

A fast response hafnium selective polymeric membrane electrode based on *N,N'*-bis(α -methyl-salicylidene)-dipropylenetriamine as a neutral carrier

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Abstract

In this study a new hafnium selective sensor was fabricated from polyvinylchloride (PVC) matrix membrane containing neutral carrier *N,N'*-bis(α -methyl-salicylidene)-dipropylenetriamine (Mesaldpt) as a new ionophore, sodium tetraphenyl borate (NaTPB) as anionic discriminator and dioctyl phthalate (DOP) as plasticizing solvent mediator in tetrahydrofuran solvent. The electrode exhibits Nernstian response for Hf^{4+} (Hafnium(IV)) over a wide concentration range (2.0×10^{-7} to 1.0×10^{-1} M) with the determination coefficient of 0.9966 and slope of 15.1 ± 0.1 mV decades $^{-1}$. The limit of detection is 1.9×10^{-7} M. The electrode has a fast response time of 18 s and a working pH range of 4–8. The proposed membrane shows excellent discriminating ability towards Hf^{4+} ion with regard to several alkali, alkaline earth transition and heavy metal ions. It can be used over a period of 1.5 months with good reproducibility. It is successfully applied for direct determination of Hf^{4+} in solutions by standard addition method for real sample analysis.

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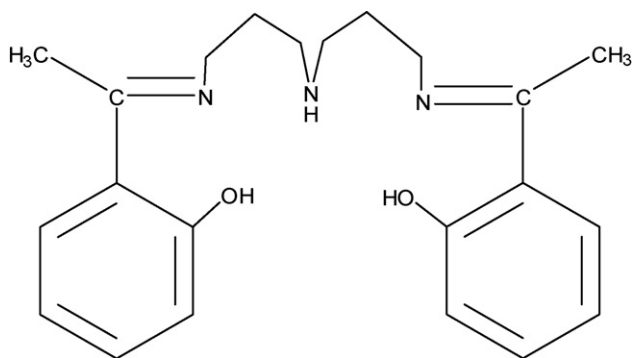
Keywords: Hafnium selective sensor; Polyvinylchloride membrane; Potentiometry; Polyvinylchloride

1. Introduction

The utility of ion sensors in the fields of environmental, agricultural and medicinal analysis is being increasingly realized regard to the rapid growth of industry and technology [1]. The most attractive and interesting aspects of this technique are the speed with which samples can be analyzed, accuracy, reproducibility, selectivity, portability of the device, non-destruction of the sample and cost effectiveness of the commercial sensors [2]. Polymeric carrier-based ion-selective electrodes (ISEs) for determination of the alkali metal cations such as sodium, potassium and lithium [3–9] have been studied numerously. The efforts are required to develop ion-selective electrodes for heavy metal ions in very low concentrations [10–13]. Hafnium is a strategic element. Its thermal neutron absorption cross section is nearly 600 times that of zirconium and because of its ability to absorb neutrons it is used to make control rods for

nuclear reactors. It also has excellent mechanical properties and exceptional corrosion–resistance properties. However due to the similarity of behavior of hafnium and zirconium its determination is difficult. The other principal uses of hafnium, as a heavy metal, are in nickel-based super alloys, nozzles for plasma arc metal cutting, and high-temperature ceramics [14]. So its determination is important. Also all hafnium compounds should be regarded as toxic although initial evidence would appear to suggest that the danger is limited but the metal dust presents a fire and explosion hazard. Overexposure to hafnium and its compounds could cause mild irritation of the eyes, skin, and mucous membranes [15]. Due to vital importance of hafnium determination in chemical, clinical and industrial analysis, many voltametric, conductometric, chromatographic and spectrometric techniques have been reported in the literatures [16–21], but most of them are sophisticated and suffer from the lack of reproducibility, so we were interested in preparation of a new solvent polymeric membrane electrode for selective monitoring of hafnium ion in solutions. In the present work, Mesaldpt that has been synthesized recently in our laboratories [22] was used as an excellent neutral ion carrier for construction of

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Scheme 1. The structure of Mesaldpt.

novel hafnium(IV)–PVC membrane electrode. The ionophore is shown in Scheme 1.

2. Experimental

2.1. Reagents and chemicals

Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) were purchased from Merck and polyvinylchloride (PVC) with high molecular weight from Fluka were used as received.

A 0.100 M stock solution of hafnium tetrachloride was prepared by dissolving an appropriate, accurate amount of HfCl_4 (Merck). A 1.0×10^{-7} to 1.0×10^{-1} M solution of hafnium ion was prepared daily by sequential dilution of the appropriate stock solution with doubly distilled water.

Nitrate salts of cations (all from Merck) were of the highest purity available. All other reagents used were of analytical reagent grade, and doubly distilled water was used throughout. Mesaldpt as an ionophore was synthesized recently in our laboratories.

2.2. Construction and calibration of electrodes

Membranes with different PVC/plasticizer ratios were studied for finding the most suitable membrane composition. The optimum composition was 30% of powdered PVC, 62% of a

plasticizer (DOP), 4% of an additive (NaTPB) and 4% of the corresponding ionophore. These were mixed in 5 mL of THF. The resulting clear mixture was slowly evaporated at room temperature until an oily concentrated mixture was obtained. A Pyrex funnel with narrow opening diameter of 3 mm was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3-mm thickness was formed. The funnel was then pulled out from the mixture and kept at room temperature for about 24 h. The funnel was then filled with an internal filling solution (1.0×10^{-3} M HfCl_4). The electrode was finally conditioned by soaking for 24 h in a 0.010 M solution of hafnium tetrachloride. An SCE (saturated calomel electrode) electrode was used as the reference internal electrode. The compositions of the membrane electrode are summarized in Table 1.

2.3. Apparatus and emf measurements

A UV–vis spectrophotometer (JASCO, model V-540) with a 1.0-cm glass cuvette was used for recording of the absorption spectra. A hafnium selective PVC electrode with general assembly shown in Scheme 2 [1,23] and a saturated calomel electrode were used as an indicating electrode and a reference electrode, respectively. The emf measurements were carried out at 25.0 ± 0.1 °C with Fanavary Tajhizat Sanjesh pH meter Model 162, a double junction SCE reference electrode. The electrode cell assembly of the following type was used:

(SCE) internal solution (1.0×10^{-3} M HfCl_4) sensor membrane (sample solution) (SCE).

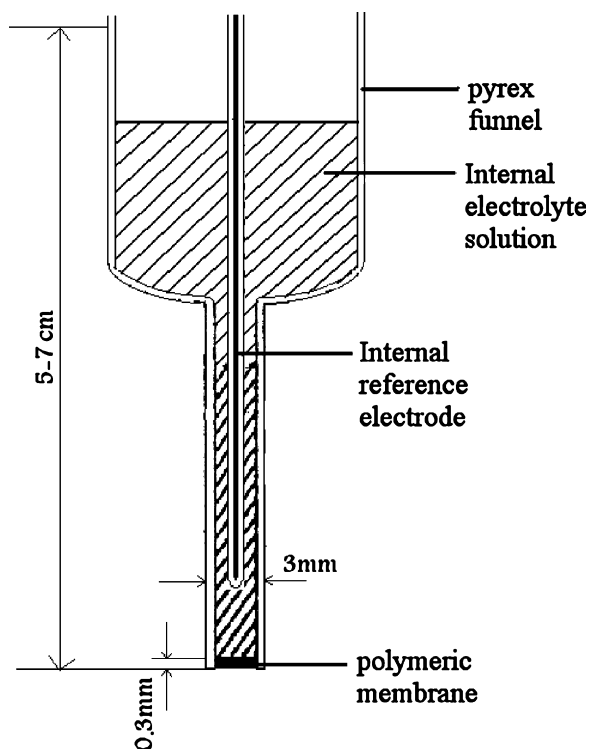
The concentration of the metal ion in the test solutions varied from 1.0×10^{-7} to 1.0×10^{-1} M. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as a logarithmic function of Hf(IV) cation activity. The activities of metal ions were based on the activity–coefficient γ which is calculated from the modified form of the “Eq. (1)” (Debye–Huckel equation) and it is applicable to any ion

$$\log \gamma = -0.511 Z^2 \left[\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} - 0.2\mu \right] \quad (1)$$

where μ is the ionic strength and Z the valency. All measurements were carried out at 25 ± 0.1 °C. All pH adjustments were made with diluted HCl and NaOH.

Table 1
Composition and optimization of membranes ingredients

No.	PVC (%)	Plasticizer (%)	Ionophore (%)	NaTPB (%)	Slope (mV decade ⁻¹)	Linear range (M)	R ²
1	28	DOP, 66	4	2	–15.7	7.0×10^{-7} to 5.0×10^{-1}	0.9878
2	26.6	DOP, 66.3	4.1	3	–18.6	5.0×10^{-7} to 5.0×10^{-1}	0.9662
3	30	DOP, 62	4	4	15.1	2.0×10^{-7} to 2.0×10^{-1}	0.9966
4	27.6	DOP, 63.4	4	5	19.8	6.0×10^{-7} to 5.0×10^{-1}	0.9747
5	30	DOP, 61.5	4	3.5	13.7	6.0×10^{-7} to 5.0×10^{-1}	0.9912
6	31	DOP, 62	4	3	15.8	2.0×10^{-7} to 5.0×10^{-1}	0.971
7	30	DOP, 31.4; DBP, 32.6	3.1	2.9	12.8	3.0×10^{-7} to 5.0×10^{-1}	0.9821
8	31	DBP, 61	4.5	3.5	11.4	3.0×10^{-7} to 5.0×10^{-1}	0.9858
9	30.4	DOP, 60.6	6	3	18	2.0×10^{-7} to 5.0×10^{-1}	0.9552
10	30.8	DOP, 59	7	3.2	15.8	3.0×10^{-7} to 5.0×10^{-1}	0.9269
11	31	DOP, 64	5	–	9.7	5.0×10^{-5} to 5.0×10^{-1}	0.8415



Scheme 2. General assembly of the proposed ISE.

2.4. Procedure for the determination of Hf ion in the real sample

Real water samples containing different hafnium concentrations were prepared by adding known amounts of hafnium to samples. The hafnium selective and reference electrodes were dipped in the samples and the hafnium concentrations were measured by direct potentiometry and using the standard addition technique.

3. Results and discussion

3.1. Preliminary potentiometry studies

In primary experiments, the proposed ligand was used, as a neutral carrier to prepare polymeric membrane electrodes for a variety of metal ions. As it can be seen from Fig. 1, among different tested cation, Hf^{4+} with the most sensitive response seems to be preferably determined with the PVC membrane based on the ligand and the emf responses gained for all other cation selective electrodes are much lower than that predicted by the Nernst equation. The results might indicate that the selectivity towards these ions is masked by the low detection limit of the electrode, which is most probably due to the transport of Hf^{4+} ions from the measuring solution to the boundary between the solution and membrane as discussed by Bakker et al. [24,25]. Among the properties of the d-block metal ions is their unique ability to adopt various coordination geometries and to form different chelate ring size with chelating ligands bearing strong σ -donor atoms [26,27]. The interaction between the metal ion and the donor atoms of the ligand is in part electrostatic leading to the

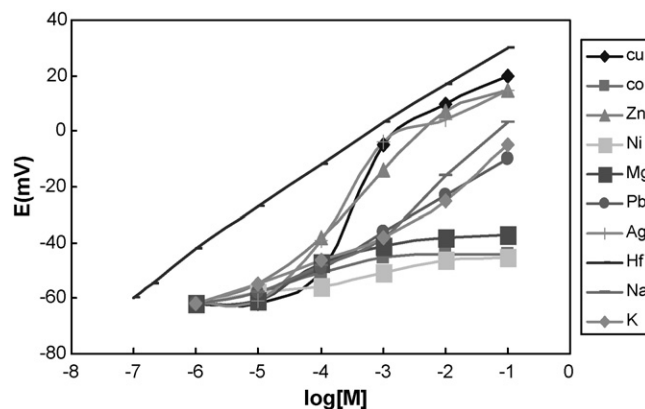
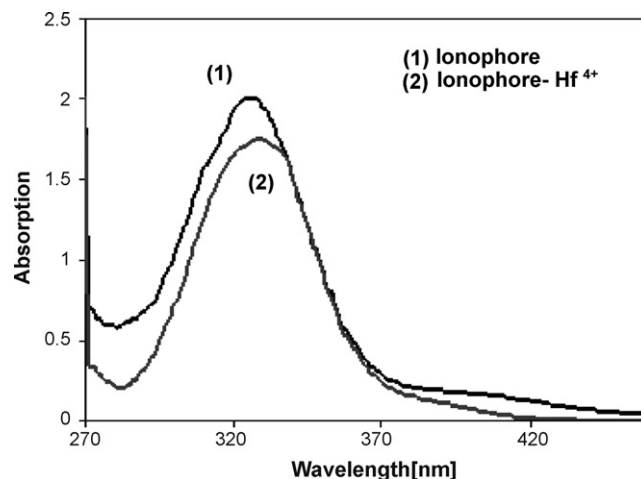


Fig. 1. Potential response of various ion-selective electrodes based on Mesaldpt.

complexes that can participate in reversible reactions. Mesaldpt is N_3O_2 pentadentate ligand that is flexible enough to provide the optimum structure for selective interaction with Hf^{4+} . Therefore, according to the UV–vis spectrum, shown in Fig. 2, it was possible to distinguish the specific interaction between the proposed ionophore and the hafnium ions. The results in Fig. 2 show that the absorption band of 1.0×10^{-4} M Mesaldpt in methanol, at wavelength of 325 nm, has shifted and changed the optical density in the presence of hafnium ions. It is well recognized that the linearity, sensitivity and selectivity obtained for a given ionophore depends strongly on the membrane composition, specially the nature and amount of plasticizer which affects the dielectric constant of the membrane phase, the state of ligands and the mobility of the ionophore molecules [28–40].

3.2. Influence of membrane composition

Besides the important role of the nature of ionophore in preparing membrane selective sensors, some other important features of the PVC membrane are known to significantly influence the linearity range, sensitivity and selectivity of ion-selective electrodes. These include the amount of ionophores, the nature of solvent mediators, the plasticizer/PVC ratio, and

Fig. 2. UV–vis absorption spectra of 1.0×10^{-4} M Mesaldpt in methanol in the absence (1) and (2) in the presence of 1.0×10^{-4} M Hf^{4+} .

especially the nature of the additives used [39]. Thus, different features of membrane preparation based on Mesaldpt for Hf^{4+} ions were optimized and the results are represented in Table 1. Ligands used as ionophores in an $\text{Hf}(\text{IV})$ ion-selective electrode should fulfill certain conditions, they have to act selective for Hf^{4+} ion over other metal cations, and they must have rapid exchange kinetics and should be completely lipophilic to prevent leaching of the ligand into the aqueous solutions [40,41]. Due to its sufficient insolubility in water and the presence of two oxygen and three nitrogen-donating atoms in its structure, the proposed ligand was expected to act as a suitable ion carrier in the PVC membrane-based sensors. The optimization of perm selectivity of membrane sensors is known to be dependent on the incorporation of additional membrane compounds. In fact, it has been observed that the existence of lipophilic-charged additives improves the potentiometric behavior of ISEs not only by reducing the ohmic resistance [42] and improving the response behavior and selectivity [43] but also, in cases where the extraction capability of the ionophore is not sufficient, by enhancing the sensitivity of the membrane electrode [44]. Moreover, the additives may catalyze the exchange kinetics at the sample–membrane interface [36]. So the polymeric membranes were investigated to measure the ability of the ionophore to act as an ion carrier in the absence and presence of the lipophilic excluders. The response of the membrane without additive gave poor sensitivity and resulted in small slope. DOP is a fairly polar plasticizer and it can have better coordination with most cations. This indicates that DOP plasticizes the membrane, dissolves the ion–association complex, and adjusts both the membrane permittivity and the mobility of the ion-exchanger sites to give the highest possible selectivity and sensitivity. Also the polar plasticizers effect deeply on the electrodes detection limits and can lower ion-pairs formation. The solvent mediator's dielectric constant influences on ISE performance characteristics but there are many limitations for this factor. If the intention for attraction between interested ion and proposed ionophore is quite suitable, there is no need of using a plasticizer with very high dielectric constant, maybe working on an intermediate solvent mediator displays much preferred results and performances. The results obtained with different membrane compositions (Table 1) show that membrane number 3 with composition of DOP:PVC:Mesaldpt:NaTPB and the percent ratio of 62:30:4:4 has the optimum composition, slope and dynamic range for detecting hafnium ions, so it was selected for preparation of the polymeric membrane electrode.

3.3. Effect of internal reference solution

Effect of the internal standard solution concentration (HfCl_4) of the membrane selective electrode on the potential response was studied by ion concentrations of 1.0×10^{-1} , 1.0×10^{-3} and 1.0×10^{-5} M (Fig. 3). The results indicated that the variation of the internal HfCl_4 concentration did not cause any considerable difference in the emf- $\log[\text{Hf}^{4+}]$ signal. Thus, the HfCl_4 concentration of 1.0×10^{-3} M, that was quite appropriate for smooth functioning of the electrode system, was selected for the internal reference solution.

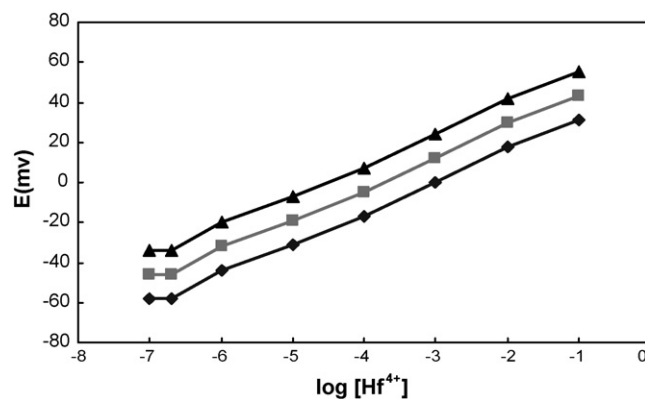


Fig. 3. Effect of the concentration of an internal reference solution on electrode response at various concentrations of 1.0×10^{-1} M (\blacklozenge), 1.0×10^{-3} M (\blacksquare) and 1.0×10^{-5} M (\blacktriangle).

3.4. Influence of pH

The effect of pH on the electrode potential at various hafnium concentrations was investigated by adding diluted solutions of HCl (0.10 M) or NaOH (0.10 M) and adjusting the pH by a pH-meter in the range of 1.0–12.0 (Fig. 4). The obtained data was listed over the range of 1.0–12.0 for 1.0×10^{-3} M $\text{Hf}(\text{IV})$ ions. The results showed that the useful pH range is 4–8 because the potential remains almost constant in this range. The sharp change in potential at higher pH values may be due to separation of H^+ from ionophore molecule by hydroxy group of the used base and significant intention toward Hf^{4+} while at lower pH values H_3O^+ ions start to contribute to the charge transport process by the membrane, thereby causing interference.

3.5. Response characteristics

ISE characterization performed with the mathematical and computational program has been shown to be very useful for determination of detection limits and selectivity constants among others [45]. Non-linear curve fitting using available common software has been used for the determination of ISE

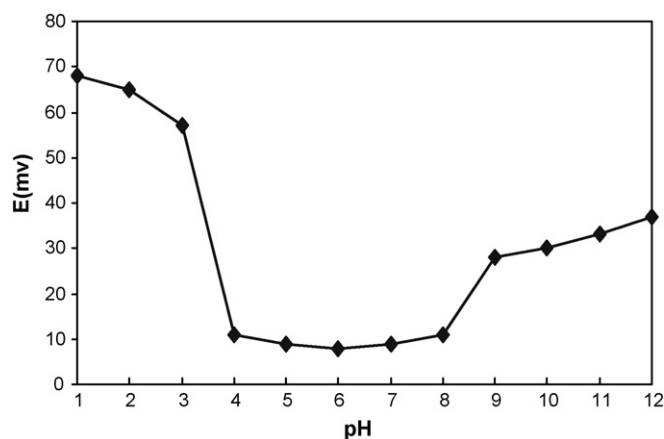


Fig. 4. Influence of pH on the potential response of the hafnium selective electrode to 1.0×10^{-3} M Hf^{4+} .

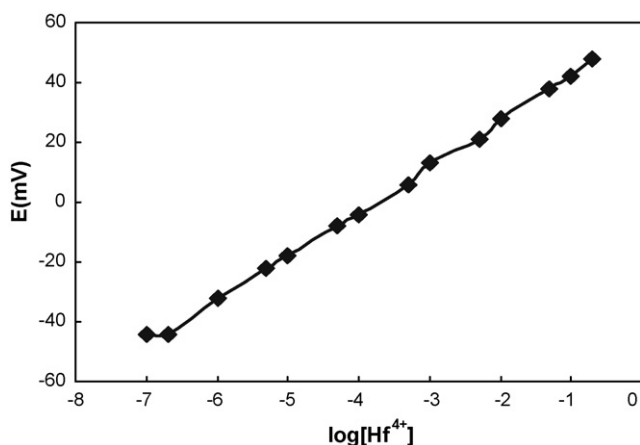


Fig. 5. Calibration graph for the proposed Hf^{4+} -ion-selective electrode.

characteristics [46]. In accordance with this, the slope, detection limit and coefficients of the hafnium selective electrode were determined by fitting the calibration data to Nikolskii–Eisenman equation or to the formula of Bakker et al. [47] for mixed-ion solutions of primary and interfering ions with different charges. The electrode exhibits a linear response ($R^2 = 0.9966$) to the activity of Hf^{4+} ion in the range about 2.0×10^{-7} to 1.0×10^{-1} M (Fig. 5). The calibration parameters obtained are included in Table 2.

The lifetime of electrodes based on ionophore in solvent polymeric membranes depends strongly on the distribution coefficient of the plasticizer and the ionophore between the membrane and aqueous phases [48]. Thus, the lifetime of electrodes must depend on the components of the solution and the measured specimens with electrodes. The lifetime of the electrodes was worked out by performing calibrations periodically

Table 2
Response characteristics of the proposed hafnium selective electrode

Slope (mV decade^{-1})	15.1 ± 0.1
Linear range (mol L^{-1})	2.0×10^{-7} to 1.0×10^{-1}
Detection limit (mol L^{-1})	1.9×10^{-7}
Response time, 2×10^{-7} to 2.0×10^{-1} mol L^{-1} (s)	<18
Working pH range	4–8
Lifetime (months)	1.5

Table 3
Conditioning time of optimized Hf–ISE

Time (day)	Slope (mV decade^{-1})	Linear range (mol L^{-1})
1	15.1 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
2	15.1 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
5	15.1 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
9	15.1 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
15	15.1 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
23	15.0 ± 0.1	2.0×10^{-7} to 2.0×10^{-1} M
35	15.0 ± 0.1	5.0×10^{-7} to 2.0×10^{-1} M
45	15.0 ± 0.1	5.0×10^{-7} to 2.0×10^{-1} M

Table 4
Potentiometric selectivity coefficient values of various interfering ions (0.01 M).

M^{n+}	$K_{\text{Hf},M}^{\text{pot}}$	M^{n+}	$K_{\text{Hf},M}^{\text{pot}}$
Na^+	1.3×10^{-2}	Cd^{2+}	2.4×10^{-2}
K^+	1.1×10^{-2}	Tl^+	3.5×10^{-2}
Mg^{2+}	6.6×10^{-3}	Ag^+	1.0×10^{-1}
Ni^{2+}	5.7×10^{-3}	Zn^{2+}	3.6×10^{-1}
Co^{2+}	6.9×10^{-3}	Cu^{2+}	5.0×10^{-1}
Mn^{2+}	2.7×10^{-2}	Zr^{4+}	8.2×10^{-2}
Pb^{2+}	2.0×10^{-2}	Al^{3+}	3.4×10^{-2}
Fe^{3+}	5.8×10^{-2}	Ce^{4+}	1.1×10^{-1}

with standard solutions and calculating the response, slope over the range 2.0×10^{-7} to 1.0×10^{-1} M HfCl_4 solution. The experimental results show that the lifetime of the present electrode was over 1.5 months. During this period, the electrode was in a hafnium tetrachloride solution and the detection limit and the slope of the electrode remained almost constant. Subsequently the electrochemical behavior of the electrode gradually deteriorated which may be due to ageing of the polymer (PVC), plasticizers and ionophore (Table 3).

The response time of the electrode was tested by measuring the time required to achieve a steady potential within 1 mV fluctuation by a rapid increase in the Hf(IV) ion concentration. The response time of the electrode based on the proposed ligand demonstrated a steady potential within 18 s.

3.6. Selectivity

The selectivity behavior is obviously one of the most important characteristics of a membrane sensor, determining whether a reliable measurement in the target sample is possible [33,49]. In order to achieve the selectivity of the proposed hafnium ion-selective electrode over other cations (M^{n+}), the method of fixed interference was employed [50]. According to this method, the potentiometric selectivity coefficients, $K_{\text{Hf},M}^{\text{pot}}$, can be evaluated from the potential measurements of solutions containing a fixed concentration of interfering ion, M^{n+} (aM^{n+} 0.01 M) and titration with Hf^{4+} solution. The potential values obtained were then plotted against the activity of the hafnium ion. The intersection of the extrapolated linear portions of this curve will indicate the activity of Hf^{4+} (a_{Hf}), which is to be used to calculate $K_{\text{Hf},M}^{\text{pot}}$

Table 5
Determination of Hf(IV) recovery by the proposed electrode in the spiked samples

Sample	Added hafnium ($\times 10^{-4}$ M)	Found hafnium ($\times 10^{-4}$ M)	Recovery (%)
Tap water	0.0	0.0	–
	2.0	1.94 ± 0.08	97.0
	4.0	3.91 ± 0.13	97.8
	6.0	6.17 ± 0.19	102.8
River water	0.0	0.0	–
	3.0	2.92 ± 0.10	98.9
	5.0	5.16 ± 0.12	103.2
	7.0	6.72 ± 0.14	96.0

Table 6
Determination of Hf(IV) in the real sample

Sample	Added hafnium ($\times 10^{-4}$ M)	Found hafnium by proposed method ($\times 10^{-4}$ M)	Found hafnium by ICP method ($\times 10^{-4}$ M)	Recovery (%)
Rafinate (1)	0.0	7.52 ± 0.11	7.84	95.9
	10.0	18.57 ± 0.17	18.84	98.6
	30.0	37.46 ± 0.14	37.84	99.0
	50.0	57.13 ± 0.21	57.84	98.8
Rafinate (2)	0.0	3.81 ± 0.09	3.92	97.2
	10.0	13.36 ± 0.12	13.92	96.0
	30.0	32.66 ± 0.15	33.92	96.3
	50.0	54.53 ± 0.22	53.92	101.1

values from the equation:

$$K_{\text{Hf,M}}^{\text{pot}} = \frac{a_{\text{Hf}}(\text{DL})}{a_{\text{M}}^{4/n}}$$

The resulting $K_{\text{Hf,M}}^{\text{pot}}$ values are summarized in Table 4. For most of the polyvalent cations used, the selectivity coefficients show low values, indicating negligible interference in the performance of the membrane electrode assembly. The selectivity coefficient of an ISE not only depends on ion charge, activity or conc. but also it can be affected by the type of interaction between ion and ionophore. For example a tetravalent ion might represent higher selectivity coefficient and strong interaction with ionophore in comparison to a univalent ion.

3.7. Applications

The new hafnium selective electrode was applied to obtain recoveries of hafnium in tap and river wastewater samples by proposed electrode with satisfactory results. The analysis was performed by using the standard addition technique. The results are summarized in Table 5. Good recoveries were obtained for all samples. The electrode was also successfully applied to the direct determination of hafnium in rafinated samples supplied by industrial site in suburbs of Isfahan city. The rafinated samples are approximately contains (0.01 M) of nitrate and chloride (0.01 M) of sodium and potassium and 4×10^{-5} M of zirconium. The hafnium content obtained from three replicate measurements in two different samples was $(7.52 \pm 0.11) \times 10^{-4}$ and $(3.81 \pm 0.09) \times 10^{-4}$ M which was found to be in agreement with that obtained by ICP (inductively coupled plasma) method (7.84×10^{-4} and 3.92×10^{-4} M, respectively). These results are represented in Table 6.

4. Conclusions

The proposed ionophore performed well as a neutral carrier in developing a new hafnium selective electrode. The electrode showed better detection limit and response time than most of the previous hafnium determining techniques and was proved suitable for the determination of hafnium in the presence of other cations. A major advantage of the present electrode concerns its facile applications. The present electrode permits direct poten-

tiometric measurement of hafnium in real samples without prior separation steps for the first time, thus considerably simplifying the determination procedure compared with other analytical methods.

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