# Design of a novel optical sensor for determination of trace gadolinium

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## ARTICLE INFO

## ABSTRACT

In this work, a highly selective and sensitive gadolinium (Gd) optical sensor based on immobilization of bis(thiophenal) pyridine-2,6-diamine (BPD), on a triacetylcellulose membrane has been reported. This optode exhibits a linear range of the Gd(III) ion concentration of $2.5 \times 10^{-6}$ M with a detection limit of $0.93 \times 10^{-8}$ M. Response time of the newly designed optode was within 1–2 min, depending on the Gd(III) ion concentration. Response of the sensor is independent of solution pH in the range of 2.0–9.0. It manifests advantages of: low detection limit, fast response time, and most significantly, very good selectivity with respect to a number of lanthanide ions (La, Ce, Sm, Tm, Ho, and Eu ions). The sensor was successfully regenerated with thiourea solutions and its response was reversible and reproducible (R.S.D. less than 1.4%). This optode was applied to determine Gd(III) in synthetic and water samples, and validated with certified reference materials (CRMs).

## 1. Introduction

Gadolinium (Gd) exhibits ferromagnetic properties below room temperature. It is used for making gadolinium yttrium garnets, which have microwave applications and are used for making phosphors for color TV tubes. Gd is also used for manufacturing compact discs and computer memories. Gadolinium together with other lanthanide oxides is widely used in the preparation of: optical glasses, glass fibers, radio-contrast agents, gasoline-cracking catalysts, polishing compounds, the construction of carbon arcs and in iron and steel industries to remove sulfur, carbon, and other electronegative elements [1].

In nuclear research, Gd and other rare earth elements are usually utilized in the form of oxides. Gadolinium acts as a neutron absorber regarding the control level regulation as well as the criticality of nuclear reactors [2]. It is most dangerous in the work environment due to the fact it dampens and its gasses can be inhaled with air. This can cause lung embolisms, especially during long-term exposure. When it accumulates in the human body, Gd can be a threat to the liver. It is dumped in the environment in many different places, mainly by the petrol-producing industries. It can also enter the environment when household equipment is thrown away. Gadolinium gradually accumulates in soils and water and this eventually leads to increasing concentrations in humans, animals and soil particles.

Gd detection has become necessary lately, because of the increasing utilization of gadolinium compounds in industry. There are many methods for low-level Gd monitoring in solution. Most of them consist of spectroscopic methods such as: inductively coupled plasma mass spectroscopy (ICP-MS) [3–7], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [8], electron spin resonance (ESR) [9–11], laser-based multi step resonance ionization [12], phosphorescence [13], spectrophotofluorimetric [14–16] ion-selective electrode (ISE) [17–21] and others methodologies [22–25]. These present low sensitivity, are time-consuming, involve multiple sample manipulations and are too expensive for most analytical laboratories. As a result, design of an inexpensive and simple technique which can provide necessary selectivity to determine Gd in the presence of other lanthanides that are very similar to Gd is of great value.

Optical sensors can be useful for Gd assessment [26] as they are easily incorporated into low-cost, easy-to-use kits. Furthermore, they can offer the required selectivity and sensitivity for environmental monitoring [27–29]. In this study, a novel gadolinium optical sensor is introduced, demonstrating the immobilization of bis(thiophenal) pyridine-2,6-diamine (BPD) on a triacetylcellulose membrane. Basic principles and theoretical description of bulk optode membranes, based on the reversible mass analyte transfer from sample in the bulk of the sensing layer have been well elucidated [30,31].

## 2. Experimental

### 2.1. Reagents

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise, and were supplied from Merk

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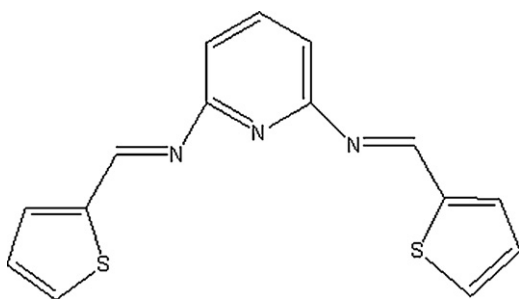  E-mail address: Ganjali@khayam.ut.ac.ir (M.R. Ganjali).

**Fig. 1.** Structure of bis(thiophenal) pyridine-2,6-diamine (BPD).

(Darmstadt, Germany). The $10^{-3}$ M gadolinium standard stock solution was prepared by dissolving 0.0173 g of $Ga_2O_3$ in a 50 mL volumetric flask and diluting to the mark with water. Working solutions were prepared daily from the stock solution by appropriate dilution with water. Universal buffer solutions were prepared from boric acid/citric acid/phosphoric acid (0.04 M each) solutions. The final pH was adjusted with the addition of a 0.2 M sodium hydroxide solution.

### 2.2. Synthesis of bis(thiophenal) pyridine-2,6-diamine (BPD)

Bis(thiophenal) pyridine-2,6-diamine (see Fig. 1) was synthesized in the usual manner by reaction of thiophene-2-carbaldehyde with 2,6-diamino pyridine in a 2:1 mole ratio in methanol as follows.

Thiophene-2-carbaldehyde (0.02 mol, 0.74 g) and 2,6-diaminopyridine (0.01 mol, 1.09 g) were placed in a 50 mL round-bottom flask equipped with a condenser and magnetic bar. Methanol (30 mL) was added to the mixture and it was refluxed for 4 h, while stirring. The solvent was evaporated and the viscous ligand was kept under vacuum while heated gently. The viscous SchiffLs base ligand was then solidified upon standing for a few days to obtain a brown product quantitatively [19].

### 2.3. Apparatus and measurement procedures

UV–vis spectra and absorbance measurements were recorded on a PerkinElmer Lambda 2 UV/vis spectrophotometer. The sensing membrane was placed and fixed in a disposable plastic cuvette and all measurements were performed in batch mode. An EcoMet p25 pH-meter with a Metrohm double junction glass electrode was used for pH adjustment. Optode membrane response to different metal ions was investigated in universal buffer (0.04 M) at pH value 8. Membrane was first exposed to buffer solution and absorbance was measured at 317 nm. Then, the sample solution was added and absorbance at 317 nm was again measured after 2 min.

### 2.4. Preparation of the membrane sensor

Transparent triacetylcellulose membranes were produced from waste photographic film tapes, which were previously treated with commercial sodium hypochlorite for several seconds in order to remove the colored gelatinous layers. Films were treated with a clear BPD solution (0.005 g) in 10 mL ethylene diamine for 3 min at ambient temperature. Afterwards, they were washed with water for the removal of ethylene diamine and the loosely trapped indicator. Membranes were finally washed with detergent solutions and water. Prepared membranes were kept under water when not in use.
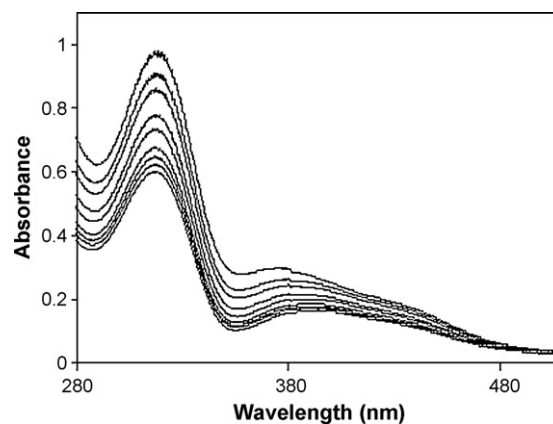


**Fig. 2.** Absorption spectra of optode film response to Gd(III) in the range of $1.0 \times 10^{-8} – 4 \times 10^{-6}$ M at pH 8.

## 3. Results and discussion

### 3.1. Spectral characteristics

Fig. 2 shows the absorption spectra of immobilized BPD on hydrolyzed cellulose acetate which was obtained after equilibration in buffer solution (pH 8), containing different concentrations of gadolinium. The spectral change is a result of the addition of Gd(III) ions and complex formation. Spectral characteristic of this optical sensor indicates two maxima at 317 and 376 nm (see Fig. 2). Spectral change was a result of Gd(III) ions addition and complex formation in the optode (see Fig. 2). Also, these two maxima shifted with increasing Gd(III) concentration in the optode (317 and 376 nm). It is important to note that the absorption spectrum of the immobilized indicator is red shift in comparison to those of their soluble form (317 and 376 nm). This observation could be attributed to the fact that the structured conformation of the immobilized indicators is more planar than that of its soluble analogue [32]. For our additional studies, the wavelength of 317 nm was selected, because of higher selectivity and sensitivity at this wavelength.

### 3.2. pH effect

pH influence on the complex was studied in the range of 2–9 by changing the universal buffer. As it can be noticed in Fig. 3, a maximum value in the sensor response was obtained at pH value 8. This pH was selected for our subsequent investigations. The observed drift at higher pH values could be due to the formation of some hydroxy complexes of the gadolinium ions in the solution.

### 3.3. Response time

An important analytical feature of any sensor is its response time. In this work, the optode film was found to reach 95% of the
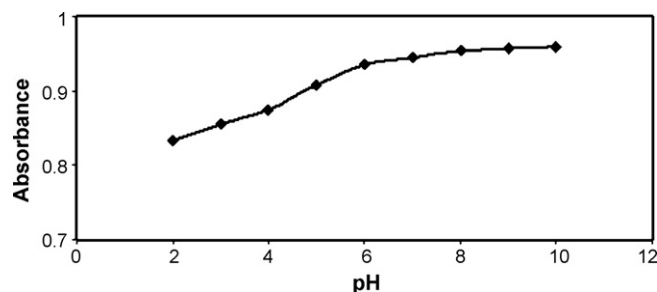


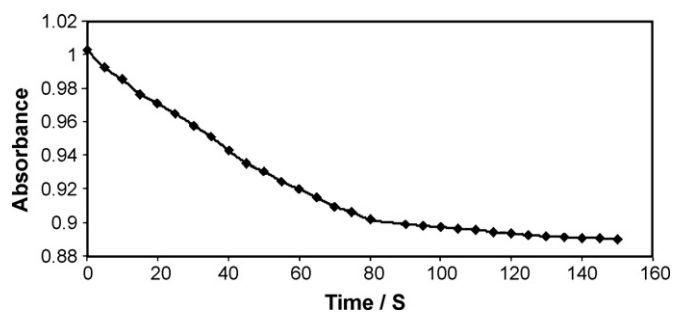**Fig. 3.** pH effect on the optode film response.

**Fig. 4.** Response time curve of the film optode at 317 nm when the film was exposed to $1.0 \times 10^{-8}$ M Gd(III) ion.

final signal at 1–2 min, depending on Gd(III) cation concentration (see Fig. 4). At high Gd(III) concentrations, a rapid response was achieved, which resulted in a large change in response. At low Gd(III) concentrations, a longer response time was produced by the optode film which is due to the fact that response time of the optode film is governed by three processes: (1) film diffusion, (2) complex formation rate between metal ion and ligand, and (3) complex dissociation rate [33].

### 3.4. Dynamic range

Fig. 5 depicts the absorption signals of the optode film to various Gd(III) ion concentrations in the range: $1.0 \times 10^{-8}$–$2.5 \times 10^{-6}$ M. The calibration graph is linear up to the Gd(III) ion concentration of: $2.5 \times 10^{-6}$ M, described by the equation:

$$\Delta Abs = 0.1601[Gd(III)] + 0.0357, \quad R^2 = 0.998$$

$\Delta Abs$ is the absorbance difference (defined as the difference between the absorbance of the immobilized BPD alone and the absorbance of Gd(III)–BPD complex), [Gd(III)] is the gadolinium ion concentration ($\mu$M), $R^2$ is the $R$-squared value of the calibration curve.

Moreover, the detection limit of the sensor film was found to be: $0.93 \times 10^{-8}$ M. In this case, detection limit can be defined as: the sample concentration yielding a signal equal to the blank signal plus three times of its standard deviation.

### 3.5. Optode regeneration

For an optode membrane to perform suitably, color change must be reversible. Tests were conducted with a number of reagents to reverse the color of Gd(III) complex. Complexing agents such
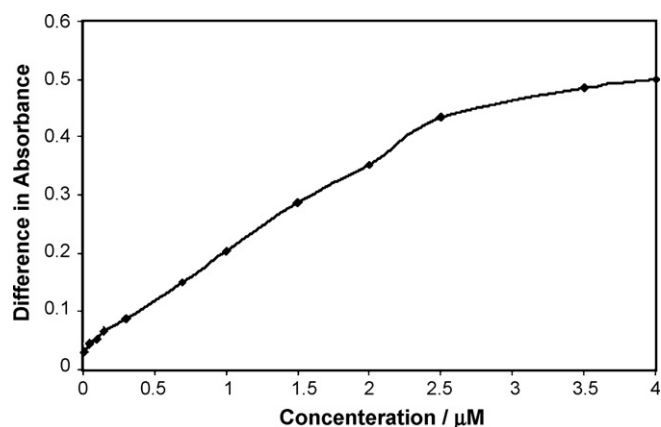
**Table 1**
Influence of the foreign ions on the Gd(III) determination of 1.0 $\mu$M.

| Interferent | Tolerance[a] limit |
|---|---|
| La$^{3+}$, Er$^{3+}$, Ca$^{2+}$, SCN$^-$ | 100 |
| Tm$^{3+}$, Dy$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Yb$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Hg$^{2+}$, Pb$^{2+}$, Na$^+$ | 1000 |
| Cu$^{2+}$, Ni$^{2+}$, K$^+$, Ag$^+$, Mg$^{2+}$, Cd$^{2+}$, CO$_3^{2-}$ | 2000 |
| NO$_3^-$, Cl$^-$, SO$_4^{2-}$ | 2500 |

[a] Maximum ratio of the foreign ions to the gadolinium ions ($1.0 \times 10^{-6}$ M) giving an error of <5%.

**Table 2**
Results of the recovery test.

| Sample | Gd(III) added ($\mu$M) | Gd(III) found ($\mu$M) | R.S.D. (%) | Recovery (%) |
|---|---|---|---|---|
| River water | 0 | ND[a] | – | – |
| | 0.050 | 0.051 | 1.4 | 102 |
| Mineral water | 0 | ND | – | – |
| | 0.500 | 0.506 | 1.2 | 101.2 |
| Drinking water | 0 | ND | – | – |
| | 1.000 | 0.998 | 1.1 | 99.8 |

[a] Not detected.

as EDTA and sulfosalicylic acid have a partial reverse effect, and prolonged exposure to them have no further improvement in reversibility of the optode. Thiourea was concluded to be the best reagent, giving a short regeneration time (less than 2 min). The on use durability of the sensor phase was obtained by subsequently placing the film in Gd(III) solutions and regenerating. After regenerating these solutions twice, a drift of about 4% was obtained in response of the sensor film.

### 3.6. Reproducibility

Repeatability and reproducibility of the optical fiber sensors are two of their important characteristics. Both parameters were studied in this research. To evaluate the discrepancies in the response for successive runs using a single sensor, the repeatability was evaluated by performing 10 determinations with the same Gd(III) standard solution. The coefficient of variation of sensor response for $0.5 \times 10^{-6}$ M Gd(III) was 1.2%. Fig. 6 shows the absorbance changes versus time for the optode membrane. For the evaluation of differences in responses of individual sensors, four membranes were prepared from the same mixture. Reproducibility was obtained by determining $0.5 \times 10^{-6}$ M Gd(III) (three determinations). Coefficient of variation of the responses between the membranes was 2.6%.



**Fig. 5.** The optode film response versus the Gd(III) ion concentration in the range of $1.0 \times 10^{-8}$–$4 \times 10^{-6}$ M at pH 8.
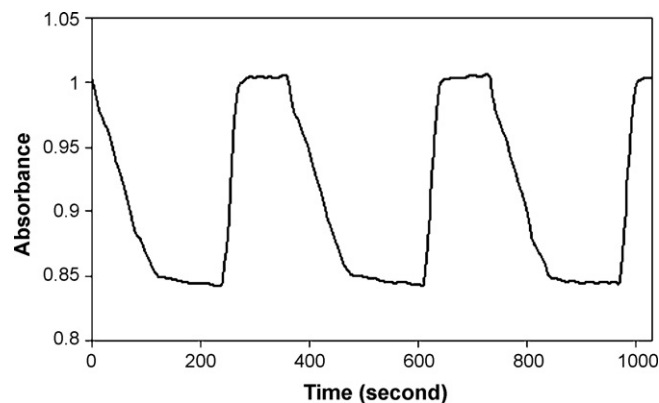


**Fig. 6.** Absorbance variation of the membrane at 317 nm for repeatedly exposing into $0.5 \times 10^{-6}$ M Gd(III) solution and 0.1 M thiourea solution.

**Table 3**
Determination of the Gd(III) ion from some real samples.

| Sample | Gd(III) added (μM) | Gd(III) found (μM) for Arsenazo method | Gd(III) found (μM) for proposed method | R.S.D. (%) for proposed method (n = 7) | RE % for proposed method |
|---|---|---|---|---|---|
| Synthetic sample 1 | 0 | ND | ND | – | – |
| | 0.01 | 0.01 | 0.01 | 0.88 | 0 |
| Synthetic sample 2 | 0 | ND | ND | – | – |
| | 0.10 | 0.11 | 0.09 | 0.92 | −1.0 |
| Synthetic sample 3 | 0 | ND | ND | – | – |
| | 1.00 | 1.02 | 1.01 | 0.96 | +1.0 |
| Mineral water | 0 | ND | ND | – | – |
| | 0.01 | 0.01 | 0.01 | 1.2 | 0 |
| Drinking water | 0 | ND | ND | – | – |
| | 0.10 | 0.14 | 0.12 | 1.1 | +2.0 |
| River water | 0 | ND | ND | – | – |
| | 1.00 | 1.07 | 1.04 | 1.3 | +4.0 |

**Table 4**
Comparison of proposed Gd(III) optical sensor with other methods for determination of gadolinium.

| Method | DL[a] (M) | LR[b] (M) | R.S.D. (%) | Samples | References |
|---|---|---|---|---|---|
| ICP-MS | $4.5 \times 10^{-7}$ | – | – | River water | [5] |
| ISE | $5.8 \times 10^{-7}$ | $1.0 \times 10^{-6}$–$1.0 \times 10^{-1}$ | – | Soil | [21] |
| Phosphorescence | – | $8.0 \times 10^{-7}$–$5.0 \times 10^{-5}$ | 2.0 | Synthetic sample | [13] |
| Optical sensor | $4.0 \times 10^{-9}$ | $1.0 \times 10^{-8}$–$2.5 \times 10^{-6}$ | 1.4 | River water | This work |

[a] Detection limit
[b] Linear range.

### 3.7. Lifetime

The lifetime of the optode film was determined by adding the buffer solution (pH 8) in a cuvette, containing the film. The signal was recorded at wavelength 317 nm over a period of time (about 10 h). No significant indicator loss occurred during that time. When the film was exposed to light, no drift in the signal took place and the optode was found to be stable during the experiment with no indicator leakage. However, the prepared membranes were kept under water when not in use to prevent them from drying out. Additionally, stability of response of the film was investigated over six weeks under ambient conditions, which indicated that the film was stable over this period.

### 3.8. Effect of the foreign ions

To determine the selectivity of the optode film, the film was tested under Gd ion concentration of $1.0 \times 10^{-6}$ M in the presence of other metal ions. Tolerance limit was taken as the concentration causing an error of ±5% in the Gd(III) assay. The results are summarized in Table 1. The surprisingly high selectivity of the optode film for Gd(III) ions over other cations used, most probably arises from the strong tendency of the complexation BPD for Gd(III) ions.

### 3.9. Recovery tests

The recovery tests were performed using three different samples. The test for each sample was carried out in triplicate measurements. As it is evident from Table 2, gadolinium recovery values were between 99.8 and 102.

### 3.10. Accuracy and analytical application

The developed Gd optical sensor device was applied to the detection of gadolinium ions in synthetic and river water samples. Table 3 lists the respective resulting data of these applications. The result, derived from seven measurements with the same sensor, was found

to be in satisfactory agreement with that determined by Arsenazo method [34]. The characteristics of the proposed gadolinium optical sensor were compared with other methods for determination of gadolinium in the literature in Table 4. The proposed sensor was also applied to Gd(III) determination concentration in the Calcareous soil (ERM®-CC690) as certified reference materials (CRMs). The results obtained for the Gd(III) sensor using calibration method was $3.3 \pm 0.2$ mg kg$^{-1}$ (while the Gd(III) concentration in CRMs was $3.2 \pm 0.4$ mg kg$^{-1}$). The comparison between two data revealed that the Gd(III) sensor can be used as an alternative tool in determination of Gd(III) ions in presence of other rare earth elements.

## 4. Conclusion

The optode described in this work is easily prepared and provides a simple, fast, and inexpensive means for the determination of Gd(III) ions. The sensor was easily prepared, readily regenerated with a thiourea solution and demonstrated a long lifetime. It is fully reversible and has a low response time. The sensor works well in a pH range of 2–9, and can be successfully employed for the determination of gadolinium ions in presence of other rare earth elements. Since the optical sensor required no solvent extraction, it could compete satisfactorily with the standard optical fibers. This optical sensor was applied to the determination of Gd(III) in synthetic and water samples.

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