Research Article

Design and Construction of a Novel Green Optode for Hafnium Determination in Real Environmental Samples

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Abstract A highly selective and sensitive Hf optode was developed, which uses a triacetylcellulose membrane to immobilize 4-(2-benzothiazolylazo)2,3-biphenyldiol (BTABPD). The membrane optode responds to hafnium ions by color changing reversibly from yellow-orange to pink in thiel buffer at pH 5.0. The proposed membrane under optimum experimental conditions exhibits a linear dynamic range of 5.0–$185\,\mathrm{ng\,cm^{-3}}$ of the Hf(IV) with detection and quantification limits of 1.58 and $4.95\,\mathrm{ng\,cm^{-3}}$, respectively. The newly developed optode has a response time of 15–30 s based on the Hf^{4+} ion level. The optode's response is determined by the pH range of 4.5–5.5. The complex's quantification and detection limits, Sandell sensitivity, molar absorptivity, Ringbom, calibration ranges, and relative standard deviation (RSD) have all been accurately calculated. The presented optode records fast response time, low detection limit, and, most significantly, excellent selectivity towards a number of lanthanide and transition ions (Sc^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, Gd^{3+}, Sm^{3+}, Lu^{3+}, Tm^{3+}, Ho^{3+}, Dy^{3+}, Eu^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+}, Sn^{2+}, Mn^{2+}, Tl^+, Ag^+, Zn^{2+}, Fe^{2+}, Cr^{3+}, and Zr^{4+} ions). The optode was regenerated successfully with thiourea and its response was reproducible (RSD $\leq 1.9\%$) and reversible. The proposed optode was successfully applied to detect Hf(IV) ions in real samples.

Keywords optode; hafnium determination; 4-(2-benzothiazolylazo)2,3-biphenyldiol; triacetylcellulose; environmental analysis

1. Introduction

The primary contaminant in zirconium compounds, which have a 2.0–3.0% Hf(IV) content, is hafnium(IV). Both hafnium and zirconium, if applied in the nuclear industry, must be separated. Hafnium absorbs neutrons much better than any other element and is resistant to corrosion; therefore, it is used to control nuclear reactions. Hafnium is applied for alloying with aluminium, iron, titanium, and other elements. It is resistant to corrosion because it is an impenetrable oxide layer on its surface and hard. Hafnium is utilized in high-temperature alloys in the ceramics sector because of its extremely high melting point [1,2].

The most methods often used for the above purpose are isotope dilution neutron activation analysis (IDNAA) [3,4], neutron activation [5], X-ray fluorescence [6], and isotope dilution mass spectrometry [7] used as standard natural hafnium solutions [1,2,3]. These procedures are usually free of interference from diverse metals [5]. Nevertheless, to counteract or minimize the influence of the matrix on the detection of the micro-component, hafnium, other methods of Hf(IV) detection require the preparation of standards using a matrix consisting of extremely pure zirconium (zirconium salts).

From an analytical perspective, it is crucial to identify Hf ions in alloys and other substances directly. Developing a highly selective and sensitive spectro-photometric method for Hf^{4+} is crucial. To increase sensitivity, inductively coupled plasma atomic emission spectrometry and electrothermal atomic absorption spectrometry were employed; however, these techniques typically need costly and time-consuming equipment, which is only available in some facilities [8,9]. These days, spectrophotometric methods are among the most used ways to identify metal ions. Hf(IV) was detected spectrophotometrically using a variety of reagents [10,11,12,13,14]. A small number of chromogenic reagents however are available for the spectrophotometric determination of Hf. Alizarin red S [15], xylenol orange [16], Arsenazo III [17,18], 4-(2-thiazolylazo)resorcinol (PAR) [19], 1-(2-pyridylazo)-2-naphthalenol (PAN) [20], and methylthymol blue [21] were recommended for spectrophotometric detection of Hf(IV). These procedures have their own advantages and disadvantages. The detection is interfered by various ions such as Cu^{2+}, Co^{2+}, Cd^{2+}, Be^{2+}, Hg^{2+}, Mn^{2+}, Pb^{2+}, Sn^{2+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, Si^{4+}, Re^{4+}, and W^{6+}. The requirement to separate the various ions from the solution before Hf determination was a drawback of these methods [21].

The determination of very low concentrations of Hf usually requires separation and preconcentration steps [22, 23,24]. The determination of the traces of Hf in presence of

Zr is very difficult by classical wet chemical methods [25]. Since Zr and Hf undergo hydrolysis and polymerization in solution with other elements, consideration must be used during sample decomposition and dissolution for these analyses. The separation of Zr and Hf is a laborious procedure because these two elements have similar chemical characteristics. Zr-Hf separation techniques include liquid-liquid extraction, ion exchange chromatography, and precipitation. Since zircon is a refractory material, quantitative dissolution requires fusion rather than acid attack [26]. Flame AAS has trouble analyzing Zr and Hf because there is not enough production of free atoms in the flame, which results in low detection limits. When zircon is dissolved using fusion mixes, the total dissolved solids increase, which causes significant issues with nebulization to ICP-OES or ICP-MS [27]. By contrast, ZrO_2 and HfO_2 can be individually determined at wide concentrations using a technique called wavelength dispersive X-ray fluorescence spectrometry (WDXRFS). Using a quick and easy sample preparation procedure including a finely ground ($< 63 \mu$m) powdered sample pellet, WDXRFS analysis yields extremely exact results in a non-destructive manner [28]. However, the use of WDXRFS requires many standard samples for reference.

Over the last three decades, the field of optical chemical sensors (optodes) has been a growing field area. Chemical sensor technology involves subsequent transduction of the analytical signals and the key processes of chemical recognition of the analytes of interest. The development of optodes [29] has been mostly dependent on the immobilization of the chromophore by either chemical (covalent bond) or physical (sol-gel, adsorption, encapsulation, etc.) procedures and incorporated in the membrane design. The immobilization process can be carried out either directly on the surface of the optical fibers (intrinsic optodes) or on the best material that can serve as a bridge between the sample and the fiber optic system (extrinsic optodes) [30]. The sensing phase consists of immobilized chromophore reagents in either inorganic or organic matrices. The absorbance behavior of the sensitive layer is changed when it reacts with the analyte. Optode design relies on metalochromic indicators and organic dyes, which are essential components for the spectrophotometric detection of various metals [31].

There is no report on the immobilization of 4-(2-benzothiazolylazo)2,3-biphenyldiol (BTABPD) on a triacetylcellulose membrane, to the best of our knowledge; BTABPD has been applied to the spectrophotometric determination of niobium(III) [32], bismuth(III) [33], titanium [34], and palladium [35]. In the present paper, an optode fabrication is described to determine ultra-trace amounts of Hf(IV) in which the sensing chromophore is BTABPD immobilized on triacetylcellulose membrane. Basic theoretical and principles description of bulk optode membranes based on the reversible mass analyte transfer from the sample in the bulk of the sensing layer have been well elucidated [30, 31]. The reaction only takes a few minutes to complete, and when measured using spectroscopic detection in the absorbance mode, the color changes from yellow-orange to pink. The membrane layer can be quickly and completely refreshed using a thiourea, which makes the optode fully reversible. The results obtained indicate that the proposed optode is an effective instrument for determining the Hf(IV) content in various environmental samples.

2. Experimental

2.1. Reagents

All chemicals and reagents were achieved from analytical reagent grade chemicals supplied from Merk (Darmstadt, Germany). A stock Hf(IV) solution was prepared by dissolving appropriate weights of $HfOCl_2 \cdot 8 H_2O$ (Merck) in $100 \, cm^3$ of $0.1 \, mol \, dm^{-3}$ HCl to make a $1,000 \, \mu g \, cm^{-3}$ solution. A $10 \, \mu g \, cm^{-3}$ working standard solution was prepared by accurate dilution of the stock ones with deionized water. Thiel buffer solutions of various pH values 2–12 were prepared as represented earlier [36]. Stock solutions of $15,000 \, ng \, cm^{-3}$ of interfering ions were prepared by dissolving appropriate weights of suitable salts in deionized water. BTABPD was synthesized using conventional diazotization and coupling methods described earlier [33].
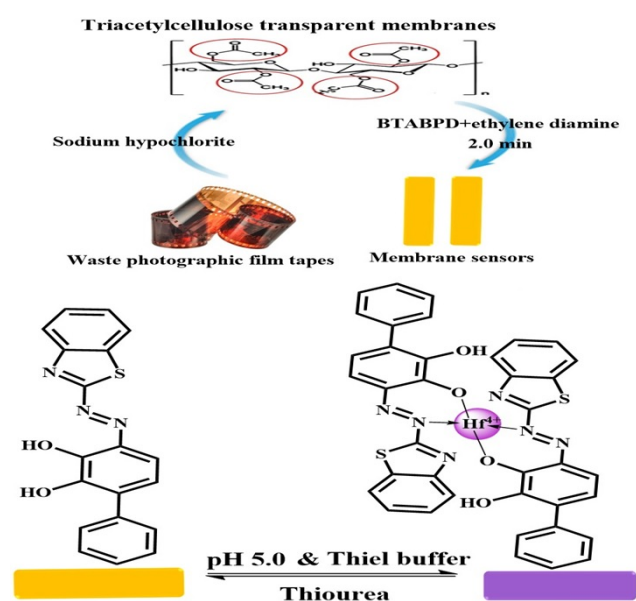
2.2. Apparatus and measurement procedures

A Hamilton syringe ($10 \, \mu$L) was used to deliver trace volumes of Hf^{4+} into the cell. The reference cell contained a membrane prepared in the same way without Hf^{4+}. A Perkin-Elmer Lambda 12 UV-vis spectrophotometer with a 10 mm quartz cell was used for all spectral measurements. All measurements were made in the λ_{max} of 616 nm. An Orion research model 601A/digital ionalyzer pH meter was used for checking the pH of solutions. A Perkin Elmer atomic absorption spectrometry model *AAnalyst* 300 was used for all GFAAS measurements.

The sensing membrane was fixed and placed in a cuvette. The length of the film is exactly as the length of the cuvette. Thus, the optode is placed in the cell and cannot move during the determinations. All measurements were performed in a batch mode. Optode membrane response to various metal ions was studied. Membrane was first exposed to buffer solution and absorbance was measured at 497 nm. Then, the sample solution was added and absorbance at 616 nm against BTABPD membrane was measured after 1 min. All results are based on six replicate measurements.

2.3. Preparation of the membrane sensor

Triacetylcellulose transparent membranes were produced from waste photographic film tapes, which were previously

Scheme 1: Representative diagram for the preparation and complexation of the formed optode.

Figure 1: Absorption spectra for $100 \, \text{ng cm}^{-3}$ Hf(IV) complexed and immobilized BTABPD at pH 5.0.

treated with commercial sodium hypochlorite for one min in order to remove the colored gelatinous layers. Films $(1 \, \text{cm} \times 4 \, \text{cm})$ were treated with a clear BTABPD $(3 \, \text{mg})$ in $10 \, \text{mL}$ ethylene diamine for 2 min at $25 \pm 2.0 \, ^\circ\text{C}$. Afterwards, they were washed with deionized water for the removal of ethylene diamine and the loosely trapped chromophore (BTABPD). Membranes were finally washed with detergent solutions and water. Prepared membranes were kept under water, when not in use [37].

2.4. General procedure

To reach equilibrium, the prepared optode membranes were inserted in a buffer of pH 5.0 for 3 min. Then, membranes were put vertically inside the sample and blank cuvettes containing $2.5 \, \text{cm}^3$ buffer of pH 5.0. The sample cell was finally titrated with Hf(IV) ions solution and the absorbance value was measured over the wavelength range of 400–740 nm after 3 min. The absorbance of optode membrane was measured, at λ_{max} of 616 nm.

2.5. Samples preparation

2.5.1. Procedure for Hf ion determination in real samples

Real water samples containing various Hf(IV) levels were prepared by adding known amounts of Hf(IV) to the samples. The Hf(IV) content of the each samples solution was detected by the proposed optode applying the standard addition technique.

River water samples (from different locations of river, Benha, Egypt) did not require previous treatment and were analyzed for Hf^{4+} ion level applying the described optode. pH of river water was adjusted by the addition of $2 \, \text{cm}^3$ of thiel buffer (pH 5.0) to $10 \, \text{cm}^3$ of river water.
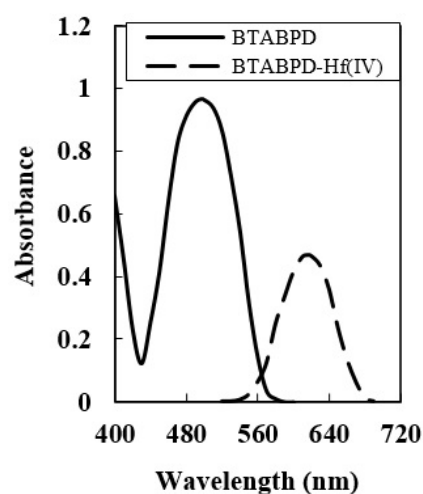
2.5.2. Determination of hafnium in zirconium oxides

In order to confirm the high usefulness and resolution of the apparatus, Hf(IV) present as an impurity in commercial high-purity zirconium oxides achieved from three various makers was determined with it. The results when compared with those obtained by ICP-AES show that the performance of the apparatus has been confirmed. In addition, it was found that the amounts of Hf(IV) contained in these so-called "high-purity" zirconium oxides are of the order expected for zirconium oxide not subjected to purification.

2.5.3. For soil and copper-based alloy

A $0.5 \, \text{g}$ of each sample was weighted and transferred into a $30 \, \text{cm}^{-3}$ platinum vessel separately to determine Hf(IV) in soil and copper-based alloy. A $10 \, \text{cm}^{-3}$ of concentrated HNO_3 and $5 \, \text{cm}^{-3}$ of concentrated HCl were added into each of the vessels. Each mixture was heated until complete evaporation of its solution. This process (digestion) was replicated three times, and then $2 \, \text{cm}^{-3}$ of concentrated HNO_3 and $5 \, \text{cm}^{-3}$ of concentrated HF were added into each vessel and heated to boiling point. The mixture was filtered and washed three times by $10 \, \text{cm}^{-3}$ deionized water. The filtrates were evaporated to a volume of $3 \, \text{cm}^{-3}$, and then the pH was adjusted to 5.0 by adding a $1 \, \text{mol dm}^{-3}$ solution of NaOH. A suitable amount of ammonium acetate salt was added so that its concentration was reached to $0.3 \, \text{mol dm}^{-3}$ in a final volume of $5 \, \text{cm}^{-3}$.

3. Results and discussion

3.1. Spectral characteristics

The absorption spectra of immobilized BTABPD on hydrolyzed cellulose acetate were represented in Figure 1, after equilibration in a buffer of pH = 5.0 containing various levels of Hf(IV) ions. The spectral characteristic of
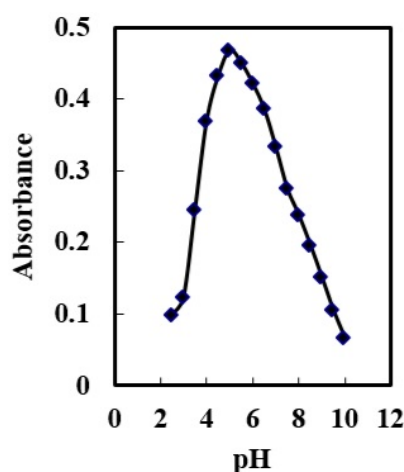
Figure 2: Absorbance of the optode in solutions containing $100 \, \text{ng cm}^{-3}$ Hf(IV) at different pH values.

the BTABPD membrane indicates a maximum band that appears at 497 nm (Figure 1). The spectral change is the result of the addition of Hf(IV) and complex formation in the optode (Figure 1). The spectral change to bathochomic shift (increase in absorption band by 119 nm) is the result of the increase of Hf(IV) ions amount in the membrane, which is due to its extraction into the membrane and complex formation. For all additional studies, the λ_{max} of 616 nm was selected, due to higher sensitivity and selectivity at this wavelength.

3.2. pH influence

The response of the optode was investigated through an examination of various buffer solutions. Experiments were conducted on acetate, phosphate, borate, thiel, and universal buffers. Thiel buffer solution was the best buffer. The effect of the pH value on the optode membrane's reaction is shown in Figure 2. The absorbance measurements were made for $100 \, \text{ng cm}^{-3}$ Hf(IV) ions in the pH range of 2.5–12 at 616 nm. It was represented that the hafnium complex was absorbed maximally at pH 5.0. In subsequent investigations, the pH was maintained a maximum absorbance at pH 5.0. Moreover, the addition of $2.0–4.0 \, \text{cm}^{-3}$ of the buffer did not affect the absorbance of the complex and the use of $2.5 \, \text{cm}^{-3}$ is recorded. At pH values lower than 5.0, the absorbance starts to increase. This phenomenon might be due to the fact that at lower pH values (pH < 5.0), complexation is weak. At pH values higher than 5.0, Hf(IV) complex decreases gradually slowly due to the dissociation of the formed complex with increasing pH values. Thus, pH 5.0 was selected for further works.

3.3. Response time

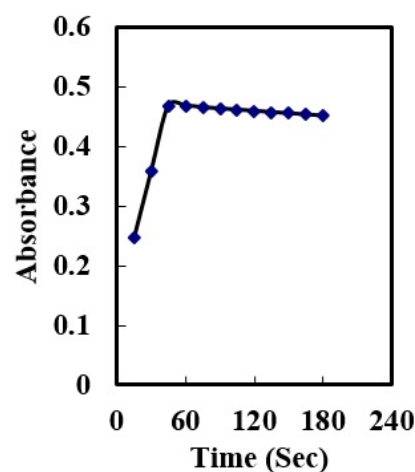After examining several immobilized phases, triacetyl-cellulose membrane was found to be the most effective.

Figure 3: Effect of response time on the absorbance of the proposed optode; conditions: [Hf(IV)] = $100 \, \text{ng cm}^{-3}$; pH = 5.0.

The response time of an optode is a crucial analytical characteristic. The optode response time is controlled by the time needed for the analyte to diffuse from the bulk to the membrane interface and to complex with the chromophore [38]. The optode response time was tested by measuring the absorbance change at 616 nm from a buffer (pH 5.0) to a buffered Hf(IV) solution of $100 \, \text{ng cm}^{-3}$. The membrane was found to reach 97.5% of the absorbance at 45–60 S depending on the amount of Hf(IV) ion (Figure 3). In general, the response time is lower in concentrated solutions than dilute ones due to strict hindrance in the membrane to form a complex. In general, the response time of the optode membrane is governed by three processes: (1) film diffusion, (2) complex formation rate between metal ion and ligand, and (3) complex dissociation rate [38]. It should be noted that the binding of the Hf(IV) ion to BTABPD is a kind of coordination to the OH group and the nitrogen of the azo group of the ligand.

3.4. Optode regeneration

To ensure proper color changing, an optode membrane must be reversible. In order to change the color of the Hf(IV) complex, several chemicals were examined. Regenerating reagents such as ethylene diamine, thiourea, SCN, and uric acid were studied. However, there was no additional improvement observed in the optode's reversibility after partial and lengthy exposure to SCN, EDTA, sulfosalicylic acid, and uric acid. Among the reagents tested, thiourea proved to be the optimal choice, as it had a quick regeneration period of about two minutes. The on use durability of the sensor phase was achieved by subsequently placing the membrane in Hf(IV) solutions and regenerating. After regeneration and for the next Hf(IV) concentration measurement, the optode should be put in buffer (pH 5.0) for 3–5 min.

3.5. Selectivity

The selectivity of the optode membrane was tested, and the BTABPD membrane was examined to determine $100\,\mathrm{ng\,cm^{-3}}$ of Hf(IV) ions in the presence of some metal ions including Sc^{3+}, Y^{3+}, La^{3+}, Ce^{3+}, Gd^{3+}, Sm^{3+}, Lu^{3+}, Tm^{3+}, Ho^{3+}, Dy^{3+}, Eu^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+}, Sn^{2+}, Mn^{2+}, Tl^{+}, Ag^{+}, Zn^{2+}, Fe^{2+}, Cr^{3+}, and Zr^{4+} ions. The tolerance limit was taken as the concentration causing an error of $\pm5.0\%$ in the absorbance for Hf(IV) determination [31]. At the applied pH value, no interference was achieved from even 6000-fold excess of the above metal ions. The surprisingly high selectivity of the BTABPD membrane for Hf(IV) ions over other cations examined most probably arises from the strong tendency of the complexation BTABPD for Hf(IV) ions.

3.6. Stoichiometry of BTABPD-Hf(IV) complex

Figure 1 shows the absorption spectra of BTABPD and the APASA-Hf(IV) complex. This gives us important information about the wavelengths at which they absorb. Notably, the peak absorption of BTABPD is at 490 nm, while the BTABPD-Hf(IV) complex has a very clear absorption band at 616 nm. To ascertain the stoichiometry of the BTABPD-Hf(IV) complex, two methods, namely, the molar ratio and Job's methods, were employed.

The molar ratio method showed that the best absorption happened at a ratio of 2.0 : 1.0 [BTABPD : Hf(IV)], which shows the formation of 2 : 1 complex. Similarly, Job's method yielded a mole ratio of 0.33, further substantiating the formation of a 2 : 1 stoichiometric ratio in the BTABPD-Hf(IV) complex. These findings, combined with the infrared (IR) spectra of BTABPD and the BTABPD-Hf(IV), provided the basis for proposing the structural representation of the complex as depicted in Scheme 2.

3.7. Analytical data

The calibration curve represented that the BTABPD membrane system obeys Beer's law in the dynamic range of $5.0\text{–}185\,\mathrm{ng}$ Hf(IV) per $\mathrm{cm^{-3}}$ in the measured samples. For a more accurate analysis, Ringbom optimum concentration range was found to be $15\text{–}170\,\mathrm{ng}$ Hg^{2+} per $\mathrm{cm^{-3}}$ in the measured phase. The linear regression equation was found as $A = 0.468\,C\,(\mathrm{ng\,cm^{-3}}) + 0.005$ $(r = 0.9985)$. The molar absorptivity was evaluated to be $8.36 \times 10^{6}\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at 616 nm, whereas Sandell sensitivity was $0.021\,\mathrm{ng\,cm^{-2}}$. The standard deviations of the absorbance measurements were evaluated from a series of 13 blank solutions. The limits of quantification $(K = 10)$ and of detection $(K = 3)$ of the procedure were illustrated according to the IUPAC definitions [39], $C_1 = KS_o/s$ where C_1 is the limit of detection, K is the constant related to the confidence interval, s is the slope of the standard curve, and S_o is the standard error of blank. The limits of quantification and
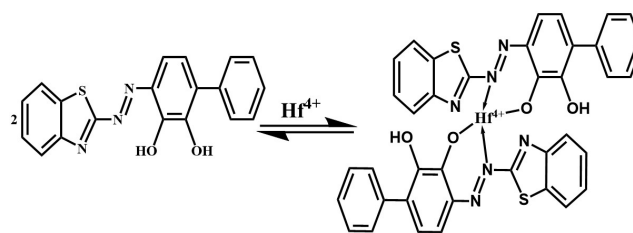
Scheme 2: Representative chemical structure of BTABPD-Hf(IV) complex.

of detection limits are found to be 4.95 and $1.58\,\mathrm{ng\,cm^{-3}}$, respectively.

3.8. Reproducibility and repeatability

Reproducibility and repeatability of the optode are two important characteristics. Both parameters were studied in this study. Reproducibility was obtained by determining $100\,\mathrm{ng\,cm^{-3}}$ of Hf^{4+} (six replicate determinations). Coefficient variation of the responses between the membranes was 2.15%.

To evaluate the discrepancies in the response for successive runs using a single optode, the repeatability was calculated by performing seven determinations with the same Hf(IV) standard solution. The coefficient of variation of optode response for $100\,\mathrm{ng\,cm^{-3}}$ Hf(IV) was 1.9%. The mean absorbance values with the standard deviation were found to be 0.382 ± 0.009 $(n = 6, 100\,\mathrm{ng\,cm^{-3}}$ Hf(IV) ion) and 0.015 ± 0.014 $(n = 6, 100\,\mathrm{ng\,cm^{-3}}$ thiourea solution). For the evaluation of differences in responses of individual optodes, four membranes were prepared from the same mixture.

3.9. Lifetime

A buffer with pH 5.0 was added to the cuvette which held the membrane to detect the optode lifetime. The absorbance at $\lambda_{\max}$ of 616 nm was measured for around 10 h. It was observed that there was no significant loss of BTABPD during this time. The experiment revealed that the optode remained stable and did not leak when exposed to light. Furthermore, there was no change in absorbance throughout the experiment. However, the prepared membranes were kept under water, when not in use, to prevent them from drying out. Moreover, the stability of the optode response was investigated over 5 weeks under ambient conditions, representing that the optode was stable over this period.

3.10. Recovery examines

Samples of minerals, tap, river, and waste water were subjected to recovery examinations using the spike approach. Each sample was measured three times. Table 1 shows that Hf(IV) can be recovered with high accuracy from solutions with a concentration ranging between 98.25% and 103.75%.

Table 1: Determination of Hf(IV) ion in spiked four water samples.

Sample	Hf(IV) added (ng cm^{-3})	Hf(IV) found (ng cm^{-3})		RSD (%)	Recovery (%)
		Proposed	ICP-AES		
Tap sample	0.00	ND[a]	ND[a]	—	—
	40.0	41.5	39.1	1.2	103.75
	80.0	78.6	81.5	1.6	98.25
Mineral water	0.00	ND[a]	ND[a]	—	—
	60.0	60.5	58.7	1.2	100.83
	120	118.7	121.1	1.8	98.92
River water	0.00	ND[a]	ND[a]	—	—
	50.0	49.2	50.6	1.1	98.40
	100	101.2	102.2	1.4	101.20
Waste water	0.00	ND[a]	ND[a]	—	—
	70.0	69.6	71.4	1.3	99.43
	140	141.0	138.3	1.7	100.71

[a]Not detected.

Table 2: Application of the proposed and ICP-AES methods to the determination of Hf in real samples.

Sample	Certified value	Measured value[a] (ng g^{-1})		t-test[b]	F-value[c]
		Proposed	ICP-AES		
Standard soil	7.0	6.9 ± 0.3	7.2 ± 0.1	2.11	4.48
	20	27.2 ± 0.6	28.3 ± 0.4	1.86	3.56
	60	59.5 ± 0.4	58.2 ± 0.6	1.59	3.23
	100	100.9 ± 0.5	98.4 ± 0.9	1.88	4.02
Copper based alloy	—	5.0 ± 1.1	5.5 ± 0.9	—	—
	50	54.4 ± 0.7	56.2 ± 1.3	1.48	3.47
	80	86.0 ± 0.5	84.1 ± 1.4	2.24	4.11
	120	124.5 ± 0.8	127.0 ± 1.7	1.65	3.78
Zirconium oxide[d]	—	22.0 ± 0.6	22.3 ± 1.8	2.11	3.95
	30	53.2 ± 0.9	51.5 ± 1.6	1.73	3.59
	60	81.1 ± 0.7	84.6 ± 2.1	1.82	4.04
	90	110.7 ± 1.0	115.0 ± 2.4	1.57	3.34
Zirconium oxide[e]	—	13.5 ± 0.5	13.2 ± 2.0	1.37	3.69
	40	53.0 ± 0.8	54.0 ± 1.8	1.66	3.81
	80	92.3 ± 0.6	95.7 ± 2.3	1.87	3.96
	120	135.5 ± 0.9	121.8 ± 1.9	2.02	4.13

[a]Mean ± standard deviation ($n = 6$).   [b]Tabulated t-value for five degrees of freedom at P (0.95) is 2.57.
[c]Tabulated F-value at P (0.95) is 5.05.   [d]Sold as 99.9% ZrO_2.   [e]Sold as 99.99% ZrO_2.

The results obtained using the spike approach were compared with those obtained using the ICP-AES approach, and they were found to be in agreement [40].

3.11. Analytical applications

The process was applied to recover additional amounts of Hf(IV) from four actual water samples to check its accuracy. Table 1 summarizes the recovery outcomes. It shows that the suggested technique can be used to calculate Hf(IV) in various matrices. The applicability of the presented procedure to determine Hf(IV) in real soil samples was tested. The reliability of the method was confirmed by conducting six replicate measurements using the same optode, and the results obtained were found to be satisfactory, as summarized in Table 2. In order to validate the proposed method, spiked real sample was tested and analyzed to assess its

performance in real-world scenarios. The accuracy and precision of the proposed procedure were evaluated by comparing the F-test (for precision) and t-value (for accuracy) with the ICP-AES method. The mean values achieved from the proposed procedure were within the acceptable range of Student's t-test and F-test at a 95% confidence level, considering five degrees of freedom [41]. The calculated values recorded in Table 2 did not exceed the theoretical values, representing good agreement between the results achieved by the proposed and the ICP-AES methods.

The presented procedure was also used to determine Hf(IV) in a new copper-based alloy and zirconium oxides, as a real sample. In this sample, Hf content is lower than the practical detection limit of ICP-AES without preconcentration, so that it cannot be analyzed by direct ICP-AES. This sample was analyzed by the coupling of

Table 3: Comparison of the proposed optode with other spectrophotometric methods for determination of Hf(IV).

Reagent	pH	λ_{max} (nm)	Range ($\mu g\,cm^{-3}$)	DL ($\mu g\,cm^{-3}$)	RSD (%)	$\varepsilon\,L\,mol^{-1}$ ($cm^{-1} \times 10^4$)	S.S. ($ng\,cm^{-2}$)	Ref.
1-(2-Pyridylazo)-2-naphthol	4.0	545	0.2–3.6	0.06	2.7	3.86	0.0046	[19]
2-Amino-3-(4-bromophenyl-azo)-8,9 dihydro-7H-pyrazolo [1,5-a]quinazolin-6-one	3.2–4.7	368	0.005–1.0	0.013	2.4	25.1	0.0032	[12]
Ficus carica tree leaves	6.0 M HCl	421	2.0–11	0.312	3.4	0.28	0.0038	[42]
Arsenazo III	9.0 M HCl	520	0.0–20	0.3	2.4	1.36	0.0023	[43]
1-(2-Thiazolylazo)-2-naphthol	2.5	590	0.0–9.0	—	2.9	3.97	0.0056	[44]
BTABPD	5.0	616	5.0–185 ($ng\,cm^{-3}$)	1.58 ($ng\,cm^{-3}$)	1.85	836	0.00021	P.M.

S.S: Sandell sensitivity.   P.M: Proposed methods.

solid phase extraction to ICP-AES. The results obtained are recorded at Table 2. The t-test showed that there was not any significant difference between the real certified amount and measured Hf(IV). Thus, the proposed membrane can be successfully applied for the determination of Hf(IV) in various real matrices.

The performance of the presented procedure was assessed by the evaluation of the t-value (for accuracy) and F-test (for precision) compared with ICP-AES method. The mean values were achieved in Student's t- and F-tests at 95% confidence limits for five degrees of freedom [41]. The results indicated that the calculated values (Table 2) did not exceed the theoretical values. A wider range of determination, more stability, higher accuracy, and less time consuming show the advantage of the presented procedure over other ones.

For the determination of low content of hafnium, the presented procedure is highly sensitive and has excellent selectivity. This fact is further confirmed by analyzing various samples of different compositions. The presented procedure was applied successfully to determine hafnium in the terbium-base alloy (72% Tb(III), 9.5% Hf(IV), and 18.5% Al(III)). The result obtained was $9.55 \pm 0.11\%$ (RSD 0.76), which confirms the validity of the presented procedure.

The characteristics of the proposed hafnium optode were compared with those of other techniques for measuring hafnium which have been previously published in the literature (as shown in Table 3). The suggested optode's linear range and detection limit are acceptable when compared to those reported in previous studies. However, after reviewing the literature, it was found that no prior research has been conducted on an optical sensor membrane with chip reagents for the measurement of Hf(IV) ions in solutions.

4. Conclusion

The optode process described in this study is a simple and affordable way to measure Hf(IV) ions. The optode has a long lifespan, is easy to make, and can be regenerated quickly with thiourea. With a high degree of selectivity for Hf(IV) over other lanthanide and transition metal ions, the optode response is reproducible. Unlike regular optical fibers, this optode does not require solvent extraction and can compete favorably. In the study, the optode was used to measure Hf(IV) in different types of water samples, including spiked samples.

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

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