

Fabrication of a New Carbon Paste Electrode Based on 5,11,17,23-tetra-*tert*-butyl-25,27-bis(pyren-1-yl-methylimido-propoxy)-26,28-dihydroxy-calix[4]arene for Potentiometric Perchlorate Determination

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A new perchlorate-selective carbon paste electrode based on a calix[4]arene derivative was prepared and evaluated in terms of construction, performance, and applications. The optimum carbon paste combination was specified as 30.0% ionophore, 30.0% graphite powder, and 40.0% 2-nitrophenyloctyl ether as binder. The proposed electrode showed a near-Nernstian slope of 56.3 ± 0.6 mV/pClO₄ in the concentration range of 1.0×10^{-6} – 1.0×10^{-1} M over the wide pH range. It has relatively short response time (6-8 s) and a long lifetime (at least 18 months). The selectivity sequence of the electrode was given according to the coefficients calculated by SSM. Furthermore, perchlorate ions in tap water, river water and human urine samples were successfully determined by direct potentiometry and the resulting mean recoveries were found in the order of 99.4%, 99.8% and 99.1%. Therefore, the proposed perchlorate-selective carbon paste electrode could be an alternative indicator electrode for potentiometric perchlorate analysis.

Keywords: Calix[4]arene; Carbon paste electrode; Potentiometry; Perchlorate-selective electrode; Determination of perchlorate

1. INTRODUCTION

As an inorganic contaminant involved in the Contaminant Candidate list of The United States Environmental Protection Agency (EPA) [1], perchlorate causes serious health problems by inhibiting iodide/iodine uptake by the thyroid, hindering the production of human hormones and regulation of their mechanism, resulting with abnormalities in child development and the thyroid cancer [2-6]. On the contrary, potassium perchlorate has been used in the treatment of hyperthyroidism due to the reason to have a similar size with iodide ions and easily take place of them in the thyroid gland.

Many fertilizers, food products, plants, soil, milk, and human urine contains perchlorate since it has been found in ground water, tap water and river water [7]. For this aim, the determination of perchlorate in water and biological fluids has gained interest because of posing a potential environmental and health risk. There are several analytical methods for direct and indirect perchlorate analysis such as volumetric titrations [8], gravimetry [9], spectrophotometry [10,11], atomic absorption spectrophotometry [12], and chromatography [3,13,14], Raman spectroscopy [15], fluorescence [16] and potentiometry [17-20]. Most of these methods except potentiometry are time consuming, require sophisticated instrumentation and sample pretreatment, need expertise, etc. Ion-selective electrodes (ISEs) based potentiometry provides simple, selective and sensitive, inexpensive and portable equipment for routine analysis of ionic and non-ionic species [21,22]. The perchlorate ion-selective electrodes have been under development for more than four decades [2,7,17,23-44]. To the best of our knowledge, only one of them was reported as a perchlorate-selective carbon paste electrode (CPE) [45]. In this paper, it was described that the developed perchlorate-selective CPE had a narrow working range of 1.0×10^{-4} – 1.0×10^{-1} M with near- or sub-Nernstian slopes.

CPEs are prepared easily by using a paste containing graphite powder, appropriate binder such as plasticizers, paraffin oil etc. and electroactive compound as a sensing material for target ion [46-48]. Furthermore, CPEs present other advantages of easy renewal of surface, lower ohmic resistance, generally stable response when compared with polymeric membrane electrodes [49-51].

The goal of this study was to fabricate a new perchlorate-selective CPE based on a calix[4]arene derivative as an electroactive compound shown in Fig. 1, since there has been only one published perchlorate-selective CPE in the literature. In addition, it was aimed to investigate whether or not a perchlorate-selective CPE with better performance characteristics could be constructed and employed as an indicator electrode to determine perchlorate ion in human urine and water samples.

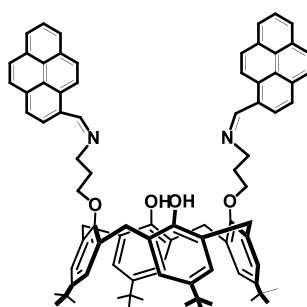


Figure 1. Chemical structure of the calix[4]arene derivative used as ionophore.

2. EXPERIMENTAL

2.1. Reagents and solutions

5,11,17,23-tetra-*tert*-butyl-25,27-bis(pyren-1-yl-methylimido-propoxy)-26,28-dihydroxy-calix[4]arene was synthesized and purified by the group in Ref.52.

Graphite powder (puriss <20 μm) and 2-nitrophenyloctyl ether (2-NPOE (selectophore grade)) were purchased from Fluka.

0.1 M stock solutions for calibration series were prepared from sodium salts of related anions (Merck/Sigma Aldrich) and diluted with deionized water supplied from ELGA Purelab Classic Ultrapure Water System (High Wycombe, Bucks, UK).

The pH of the calibration solutions were kept constant at pH 4.0 by 0.1 M acetic acid/acetate buffer. pHs were changed by HCl and NaOH solutions purchased from Merck. NaCl solutions were prepared from solid compound obtained from Merck.

Tap water and river water samples were supplied and stored by standard method reported in Ref. 53. Human urine sample was taken from a smoking person.

2.2. Electrode fabrication

Ionophore (30% w/w), graphite powder (30% w/w) and 2-NPOE (40% w/w) were homogeneously mixed in a petri dish for 30-40 minutes. The resulting composite mixture was then fully filled into the cavity of the electrode body (BASi MF-2010) to prepare calix[4]arene modified perchlorate-selective carbon paste electrode. Finally, the electrode surface was polished on the weighting paper and washed with deionized water. Also, unmodified carbon paste electrode without ionophore was constructed in the similar technique.

2.3. Apparatus and electrochemical measurements

All potential and pH measurements were carried out with the following electrochemical cell by using Mettler- Toledo Seven Multi pH / ion meter (Schweizenbach, Switzerland) at 20 ± 1 °C:

Reference electrode (Ag/AgCl) | test solution | Perchlorate-selective CPE

CHI660D Electrochemical Workstation (Austin, TX, USA) was used for the chronopotentiometric and impedance measurements. In this system, the proposed carbon paste electrode (working electrode), BASi MF 2052 reference electrode (Ag/AgCl electrode) and BASi MW-1032 counter electrode (platinum wire) were used.

EMF-time ($E-t$) plots were drawn from chronopotentiometric data obtained by successive addition of stock NaClO_4 solutions to pH 4.0 buffer solutions containing 0.1 M NaCl. The impedance spectra of the carbon paste electrode were recorded in the same media with different concentrations of analyte solutions. The experimental parameters for impedance measurements were as followed: $0.1-1.0 \times 10^5$ Hz frequency range, 0.2 V initial potential and 0.005 V amplitude.

2.4. Sample preparation and analysis

Certain amounts of human urine and water samples were diluted to 50.0 mL by adjusting their pH to 4.0 with acetate buffer solution and the potentials were measured for each sample. By using the related potentials, the perchlorate concentrations were found from the calibration curve recorded prior

to the sample analysis step according to direct potentiometry. The recovery studies of three samples were performed by spiking with different quantities of standard perchlorate solutions.

3. RESULTS AND DISCUSSION

3.1. Composition of the sensing carbon paste

As well known, it is worth pointing out that the performance characteristics of ISEs depend on the composition of selective surfaces. Thus, the influence of paste composition was evaluated by varying the graphite powder/calix[4]arene ratio and keeping the binder (2-NPOE) constant at 40%. Four carbon paste electrodes with different paste compositions were prepared and their response characteristics were summarized in Table 1. The calix[4]arene free CPE (Electrode no.1) showed sub-Nernstian response (22.7 ± 0.8 mV/decade) in the linear range of 1.0×10^{-1} – 1.0×10^{-4} M for perchlorate ions. When the calix[4]arene amount was changed as 7.5 (Electrode no.2), 15.0 (Electrode no.3) and 30.0% (Electrode no.4), in which the graphite powder/calix[4]arene ratios were 7, 3 and 1, respectively, the slope of the electrode rised up to 45.2 ± 1.1 mV/decade for Electrode no.2, 48.3 ± 0.4 mV/decade for Electrode no.3 and 56.3 ± 0.6 mV/decade for Electrode no.4 in the linear concentration range of 1.0×10^{-1} – 1.0×10^{-6} M by increasing the calix[4]arene percentage in the carbon paste. It was decided that the calix[4]arene dopped perchlorate-selective CPE composed of 30.0% ionophore, 30.0% graphite powder and 40.0% 2-NPOE (Electrode no.4) was found to be optimal for perchlorate sensing. It was concluded that the selectivity of the CPEs depended to a large extent of the ionophore ratio in the paste as well as the other types of ISEs. By comparison with the slopes (57.7, 50.2, and 45.8 mV/decade) and the working ranges (1.0×10^{-1} – 1.0×10^{-4} M) of the CPE reported in Ref. 45, the proposed perchlorate-selective CPE exhibited better performance (56.3 ± 0.6 mV/decade and 1.0×10^{-1} – 1.0×10^{-6} M).

Table 1. Composition and response characteristics of the calix[4]arene dopped perchlorate-selective CPE

Electrode	Paste Composition (%)*			Response Characteristics ($N=5$)		
	Ionophore	Graphite	Graphite/ 2-NPOE	Slope \pm ts/\sqrt{N} (mV/decade)	Linear range (M)	Detection limit (M)
1	–	60.0	1.5	22.7 ± 0.8	1.0×10^{-1} – 1.0×10^{-4}	1.8×10^{-5}
2	7.5	52.5	1.31	45.2 ± 1.1	1.0×10^{-1} – 1.0×10^{-6}	1.3×10^{-6}
3	15.0	45.0	1.12	48.3 ± 0.4	1.0×10^{-1} – 1.0×10^{-6}	5.0×10^{-7}
4	30.0	30.0	0.75	56.3 ± 0.6	1.0×10^{-1} – 1.0×10^{-6}	4.8×10^{-7}

* 2-NPOE percentage kept at 40% in carbon paste

Moreover, it is stated in the literature that the selectivity and the sensitivity of CPEs were related to the graphite powder/binder ratio used. It was also expressed that the most proper ratio was 1.00 and the ratios smaller than 0.90 were not applicable. As seen in Table 1, the ratios of 0.75–1.31 were investigated. The best ratio was found as 0.75 that provided satisfactory selectivity for perchlorate ion which is not in accordance with literature [54]. This difference can be attributed to the presence of additional components rather than the graphite powder and the binder used in carbon pastes.

3.2. Characterization of the sensing surface

It was pointed out that the response characteristics of ISEs depended on the surface morphology [55]. Therefore, the scanning electron microscope (SEM) images of the surface of calix[4]arene doped perchlorate-selective CPE (Electrode no.4) with the optimum carbon paste composition were investigated and given in Fig. 2a together with that of ionophore free electrode (Fig. 2b). As can be seen in these SEM images, CPEs appeared to have a rough surface while the calix[4]arene (ionophore) was observed to be distributed homogeneously. This situation indicated that 2-NPOE was the appropriate binder to create uniform paste combining graphite powder and ionophore together.

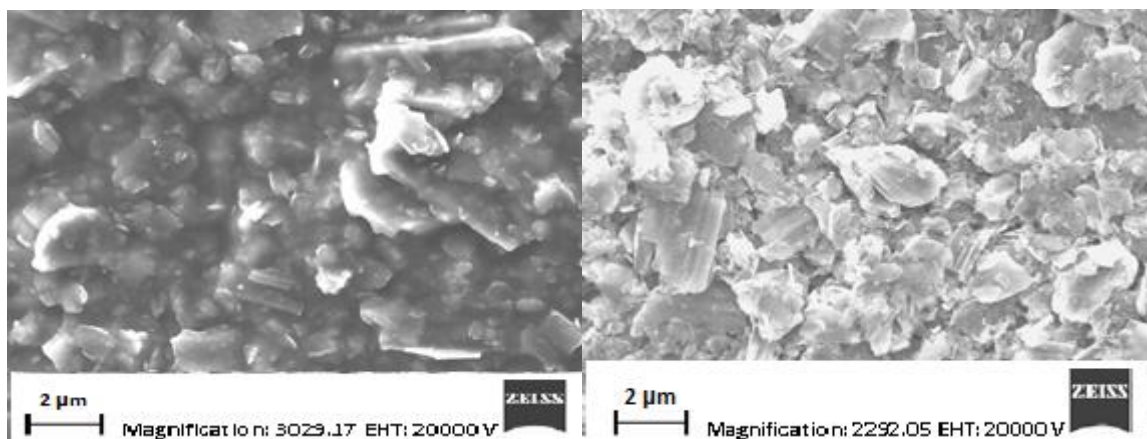


Figure 2. SEM images of the surfaces for CPEs (a) with 30% ionophore and (b) without ionophore.

In order to have an idea about the response mechanism of the proposed CPE, the Nyquist plots were drawn by changing the perchlorate concentration (1.0×10^{-2} – 1.0×10^{-5} M) in the test solution containing 0.1 M NaCl at pH 4.0 using electrochemical impedance spectroscopy (EIS) (Fig. 3). At high frequencies, these plots include a semicircle section related to the ion transfer limited process and a linear section corresponding to the diffusion process is observed at low frequencies [56,57]. Fig. 3 demonstrated that Nyquist plots had well-shaped semicircles and linear portions for all analyte concentrations. The bulk resistances of these impedance spectra were reduced while the perchlorate concentration rised. The observed decrease in resistance with the increasing ion concentration can be attributed to the transfer of target ion to the electrode surface resulting from the interaction between

perchlorate ion and the ionophore. This phenomenon can be concluded that perchlorate ions were introduced to the cavity of the ionophore and/or binded nitrogen atoms in the calix[4]arene via possible hydrogen bonding.

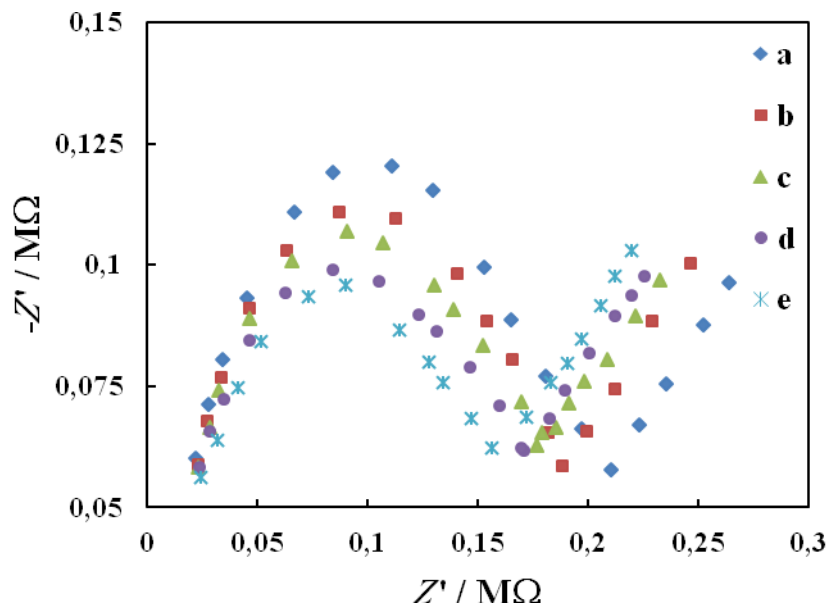


Figure 3. Influence of sodium perchlorate concentrations on the impedance spectra of the CPE (a) acetic acid/acetate buffer solution (b) 1.0×10^{-5} M (c) 1.0×10^{-4} M (d) 1.0×10^{-3} M (e) 1.0×10^{-2} M.

3.3. Influence of pH

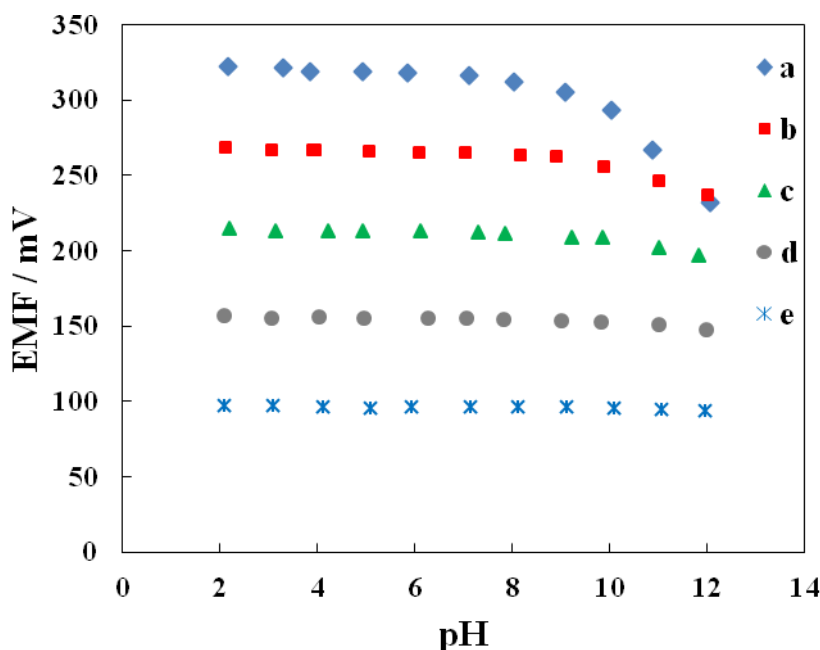


Figure 4. Influence of pH on the response of the perchlorate- selective CPE: (a) 0, (b) 1.0×10^{-5} , (c) 1.0×10^{-4} , (d) 1.0×10^{-3} and (e) 1.0×10^{-2} M NaClO_4 .

The influence of pH on the response of the presented CPE was studied in different perchlorate concentrations (1.0×10^{-5} – 1.0×10^{-2} M) by adjusting the pH with HCl and NaOH solutions in the range of 2.0–12.0 and the related graphics were illustrated in Fig. 4. In the perchlorate free media, the observed drift at pH values higher than 9.0 in Fig. 4a, may be due to the OH^- sensitivity of calix[4]arene. Fig. 4b and 4c presented the similar OH^- effect on the potential response in the low perchlorate concentrations (1.0×10^{-5} and 1.0×10^{-4} M) resulted from the competition of the ClO_4^- with OH^- . On the other hand, the potential response of the CPE remained almost constant between pH 2.0–12.0 in 1.0×10^{-3} and 1.0×10^{-2} M NaClO_4 containing solution (Fig. 4d and 4e) due to the dominant interaction of perchlorate with ionophore at pH values higher than 9.0, too.

3.4. The performance characteristics

Calibration curve was obtained by using the data from pH-ion meter measurements and given in Fig. 5 together with error bars for five replicates. The electrode behavior was quite similar when recording potential values either from low to high perchlorate concentrations or vice versa. The data from chronopotentiometric $E-t$ measurements (Fig. 6) were also evaluated to plot another calibration curve and the same results in terms of the working range, the slope, the detection limit, response time, the potential stability and the lifetime of the electrode were observed. In order to investigate these performance characteristics, International Union of Pure and Applied Chemistry (IUPAC) recommendations were taken in consideration with both of this data. Consequently, the CPE with optimum carbon paste composition had linear response in the range of 1.0×10^{-6} – 1.0×10^{-1} M with a near-Nernstian slope of 56.3 ± 0.6 mV/p ClO_4 with detection limit of 4.8×10^{-7} M.

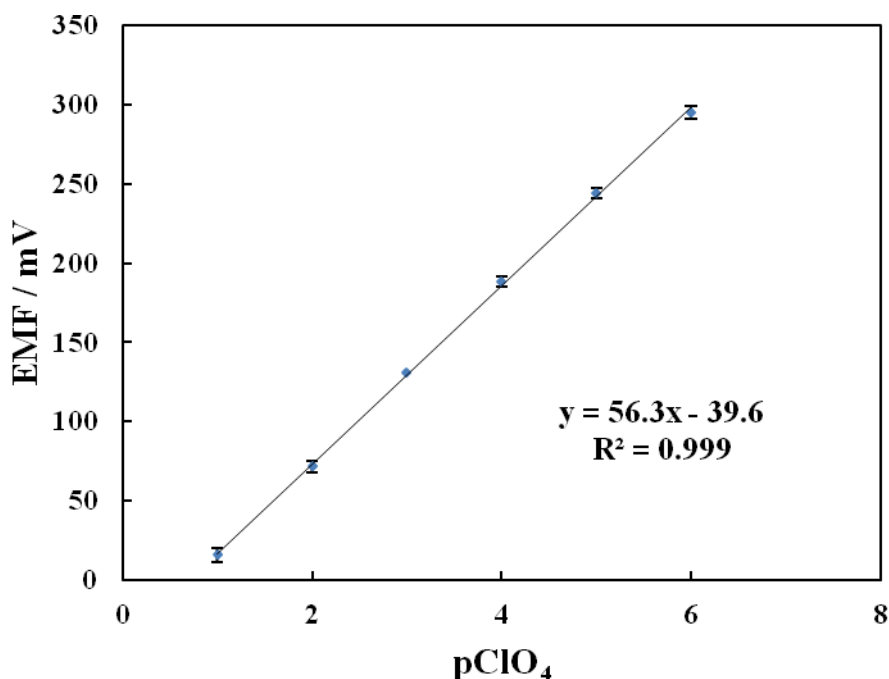


Figure 5. Calibration curve of the proposed perchlorate- selective CPE at pH 4 ($N= 5$).

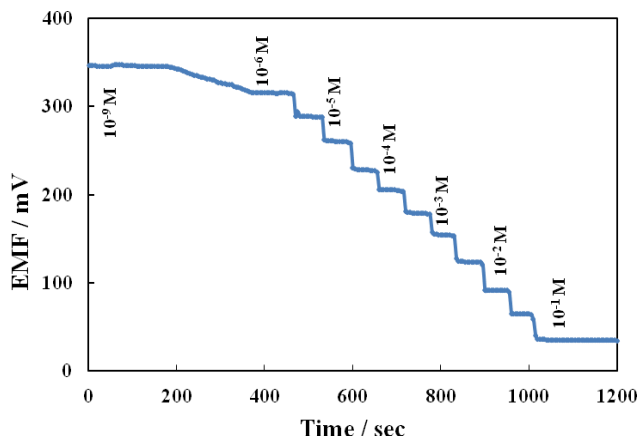


Figure 6. Dynamic response of the perchlorate- selective CPE obtained by successive additions of NaClO₄ at pH 4.

It is well known that the dynamic response time of ISEs is critical importance for any sample analysis. The response time was found as 6-8 s from *E-t* experiments which were carried out with recording the time needed to achieve 95% equilibrium potential value after the addition of perchlorate solution to access the suitable concentration over the working range. This short response time can be due to the fast and reversible perchlorate ion exchange across the carbon paste- test solution interface. Potentials were also found stable for approximately 25 min. The stability and the lifetime of the electrode were determined by plotting two calibration curves per day and the electrode response had no significant deviation over 18 months.

Table 2. Comparison of performance characteristics of some solid-contact perchlorate-selective electrodes with the proposed CPE

Ionophore*/ Electrode** Type	Slope, mV/pClO ₄	Linear Range, M	DL, M	pH range	ResponseTime, s	Lifetime, month	Ref.
I / CGE	59.3 ± 0.2	1.0×10 ⁻⁷ - 1.0×10 ⁻²	8.4×10 ⁻⁸	2.5–9.0	9	>2	[7]
II / CPtE	50.4±1.9	1.0×10 ⁻⁶ - 1.0×10 ⁻¹	8.7×10 ⁻⁷	2.0-8.0	≤4	>2	[20]
III / CGCE	53.6±0.4	1.0×10 ⁻⁶ - 3.0×10 ⁻²	7.0×10 ⁻⁷	4.0-10.0	-	>2	[31]
IV / CGCE	58.2±0.3	1.5×10 ⁻⁷ - 2.7×10 ⁻¹	1.0×10 ⁻⁷	2.5–9.5	8	2	[34]
V / CGCE	58.6±0.4	5.0×10 ⁻⁷ - 1.9×10 ⁻¹	4.0×10 ⁻⁷	2.0-9.0	<10	>1	[39]
VI / CGE	59.4±0.9	1.0×10 ⁻⁶ - 5.0×10 ⁻¹	5.0×10 ⁻⁷	3.0-12.0	<5	>2	[40]
VII / ERPMCGE	54.1 ±0.7	1.2×10 ⁻⁷ - 1.0×10 ⁻³	7.7×10 ⁻⁸	3.5–11.0	60 s	3	[43]
VIII / CPE	57.7±1.5	1.0×10 ⁻⁵ - 1.0×10 ⁻¹	2.5×10 ⁻⁵				[45]
IX / CPE	56.3±0.6	1.0×10 ⁻⁶ - 1.0×10 ⁻¹	4.8×10 ⁻⁷	2.0-9.0	6-8	>18	This work

* I: Zinc complex of 6,7:13,14-dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetra-azacyclotetradecane-6,13-diene; II: Calix[4]arene; III: Phosphorus(V) tetraphenylporphyrin complex; IV: [Pt(*p*-MeOC₆H₄)₂(NN)] (NN= 2,2'-bipyridyl); V: [Pt(MeC₆H₄)₂(dppm)] complex; VI:

Co(5-NO₂ Salen)(PBU₃)]ClO₄•H₂O; VII: Bisnaphthalimidopropyl Polyamine; VIII: Tricresyl phosphate; IX: Calix[4]arene.

** CGE: Coated Graphite Electrode; CPtE: Coated Pt Electrode; CGCE: Coated Glassy Carbon Electrode; ERPMCGE: Epoxy Resin/Polimeric Membrane Coated Graphite Electrode; CPE: Carbon Paste Electrode.

As can be seen from Table 2, the proposed electrode can compete with other solid-contact electrodes in the literature in terms of performance characteristics such as slope, linear range, detection limit (DL) and response time. Moreover, most of the ionophores in previously reported perchlorate-selective solid-contact electrodes were metal complexes [7,31,34,39,40] and their membranes were based on PVC [7,20,31,34,39,40,43]. However, in this study a neutral calix[4]arene derivative was employed. The proposed electrode had much more superior lifetime than all these electrodes. This could be attributed to the decomposition of metal complexes used as ionophore, and/ or the leaching of membrane components from PVC membranes.

To decide whether a repeatable and reproducible electrode was developed or not, successive calibration curves ($N=5$) were drawn by the use of same CPE and five separate CPEs with the same composition, respectively. As it is obvious from small error bars in calibration curves, the relative standard deviations of the slope values were found to be smaller than 5%, therefore the results showed that calix[4]arene doped perchlorate-selective CPE had good repeatability and reproducibility.

3.5. Selectivity

The potentiometric selectivity behavior of an electrode which controls the accuracy of real sample analysis, is one of the most important criteria. For this purpose, the separate solution method (SSM), recommended by IUPAC, was used to calculate the selectivity coefficients for the proposed CPE with respect to variety of anions [58,59]. The following selectivity order was obtained according to the resulting values:



The selectivity sequence of this CPE was differ from the Hofmeister series [60]. This situation was thought to be arised from relatively selective interaction of perchlorate with calix[4]arene. The electrode displayed significant selectivity for perchlorate over many common organic and inorganic ions except salicylate, iodide and benzoate. Moreover, no interference was exhibited by chloride ions, a universal contaminant, which is an important advantage.

3.6. Potentiometric determinations

Human urine, tap water, and river water samples were used to evaluate the applicability of the electrode for perchlorate analysis. The results were obtained from four replicate measurements by recording the potentials and calculating perchlorate concentration using direct potentiometry, and

listed in Table 3. Each sample was spiked with certain amount of standard perchlorate solution, then total perchlorate concentration was calculated and recovery percentages were summarized in the table. As it is obvious, mean recoveries were accomplished around 100% for all samples. In conclusion, the presented electrode was found to work successfully for perchlorate analysis in human urine and water samples under laboratory conditions without any pretreatment process.

Table 3. The recovery values calculated for each sample by using the perchlorate-selective carbon paste electrode

Sample	Added ($\mu\text{g}\cdot\text{mL}^{-1}$)	Found ($\mu\text{g}\cdot\text{mL}^{-1}$)	Recovery %
Tap water	0	0.15	-
	1.97	2.08	98.1
	4.91	5.02	99.2
	14.73	14.56	97.8
	19.50	20.13	102.4
			<i>Mean Recovery 99.4</i>
River water	0	0.21	-
	1.97	2.16	99.1
	4.91	5.23	102.1
	14.73	14.68	98.3
	19.50	19.67	99.8
			<i>Mean Recovery 99.8</i>
Human urine	0	1.27	-
	19.50	20.06	96.6
	68.26	69.88	100.5
	117.41	117.93	99.4
	165.57	166.52	99.8
			<i>Mean Recovery 99.1</i>

4. CONCLUSIONS

5,11,17,23-tetra-*tert*-butyl-25,27-bis(pyren-1-yl-methylimido-propoxy)-26,28-dihydroxy-calix[4]arene was performed well as an ionophore in the preparation of CPE for perchlorate sensing. The proposed CPE with wide working range of 1.0×10^{-6} – 1.0×10^{-1} M, a near-Nernstian slope of 56.3 ± 0.6 mV/pClO₄ and detection limit of 4.8×10^{-7} M has a very long lifetime (>18 months), short response time, good repeatability and reproducibility. The findings related to the CPE revealed that its performance characteristics were a lot better than the only one perchlorate-selective CPE previously reported in literature [45].

It is believed that the obtained results could make a good contribution to the literature. In the future, an ion chromatography detector could be developed by using this type of CPE due to the selective behavior of ionophore to some anions other than perchlorate.

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