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Direct analysis of thorium(IV) ions concentration in water samples using a new carbon paste electrode

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Abstract

The radioactive and hazardous nature of thorium demands the fabrication of efficient electrodes for its sensitive and selective monitoring in aqueous environments. The present paper reports the construction and characterization of a new carbon paste electrode (CPE) chemically modified by octyl phenyl acid phosphate (OPAP) as a selective recognition agent for the potentiometric assay of thorium(IV) ions. Improved sensitivity, electrical conductivity, and selectivity were achieved by incorporating oxidized multi-walled carbon nanotubes (o-MWCNTs) into the carbon paste composition. The electrochemical performance of the developed electrode was evaluated regarding the paste ingredients, response time, and working pH range. The standard CPE potentials, $E°$, were determined at various temperatures and the isothermal temperature coefficient was calculated. The optimized CPE showed a Nernstian slope of 14.65 ± 0.38 mV decade^{-1} over the concentration range of 4.82×10^{-7}–1.00×10^{-1} mol L^{-1}. The electrode possessed a short response time (9 s), independence of the solution pH over the range of 2.5–5.5, and a relatively long operational lifetime ($>$ 3 months). The selectivity coefficients indicated the good discrimination ability of the developed CPE towards thorium(IV) ion compared to various common ions. Aiming to judge the practical utility of the developed CPE, it was successfully used for the potentiometric analysis of thorium(IV) ions in various real aqueous matrices with sensible results.

Keywords Modified carbon paste electrode · Potentiometric sensor · Ion-selective electrodes · Thorium(IV) ions determination · Oxidized multi-walled carbon nanotubes

Introduction

Carbon paste electrodes (CPEs) are promising electrochemical sensors with distinct physicochemical and electrochemical properties [1]. CPEs are commonly popular due to their very attractive properties such as non-toxic nature, biocompatibility, chemical inertness, electrochemical behavior stability, very low background current, easy preparation, low ohmic resistance, robustness, absence of an internal solution, surface regeneration, fast response time, long operational lifetime, and modification ability [2–4]. CPEs are especially convenient to develop electrode materials modified with various compounds hence giving the electrode specific

pre-determined characteristics [5]. CPEs usually have carbon powder as an electrical conductor dispersed in a non-conductive and chemically inert binder with low volatility and high viscosity to offer mechanical stability to the paste [6]. Graphite poses both metallic and nonmetallic characteristics making it a useful material for electrode preparation [7]. The exceptional advantages of CPEs have attracted considerable attention [8], where numerous sensing electrodes are being developed to determine various organic and inorganic substances, employing chemically-modified CPEs [8–10].

Incorporating a selective additive (modifier) in the carbon paste was reported to boost the selectivity and sensitivity of the CPEs [11]. Such modifiers can be a polymer, nanomaterials, or a ligand; where the CPE performance towards sensing the target species relies on the chemical nature and characteristics of the modifier added to the paste [12–14]. Among all modifying additives, the ionophores play a pivotal role in promoting the selectivity and sensitivity of the modified electrodes. Thus, by adding an appropriate ionophore to the carbon paste, the chemically modified CPE

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would reveal high selectivity to the target analyte enabling its measurement without prior interferent removal steps [2]. Moreover, the inclusion of nano substances in the electrode matrix, as ion-to-electron transducers, is an effective means for the sensitive determination of various ions. Nanomaterials decrease the resistance and increase the surface area of the electrode, leading to a significant performance enhancement [15]. Recently, multi-walled carbon nanotubes (MWCNTs) have become among the most extensively utilized nanomaterials to enhance the electroanalytical performance of many chemically modified electrodes [16, 17]. MWCNTs are composed of sp^2 carbon units having several layers of graphite sheets, with distinctively exceptional electrical, electronic, mechanical, and chemical characteristics [2]. Adding MWCNTs to the CPE matrix as a modifier would enhance the electrode performance by increasing the velocity of the electron transfer. Several papers reported that MWCNTs enhance the electrode conductivity leading to a better detection limit and sensitivity [18].

Thorium quantification in diverse matrices is of special interest to both environmental science and nuclear fuel chemistry [19, 20]. Thorium and its compounds are extensively utilized in diverse industrial applications [21]. Thorium is a nuclear-power fuel alternative for the traditional uranium-based reactors, thus, it is seen as a key energy source for the growing world demand for energy [22]. Although nuclear power plants are designed to be safe, the waste of those plants can be radioactive if not adequately treated [23]. Natural water contaminated with thorium possess significant hazards for the biota and particularly for human health [24]. Thorium intake in living bodies increases the risk of developing lung, bone, and pancreatic cancer. Thorium has been traditionally measured by a number of spectrometric and spectroscopic instrumental methods, including X-ray fluorescence, inductively coupled plasma-mass spectrometry, neutron activation analysis, and electrothermal atomic emission spectroscopy [25, 26]. Although those techniques are sensitive, they are of high cost, time-consuming, entail complicated equipment, need frequent maintenance, and require sample pretreatment ahead of thorium(IV) determination [19, 27].

In this regard, ion selective electrodes (ISEs) represent a good candidate for thorium monitoring owing to the advantages of low cost, fast analysis, high performance, low maintenance, no sample pretreatment, and the possibility of miniaturization and integration into standalone sensing units [28]. Even though some attention has been paid to the potentiometric monitoring of thorium ions, only a few reports are available in the literature and thus the need for more ISEs is notable [29–34]. A number of ionophores have been introduced for the fabrication of thorium ISEs including 2-(diphenyl phosphorothioyl)-N′,N′-diphenyl acetamide [29], calix[4]arenes [30, 31],

dibutyl(8-hydroxyquinolin-2-yl) methylphosphonate [27], Aliquat-336 [32], dithio-tetraaza macrocyclic compound [33], morpholine derivative [34], and thorium oxinate [35].

Recently, we have used a synthesized morpholine derivative as ionophore to fabricate a screen-printed electrode for thorium(IV) ions [34]. The developed electrode exhibited good response characteristics and was successfully applied to the determination of thorium content. Therefore, and considering the shortage of reported thorium(IV)-ISEs, we were still interested in developing sensitive and selective electrodes for the potentiometric quantification of thorium ions. In reviewing the literature, we found no work reporting the development of potentiometric CPE for thorium(IV) ions. Furthermore, despite the high extraction efficiency reported for organophosphorus extractants towards thorium(IV) ions [36, 37], their employment as sensing materials for thorium ISE needs to be further investigated. In this context, in this work, we developed a CPE modified by octyl phenyl acid phosphate and o-MWCNTs for the effective analysis of thorium(IV) ions. The performance of the developed CPE was comprehensively assessed and it was efficiently applied in analyzing thorium content in aqueous samples. Coupling of OPAP with o-MWCNTs was noticed to boost the signal transducers and enhance the potentiometric characteristics of the developed CPE.

Experimental

Chemicals and apparatus

Graphite powder (GP) (synthetic 1–2 µm), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), dioctyl phthalate (DOP), and multi-walled carbon nanotubes (MWCNTs), were acquired from Sigma-Aldrich. OPAP was supplied by Mobil Chemical Company. Thorium nitrate was used in this work to prepare the working solutions. For interference studies, the used metal solutions were made from analytical grade nitrate salts.

For electrochemical measurements, a potentiometric ion analyzer (Nico-2000, UK) and Ag/AgCl with a saturated KCl inner solution reference electrode were used. An inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo-iCAP6500) was used for the standard spectrometric measurements of thorium ions.

Functionalization of MWCNTs

The functionalization of MWCNTs was conducted via ultrasound-assisted acid oxidation [38]. First, the dispersion and ultrasonication of MWCNTs in an acidic mixture of concentrated H_2SO_4 and HNO_3 were conducted for 1 h at ambient temperature followed by 4 h at 70 °C. Then,

Scheme 1 Schematic diagram of CPE preparation and the potentiometric cell set-up
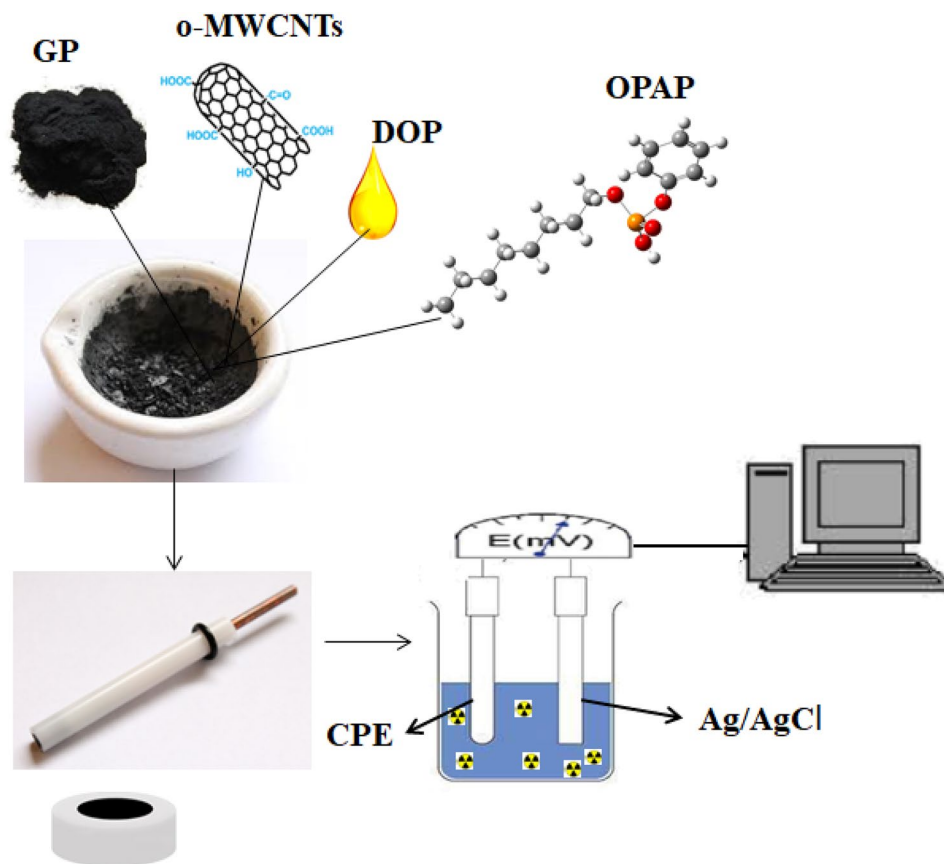
the functionalized o-MWCNTs were filtered, washed with deionized water until neutral pH was obtained, and finally dried.

Fabrication of the working electrodes

To prepare the working CPEs, certain amounts of GP, OPAP, o-MWCNTs, and KTpClPB were transferred to a mortar, mixed with the plasticizer, and then thoroughly homogenized. The resulting paste was packed carefully in an electrode body of piston-type Teflon holder avoiding air penetration (Scheme 1). Bare CPE was prepared as a blank electrode in the same manner without the addition of OPAP, KTpClPB, or o-MWCNTs. The external surface of the CPE was smoothed by a wet filter paper and then the CPE was conditioned in thorium solution (1.0×10^{-3} mol L^{-1}) for 5 min before measurements. When necessary, the CPE surface renewal was conducted mechanically via pressing out a little amount of the paste from the electrode body and smoothing it as described earlier.

Potential measurements

The potential measurements were performed at the room temperature in an electrochemical cell containing the developed CPE as the working electrode and Ag/AgCl as the reference electrode. Both electrodes were connected to a potentiometric ion analyzer. The cell setup can be represented as follows: carbon paste electrode|sample Th(IV) ion solution|Ag/AgCl–KCl (satd.) (Scheme 1).

The calibration graph was drawn by plotting the potential, E, versus the logarithm of the various concentrations of thorium(IV) ions.

Results and discussion

Organophosphorus acid extractants have been a subject of extensive research as potential carriers for lanthanides and actinides ISEs [39]. In this regard, we investigated the feasibility of using OPAP as a modifier immobilized in CPE to develop selective thorium(IV) potentiometric sensor. In preliminary tests, the potentiometric response of the modified CPE towards various cations was studied. The results revealed that the OPAP-based CPE exhibited remarkable
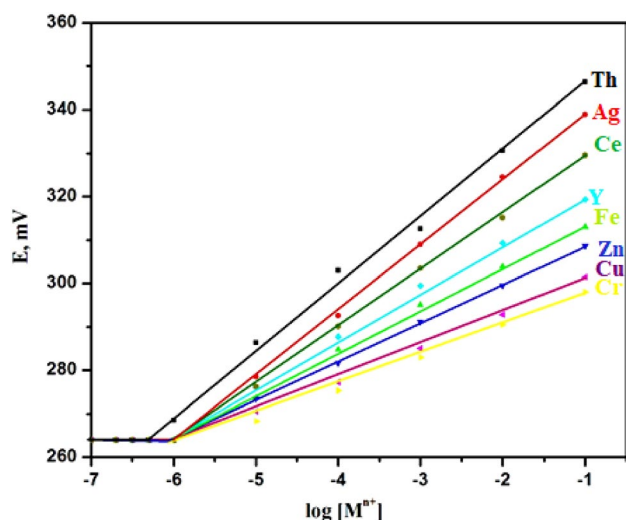
Fig. 1 Potential response of the developed CPE towards various cations

selectivity and sensitivity to thorium(IV) ions compared to the tested metal ions (Fig. 1). Additionally, a Nernstian potential response was obtained for thorium ions, while the response determined for other cations was much lower than that predicted by the Nernst equation. This behavior could result from the selective behavior of OPAP toward thorium(IV) ions compared to other metal ions and indicates the practicability of the developed electrode for thorium potentiometric quantification.

Optimization of the CPE composition

The sensitivity and selectivity of CPE are significantly affected by the paste composition and the nature of the used additives. Thus, the impact of the paste constituents on the

potentiometric response characteristics of the developed CPE was studied and the corresponding results were listed in Table 1. The unmodified CPE (no. 1–2) displayed a weak, unreliable, and nonlinear response towards thorium(IV) ions. As can be seen from Table 1, changing the ratio of the solvent mediator (DOP) to graphite has no significant influence on the CPE response. Upon adding OPAP, a sub-Nernstian slope was noticed over a wider linear dynamic range. A lipophilic additive was added to the paste to improve the CPE response, and the results revealed that KTpClPB led to a near-Nernstian response with a better slope (CPEs no. 4–5). The existence of KTpClPB in the ingredients reduced the ohmic resistance, improved the response behavior, and increased the electrode sensitivity [40, 41].

For more enhancements, we tested o-MWCNTs as suitable additives in conjunction with OPAP to modify the CPE. Data in Table 1 showed that the addition of o-MWCNTs resulted in better slope of the calibration curve, improved dynamic working range, and lower detection limit. This improvement stems from the distinguished properties of o-MWCNTs, including large surface area, highly porous structure, chemical stability, hydrophobicity, and high electron transferability [42, 43]. These characteristics enhanced the paste homogeneity, increased the conductivity of the CPE, and supported the extraction of thorium(IV) ions into the CPE surface which resulted in an improved electrochemical response [44]. It is worth mentioning that CPE no. 7 showed the lowest detection limit, a Nernstian slope, and the highest regression coefficient; therefore, 30% graphite, 60% DOP, 6% OPAP, 2% KTpClPB, and 2% o-MWCNTs were used as the optimum CPE composition for subsequent studies. Figure 2 depicts the potential response of the CPE no. 7 to varying concentrations of thorium(IV) ions. The calibration curve slope was 14.65 ± 0.38 mV decade^{-1}, while the detection limit was 4.82×10^{-7} mol L^{-1}.

Table 1 Optimization of the paste ingredients

| No | Composition % (w/w) | | | | | Electrode characteristics | | |
	GP	DOP	OPAP	KTpClPB	o-MWCNTs	Slope (mV decade^{-1})	Linear Range (mol L^{-1})	R^2
1	70	30	–	–	–	6.56 ± 2.71	$1.00 \times 10^{-4} – 1.00 \times 10^{-1}$	0.756
2	65	35	–	–	–	6.85 ± 1.38	$1.00 \times 10^{-4} – 1.00 \times 10^{-1}$	0.847
3	62	33	5	–	–	11.76 ± 1.01	$1.00 \times 10^{-6} – 1.00 \times 10^{-1}$	0.881
4	61	32	6	2	–	13.09 ± 1.73	$1.00 \times 10^{-6} – 1.00 \times 10^{-1}$	0.921
5	61	30	6	3	–	13.89 ± 0.55	$1.00 \times 10^{-6} – 1.00 \times 10^{-1}$	0.974
6	60	30	6	3	1	14.24 ± 0.62	$7.23 \times 10^{-7} – 1.00 \times 10^{-1}$	0.982
7	60	30	6	2	2	14.65 ± 0.38	$4.82 \times 10^{-7} – 1.00 \times 10^{-1}$	0.998
8	59	28	7	3	3	14.16 ± 0.54	$7.23 \times 10^{-7} – 1.00 \times 10^{-1}$	0.993
9	58	27	7	4	4	13.71 ± 1.02	$8.00 \times 10^{-7} – 1.00 \times 10^{-1}$	0.974
10	60	30	6	1	3	13.91 ± 0.99	$8.00 \times 10^{-7} – 1.00 \times 10^{-1}$	0.977
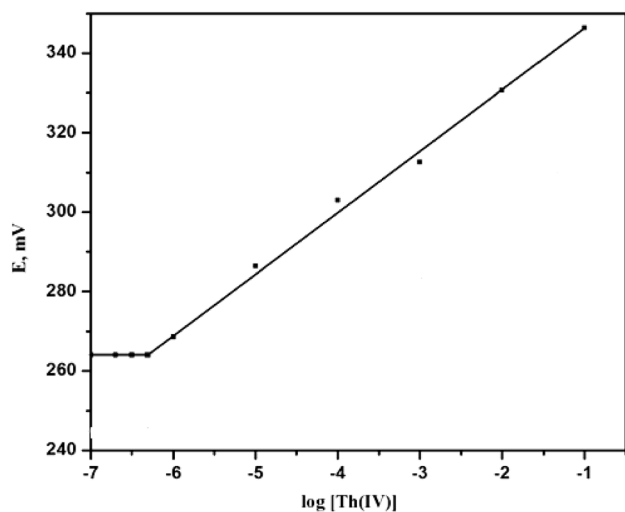
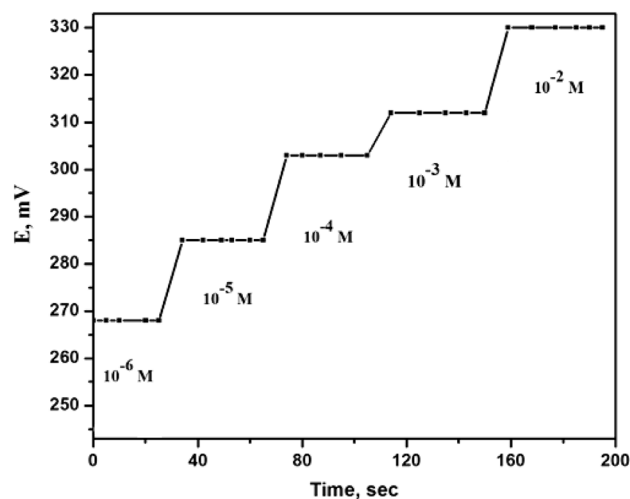**Fig. 2** Calibration curve of the developed Th(IV)-CPE

Fig. 4 Dynamic response of the developed Th(IV)-CPE
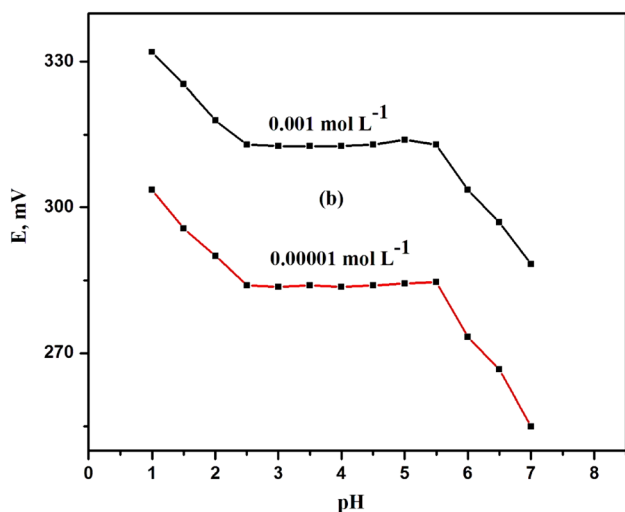
Fig. 3 Effect of pH of the test solution on the response of the developed Th(IV)-CPE

Fig. 5 Life cycle of the developed Th(IV)-CPE

pH dependence of the CPE response

Because hydrogen and hydroxyl ions frequently interfere with the potentiometric electrode performance, their effect on the CPE response was investigated. The pH response profile for the developed CPE was monitored over various pHs using 1.0×10^{-3} and 1.0×10^{-5} mol L^{-1} thorium(IV) solutions. As displayed in Fig. 3, the potential remained constant even with the pH change from 2.5 to 5.5, indicating the applicability of the developed CPE within this pH range. Potential fluctuations were observed above and below this range. The decrease in potentials at higher pHs is caused by thorium(IV) ion hydrolysis, which resulted in a decrease in free thorium(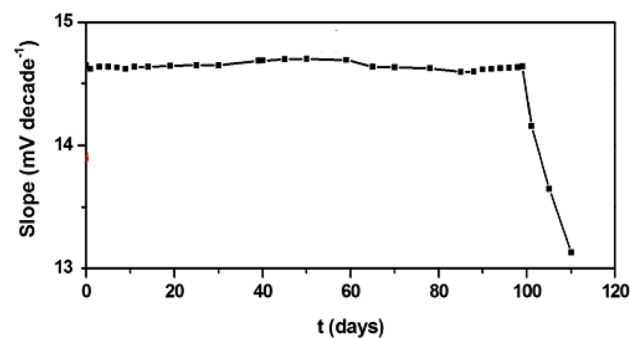IV) ions in the test solution and the formation of various thorium hydroxide complexes that were not detected by the CPE [37]. On the other side, at lower pHs, the observed potential drift is due to the ligand protonation and hydronium ions interference [33].

Dynamic response time and lifespan

Time is a significant aspect when evaluating the ISE performance for the subsequent analytical applications. Herein, we determined the practical response time by successive immersion of the developed CPE at solutions with different thorium(IV) concentrations, $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ mol L^{-1}, each of which had a tenfold increase, and recording the needed time for potential reading within ± 1 mV of the final value. As indicated in Fig. 4, the average response time over the entire concentration range was about 9 s. The equilibrium potential was reached fast because o-MWCNTs lowered the CPE resistance and

thus facilitated the electron transfer at the CPE/Th(IV) interface leading to a fast response time.

The lifetime of ISEs is the time interval between the ISE construction and the variation of its response characteristics. The lifetime of the developed CPE was monitored through periodical calibration in thorium(IV) solutions to evaluate the CPE's capability to retain its performance for a definite duration. The experimental results displayed in Fig. 5 show that no remarkable change in the calibration curve slope was noticed for 100 days. The observed long stability of the developed CPE results from the surface renewability and low water penetration [45]. After that period, there is a gradual decrease in the electrode potentiometric slope, which deviates from the Nernstian behavior.

Selectivity studies

Since the real samples could include various inferring species, the selectivity behavior of the electrode is an important feature that determines its suitability for real-life applications [46]. Selectivity coefficients describe the ISE's ability to discriminate between the target ion and interfering species (J). Low selectivity coefficient values express the electrode preference for the primary analyte over other species in the test solution. Herein, we determined the selectivity coefficients of the developed CPE via the matched potential method (MPM). According to the MPM method, the selectivity coefficients are defined as the activity ratio of primary and interfering ions that give similar potential change under identical conditions. In practice, a specific concentration of the thorium (IV) ions was added to a standard reference solution containing fixed thorium concentration (1.0×10^{-5} mol L^{-1}), and the potential was recorded. Then, in other experiments, interfering ions (J^{n+}) were continuously added to a similar standard thorium(IV) solution till the same potential value was obtained [47]. The selectivity coefficients $K_{Th,J}^{MPM}$ were then calculated by the resulting

thorium ion to interfering ion activity ratio. The selectivity coefficient values listed in Table 2 don't show a significant interference for several cations and indicate that the developed CPE possesses a good selectivity towards thorium(IV) ions with respect to various monovalent, bivalent, and trivalent ions.

Temperature dependence of the CPE response

The solution temperature could have a significant impact on the ISE measurement process. Thus, we tested the developed CPE's thermal stability by measuring the electrode potential and constructing the calibration graphs under varying temperatures within the range of 10–60 °C. The developed CPE exhibited a good Nernstian response in the temperature range under study, which indicates that the temperature variation in this definite range could hardly influence the potentiometric performance of the developed CPE.

The isothermal temperature coefficient was computed, according to the literature, using the standard cell potentials (ΔE) that were calculated from the corresponding calibration curves at various temperatures [11]. The slop of the ΔE Vs t-25 plot (Fig. 6) represents the isothermal coefficient as 0.0001 mV °C^{-1}, indicating the high thermal stability of the developed CPE.

Table 2 Selectivity coefficient values calculated for the developed CPE (no. 7) for various interfering ions (J) using matched potential method

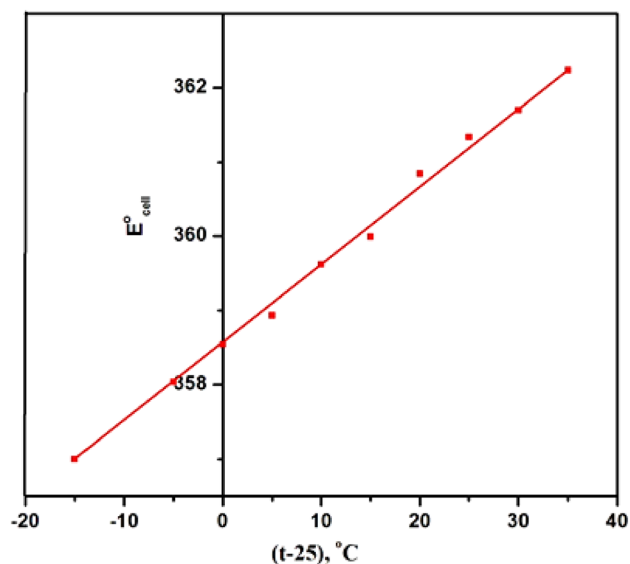| Interfering ions	$K_{Th,J}^{MPM}$	Interfering ions	$K_{Th,J}^{MPM}$
Ce^{3+}	9.13×10^{-2}	Hg^{2+}	1.36×10^{-2}
La^{3+}	5.51×10^{-2}	Cu^{2+}	6.24×10^{-3}
Nd^{3+}	7.81×10^{-2}	Zn^{2+}	4.25×10^{-3}
Y^{3+}	8.66×10^{-2}	Mg^{2+}	1.15×10^{-4}
Fe^{3+}	1.98×10^{-2}	Ba^{2+}	2.42×10^{-5}
Cr^{3+}	5.44×10^{-4}	Ca^{2+}	2.40×10^{-5}
Bi^{3+}	3.12×10^{-4}	K^{+}	6.06×10^{-5}
Al^{3+}	7.06×10^{-4}	Na^{+}	7.38×10^{-5}

Fig. 6 Effect of temperature on the response of the developed Th(IV)-CPE

Real samples analysis

Thorium concentration was measured in some real samples to test the analytical application of the developed CPE. The samples included formation water collected from various petroleum companies (sample 1 Alexandria, samples 2 and 3 Western Desert, and sample 4 Red Sea governorates). For each sample, an aliquot of standard thorium(IV) solution was injected and the concentration was potentiometrically measured. The calibration plot, obtained under the optimized experimental conditions, was employed to calculate uranium content in the samples. The results listed in Table 3 show good recovery percentage values ranging from 97.60

to 99.50% and good precision as indicated by the relative standard deviation values (less than unity). Additionally, the results agreed well with those values determined by the ICP-OES which further reflects accuracy of the developed CPE.

Precision and accuracy

To assess the repeatability of the developed CPE accuracy and precision were studied by measuring known thorium amounts added to the real samples at different spiking levels. Intraday repeatability was computed by measuring the potentials in five replicates on the same day while inter-day variations were calculated from repeated analyses over three

Table 3 Determination of Th(IV) ions in spiked real samples using the developed CPE

Sample no	[Th(IV)] added (mg mL^{-1})	CPE			ICP-OES		
		Found^a (mg mL^{-1})	R.S.D (%)	Recovery (%)	Found^a (mg mL^{-1})	R.S.D (%)	Recovery (%)
1	0.35	0.348	0.542	97.73	0.341	1.176	97.43
	0.50	0.494	0.836	98.80	0.487	1.184	97.40
2	0.25	0.249	0.483	97.60	0.245	1.015	98.00
	0.40	0.398	0.506	99.52	0.391	1.073	97.75
3	0.30	0.299	0.761	98.67	0.291	1.251	98.10
	0.45	0.448	0.905	99.56	0.442	1.064	98.22
4	0.35	0.349	0.669	98.71	0.344	1.001	98.29
	0.50	0.498	0.923	99.50	0.489	1.059	99.80

^{a}Average of three replicate measurements

Table 4 Evaluation of intra- and inter-days precision and accuracy of CPE in different real samples

Sample no	[Th(IV)] added (mg mL^{-1})	Intra-day			Inter-day		
		[Th(IV)] found (mg mL^{-1})	Recovery (%)	RSD%	[Th(IV)] found (mg mL^{-1})	Recovery (%)	RSD%
2	0.25	0.248	99.20	0.244	0.244	97.60	1.001
	0.40	0.395	98.75	0.399	0.393	98.25	0.891
3	0.30	0.296	98.67	0.693	0.295	98.33	0.801
	0.45	0.447	99.33	0.331	0.444	98.67	0.661

Table 5 Comparing the response characteristics of the developed CPE with some reported Th(IV)-ISEs

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
This work	14.65	9	2.5–5.5	> 3	1.00×10^{-7}–1.00×10^{-1}	4.82×10^{-7}
[33]	14.2	10	3.5–9.5	5	1.00×10^{-6}–1.00×10^{-1}	8.00×10^{-7}
[30]	15.5	15	2.3–4.0	6	1.00×10^{-5}–1.00×10^{-3}	7.90×10^{-6}
[31]	13.9	< 10	3.15–6.5	2	2.00×10^{-7}–1.00×10^{-2}	9.00×10^{-8}
[29]	15.2	30	3.0–9.0	2	1.00×10^{-6}–1.00×10^{-2}	6.30×10^{-7}
[35]	15.5	30	3.0–5.0	2	5.00×10^{-6}–1.00×10^{-1}	1.60×10^{-6}
[27]	31.2	5	4.0–6.5	3	1.00×10^{-7}–1.00×10^{-1}	1.00×10^{-8}
[34]	14.30	11	2.5–9.0	6	4.00×10^{-7}–1.00×10^{-1}	4.00×10^{-7}

successive days, respectively. The calculated recovery and RSD % values (Table 4) indicated that the results were of satisfactory precision.

Comparison of the developed CPE with literature

To remark on the effectiveness of the developed CPE, it was compared with previously reported thorium-ISEs in terms of detection limit (DL), potentiometric slope, usable pH range, dynamic response time, and linear working range. From the data given in Table 5, it is clear that the developed electrode offers good response characteristics superior to or within the same ranges compared to those previously reported for thorium(IV) ions.

Conclusions

The development and application of CPE modified by OPAP and o-MWCNTs for the selective direct determination of thorium(IV) ions were described in this study, for the first time. The developed electrode presented a good Nernstian response over a wide linear range. Thorium(IV) concentrations as low as 4.82×10^{-7} mol L^{-1} can be accurately measured using the developed electrode. pHs within 2.5–5.5 could hardly affect the electrode performance and the noticed fast response time of the developed electrode could facilitate its application in routine analysis. The developed CPE revealed good thermal stability, long operational lifetime, and high selectivity to thorium(IV) ions against different interfering species. The performance of the developed CPE in real samples was analyzed and it revealed good recoveries comparable to the reference method with satisfactory precision. The obtained results showed that the developed CPE allows for convenient, fast, and accurate thorium(IV) ions monitoring.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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