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An optical chemical sensor for thorium (IV) determination based on thorin

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ABSTRACT

A selective method for the determination of thorium (IV) using an optical sensor is described. The sensing membrane is prepared by immobilization of thorin–methyltrioctylammonium ion pair on triacetylcellulose polymer. The sensor produced a linear response for thorium (IV) concentration in the range of 6.46×10^{-6} to 9.91×10^{-5} mol L^{-1} with detection limit of 1.85×10^{-6} mol L^{-1}. The regeneration of optode was accomplished completely at a short time (less than 20 s) with 0.1 mol L^{-1} of oxalate ion solution. The relative standard deviation for ten replicate measurements of 2.15×10^{-5} and 8.62×10^{-5} mol L^{-1} of thorium was 2.71 and 1.65%, respectively. The optode membrane exhibits good selectivity for thorium (IV) over several other ionic species and are comparable to those obtained in case of spectrophotometric determination of thorium using thorin in solution. A good agreement with the ICP-MS and spiked method was achieved when the proposed optode was applied to the determination of thorium (IV) in dust and water samples.

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1. Introduction

Thorium is a radio element that is often used as a fuel for nuclear reactors besides its industrial applications. The main sources of thorium in nature are soil, rocks, plants, sand and water [1,2]. Normally, very little amounts of thorium in lakes, rivers and oceans get into the fish or seafood. But there may be more thorium than normal near an uncontrolled hazardous waste site which could have acute toxicological effects for human. The continuous exposure to thorium may cause an increased chance of developing cancer of the lung, pancreas or bone and changes in genetic material of body cells [3]. Thus, the analytical determination of this element is useful in environmental science and also in view of their applications in geochemistry and nuclear fuel chemistry.

The determination of thorium by the instrumental techniques such as ICP-AES, ICP-MS and NAA is still difficult because of insufficient sensitivity, lack of selectivity, presence of complex matrix, poor precision and accuracy [4–7].

In recent years, among a wide variety of methods, optical sensors (optodes) have been applied to various heavy metal assays [8–10]. The optodes have gained notable practical reliability and can be considered as inexpensive alternative to certain conventional analytical methods. These sensors are simple devices that use chemical sensing elements and optical transduction for the signal processing. The optical sensors offer further advantages as freedom from electrical noise and ease of miniaturization, as well as the possibility of remote sensing [11].

Polymers have been widely used as support materials for a broad range of optical sensors. They have many desirable features and compare well with sol–gel matrices for most applications [12,13]. Because of their transparency, the polymers are most often used in optodes with visible spectrophotometric detections. The most widely used polymers in optical sensors are polyvinyl chloride (PVC) [14–16] and cellulose derivatives such as acetylcellulose [17–20]. Many factors must be controlled for preparation of a good optode based on a PVC membrane, particularly the solubility parameter of additives [21], whereas, the optical sensor based on acetylcellulose is prepared easily in a short time.

Optical sensors using polymer membrane containing an ionophore that form a complex with the analyte to produce a distinctive color change are of great interest for the trace analysis of heavy metal ions. Most of these ionophores are water soluble. Therefore their immobilization into or onto a solid support is an important factor for producing a suitable sensing membrane. Among different strategies, the lipophilization of the ionophore molecule by formation of an ion pair is the most commonly used method which can slow down the process of leaching [22–24].

A few optical sensors for the determination of thorium have been reported in the literature. Safavi and Sadeghi [25] described a thorium sensing membrane by incorporating 4-(p-nitrophenylazo)-pyrocatechol as ionophore in plasticized PVC. The proposed optical sensor displays a linear range of 8.66×10^{-6} to 2.00×10^{-4} mol L^{-1} of thorium with a limit of detection of 6×10^{-6} mol L^{-1}. In another research Khayatzadeh Mahani et

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al. [26] presented an optode for the determination of thorium based on immobilization of synthesized ligand (triazene-1,3-di(2-methoxyphenyl) on PVC membrane. The linear concentration range for the determination of thorium by this sensor was 1.33–28.49 μg ml^{-1} (5.73×10^{-6} to 1.23×10^{-4} mol L^{-1}). This sensor could not be regenerated and was used as a probe for the determination of thorium. The optical ligand–thorium complex sensors using arsenazo III, thorin and thionin as complexation reagents were studied by Gumrah et al. [27]. They immobilized the complexation dyes onto poly(ethylene imine)(PEI)-attached poly(chloromethylstyrene)(PCMS) polymeric beads and compared the formation constants obtained in dip probe, flow cell and microchip systems.

In the present study, a selective optical sensor for the determination of thorium (IV) has been developed by immobilization of thorin as the sensitive reagent on triacetylcellulose membrane. The effective immobilization of thorin is performed using the formation of an ion pair between thorin and methyltrioctylammonium chloride by a simple approach.

2. Experimental

2.1. Apparatus

A GBC UV–vis spectrophotometer model Cintra 101 (Australia) was used for recording the spectra, and the absorbance measurements were made using a PerkinElmer and CO GMBH (Germany) UV–vis spectrophotometer model 550S. The sensing membrane was placed in a glass cell and all measurements were performed in a batch mode.

Measurement of pH was performed using a Metrohm 632 (Switzerland) pH-meter with a combined glass electrode.

2.2. Reagents and solutions

All reagents were of analytical grade and double distilled water was used throughout the experiments.

A 4.58×10^{-3} mol L^{-1} of thorium (IV) stock solution was prepared by dissolving 0.2530 g of $Th(NO_3)_4$. 4 H_2O (Baker Analyzed) in water containing small amounts of HNO_3 and diluting to 100 mL in a volumetric flask. Working solutions were prepared by adequate dilution of the stock solution. Glycine buffer solution was prepared by dissolving of 1.5 g of glycine (Merck) in water and diluting to 200 mL. The pH of this solution was adjusted to 2.8 by the addition of hydrochloric acid [28].

2.3. Preparation of optical sensor

The following procedure for the preparation of sensor was performed in order to immobilize thorin on triacetylcellulose membrane. For this purpose, the transparent triacetylcellulose membrane was produced from waste photographic film that had been previously treated with commercial sodium hypochlorite in order to remove colored gelatinous layers [29]. This clean and dry membrane was placed in the solution containing 0.020 g of thorin (Merck), 0.12 g methyltrioctylammonium chloride (Merck) and 10 mL ethylenediamine (Merck) for 15 min at ambient temperature. Then it was washed with water for removing the additional reagents. The obtained membrane was stored under water when not in use.

2.4. Analytical procedure

An aliquot of thorium (IV) solution and 5 mL of glycine buffer at pH 2.8 were added to 25 mL volumetric flask and diluted to mark with water. A few mL of this solution was transferred to spectrophotometer cell in which the optical membrane with area 27 mm × 10 mm and thickness of 0.28 mm was mounted into it. The cell was shaken and the absorbance was measured at 554 nm against a blank membrane after 7 min.

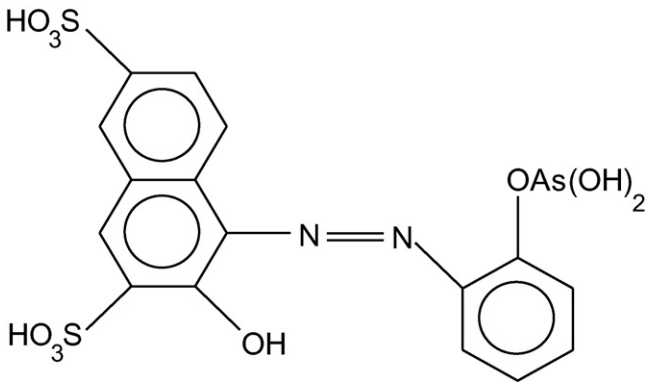

Fig. 1. Chemical structure of thorin.

2.5. Preparation of dust sample

10 g of dust sample was digested with a mixture of 20 mL concentrated hydrochloric acid and 5 mL of concentrated nitric acid at room temperature, then it was heated to 100 °C. After the evolution of NO_2 fumes, the mixture was evaporated almost to dryness. Then 10 mL of above acid mixture was added to the residue and evaporated to dryness again. After evaporation, 10 mL of distilled water was added and the resulting mixture was filtered [4]. The pH of filtrate was adjusted to 2.5 by sodium hydroxide and the analytical procedure was applied.

3. Results and discussion

3.1. Sensing reagent and spectral characteristics

To design an optical sensor a sensing reagent must be selected considering various aspects, such as the rate of response, sensitivity and selectivity.

2-(2-Hydroxy-3,6-disulpho-1-naphthylazo)benzene arsonic acid (thorin) is a spectrophotometric reagent for the determination of thorium. Thorin reacts with thorium (IV) in acidic medium to yield a red complex [30]. The presence of $-SO_3H$ groups in chemical structure of thorin (Fig. 1) denoted that this reagent is soluble in water and cannot be immobilized effectively on triacetylcellulose membrane, as proved by experiment. The use of methyltrioctylammonium chloride can help immobilizing thorin on the membrane by formation of a lipophilic ion pair. Therefore addition of a small amount of methyltrioctylammonium chloride to the thorin solution in ethylenediamine changed the membrane color to orange which indicate the adsorption of thorin–methyltrioctylammonium ion pair on triacetylcellulose [22]. By placing this membrane in acidic solution of thorium (IV), the color was changed to pink.

The absorbance spectra of the sensing membrane in the presence of different concentrations of thorium (IV) against a blank membrane are shown in Fig. 2. The spectra indicate that the absorbance at maximum wavelength, 554 nm, increased with increasing of thorium (IV) concentration. Thus this wavelength was selected for measuring the absorbance of optode.

3.2. The effect of variables on sensor response

The membrane composition has significant influence on transparency, homogeneity and sensitivity of the sensor [17,31].

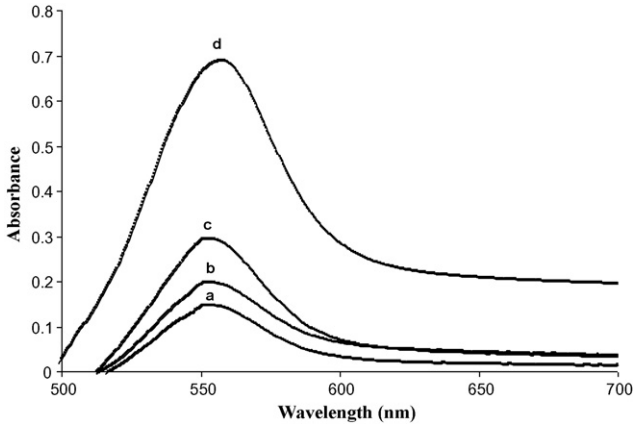

Fig. 2. Absorption spectra of optode against a blank membrane in the presence of different concentrations of thorium (IV) at pH = 2.8, (a) 4.31×10^{-5}, (b) 8.62×10^{-5}, (c) 2.15×10^{-4}, (d) 4.31×10^{-4} mol L^{-1} of thorium (IV).

Therefore the effect of solvent types, amount of methyltrioctylammonium chloride and thorin plus preparation time on the response characteristics was studied.

The obtained results indicated that the immobilization of thorin–methyltrioctylammonium ion pair was effectively performed in a short time when using ethylenediamine as solvent. As mentioned in previous works [19,20] the hydrolyzed cellulose film in ethylenediamine shaped the porous structure in the polymer, which minimizes barriers of mass transport.

The effect of amount of methyltrioctylammonium chloride on the sensor response was investigated. The results denoted that at low amounts the response is decreased and higher values caused the membrane to become opaque. The highest response was obtained when using 0.12 g of methyltrioctylammonium chloride, thus this value was selected for preparation of optode. In another experiment, the effect of thorin amounts on the optode response was studied in the range of 0.015–0.025 g. The maximum response was obtained when 0.020 g of thorin was used. The amount of thorin immobilized on the surface of the membrane was determined by desorbing the reagent in a mixture of 5 mol L^{-1} sulphuric acid and acetonitrile (1:1) and measuring by spectrophotometer. The results showed that 1.8×10^{-4} g thorin was immobilized on the membrane.

The preparation time of sensing membrane is also a significant parameter. The obtained results showed that maximum response is obtained at 15 min (Fig. 3) but above 18 min the membrane began to dissolve and to deform. Thus the optode was prepared

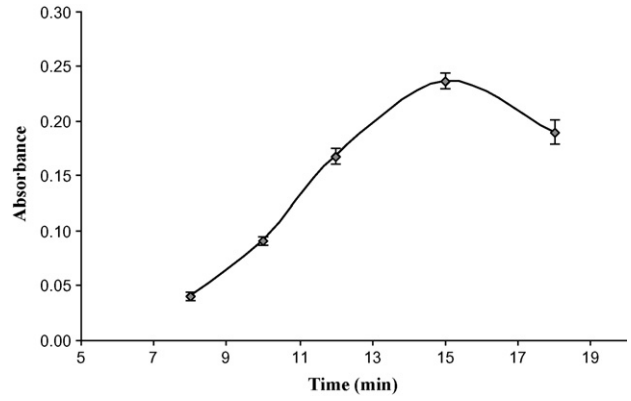

Fig. 3. Effect of preparation time of sensing membrane on the sensor response for solution containing 8.62×10^{-5} mol L^{-1} of thorium (IV), each point refers to the mean of triplicate measurements.

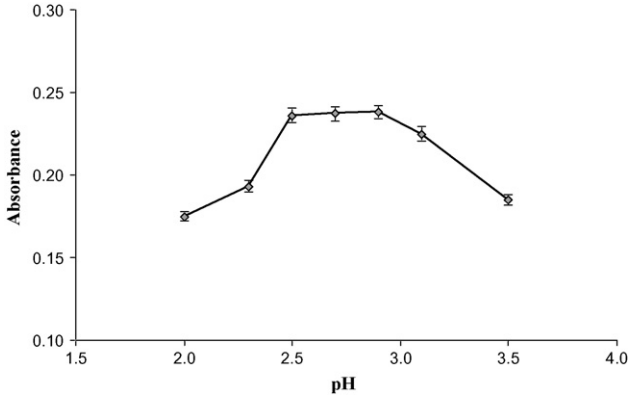

Fig. 4. Effect of pH on the optode response for solution containing 8.62×10^{-5} mol L^{-1} of thorium (IV), each point refers to the mean of triplicate measurements.

by treating triacetylcellulose membrane with a solution containing 0.12 g methyltrioctylammonium chloride and 0.020 g thorin in 10 mL ethylenediamine for 15 min.

To achieve higher sensitivity, the effect of the pH of the thorium (IV) solution over the range of 2.0–3.5 on the response of the optode was investigated. The appropriate pH was obtained by the addition of diluted nitric acid to the thorium solution. As it is obvious from Fig. 4 the maximum response was obtained at pH 2.5–2.9. At pH values less than 2, the thorin had leakage from the membrane. Also at higher pH values the thorium ion was hydrolyzed in aqueous solution and insoluble hydroxide was formed [28].

For adjusting pH, the effect of formate, citrate and glycine buffers at pH 2.8 on the sensor response was studied. The thorium (IV) solution became turbid in the presence of the formate and citrate buffers. Therefore the glycine buffer at pH 2.8 was chosen for further studies.

The influence of the electrolyte concentration on the membrane response was investigated by adding different amounts of potassium nitrate. The results indicate that this parameter has no effect on the response of sensor to the thorium (IV), up to 0.07 mol L^{-1} of potassium nitrate and above this concentration the response is reduced slightly. This is due to a decrease in the activity of thorium (IV) ion at higher concentration of electrolyte which reduces the interaction of thorium (IV) ion with thorin in the membrane.

3.3. Equilibrium response time and regeneration of optode

The equilibrium response time is a very important factor in optical sensors. For this purpose, the absorbance changes of the membrane were recorded versus time at 554 nm using selected experimental conditions for 2.15×10^{-5} and 8.62×10^{-5} mol L^{-1} of thorium (IV). The obtained response curves for both concentrations of thorium are shown in Fig. 5. It can be noted that well over 98% of the total response can be achieved within 7 min.

One of the main characteristics of an optical sensor is its regeneration which allows using the sensor many times leading to consumption of small amount of reagent. Therefore the effect of tartrate, oxalate and EDTA solution were studied as regenerating reagents. The best results were obtained using 0.1 mol L^{-1} of oxalate ion solution which provided a complete regeneration at a short time (less than 20 s).

3.4. Analytical parameters

The corresponding calibration graph based on absorbance versus thorium (IV) concentration was linear in the range of 6.46×10^{-6} to 9.91×10^{-5} mol L^{-1}. The equation for the regression

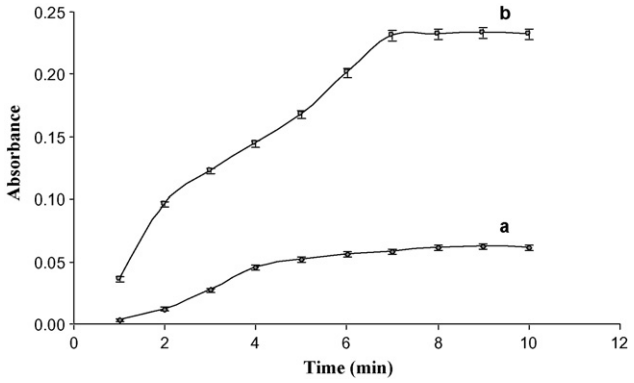

Fig. 5. Absorbance as a function of time when the concentration of thorium (IV) was (a) 2.15×10^{-5} and (b) 8.62×10^{-5} mol L^{-1}, each point refers to the mean of triplicate measurements.

Table 1
Effect of foreign ions on the determination of 4.31×10^{-5} mol L^{-1} of thorium (IV).

Foreign ions	Tolerance ratio ([M]/[Th])
Na^+, K^+, Mg^{2+}	1000
Cu^{2+}, Cd^{2+}, Ni^{2+}, Cr^{3+}, SO_4^{2-}	500
Zn^{2+}, Zr(IV), Br^-, I^-	200
Co^{2+}, Mn^{2+}, Fe^{3+}, Ca^{2+}, V(IV)	50
CO_3^{2-}, F^- [a]	
Al^{3+}, Ga^{3+}, Hg^{2+}, Ti(IV), tartrate	20
La^{3+}, As^{3+}, Sb^{3+}	3

[a] Masked by Fe^{3+}

line was $A = 2778.2C + 1.4 \times 10^{-3}$ with correlation coefficient (r) of 0.9985, where C is concentration of thorium (IV) in mol L^{-1} and A is absorbance of optode against the blank membrane at 554 nm under optimized conditions. The detection limit, defined as the average blank signal plus three times of its standard deviations ($n = 10$), is equal to 1.85×10^{-6} mol L^{-1} (0.43 μg mL^{-1}).

3.5. Reproducibility and lifetime

The reproducibility of the sensor using a single membrane was assessed by performing ten replicate measurements for 2.15×10^{-5} and 8.62×10^{-5} mol L^{-1} of thorium (IV) solutions. The mean absorbance values at 554 nm with their standard deviations were found to be reproducible to 0.071 ± 0.002 (for 2.15×10^{-5} mol L^{-1}) and 0.239 ± 0.004 (for 8.62×10^{-5} mol L^{-1}); the corresponding R.S.D. for thorium determination was 2.71 and 1.65%, respectively.

The reproducibility between days ($n = 5$) and between different membranes ($n = 4$) was also evaluated by recording the absorbance under optimum conditions for 8.62×10^{-5} mol L^{-1} of thorium (IV). The results showed that R.S.D. value for these measurements was less than 4%.

To study the lifetime of the optode, the response value of the membrane in contact with 8.62×10^{-5} mol L^{-1} of thorium (IV) was recorded after keeping the membrane in water over two weeks. The obtained results denoted that the absorbance values of the optode under optimum conditions only decreased by 3.8% over a period of two weeks.

Table 2
Determination of thorium in dust sample by proposed optode and comparison with ICP-MS.

Sample	Thorium found (μg g^{-1}) [a]		
	Proposed method	ICP-MS method	Relative error (%)
1	5.55 ± 0.19	5.70 ± 0.15	2.63
2	5.20 ± 0.18	5.70 ± 0.15	8.77

[a] Mean ± standard deviation ($n = 3$).

Table 3
Determination of thorium in water samples.

Water samples	Amount of thorium (IV) (mol L^{-1})		Recovery (%)
	Added	Found [a]	
Karun River [b]	–	$1.03 (\pm 0.04) \times 10^{-5}$	–
	4.31×10^{-6}	$1.46 (\pm 0.04) \times 10^{-5}$	100
	8.62×10^{-6}	$1.93 (\pm 0.03) \times 10^{-5}$	102
Khor Musa Estuary	–	$1.86 (\pm 0.04) \times 10^{-5}$	–
	4.31×10^{-6}	$2.25 (\pm 0.03) \times 10^{-5}$	98
	8.62×10^{-6}	$2.72 (\pm 0.04) \times 10^{-5}$	100

[a] Mean ± standard deviation ($n = 3$).
[b] Taken from polluted area.

3.6. Selectivity of the optode

Potential interference of cations and anions in the determination of thorium (IV) using the proposed method were studied by adding different amounts of foreign species to samples containing 4.31×10^{-5} mol L^{-1} of thorium (IV). The tolerance limit was defined as the maximum concentration of foreign ion causing an error of less than ±5% in the determination of thorium. Table 1 lists the ratios of the species assayed to be tolerated. Similar selectivity results have been observed when thorin was used for the determination of thorium in solution [32].

3.7. Analytical application

The application and validation of the proposed optical sensor was verified by employing method to dust and water samples.

The dust sample was collected from suburb of Ahvaz (Khuzestan Province, Iran). The reported values by ICP-MS and observed amounts for thorium in dust sample are given in Table 2. The results of two methods were compared by performing t-test. It showed that there are no significant difference between the two results at 95% and 98% confidence level for samples 1 and 2, respectively.

Two water samples were selected from Karun River (Khuzestan Province, Iran) and Khor Musa Estuary (Khuzestan Province, Iran), which are industrial regions. The possibility of applying the present optical sensor for analysis of water samples was tested by determining the recovery of known amounts of thorium (IV) ion added to the samples. The given results in Table 3 show good agreement between added and detected concentration of the thorium in real samples.

Table 4
Comparison of proposed optode with previously reported optodes.

Method	LOD (mol L^{-1})	Linear range (mol L^{-1})	Response time (min)	Regeneration time(s)	Ref.
Optode based on NAP [a]	6×10^{-6}	8.66×10^{-6} to 2.00×10^{-4}	8.8–12.5	10–20	[25]
Optode based on TMP [b]	4.96×10^{-6}	5.73×10^{-6} to 1.23×10^{-4}	Immediately	Not regenerated	[26]
Optode based on thorin	1.85×10^{-6}	6.46×10^{-6} to 9.91×10^{-5}	7	<20	Proposed optode

[a] 4-(*p*-Nitrophenyl azo)-pyrocatechol.
[b] Triazene-1,3-di(2-methoxyphenyl).

4. Conclusion

A selective optical sensor for the determination of thorium (IV) was developed by physical immobilization of thorin on triacetylcellulose membrane. The use of methyltrioctylammonium chloride facilitates adsorption of thorin on the membrane by formation of an ion pair according to a simple method. The sensor can be regenerated readily and its response is very reproducible. In comparison with spectrophotometric method [30] the proposed optode uses low amount of thorin for thorium (IV) determination, because the sensing membrane could be regenerated many times and used without any loss of sensitivity. The advantageous features of purposed thorium sensor in comparison with previously reported optodes [25,26] are ease of fabrication, lower detection limit and response time and readily regenerated. The comparison of the results is given in Table 4. The presented sensor offers good accuracy, precision and reproducibility that make it useful for analysis of thorium in dust and water samples.

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