 , (2 mmol) was added to a solution of HL ligand (2 mmol, 0.434 g) in methanol (30 mL) and the resulting solution was stirred at room temperature. The resulting green solution was filtered and allowed to crystallize at room temperature. Green needle-shaped crystals appeared upon slow evaporation of the solvents at room temperature and then were washed with ethanol and dried in air. The product had the following properties: Yield of 67%. Anal. Calcd. for $\text{C}_{12}\text{H}_{13}$

BrCuN_2O_2 : C, 39.96; H, 3.63; N, 7.77. Found: C, 40.26; H, 3.46; N, 7.83. IR (KBr, cm^{-1}): $\nu_{\text{C=N}} = 1550$, $\nu_{\text{C=O}} = 1589$. The electronic spectra in CH_3OH were characterized as λ_{max} (nm), ($\log \epsilon$): 683 (1.92), 375 (5.04), 237 (4.99).

2.2. Preparation of ion-selective electrode

A general procedure was used to prepare the PVC membrane. A mixture of a plasticizer (DOP), an ionophore (CuLBr), PVC, and an additive (MTOAC) was dissolved in THF, and the solution was mixed well. The best performance was recorded with a membrane composition of PVC: DOP: Ionophore: MTOAC as 30.3: 62: 4: 3.7 (w/w %). The total mass of these compounds should be 0.1 g [31]. The resulting mixture was transferred into a small flat bottom glassy dish. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A PVC pipe with an opening of about 3 mm and a length of 2 cm was dipped into the mixture for about 6 seconds to form a 0.3-mm-thick transparent membrane. Then, it was kept at room temperature for about 24-48 hours. In the next place, the tube was filled with an internal filling solution (1.0×10^{-2} M sodium citrate). Also, an Ag/AgCl electrode was used as an internal reference electrode.

2.3. Potential measurement

A citrate-selective PVC electrode and a saturated calomel electrode (SCE) were used as an indicator electrode and a reference electrode respectively.

The representation of the electrochemical cell for the EMF measurements is as follows:
 $\text{Ag}|\text{AgCl}|\text{KCl} (3.0 \text{ M}) | \text{internal solution} (1.0 \times 10^{-2} \text{ M sodium citrate}) | \text{PVC membrane} | \text{test solution} || \text{SCE}$

All potentials were measured at the of temperature 25 ± 1 °C using a digital pH/mV meter, Model 691 Metrohm. The performance of the electrode was investigated by measuring its potential in citrate solutions prepared in the concentration range of 1.0×10^{-8} – 1.0×10^{-1} M and gradually diluted at a constant pH. Additionally, pH changes were measured using a pH meter (Metrohm) and a pH electrode (Metrohm). The pH meter was calibrated using a phosphate buffer at the pH of 7.0 and an acetate buffer at the pH of 4.0. The potentiometric selectivity ($K_{Ci, M}$) was obtained by the Matched Potential Method (MPM).

2.4. Preparation of juice samples to measure citrate anions

First of all, a sodium hydroxide was standardized. Then, using the standardized sodium hydroxide, titration was done for 10 mL of a pineapple juice. This method was considered as a reference method [32]. Also, through potentiometry and using a calibration curve, the citrate concentration was measured. In this technique, 10 mL of the pineapple juice was put in the potentiometric cell and diluted with distilled water to an appropriate volume. Then, the potential value shown on the device was recorded. Using this value and the calibration curve equation, an unknown concentration was obtained. This concentration was then compared to the reference concentration.

3. RESULTS AND DISCUSSION

3.1. Potentiometric measurements

3.1.1. Effect of membrane composition and response characteristics

The responses of different anions were plotted as the negative log of concentration, and the potential values were obtained for different anions. As shown in Fig. 2, the best response was seen for the citrate ions, as compared to the other anions.

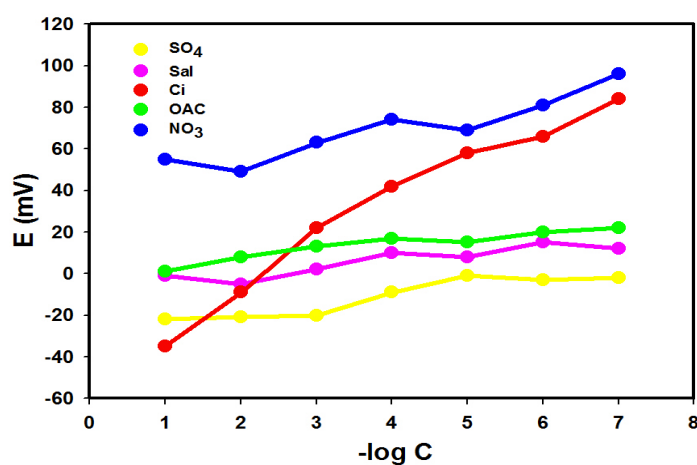


Fig. 2. Comparison of the potentiometric response of different anions with internal solution 1.0×10^{-2} M

ISEs of this kind enable controlled variation of their electrochemical characteristics via modification of the chemical structure of the active substance of the membrane, ionophore, capable of selective complexation with target ions [33]. It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition [34]. Thus, the several membrane compositions were investigated by varying the proportions of the ionophore, the plasticizer, the PVC, and the ionic additive. A combination of electrodes 5 and 6 (Table 1) indicated that the potentiometric response of the membrane would greatly improve with the addition of the lipophilic cationic additive (MTOAC) to the membrane, which has a useful influence on the performance of the membrane electrode. In fact, the lipophilic salts not only reduce the membrane resistance but also enhance the response behavior and selectivity and reduce interferences in the sample anions. [35,36] The ionophore used here is a neutral complex which forms a negative complex with citrate ions in the membrane. As a result, the ionic additive (MTOAC) neutralizes the negative charge in the membrane and blocks the entry of counter ions with a positive charge into the membrane.

The membrane solvent has to be physically compatible with the polymer (i.e. have plasticizer properties), so as to give a homogeneous organic phase. Additionally, it may affect the selectivity behavior. A polar dioctyl phthalate (DOP) is the most important PVC plasticizer [37] that the mixing of polyvinyl chloride (PVC) with dioctyl phthalate (DOP) shows two stages of gelation and fusion [38]. Good results are obtained with plasticized (DOP). Irrespective of the ionophore concentration, the slope was relatively larger when the DOP-PVC weight ratio was almost 2. The amount and the nature of the plasticizer influence the sensitivity of the electrode by influencing the dielectric constant of the membrane phase, and the mobility of the ionophore is, thus, affected in the matrix [39].

As Table 1 indicates, the percentages of all the components are relatively changed. On the ion-selective membrane electrodes, both lipophilic salts and ionophores have impacts on the selectivity of the electrodes (although the other components, too, bear their effects on the viscosity and other parameters). A change in the percentage of one component can lead to a change in the behavior of another component. Therefore, in this study, we placed the behavior of a component on the basis of its response. The optimized composition of the membrane was 4% ionophore, 62% membrane solvent, 30.3% PVC, and 3.7% additive (electrode 5). The calibration curve exhibited a good Nernstian slope of 19.7 ± 0.3 mV decade⁻¹ and a detection limit of 6.3×10^{-8} M. In addition, once the concentration of the internal electrode solution was changed, the linear range extended to 1×10^{-1} - 1×10^{-7} M.

The results demonstrate that optimal concentration of primary ion in the inner electrolyte, $C_{I,inner}^0$, is dictated by two limiting cases. If $C_{I,inner} > C_{I,inner}^0$, leaching of primary ions from the membrane occurs, whereas $C_{I,inner} < C_{I,inner}^0$, results in abrupt decrease of the EMF corresponding to the depletion of primary ions at the membrane/sample interface, and an

equivalent release of the interfering ion J^+ . Depletion is accompanied by the super-Nernstian response slopes and was observed and extensively studied not only by model calculations but also experimentally [40-45]. It is somehow related to the earlier observed Hulanicki effect, taking place when the membrane is brought in contact with a preferred ion of low concentration that is not initially contained in the membrane; the measuring ions in the Nernst diffusion layer adjacent to the membrane are depleted since the membrane acts as an effective sink that extracts these ions. It seems that the inward flux of primary ions is largely influenced by the particles in the outer surface layer of the membrane [46].

Table 1. Optimized membrane compositions and their potentiometric response properties in citrate-ISE (values in the table are mass ratio in percent)

No.	PVC %	DOP%	Ionophore%	Additive%	Slope, mV/decade	Linear dynamic range, M
1	32	60	5.0	3.0	26.0±1.0	1.0×10^{-6} – 1.0×10^{-1}
2	32	59	6.0	3.0	23.5±0.9	1.0×10^{-6} – 1.0×10^{-1}
3	31	64	5.5	2.5	24.0±0.2	1.0×10^{-5} – 1.0×10^{-1}
4	33	64	3.0	2.9	20.0±0.3	1.0×10^{-6} – 1.0×10^{-1}
5	30.3	62	4.0	3.7	19.7±0.3	1.0×10^{-7} – 1.0×10^{-1}
6	30	61	4.0	4.0	18.2±0.2	1.0×10^{-7} – 1.0×10^{-1}
7	33	62	5.4	3.4	29.8±1.0	1.0×10^{-5} – 1.0×10^{-1}
8	32	59	5.4	3.5	17.8±0.9	1.0×10^{-6} – 1.0×10^{-1}

3.1.2. Effect of pH on potential electrode

The pH dependence of the electrode potential was tested over the range of 2.0–13.0 for the citrate ions in the concentration of 1.0×10^{-3} M as shown in Fig. 3. The pH levels of the solutions were adjusted by adding required amounts of hydrochloric acid and sodium hydroxide. The results showed that the sensor is suitable for citrate determination in the wide pH range of 8.0–12.0, as the potentials remain constant in this range. At high pH values, the structure of a complex may undergo a change, which leads to the malfunctioning of the ionophore. As a result, the potential changes. while, at lower pH values, it is due to the protonation of citrate ions. Additionally, the potential changes at a low pH can be attributed to the interference of the hydronium ion in the ionophore complex [47,48].

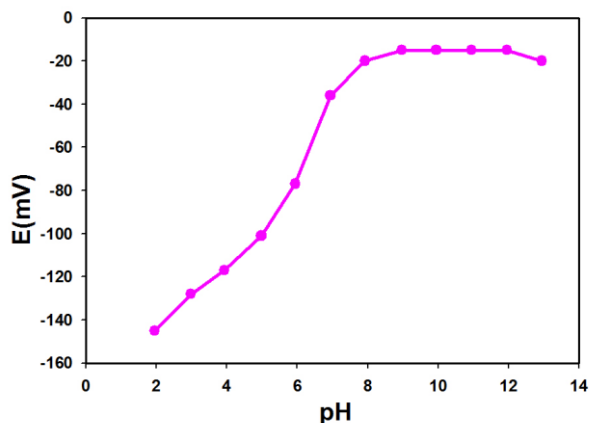


Fig. 3. pH effect on the potential response of the citrate anion-selective electrode.

3.1.3. Response time, repeatability and lifetime

The response time is an important factor for any ion selective electrode [49]. The response time is defined as the time between the addition of analyte to the sample solution and the time when a steady-state potential with less than 0.1 mV/min changes is achieved [50].

The response time of the electrode was measured after continuous submergence of the electrode in a series of citrate solutions, in each of which the citrate concentration increased tenfold, from 1.0×10^{-8} to 1.0×10^{-1} M. The static response time was, thus, found to be 15 seconds for the citrate concentration of 1.0×10^{-7} M. However, in higher concentrations, the response time was lower and reached 5 seconds for the citrate concentration of 1.0×10^{-1} M. This observation can be related to the fast exchange kinetics of the association-dissociation of citrate ions with the ionophore at the solution-membrane intermediate. The sensing behavior of the membrane electrode did not depend on whether the potentials were recorded from low to high concentrations or vice versa [51]. The actual potential versus time plot is shown in Fig. 4.

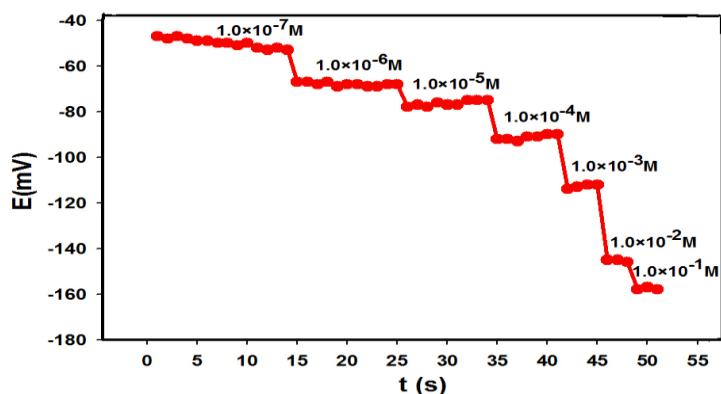


Fig. 4. Response time of the citrate anion-selective electrode

An investigation was also made of the repeatability and stability of the electrodes. Generally speaking, a measuring device is expected to yield a result that is as close to the real value as possible (i.e. to have accuracy) and to do this with sufficient reproducibility (i.e. to have precision). These two features are essential if individual results are to be dependable. In the present study, the standard deviations of 20 replicated measurements for the PVC sensor were ± 0.63 and ± 0.85 mV in citrate ion concentrations of 1.0×10^{-2} and 1.0×10^{-3} M respectively.

The long-term stability of the electrode was studied by periodically recalibrating it in standard solutions and numerating the response slope over the range of 1.0×10^{-8} – 1.0×10^{-1} M. The lifetimes of the electrodes were determined by recording their potentials and plotting their calibration curves once a day. As observed, there was no significant change in the slope and the linear range of an electrode. The membrane PVC electrode was tested over a period of 21 days to investigate its stability. During this period, the electrode was kept in a dark place and at room temperature. This lifetime may be caused by the high lipophilicity of the ionophore that remains in the membrane for a long time. The results of this study are presented in table 2.

Table 2. The effect of the time on potentiometric response of citrate ion electrode

Time (day)	Slope (mV/decade)	Linear Range (M)
1	$19.6 \pm .1$	1.0×10^{-7} - 1.0×10^{-1}
2	$20.5 \pm .7$	1.0×10^{-7} - 1.0×10^{-1}
7	$18.1 \pm .2$	1.0×10^{-7} - 1.0×10^{-1}
10	$17.9 \pm .1$	1.0×10^{-7} - 1.0×10^{-1}
14	$17.4 \pm .5$	1.0×10^{-6} - 1.0×10^{-1}
21	$16.7 \pm .3$	1.0×10^{-6} - 1.0×10^{-1}
30	$16.0 \pm .2$	1.0×10^{-5} - 1.0×10^{-1}
35	$15.4 \pm .4$	1.0×10^{-5} - 1.0×10^{-1}
40	$13.9 \pm .1$	1.0×10^{-5} - 1.0×10^{-1}

3.1.4. Selectivity of electrode

Selectivity is the most important characteristic of an ion-selective electrode (ISE) membrane and explains its specificity towards a primary ion in the presence of interfering ions. For polymer membranes, interferences by other sample ions are mainly dictated by their competitive extraction into the membrane phase. Consequently, the ISEs response can be fully predicted from thermodynamic constants, ionophore and ionic sites concentrations and, in the case of ionophore-based membranes, from the complex formation constants of each ion-ionophore complex in the membrane [52]. The potentiometric selectivity coefficients

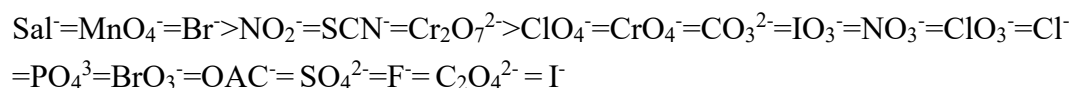
($K^{\text{pot}}_{\text{Ci,j}}$) of the sensor were determined by the matched potential method (MPM). The MPM is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation. According to this method, the specified activity (concentration) of the primary ion is added to a reference solution and the potential is measured. In a separation experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, $K^{\text{MPM}}_{\text{Ci,X}}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{\text{MPM}}_{\text{Ci,X}} = \Delta a_{\text{Ci}} / a_{\text{X}}$ [53]. The resulting values of the selectivity coefficients are given in table 3.

Table 3. Selectivity coefficients of the citrate selective electrode for various interfering

Interfering ion	K_{MPM}	Interfering ion	K_{MPM}
ClO_4^-	1×10^{-3}	CrO_4^-	1×10^{-3}
IO_3^-	1×10^{-3}	CO_3^{2-}	1×10^{-3}
Sal^-	1×10^{-1}	NO_2^-	1×10^{-2}
SCN^-	1×10^{-2}	NO_3^-	1×10^{-3}
ClO_3^-	1×10^{-3}	Cl^-	1×10^{-3}
PO_4^{3-}	1×10^{-3}	MnO_4^-	1×10^{-1}
BrO_3^-	1×10^{-3}	$\text{Cr}_2\text{O}_7^{2-}$	1×10^{-2}
OAC^-	1×10^{-3}	SO_4^{2-}	1×10^{-3}
Br^-	1×10^{-1}	F^-	1×10^{-3}
$\text{C}_2\text{O}_4^{2-}$	1×10^{-3}	I^-	1×10^{-3}

As it can be seen, the anions that cause the most interference with the electrode are bromide, salicylate and permanganate.

The selectivity coefficients presented in the table with the respective patterns are as follows:



The obtained patterns show that the anti Hofmeister series are as follows:



The reason why the selectivity coefficients of this electrode do not comply with the Hofmeister series and show anti-Hofmeister behavior is thought to be due to the possible interaction of the anions with copper [54].

3.1.5. Comparison with other citrate-selective electrodes

The properties of our electrode, as compared to other citrate-selective electrodes, are shown in table 4. As it can be seen, the potentiometric linear range, detection limit and response time of this electrode are improved as compared to other electrodes except one of them, Nezamzadeh-Ejchieh and Hasheminejad presented a citrate polymeric membrane sensor with the response time of 10 seconds [28]. However, in this work, the linear range reached 1.0×10^{-7} to 1.0×10^{-1} M using the potentiometric technique, which was much better than those of other electrodes [1,25,26,28,29].

Table 4. Comparison of the proposed electrode properties with the other citrate-selective electrodes

Ref.	Methods	Nernstian slope (mV/decade)	Linear range (M)	Detection limit (M)	Response time (s)
[1]	Potentiometry	29.0±1.0	1.0×10^{-5} to 1.0×10^{-3}	Not reported	Not reported
[25]	Potentiometry ^b	61.9	5×10^{-5} (LLLR) ^a	3.0×10^{-6}	120
[26]	Potentiometry ^c	55.5±0.39	7.0×10^{-5} to 7.0×10^{-3}	5×10^{-6}	30
		55.5±0.35		6×10^{-6}	40
[28]	Potentiometry	-29.9±0.2	5.0×10^{-5} to 5.0×10^{-2}	3.0×10^{-5}	10
[29]	Potentiometry	-19.34± 0.83	4×10^{-5} to 10^{-1}	9×10^{-6}	Not reported
Present work	Potentiometry	19.7±0.3	1.0×10^{-7} to 3.0×10^{-1}	6.3×10^{-8}	15

^a Lower limit of linear range; ^b Potentiometric measurements were used for study of two types of electrode; ^c Potentiometric measurements were carried out by a coated graphite electrode (CGE)

3.2. ANALYTICAL APPLICATIONS

To evaluate the applicability of the anion-selective electrode prepared for citrate ions, a juice sample was measured through potentiometric and titration procedures. Titration of NaOH (1.0×10^{-1} M, 4.5 mL) with a 10.0 mL juice sample was performed using phenolphthalein as an indicator to determine the equivalence point. The results, summarized in table 5, indicate a good agreement between the potentiometric and the titration procedures. In addition, t-test was used for a confidence level of 95%, and triplicate measurements were done for each sample. The measurements by the sensor were repeated under identical

conditions. So, because the reference value was (4.5×10^{-2} M), the results could be considered acceptable. As it was found, the amount of citrate in a juice sample can be accurately determined with the proposed electrode.

Table 5. Determination of citrate concentration in juice sample using potentiometric and titration manners

Sample	Comparison of potentiometric results with those of the titration method in three measurements		t-test for confidence level of 95%, ($t_3=2.78$)
	Potentiometry/M	Titration/M	t-test
1	$4.2(\pm 0.2) \times 10^{-2}$	4.5×10^{-2}	0.5
2	$4.3(\pm 0.1) \times 10^{-2}$	4.5×10^{-2}	0.2
3	$4.1(\pm 0.3) \times 10^{-2}$	4.5×10^{-2}	0.6

4. CONCLUSION

The additives, which increase the plasticity or fluidity of the material to which they are added, are called plasticizers. Normally, the composition of the solvent polymeric membranes, used in the ionselective devices, is about 30-33% (w/w) PVC and 60-66% of a membrane solvent [55]. Through this paper, a new anion-selective electrode was prepared that, the performance of this electrode was investigated using potentiometric. Potentiometric results indicate that this electrode has a good Nernstian slope of 19.7 ± 0.3 mV decade⁻¹ in the linear concentration range of 1.0×10^{-7} to 1.0×10^{-1} M and a detection limit of 6.3×10^{-8} M. The proposed method has superior reproducibility, a wide linear range, good selectivity, time saving and a Nernstian slope. These are all important lineament of the system and in general, the ISE proposed here could compete with the many sophisticated methods currently available.

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