



Development of a new chemically modified carbon paste electrode for selective determination of urinary and serum oxalate concentration



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ABSTRACT

The construction and evaluation of a novel modified carbon paste electrode with high selectivity toward oxalate ion are described. The constructed carbon paste potentiometric sensor for oxalate ion is based on the use of a zirconium salan complex as a good ionophore in the carbon paste matrix. The electrode exhibits a Nernstian slope of 29.1 mV/decade to oxalate ion over a wide concentration range from 1.5×10^{-6} to $3.9 \times 10^{-2} \text{ mol L}^{-1}$ with a low detection limit of $7.0 \times 10^{-7} \text{ mol L}^{-1}$. The electrode possesses fast response time, satisfactory reproducibility, appropriate lifetime, and most importantly, good selectivity toward $\text{C}_2\text{O}_4^{2-}$ relative to a variety of common anions. The potentiometric response of the electrode is independent of the pH of the test solution in the pH range 2.5–8.0. The modified carbon paste electrode was successfully applied as an indicator electrode in potentiometric titration and potentiometric determination of oxalate ion in mineral water, blood serum and urine samples.

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1. Introduction

Oxalate is an important anion in food industries and clinical analysis. High oxalate content in urine or blood accompanies a number of maladies including renal failure, vitamin deficiencies, intestinal diseases and hyperoxaluria [1]. It has also been shown that increased urinary oxalate excretion may lead to the development and formation of renal and urinary tract stones [2–4]. Calcium oxalate may be ingested as a dietary constituent or may be produced in the body as an end product of amino acid or ascorbate metabolism. Therefore, the quantification of urinary oxalate is very important for diagnosis and management of these diseases. Furthermore, since treatment sometimes involves a low oxalate diet, measurement of the oxalate content in food-stuffs is also important. Thus, it is necessary to have available convenient and accurate methods for oxalate determination in different samples. In recent years, various techniques such as amperometry [5,6], spectrophotometry [7–9], spectrofluorimetry [10], chemiluminescence [11], isotope dilution mass spectrometry [12] and chromatography [13–15] have been developed for the oxalate ion determination. However, most of these methods are

either time-consuming or require expensive and sophisticated instruments, well controlled experimental conditions and some sample pretreatments. Thus, a simple, sensitive and inexpensive determination method for oxalate ion in different samples is still required. Although a few selective electrodes were reported for oxalate [16–18], these electrodes were conventional polymeric membrane electrodes which suffered from disadvantages such as low mechanical stability and interferences of some organic species. These disadvantages can significantly limit their practical applications.

Among the current analytical techniques, ion-selective electrode (ISE) is widely used due to a lot of advantages which are not available in many of other analytical methods [19]. Analyses with ISEs have enabled the activity of various species to be measured directly and, in most instances, selectively without prior separation of the active substance from the formulation matrix. Moreover, analyses based on ISEs are simple, rapid, low cost, precise and accurate with a wide concentration range and applicable to colored and turbid solutions [20]. Thus, during the last three decades, many efforts have been focused on the introduction of ISEs with different configurations. Chemically modified carbon paste electrodes (CMCPEs) have been successfully applied as potentiometric sensors for determination of various inorganic and organic species [21–24]. Compared to other types of ISEs, potentiometric CMCPEs possess advantages of simple preparation, ease of regeneration, stable potentiometric response and very low

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ohmic resistance [25]. The latter property is related to the formation of a very thin film of the pasting liquid coated on the small particles of carbon powders [26]. The operation mechanism of the CMCPs depends on the properties of the modifier materials used to impart selectivity towards the target species [21]. So, by application of appropriate ionophores into the composition of the CMCPs, these electrodes exhibit high selectivities which the primary species can be measured without any interferences and separation steps [22]. With respect to the importance of the selective determination of oxalate ion in clinical and biological analysis, development of a potentiometric CPE with wide linear range and good selectivity for easy, fast and selective determination of oxalate in different media can be highly valuable.

Currently, a considerable effort has been invested in developing new chelating ligand systems for metal ions. Thus, their complexes may lead to having attractive characteristics for application in ISEs as anion carriers. The tetradentate diaminodiphenolate ligands, also known as tetrahydrosalen or salan ligands, are attracting increasing interest due to their rich coordination chemistry [27,28]. They can be obtained from the reduction of salen precursors. Salan ligands lead to well-defined complexes that allow the tuning of the metal geometry and the electronic and steric properties by simply varying of the ligand structure and substitution pattern. Thus, with respect to the unique properties of salan complexes, in this paper the application of a zirconium-salan complex (Scheme 1, 3) as an ion carrier for preparation of a potentiometric carbon paste sensor was investigated. The constructed sensor represented excellent response characteristics to oxalate ion. The obtained results showed that the sensor exhibited a low detection limit and also excellent selectivity and sensitivity toward oxalate ion, features which permit the direct determination of $\text{C}_2\text{O}_4^{2-}$ concentration in different media without prior separation steps.

2. Experimental

2.1. Reagents

Reagent grade, dibutyl phthalate (DBP), dioctyl phthalate (DOP), dioctyl sebacate (DOS), paraffin oil (PO) and graphite powder (all from Merck) were used as received. Sodium and potassium salt of anions (all from Merck) were of highest purity

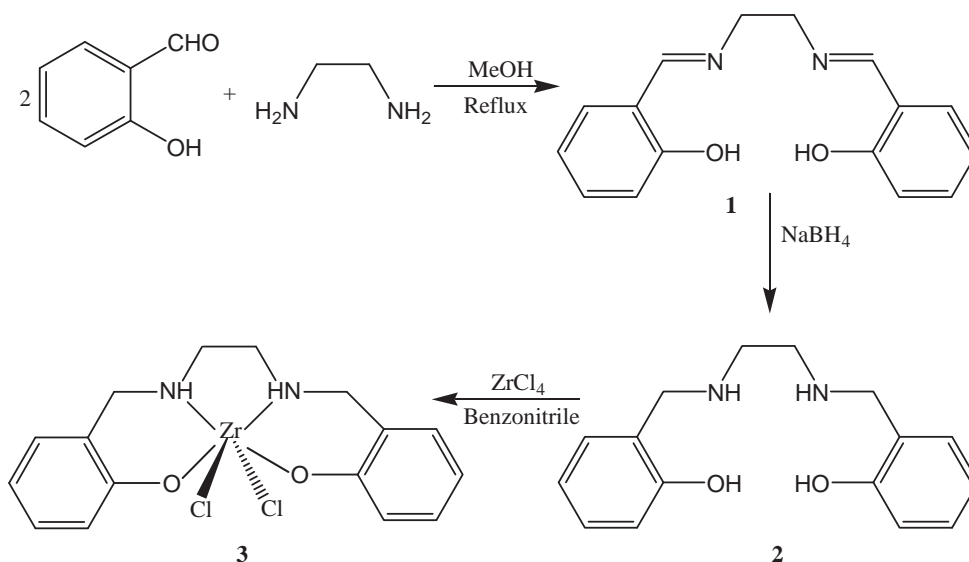
available and used without any further purification. All other chemicals were purchased from Merck chemical company and used as received. Doubly distilled water was used throughout. A stock solution of $2 \times 10^{-1} \text{ mol L}^{-1}$ sodium oxalate was prepared by dissolving 2.680 g of sodium oxalate in 100 mL of water. Solutions of different concentrations were made by serial dilution of this stock solution. The pH adjustments were made with dilute hydrochloric acid or potassium hydroxide solution as required. Blood serum and urine samples were obtained from healthy volunteers.

2.2. Synthesis of ionophore

The salan and its zirconium complex were prepared according to the reaction presented in Scheme 1. The reaction of salicylaldehyde with ethylenediamine in methanol (5 mL) afforded salen- H_2 (1) as a lemon yellow powder (yield 81%), which was further reacted with NaBH_4 in methanol (5 mL) for 2 h at ambient temperature. Removal of the solvent on a rotary evaporator followed by treatment with water afforded salen- H_4 (2) as a colorless powder (yield 71%). To a solution of salen- H_4 (2) in benzonitrile was added zirconium chloride. The reaction mixture was stirred for 6 hours, in which a yellow precipitate was formed. The precipitate was filtered and washed with methanol and acetonitrile, yielding a yellow powder of Zr-salan (3) complex (yield 71%). Anal. Calc. for $[\text{C}_{16}\text{H}_{18} \text{Cl}_2\text{N}_2\text{O}_2\text{Zr}]$ (3): (MW: 432.44), C, 44.44; H, 4.2; N, 6.48%. Found: C, 44.71; H, 3.70; N, 6.47%. IR (KBr, v/cm^{-1}): 3250 $\text{v}(\text{N-H})$, 3240 $\text{v}(\text{C-H})$, 1570 $\text{v}(\text{C}=\text{C})$ (aromatic), 1117 $\text{v}(\text{CO})$ (phenolic). ^1H NMR (400 MHz, DMSO-d_6 , δ/ppm): 6.9–7.2 (m, 4H, ArH), 6.70 (t, 2H, $J=7.6$, ArH), 6.61 (d, 2H, $J=7.6$, ArH), 5.23 (d, 2H, $J=14.3$, ArCH_2N), 3.60 (d, 2H, $J=14.3$, ArCH_2N), 3.45 (s, 2H, NH), 3.08 (d, 2H, $J=9.5$, $\text{N}(\text{CH}_2\text{CH}_2\text{N})$), 2.15 (d, 2H, $J=9.5$, $\text{N}(\text{CH}_2\text{CH}_2\text{N})$). ^{13}C NMR (100.64 MHz, DMSO-d_6 , δ/ppm): 158.60, 128.67, 128.42, 121.12, 119.56, 117.90, 64.32, 51.11. Ms (m/e)=428 $[\text{M}^+]$.

2.3. Electrode preparation

The modified carbon paste electrodes containing Zr-salan complex as ionophore were generally prepared by hand mixing various amounts of graphite powder and ionophore in a mortar for at least 10 min until the ionophore was uniformly dispersed through the graphite powder. Then, paraffin oil was added to this mixture and the mixture was mixed again until a uniform paste



Scheme 1. The synthetic routes of the Zr-salan complex.

was obtained. The paste was packed in the end of a disposable polyethylene syringe (3 mm i.d.), the tip of which had been cut off with a razor blade. Electrical contact to the carbon paste was made with a copper wire. Fresh surface was obtained by applying manual pressure to the piston. The resulting fresh surface was polished on a white paper until the surface had a shiny surface.

2.4. EMF measurements

All EMF measurements with the carbon paste electrodes were carried out with the following cell assembly:

Ag/AgCl, KCl (satd)|test solution|carbon paste|Cu

A Metrohm ion analyzer model 654 was used for the potential measurements. The EMF observations were made relative to a double-junction silver/silver chloride electrode (Metrohm) containing saturated solution of KCl with the chamber filled with a potassium nitrate solution.

Suitable increments of oxalate solution were added to 20 mL of 1.0×10^{-7} mol L⁻¹ oxalate solution to cover the concentration range 5.0×10^{-7} – 6.0×10^{-2} mol L⁻¹ and the EMF values were recorded after each addition. Calibration graphs were then constructed by plotting the recorded potentials versus log[C₂O₄²⁻]. The obtained graphs then employed for the characterization of the CPE.

2.5. Determination of oxalate in urine and serum samples

Aliquots of 5 mL human blood serum or urine sample were transferred to a 50 mL calibrated flask, made up to the mark with buffer solution (pH=7.0) and shaken for 5 min. 20 mL of this solution was transferred into a 50 mL beaker. Different amounts of oxalate ion were spiked into the beaker solution separately, and then oxalate content of the solution was determined by the proposed CPE, using a standard addition method.

3. Results and discussion

3.1. Preliminary potentiometric studies

Previous studies revealed that the anion selective electrodes based on Schiff base metal-ion complexes exhibited anion selectivity deviating from Hofmeister series [23,29–32]. In these selective electrodes, the anion selectivity is mainly governed by specific interaction between central metal and anion rather than the lipophilicity of the anion or simple opposite charge interaction with anion. Therefore, the anion selectivity behavior is influenced by both the properties of the central metal ion and the structure of the organic ligand [33]. Thus, we were interested to investigate the possibility of the use of the zirconium-salan complex (Scheme 1, 3), the reduced form of Schiff base complex, as an anion carrier in a carbon paste matrix. Therefore, in the preliminary experiments, the potentiometric responses for various anions were investigated with the modified CPEs based on Zr-salan complex as ion carrier. The potential responses of the modified CPE to different anions in the concentration range 5.0×10^{-7} – 1.5×10^{-3} mol L⁻¹ were shown in Fig. 1. It was observed that except for C₂O₄²⁻ ion, the slopes of the corresponding potential versus pM plots were much lower than the expected Nernstian slopes of 59 and 29.5 mV/decade for uni- and bivalent anions, respectively. The modified CPE produced the most sensitive potential response for the oxalate ion over the studied concentration range. Therefore, the Zr-salan complex was selected to construct a C₂O₄²⁻-selective CPE and performance of the electrode for oxalate ion was studied in detail.

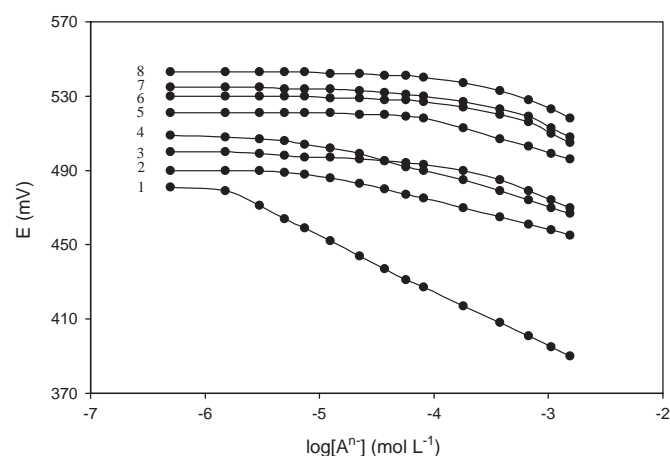


Fig. 1. Potential responses of modified CPE with Zr-salan complex to various anions: (1) C₂O₄²⁻; (2) NO₃⁻; (3) Br⁻; (4) I⁻; (5) SCN⁻; (6) Cl⁻; (7) NO₂⁻; (8) SO₄²⁻.

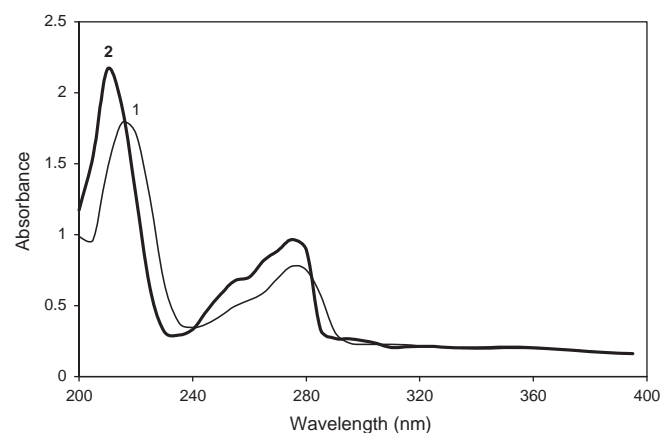


Fig. 2. UV/Vis absorption spectra of 1.0×10^{-4} mol L⁻¹ solution of Zr-salan in the (1) absence and (2) the presence of 1.0×10^{-4} mol L⁻¹ of Na₂C₂O₄ in dry acetonitrile.

It is well-known that in the case of ionophores based on different metal ion complexes, in addition to the electrostatic interaction between the central metal ion and analyte anion, there is a coordination action between both species involved [34–38]. Thus, the selectivity sequence is dominated by both electrostatic and coordination forces. So, it is expected that both the nature of the central metal ion and the coordination ligand properties play important roles in determining the selectivity of the ionophore towards a specific anion. Therefore, UV/Vis was used as a suitable tool to show specific interaction between the Zr-salan complex and oxalate anion. As illustrated in Fig. 2, in acetonitrile, the complex (1.0×10^{-4} mol L⁻¹) showed two absorption peaks at 215 and 276 nm. The addition of an equimolar amount of sodium oxalate to this solution resulted in a distinct increase in both bands and also a wavelength blue shift to 210 and 270 nm, respectively. The observed spectral shifts, together with the substantial increase in absorbance, after contact of the carrier solution with C₂O₄²⁻ ions, revealed a specific interaction between the ionophore in the membrane and oxalate ions. Such interaction is most likely explained by the selective axial ligation [39,40] between the metal ion center and oxalate anion. Moreover, to obtain a clue about the extent of selectivity of the ionophore complex to the oxalate ion, the influences of other anions such as SCN⁻, I⁻, ClO₄⁻ and SO₄²⁻ on the spectrum of the Zr-salan complex were also investigated, and almost no detectable spectral changes were observed. This revealed high selectivity of the CPE to oxalate ion.

3.2. Optimization of membrane components

The sensitivity, selectivity and linearity of the selective carbon paste electrodes depend not only on the nature and amount of ionophore, but also significantly on the membrane composition and the properties of pasting liquid [41,42]. Since the nature of pasting liquid in CPEs influences the dielectric constant of the carbon paste and the mobility of the ionophore molecules [41,43], it was expected that kind of pasting liquid plays an important role in determining the carbon paste electrode characteristics. Thus, the effect of amount of ionophore and also different pasting liquids (PO, DOS, DBP and DOP) on the potential response of the modified CPE was investigated and the results were summarized in Table 1. As seen from Table 1, the key ingredient in the membrane is the ionophore. In fact, in the absence of ionophore, the resulting electrode (no. 1) revealed a very limited slope and linear range. The linear dynamic range and slope of the electrode response were improved on increasing the amount of Zr-salan complex ionophore up to 7.5% (no. 6). Moreover, among four pasting liquids examined, paraffin oil (PO) resulted in the best sensitivity and linear range. Therefore, among different carbon paste compositions tested, composition with 7.5% ionophore, 61.7% graphite powder and 30.8% paraffin oil offers the best sensitivity, widest linear range and a Nernstian slope of about 29.1 mV per decade.

3.3. Response characteristics of the modified carbon paste electrode

The EMF response of the proposed modified CPE based on Zr-salan complex (prepared under optimal membrane ingredients) at varying concentrations of oxalate ions (Fig. 3) indicated a linear range from 1.5×10^{-6} to 3.9×10^{-2} mol L⁻¹ ($r=0.998$). The slopes of the calibration curves were 29.1 ± 0.3 mV/decade ($n=4$) of $C_2O_4^{2-}$ concentration. The limit of detection, as determined from the intersection of two extrapolated segments of the calibration graph, was 7.0×10^{-7} mol L⁻¹.

The average time required for the modified CPE to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of $C_2O_4^{2-}$ solutions, each having 10-fold difference in concentration, was less than 9 s over the entire concentration range and the potentials stayed constant after this time. The standard deviation of the potential responses every 10 min over a period of 3 h in a 1.0×10^{-4} mol L⁻¹ solution of

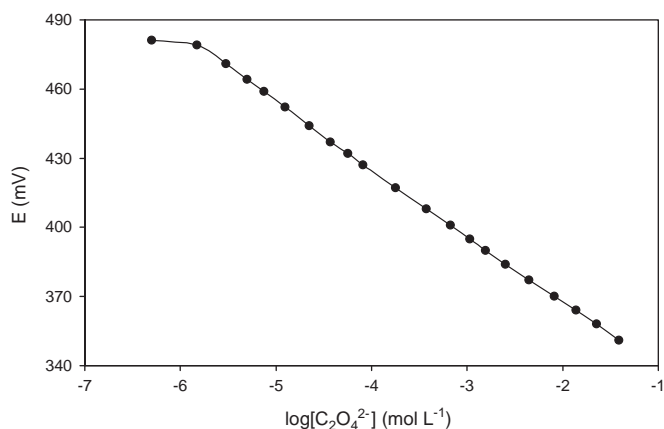


Fig. 3. Calibration graph for the CPE under optimum conditions.

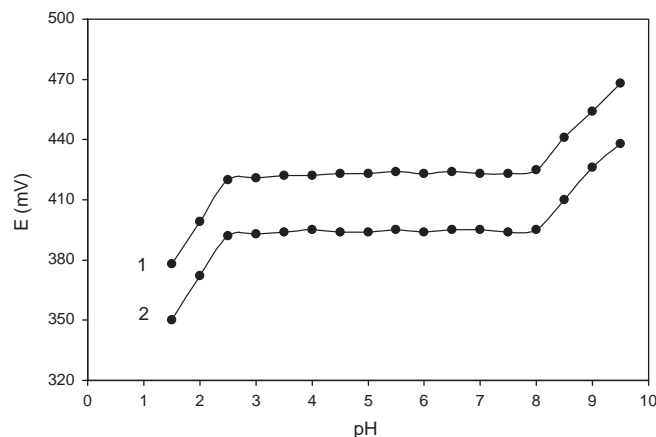


Fig. 4. Effect of pH of the test solution on the potential response of the CPE at two concentrations: (1) 1.0×10^{-4} mol L⁻¹; (2) 1.0×10^{-3} mol L⁻¹.

$C_2O_4^{2-}$ ion was 0.8 mV ($n=18$) that revealed good stability of potential responses of the proposed electrode. Moreover, the potential readings for the CPE dipped alternatively into stirred solutions of 1.0×10^{-3} and 1.0×10^{-4} mol L⁻¹ of $C_2O_4^{2-}$ represented a standard deviation of 0.9 mV ($n=6$). This very low standard deviation showed good reversibility of the CPE, so the electrode can be considered as a reusable electrode.

The lifetime of an ISE is usually defined as the time interval between the first construction of the electrode and the moment when at least one of its response characteristics changes. The relative lifetime of the proposed CPE was studied by periodically obtaining the slope and linear range of the calibration curve over the range of 5.0×10^{-7} – 6.0×10^{-2} mol L⁻¹ $C_2O_4^{2-}$ solutions. The experimental results showed that the lifetime of the modified CPE was more than 2 months. During this time the detection limit and slope of the electrode remained almost constant.

3.4. Effect of pH

The pH dependence of the potential response of the proposed CPE at two different concentration of oxalate ion in the pH range of 1.0–10.0 was tested and the results were shown in Fig. 4. As it can be seen, the electrode potential was independent of pH in the range of 2.5–8.0. This can be taken as the working pH range of the electrode suitable for oxalate ion determination. Subsequently, in the oxalate determination processes, the solution pH values were adjusted at 7.0 when required. It is noteworthy that at pH lower than about 4.0, divalent oxalate ion ($C_2O_4^{2-}$) started to be as monovalent ion ($pK_2=4.27$), so lower interaction of oxalate ion

Table 1
Optimization of membrane ingredients.

No.	Composition(%)			Slope (mV/decade)	Linear range (mol L ⁻¹)
	Graphite powder	Binder	Ionophore		
1	66.7	PO, 33.3	0.0	12.2	1.2×10^{-5} – 1.4×10^{-2}
2	65.4	PO, 32.6	2.0	16.3	7.5×10^{-6} – 1.4×10^{-2}
3	62.7	PO, 31.3	6.0	20.4	5.0×10^{-6} – 1.4×10^{-2}
4	62.0	PO, 31.0	7.0	23.1	5.0×10^{-6} – 1.4×10^{-2}
5	62.7	DOP, 62.7	6.0	15.8	7.4×10^{-6} – 1.4×10^{-2}
6	61.7	PO, 30.8	7.5	29.1	1.5×10^{-6} – 3.9×10^{-2}
7	61.7	DOS, 30.8	7.5	22.3	5.7×10^{-5} – 2.2×10^{-2}
8	61.7	DBP, 30.8	7.5	21.1	8.2×10^{-5} – 2.2×10^{-2}
9	61.7	DOP, 30.8	7.5	23.4	3.7×10^{-5} – 1.4×10^{-2}
10	61.3	PO, 30.7	8.0	35.9	7.5×10^{-6} – 2.2×10^{-2}

with ionophore was expected. However, this could be compensated with higher response of the monovalent ion ($z = -1$), and the potential could remain constant until 2.5. At lower pH values potential decreased, most probably due to the instability of the ionophore due to the nitrogen sites protonation or more formation of monovalent oxalate anions [17]. On the other hand, the increase in potentials above pH 8.0 would be presumably due to the interference of OH^- on coordination interaction between oxalate ions and complex ionophore.

3.5. Selectivity

The basic parameter characterizing the analytical properties of each new selective electrode is its selectivity coefficients. The selectivity behavior is the most important characteristic of an ion selective electrode as it determines the applicability of any sensor in the presence of foreign ions in the samples. Selectivity interprets relative electrode response for the primary anion (i) over other anions which are present in the solution (j), which is usually expressed in terms of potentiometric selectivity coefficient (K_{ij}^{pot}). The potentiometric selectivity coefficients for the proposed modified CPE were determined by the fixed interference method (FIM) [44,45] at 0.1 mol L^{-1} concentration of the interfering species. The resulting selectivity coefficients were listed in Table 2. From the data given in Table 2, it is revealed that the proposed oxalate sensors have good selectivity toward oxalate anion with respect to anions such as, iodide, thiocyanate, perchlorate and nitrate. So, the disturbance produced by these anions is negligible in the determination process of oxalate ions in the presence of foreign anions.

In Table 2, the analytical performance and selectivity coefficients of the proposed CPE based on the Zr-salan complex are compared with the corresponding values previously reported for the usual PVC membrane oxalate-selective electrodes [16,17]. As seen, the proposed CPE showed somewhat similar, in most cases, or superior, in some cases, response characteristics and

selectivity behavior to the PVC membrane electrode reported previously. It should be noted that the lack of internal solution and more mechanical stability are further advantages of the proposed CPE over the usual liquid membrane selective electrodes.

3.6. Analytical applications

The proposed oxalate-selective electrode was found to work under laboratory conditions. It was successfully used as an indicator electrode in potentiometric titration of 20.0 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{C}_2\text{O}_4^{2-}$ solution with a 0.1 M CaCl_2 solution. The resulting titration curve was shown in Fig. 5. As it can be seen, the titration curve has a distinct and accurate equivalent point, and the amount of oxalate concentration can be accurately determined by the proposed electrode.

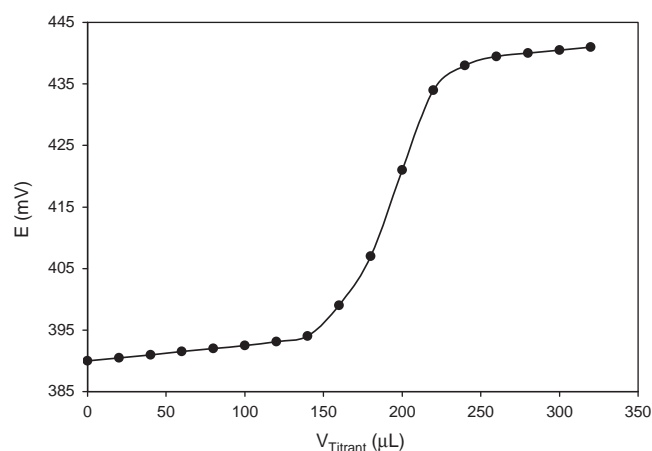


Fig. 5. Potentiometric titration curve of 20 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{C}_2\text{O}_4^{2-}$ with 0.1 mol L^{-1} of CaCl_2 .

Table 2

Selectivity coefficients ($\log K_{\text{Oxa},j}^{\text{pot}}$) and response characteristics of the proposed CPE and the previous reported PVC membrane oxalate-selective electrodes.

Anion	The proposed CPE	References	
		[16]	[17]
CN^-	−3.8	–	−3.9
Cl^-	−3.3	–	−3.6
F^-	−3.8	–	−4.6
I^-	−3.0	−4.3	−3.7
Br^-	−3.4	−3.8	−3.8
ClO_4^-	−3.5	−1.3	−2.2
SCN^-	−3.5	−2.5	−2.6
NO_3^-	−2.9	−3.8	−3.8
HCO_3^-	−3.2	−2.8	−4.9
PO_4^{3-}	−3.4	−2.5	–
SO_4^{2-}	−3.9	−1.1	−2.3
NO_2^-	−3.6	−4.8	−4.1
$\text{S}_2\text{O}_3^{2-}$	−4.2	–	–
OAc^-	−2.2	−2.5	−2.4
Urea	−3.7	–	–
Citrate	−3.4	–	−4.9
Salicylate	−3.5	–	–
Glycine	−2.9	–	–
Ascorbate	−3.2	–	–
Lactate	−3.3	–	–
Linear range (mol L^{-1})	1.5×10^{-6} – 3.9×10^{-2}	1.0×10^{-7} – 1.0×10^{-1}	1.0×10^{-6} – 1.0×10^{-1}
Detection limit (mol L^{-1})	7.0×10^{-7}	4.5×10^{-7}	3.0×10^{-7}
Slope (mv/decade)	29.1 ± 0.3	28.4 ± 0.4	28.7 ± 0.1
pH range	2.5–8.0	5.0–10.5	2.0–7.8
Response time (s)	9	5–10	5–15
Stability (month)	> 2	2	> 2

Table 3
Determination of oxalate ions in mineral water, human serum and urine samples.

Sample	Oxalate ($\mu\text{g mL}^{-1}$)		Recovery (%)	<i>t</i> -value (3.18) ^b
	Added	Found ^a		
Mineral water	25.0	24.6 ± 0.3	98.4	2.67
	50.0	50.8 ± 0.7	101.6	2.29
	500.0	496.0 ± 2.8	99.2	2.86
Human serum	25.0	24.5 ± 0.4	98.0	2.50
	50.0	50.9 ± 0.9	101.8	2.00
	500.0	495.9 ± 2.9	99.2	2.83
Urine	25.0	25.4 ± 0.4	101.6	2.00
	50.0	49.4 ± 0.7	98.8	1.71
	500.0	495.8 ± 3.1	99.2	2.70

^a Average value of four replicate measurements.

^b *t*-value tabulated at 95% confidence limit and three degrees of freedom.

The selectivity coefficients obtained for the proposed CPE made it suitable for oxalate assay in real samples. With respect to the importance of the determination of oxalate ion concentration in water and biological samples [1,4], the electrode was applied to the determination of oxalate ion in mineral water (Damavand mineral water, marketed in Iran), human blood serum (prepared from a clinical laboratory), and urine samples as good matrices to test the applicability of the electrode experimentally. Different amounts of $\text{C}_2\text{O}_4^{2-}$ ions were spiked into the mineral water, human blood serum and urine samples and the oxalate contents of the samples were measured by standard addition method. The oxalate concentrations in the samples were assessed during four consecutive days and then the mean results were calculated. The results were summarized in Table 3. The calculated *t*-values for method validation were also shown in Table 3. As seen, the recoveries were quantitative at the various $\text{C}_2\text{O}_4^{2-}$ ion concentrations tested in different samples, which revealed that the proposed electrode can be applied for the determination of oxalate ion concentration with satisfactory accuracy and precision in different samples. Also, the *t*-values were found in the range 1.71–2.86 which are lower than the tabulated value at 95% confidence limit and 3 degrees of freedom (3.18). This means that there is no significant difference between the mean values obtained and real values.

4. Conclusions

This work reveals that the proposed modified carbon paste electrode based on zirconium salan complex can be used as a useful analytical tool and interesting alternative for the determination of oxalate ion in different samples. The electrode shows good sensitivity and detection limit, reasonable selectivity, long term stability and applicability over a wide pH range. The electrode characteristics such as linear range, detection limit, life and response time, and specially selectivity, are comparable to the previously reported usual PVC membrane oxalate-selective electrodes. Another major advantage of the proposed CPE concerns its application. The electrode permits the direct measurement of oxalate ion in different real samples such as mineral water, blood serum and urine without prior separation steps.

Acknowledgments

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