

# A New Optical Sensor for Selective Monitoring of Nickel Ion Based on A Hydrazone Derivative Immobilized on the Triacetyl Cellulose Membrane

Kamal Alizadeh\* and Nasim Abbasi Rad

Department of Chemistry, Lorestan University, Khorramabad, Iran

## Abstract

A new highly selective optical sensor was prepared by de-esterification of triacetyl cellulose transparent film and chemical immobilization of 1-acenaphthoquinone 1-thiosemicarbazone (**L**) on it. The absorbance variation of immobilized 1-acenaphthoquinone 1-thiosemicarbazone on hydrolyzed cellulose acetate film of upon addition of  $1.5 \times 10^{-5}$  mol L<sup>-1</sup> aqueous solutions of Zn<sup>2+</sup>, Pb<sup>2+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, CrO<sub>4</sub><sup>2-</sup>, Hg<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, Ti<sup>+</sup> and Fe<sup>3+</sup> indicated a substantiality much larger variation for the Nickel ion in compare to other studied ions. Consequently, the new hydrazone derivative **L** possesses a high selectivity towards this metal ion. Influences of various experimental parameters on Ni<sup>2+</sup> sensing, including the reaction time, the solution pH and the concentration of reagents were studied. A linear relationship was observed between the variance in membrane absorbance ( $\Delta A$ ) at 337 nm and Ni<sup>2+</sup> concentrations in a range from  $5.01 \times 10^{-10}$  to  $2.04 \times 10^{-5}$  mol L<sup>-1</sup> with a detection limit ( $3\sigma$ ) of  $1.00 \times 10^{-10}$  mol L<sup>-1</sup>. No significant interference from 100 times concentrations of a number of potentially interfering ions was detected for the nickel ion determination. The sensor showed a good durability and short response time with no evidence of reagent leaching. The optical sensor was successfully applied to the determination of nickel in real water samples.

**Keywords:** Optical sensor; Nickel ion; Triacetyl cellulose membrane; Hydrazone derivative; Spectrophotometric

## Introduction

In the recent years, pollution of the environment by heavy metals has received considerable attention. Nickel is a moderate toxic element compared to other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer. Moreover, nickel can cause a disorder known as nickel-eczema [1,2]. Nickel is an excellent alloying metal in steel industry and is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals [3]. This metal normally occurs at very low level in the environment, so sensitive methods are needed to detect it in most environmental samples. Thus, the development of simple methods for selective determination of nickel in trace amounts in different matrices is critical.

Optical sensors have found great interest in recent years as they have many uses in clinical analysis, environmental analysis, and process control [4]. Optical chemical sensors (optodes), are usually based on acid-base indicators, which can be adsorbed on the surface of support materials [5-7]. Several different support materials including lipophilic polymers and plasticizers, hydrophilic polymers, ionic polymers, sol-gel glass and molecularly imprinted polymers have been used for preparation of optical sensors [5-8]. Covalently immobilized dyes, in contrast to the physically adsorbed or entrapped dyes, do not suffer from leaching or hysteresis and exhibit long lifetimes [8].

Optodes are simple and selective tools for the determination of heavy metal ions that have been extensively developed in recent years. Optodes are generally used in combination with inexpensive spectrophotometric or spectrofluorometric techniques to provide simple and fast determination methods with enhanced selectivity and low detection limits [9-13].

Fabrication of membrane optical sensors have been reported for many cations including Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup> [14-22]. Use of transparent triacetyl cellulose and agarose membranes as

supports for preparation of covalently immobilized optical sensors for some ions determination were reported by different laboratories. It was shown that these membranes can be easily manufactured and simply activated and functionalized with an ionophore. In construction of optical sensors, ionophores play an important role. The compounds contain some donor atoms have been frequently used as ionophores in construction of membrane sensors because of their ability to form stable complexes with transition metal ions. They produce remarkable selectivity, sensitivity and stability for a specific ion [23-26].

In the present study, a hydrazone derivative ligand 1-acenaphthoquinone 1-thiosemicarbazone, **L** (Figure 1) [27,28], is covalently immobilized on a triacetyl cellulose membrane to be used as an effective ionophore with N and O donor atoms for construction of a selective optical sensor for the spectrophotometric determination of Ni<sup>2+</sup> in aqueous solutions. The studied compound as an ionophore is the family of hydrazone which is a kind of asymmetric Schiff's base. Schiff's bases (also called azomethines or imines) are functional groups with the general formula of R<sub>1</sub>R<sub>2</sub>C=N-R<sub>3</sub>. Schiff's base can be divided into two groups; symmetric and asymmetric Schiff's base. Hydrazones are the members of the asymmetric Schiff's bases. Hydrazones are a class of organic compounds with the general structure of R<sub>2</sub>C=NNR<sub>2</sub> which are related to ketones and aldehydes by the replacement of the oxygen with NNR<sub>2</sub> functional group. These compounds are commonly

\*Corresponding author: Kamal Alizadeh, Department of Chemistry, Lorestan University, Khorramabad, Iran, Tel: +986633120612; Fax: +986633120612; E-mail: Alizadehkam@yahoo.com (or) Alizadeh.k@lu.ac.ir

Received May 24, 2016; Accepted June 10, 2016; Published June 17, 2016

Citation: Alizadeh K, Rad NA (2016) A New Optical Sensor for Selective Monitoring of Nickel Ion Based on A Hydrazone Derivative Immobilized on the Triacetyl Cellulose Membrane. J Anal Bioanal Tech 7: 322. doi:10.4172/2155-9872.1000322

Copyright: © 2016 Alizadeh K, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

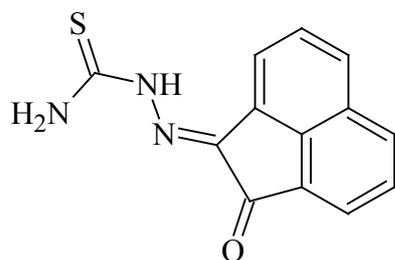


Figure 1: Chemical structure of 1-acenaphthoquinone 1-thiosemicarbazone.

formed through the reaction of hydrazine on ketones or aldehydes [29-31].

## Experimental Section

### Materials and instruments

All reagents were of analytical reagent grade and were used as received. Deionized double-distilled water was used throughout and test solutions were buffered in a 0.02 mol L<sup>-1</sup> solution of acetic acid/sodium acetate and pH adjusted with dropwise addition of 1 mol L<sup>-1</sup> solution of HCl or NaOH. The Schiff's base L, with the chemical name of 1-acenaphthoquinone 1-thiosemicarbazone, was synthesized and purified using a previously reported method [27,28].

A Jenway (USA) model 3020 pH meter with a combined glass electrode was used after calibration against standard Merck buffers for pH determinations. A Shimadzu (Japan) model 1650PC double-beam spectrophotometer was used for running the electronic absorption spectra (controlled to  $\pm 0.1^\circ\text{C}$ ). A home-made polyacrilamide holder was used for holding triacetyl cellulose membranes inside the quartz cells of the spectrophotometer. A totally glass Fisons (UK) double distiller was used for preparation of doubly distilled water.

### Procedures

A method described elsewhere was used for the preparation of transparent triacetyl cellulose membranes. They 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 [26,32]. The triacetyl cellulose transparent film was hydrolyzed in order to deesterify the acetyl groups and to increase the porosity of the membrane by treating the membrane into 0.10 M NaOH solution for 24 h. The films were treated with a solution of 0.007 g of the compound L, in 10 ml ethylene diamine for 2 min at ambient temperature. Afterwards, they were washed with water for the removal of ethylene diamine and the loosely trapped indicator. The prepared membranes were kept under water, when not in use. A 1 cm  $\times$  2 cm piece of the fabricated membranes sensor was cut and mounted in a polyacrilamide holder and placed inside the quartz cell of the spectrophotometer. The cell was then used as usual for the absorbance determinations. All the measurements on the transparent triacetyl cellulose membrane were performed in aqueous medium.

The recommended procedure was applied to the determination of nickel in several real water samples collected from the west of Iran, Kermanshah. The pH was adjusted to 6.0 before analysis, without any further treatment. For analysis, about 2.5 ml of the samples were transferred into a 1 cm quartz cell equipped with the membrane sensor. The absorbance's were then measured at 337 nm and subtracted from an absorbance reading for a buffer solution at the same wavelength. The Ni<sup>2+</sup> concentration was then derived using an ordinary calibration curve method.

## Results and Discussion

### Preliminary studies

In preliminary studies, we recorded the absorbance variations followed by absorbance readings at maximum wavelength of immobilized 1-acenaphthoquinone 1-thiosemicarbazone on hydrolyzed cellulose acetate into a quartz cell of the spectrometer. They occur upon addition of  $1.5 \times 10^{-5}$  mol L<sup>-1</sup> aqueous solutions of Zn<sup>2+</sup>, Pb<sup>2+</sup>, K<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, CrO<sub>4</sub><sup>2-</sup>, Hg<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>, Tl<sup>+</sup> and Fe<sup>3+</sup> which was obtained after equilibration at pH 6. According to the shape reported in Figure 2, It should be noted that the largest variation is observed for Ni<sup>2+</sup>, whereas for the other studied ions, negligible or small variations in the absorbance maximum is observed by increasing the concentration of corresponding ions. Based on the relatively high selectivity of 1-acenaphthoquinone 1-thiosemicarbazone for Ni<sup>2+</sup>, as was concluded from its absorbance variation, the mentioned compound, L was expected to possess a high selectivity towards this metal ion.

Immobilization of ligand L on a triacetyl cellulose transparent film changed, in some extent, its optical properties. The absorbance maximum of L showed a blue shift from 417 nm to about 337 nm upon the immobilization as is obvious from Figure 3. This can suggest that the structured conformation of the immobilized 1-acenaphthoquinone 1-thiosemicarbazone compound is less flat than that of its soluble analogue [26]. Furthermore, it is evident that the first region of spectra at about 200-300 nm for the membrane sensor in compare to the dissolved form of L, in methanol was disappeared too.

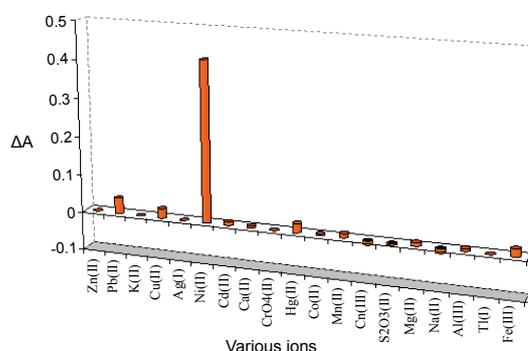


Figure 2: The absorbance variations of the 1-acenaphthoquinone 1-thiosemicarbazone membrane sensor at maximum wavelength for the studied ions.

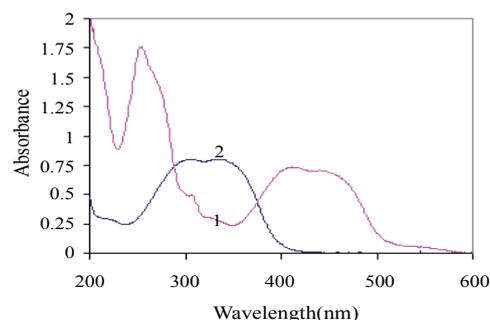


Figure 3: The curves 1 and 2 show the absorbance spectra of the 1-acenaphthoquinone 1-thiosemicarbazone in methanol solution ( $1 \times 10^{-4}$  mol L<sup>-1</sup>) and after immobilization on a triacetyl cellulose membrane, respectively. The blue shift observed for L (curve 2) upon immobilization on the membrane.

Figure 4 show the absorption spectra of immobilized 1-acenaphthoquinone 1-thiosemicarbazone on hydrolyzed cellulose acetate which was obtained after equilibration at pH 6.0 containing different concentrations of  $\text{Ni}^{2+}$ . The spectral characteristic of this optical sensor indicate maxima at 337 nm. It is evident that the membrane absorbance at 337 nm decrease by increasing  $\text{Ni}^{2+}$  concentration as a result of the complex formation in the optode. During the titration, no measurable spectral shift was observed, which is typical for an absorption process involving a strong complex formation [26].

### Effect of pH on the sensor response

The response characteristic of the prepared membrane sensor was highly dependent to pH. Since variation of pH changed the absorbance of both the free and complexed forms of the immobilized L, for the study of the effect of pH absorbance differences ( $\Delta A$ ) before and after addition of  $\text{Ni}^{2+}$  was followed in a pH range of 4 to 10. As shown in Figure 5, the change in absorbance increased rapidly by changing the pH from 4 to about 5.5, while it was decreased at pH values higher than 6.5. The diminished response at the low pH region may be explained by the extraction of  $\text{H}^+$  from the test solution into the membrane, via protonation of the donor atoms of L, resulting in an expected change in the formation of a  $\text{Ni}^{2+}$ -L complex. On the other hand the reduced optical response of the proposed sensor due to a possible of  $\text{Ni}^{2+}$  hydrolysis in higher pH values. Thus, a pH of 6.0 was considered as optimum and used for further studies [33].

### Calibration curve of the sensor

The dynamic working ranges for the proposed membrane sensor was studied by stepwise addition of  $\text{Ni}^{2+}$  to a series of test solutions followed by the absorbance difference monitoring at 337 nm. It was found that the absorbance decreased continuously by increasing the Ni(II) concentration and the membrane was saturated when the  $\text{Ni}^{2+}$  concentration exceeded  $10^{-4}$  mol  $\text{L}^{-1}$ . Under the specified experimental conditions, the calibration curve in a logarithmic scale for  $\text{Ni}^{2+}$  was linear from  $5.01 \times 10^{-10}$  to  $2.04 \times 10^{-5}$  mol  $\text{L}^{-1}$ . According to the definition of IUPAC, the limit of detection (LOD,  $3\sigma$ ) of this method was  $1.00 \times 10^{-10}$  mol  $\text{L}^{-1}$  which is sufficiently low for  $\text{Ni}^{2+}$  monitoring in environmental samples [10,34,35]. The regression equation for the calibration curve shown in Figure 6 was  $\Delta A = 0.097 \times \text{Log}(\text{Ni}^{2+}) + 0.925$  with a correlation coefficient ( $R^2$ ) of 0.994.

### The sensor response time

The response time of the  $\text{Ni}^{2+}$  sensor was calculated by plotting the absorbance as a function of time at two levels of  $\text{Ni}^{2+}$  concentrations. As shown in Figure 7 the profile of the response of  $\text{Ni}^{2+}$  optical sensor at 337 nm with time, the absorbance gets to 95% of the steady state signal in about 1 min. In general the response time decreased by increasing the analyte concentration. This may be explained by the fact that at a higher analyte concentration the rate of its diffusion in the membrane phase may be increased [10,34].

### Effect of interfering ions

Perhaps the most important characteristics of an ion-selective optode are its selectivity, which reflects its relative response for primary ion over diverse ions present in solution. Thus, the influence of several potentially interfering ions on the response behavior of the membrane sensor was studied. To investigate the selectivity of the proposed  $\text{Ni}^{2+}$  optical membrane sensor, the absorbance of a fixed concentration of nickel ion, at  $1.0 \times 10^{-8}$  mol  $\text{L}^{-1}$  level, in a solution of pH=6.0 was recorded before ( $\Delta A_0$ ) and after ( $\Delta A$ ) addition of some

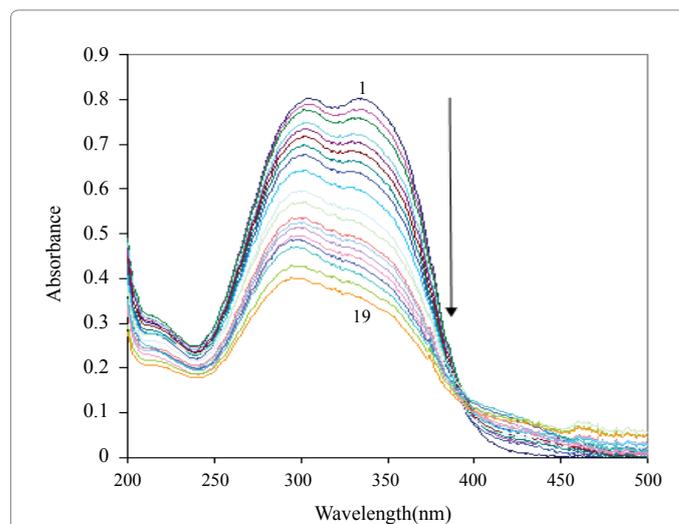


Figure 4: The absorption spectra resulting from spectrophotometric titration of the proposed sensor, under the optimal experimental conditions. The arrows show the directions of absorbance changes by increasing the concentration of  $\text{Ni}^{2+}$ .

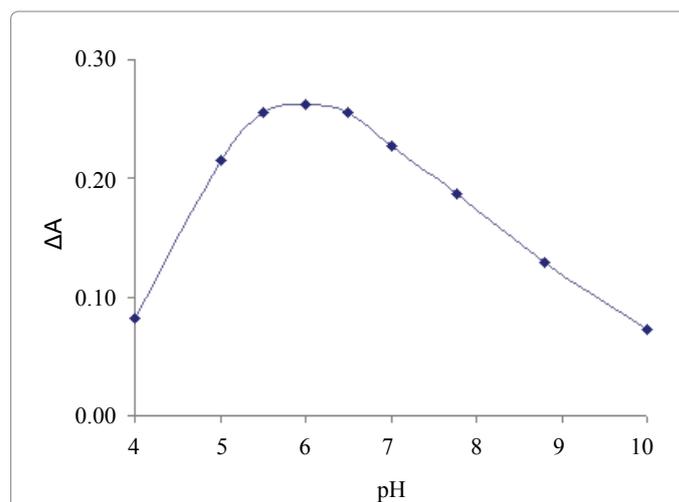
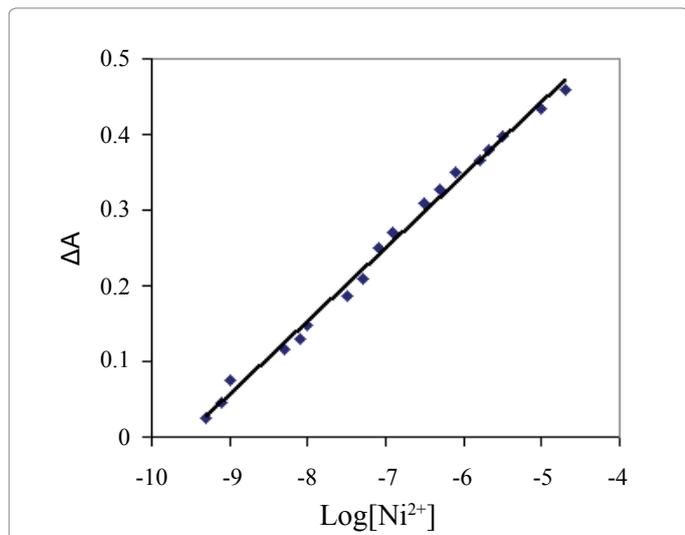


Figure 5: Effect of measurement pH on the absorbance differences between the free and complexed forms of the immobilized L. The absorbances were measured at 337 nm in a 0.05 mol  $\text{l}^{-1}$  acetate buffer and a buffered  $1.0 \times 10^{-7}$  mol  $\text{L}^{-1}$   $\text{Ni}^{2+}$  solution, respectively.

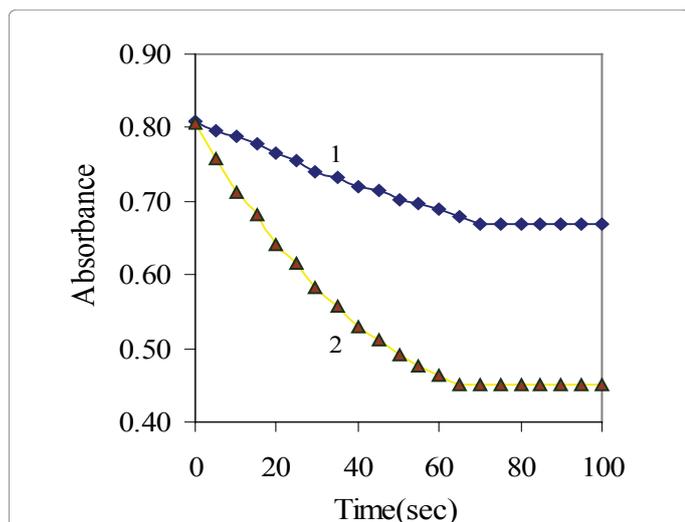
potentially interfering ions such as  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Tl}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Li}^+$ ,  $\text{Ba}^{2+}$  and  $\text{Ce}^{3+}$  at concentrations up to 100 times of the analyte ion. The resulting relative error is defined as  $\text{RE}(\%) = [(\Delta A - \Delta A_0) / \Delta A_0] \times 100$ . The results of the selectivity studies are summarized in Figure 8. The data clearly indicate that, for all the studied metal ions, the relative error is up to 4%, which demonstrated that the studied interfering ions with a concentration of at least 100 times of  $\text{Ni}^{2+}$  ion, have no significant effect on the analytical signal [21,34,35].

### Regeneration and reproducibility of the sensor

Multiple usage of an optical sensor is feasible if the sensor can be easily regenerated and give reproducible responses. Different compounds, EDTA and  $\text{SCN}^-$  solutions with different concentrations were tested for regeneration of the membrane sensor and desorption of



**Figure 6:** The logarithmic scale calibration curve for the 1-acenaphthoquinone 1-thiosemicarbazone membrane sensor at 337 nm.



**Figure 7:** Plot of absorption vs. time of the sensor at 337 nm for two  $\text{Ni}^{2+}$  concentration levels of  $5.0 \times 10^{-9}$  and  $1.0 \times 10^{-6} \text{ mol L}^{-1}$  according to curves 1 and 2, respectively.

$\text{Ni}^{2+}$  from it, see Figure 9. The best reagent was an EDTA solution with a concentration of  $0.1 \text{ mol L}^{-1}$  or higher, which can efficiently remove any adsorbed  $\text{Ni}^{2+}$  from the membrane and returns its absorbance to its initial value for membrane ( $\Delta A \approx 0$ ) in less than about three minute.

The reproducibility of the sensor response was tested by its multiple usages for  $\text{Ni}^{2+}$  monitoring in test solutions at two concentration levels of  $1.0 \times 10^{-9}$  and  $1.0 \times 10^{-7} \text{ mol L}^{-1}$ . After each absorbance reading, the membrane was cleaned by  $0.1 \text{ mol L}^{-1}$  EDTA solution, pure water and a  $0.05 \text{ mol L}^{-1}$  acetate buffer solution, respectively. As shown in Figure 10, good reproducibilities were obtained at both  $\text{Ni}^{2+}$  concentration levels. The corresponding RSD values were 1.45% and 0.83%, respectively [21,34,35].

### Lifetime and stability

The life time of the membrane sensor was tested over a period of 4 months during which the membranes were stored in water [5,36-

38]. The mean absorbances of the membranes at 337 nm were found to be  $0.801 (\pm 0.025)$  and  $0.805 (\pm 0.020)$ , before and after this period, respectively. Hence, the membranes are stable within this period with a minimum life time of 4 months. Also no evidence of the ionophore leaching or signal drift was observed during multiple usages of the membrane.

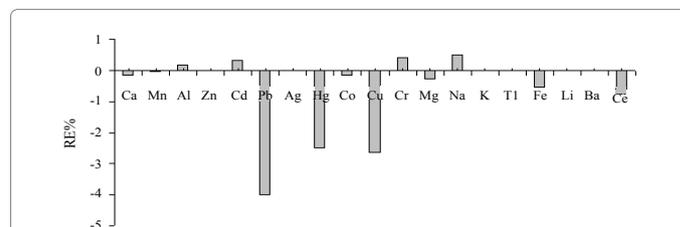
Additionally, the short-term stability of the optode membrane was investigated by monitoring its absorbance values during its contact with a  $1.0 \times 10^{-7} \text{ M}$  solution of  $\text{Ni}^{2+}$  at pH 6.0 over a period of 6 hours. From the absorbance measurements in 30 min intervals ( $n=2$ ), it was found that the response was almost unchanged with only 1.0% increase in absorbance at tested wavelength after the 6 hours monitoring [34].

### Application

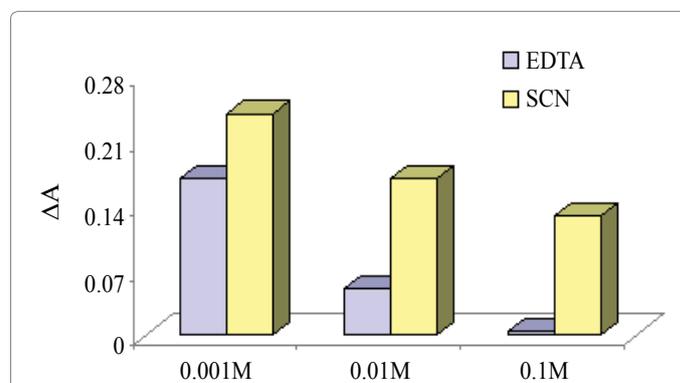
The proposed  $\text{Ni}^{2+}$ -selective optical sensor was used for the determination of  $\text{Ni}^{2+}$  in two natural water samples. The data given in Table 1 show a good agreement between the measured values using the proposed method and those obtained by the atomic absorption spectrometry (AAS) laboratory at Razi University, Kermanshah, Iran. It may be concluded that the proposed membrane sensor is selective to  $\text{Ni}^{2+}$  and may be used for monitoring of this ion in real water samples.

### Conclusion

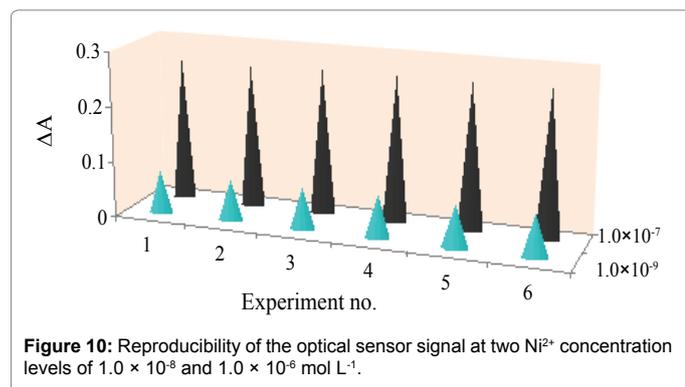
The  $\text{Ni}^{2+}$  optical sensor that is prepared on the basis of 1-acenaphthoquinone 1-thiosemicarbazone in this study shows very good selectivity for  $\text{Ni}^{2+}$  over other common metal ions. The proposed sensor showed very favorable optical properties for its use as an optical sensor, such as high selectivity, adequate life time, fast and reproducible regeneration, low cost and simple fabrication and handling. The sensor



**Figure 8:** Interferences from different metal ions to the spectrophotometric determination of  $\text{Ni}^{2+}$  ion for the 1-acenaphthoquinone 1-thiosemicarbazone membrane sensor at pH 6. Concentration of  $\text{Ni}^{2+}$  and the diverse ions were  $1.0 \times 10^{-8}$  and  $1.0 \times 10^{-6} \text{ mol L}^{-1}$ , respectively.



**Figure 9:** Regeneration of the membrane in the presence of different concentrations of EDTA and  $\text{SCN}^-$ . Experimental conditions: wavelength, 337 nm; measurement pH was 6.0.



**Figure 10:** Reproducibility of the optical sensor signal at two Ni<sup>2+</sup> concentration levels of  $1.0 \times 10^{-8}$  and  $1.0 \times 10^{-6}$  mol L<sup>-1</sup>.

Samples	Ni <sup>2+</sup> (mol L <sup>-1</sup> ) <sup>a</sup>	
	Measured value (Triacetyl cellulose membrane)	Reference value (AAS)
Gharahsoo River water	$1.68 (\pm 0.22) \times 10^{-7}$	$1.73 (\pm 0.23) \times 10^{-7}$
Spring water	$1.21 (\pm 0.19) \times 10^{-7}$	$1.25 (\pm 0.20) \times 10^{-7}$

<sup>a</sup>values in the parentheses are standard deviation based on the three replicate analyses

**Table 1:** Application of the membrane sensor for the determination of Ni<sup>2+</sup> in different real samples.

can be regenerated readily with an EDTA solution and demonstrated a long life time with the possibility of multiple uses for environmental monitoring of Ni<sup>2+</sup>. Due to the advantages of the proposed method with respect to previously reported ones it may be used as an alternative method for Ni<sup>2+</sup> determination over a range of  $5.01 \times 10^{-10}$  to  $2.04 \times 10^{-5}$  mol L<sup>-1</sup> values without any significant interference from other metal ions.

### Acknowledgements

The authors thank the Lorestan University for supporting this study.

### References

- Ferreira SLC, Santos WNL dos, Lemos VA (2001) On-line preconcentration system for nickel determination in food samples by flame atomic absorption spectrometry. *Anal Chim Acta* 445: 145-151.
- Underwood EJ (1977) Trace elements in human and Animal Nutrition. Fourth edn. Academic Press, New York, USA.
- Hu NL, Gao HW, Zhang B, Zhan GQ (2005) Simultaneous determination of cobalt and nickel in wastewater with 2-hydroxyl-5-benzeneazoforomoamithiozone by spectral correction technique. *J Chin Chem Soc* 52: 1145-1152.
- Wu MH, Lin JL, Wang J, Cui Z, Cui Z (2009) Development of high throughput optical sensor array for on-line pH monitoring in micro-scale cell culture environment. *Biomed Microdevices* 11: 265-273.
- Mohr GJ, Wolfbeis OS (1994) Optical sensors for a wide range of pH based on azo dyes immobilized on a novel support. *Anal Chim Acta* 292: 41-48.
- Wang E, Chow KF, Kwan V, Chin T, Wong C, et al. (2003) Fast and long term optical sensors for pH based on sol-gels. *Anal Chim Acta* 495: 45-50.
- Safavi A, Bagheri M (2003) Novel optical pH sensor for high and low pH values. *Sens Actuators B* 90: 143-150.
- Alizadeh K, Nemati H, Zohrevand S, Hashemi P, Kakanejadifard A, et al. (2013) Selective dispersive liquid-liquid microextraction and preconcentration of Ni(II) into a micro droplet followed by ETAAS determination using a yellow Schiff's base bisazanyl derivative. *Mater Sci Eng C* 33: 916-922.
- Amini MK, Khezri B, Firooz AR (2008) Development of a highly sensitive and selective optical chemical sensor for batch and flow-through determination of mercury ion. *Sens Actuators B* 131: 470-478.
- Hashemi P, Abolghasemi MM, Alizadeh K, Afzari Zarjani R (2008) A calmagite immobilized agarose membrane optical sensor for selective monitoring of Cu<sup>2+</sup>. *Sens Actuators B* 129: 332-338.
- Dridi C, Ben Ali M (2008) Electrical and optical study on modified thiacalix(4) arene sensing molecules: Application to Hg<sup>2+</sup> ion detection. *Mater Sci Eng C* 28: 765-770.
- Yang Y, Jiang J, Shen G, Yu R (2009) An optical sensor for mercury ion based on the fluorescence quenching of tetra(p-dimethylaminophenyl)porphyrin. *Anal Chim Acta* 636: 83-88.
- Han ZX, Luo HY, Zhang XB, Kong RM, Shen GL, et al. (2009) A ratiometric chemosensor for fluorescent determination of Hg(2+) based on a new porphyrin-quinoline dyad. *Spectrochim Acta A Mol Biomol Spectrosc* 72: 1084-1088.
- Hisamoto H, Watanabe K, Nakagawa E, Siswanta D, Shichi Y, et al. (1994) Flow-through type calcium ion selective optodes based on novel neutral ionophores and a lipophilic anionic dye. *Anal Chim Acta* 299: 179-187.
- O'Neill S, Conway S, Twellmeyer J, Egan O, Nolan K, et al. (1999) Ion-selective optode membranes using 9-(4-diethylamino-2-octadecanoatestyryl)-acridine acidochromic dye. *Anal Chim Acta* 398: 1-11.
- Tóth K, Thu Lan BT, Jeney J, Horváth M, Bitter I, et al. (1994) Chromogenic calix[4]arene as ionophore for potentiometric and optical sensors. *Talanta* 41: 1041-1049.
- Shortreed MR, Dourado S, Kopelman R (1997) Development of a fluorescent optical potassium-selective ion sensor with ratiometric response for intracellular applications. *Sens Actuators B* 38-39: 8-12.
- Ensafi A, Bakhshi M (2003) A stable optical film sensor based on immobilization of 2-amino-1-cyclopentene-1-dithiocarboxylic acid on acetyl cellulose membrane for Ni(II) determination. *Sens Actuators B* 96: 435-440.
- Shamsipur M, Poursaberi T, Karami AR, Hosseini M, Momeni A, et al. (2004) Development of a new fluorimetric bulk optode membrane based on 2,5-thiophenylbis(5-tert-butyl-1,3-benzoxazole) for nickel(II) ions. *Analytica Chimica Acta* 501: 55-60.
- Alizadeh N, Moemeni A, Shamsipur M (2002) Poly(vinyl chloride)-membrane ion-selective bulk optode based on 1,10-dibenzyl-1,10-diaza-18-crown-6 and 1-(2-pyridylazo)-2-naphthol for Cu<sup>2+</sup> and Pb<sup>2+</sup> ions. *Anal Chim Acta* 464: 187-196.
- Shamsipur M, Hosseini M, Alizadeh K, Alizadeh N, Yari A, et al. (2005) Novel fluorimetric bulk optode membrane based on a dansylamidopropyl pendant arm derivative of 1-aza-4,10-dithia-7-oxacyclododecane ([12]aneNS2O) for selective subnanomolar detection of Hg(II) ions. *Anal Chim Acta* 533: 17-24.
- Kim SH, Han SK, Park SH, Lee SM, Mi Lee S, et al. (1999) Use of squarylium dyes as a sensing molecule in optical sensors for the detection of metal ions. *Dyes and Pigments* 41: 221-226.
- Ganjali MR, Poursaberi T, Hajiagha-Babaei L, Rouhani S, Yousefi M, et al. (2001) Highly selective and sensitive copper(II) membrane coated graphite electrode based on a recently synthesized Schiff's base. *Anal Chim Acta* 440: 81-87.
- Gholivand MB, Ahmadi F, Rafiee E (2006) A novel Al(III)-selective electrochemical sensor based on N,N'-bis(salicylidene)-1,2-phenylenediamine complexes. *Electroanalysis* 18: 1620-1626.
- Ganjali MR, Rezapour M, Norouzi P, Salavati-Niasari M (2005) A new pentadentate S-N Schiff's-Base as a novel ionophore in construction of a novel Gd(III) membrane sensor. *Electroanalysis* 17: 2032-2036.
- Alizadeh K, Rezaei B, Khazaeli E (2014) A new triazine-1-oxide derivative, immobilized on the triacetyl cellulose membrane as an optical Ni<sup>2+</sup> sensor. *Sens Actuators B* 193: 267-272.
- Hahn R, Herrmann WA, Artus GRJ, Kleine M (1995) Biologically relevant metal coordination compounds: MoVI O<sub>2</sub> and nickel(II) complexes with tridentate aromatic Schiff bases. *Polyhedron* 14: 2953-2960.
- Su X, Aprahamian I (2014) Hydrazone-based switches, metallo-assemblies and sensors. *Chem Soc Rev* 43: 1963-1981.
- Alizadeh K, Seyyedi S, Avanes A, Ganjali MR, Faridbod F (2011) Concentration and Temperature Effects on the Electronic Absorption Spectra of 1-pyridinyl-2-methylene-benzenecarbohydrazonic Acid Following Solvatochromic Studies. *Acta Chim Slov* 58: 251-255.
- Faridbod F, Ganjali MR, Dinarvand R, Norouzi P, Riahi S (2008) Schiff's bases and crown ethers as supramolecular sensing materials in the construction of potentiometric membrane sensors. *Sensors* 8: 1645-1703.

31. Alizadeh K, Ghiasvand AR, Borzoei M, Zohrevand S, Rezaei B, et al. (2009) Experimental and computational study on the aqueous acidity constants of some new aminobenzoic acid compounds. *J Mol Liq* 149: 60-65.
32. Noroozifar M, Khorasani Motlagh M, Taheri A, Zare Dorabei R (2008) Diphenylthiocarbazone immobilized on the triacetyl cellulose membrane as an optical silver sensor. *Turk J Chem* 32: 249-257.
33. Hashemi P, Hosseini M, Zargoosh K, Alizadeh K (2011) High sensitive optode for selective determination of Ni<sup>2+</sup> based on the covalently immobilized thionine in agarose membrane. *Sens Actuators B* 153: 24-28.
34. Alizadeh K, Parooi R, Hashemi P, Rezaei B, Ganjali MR (2011) A new Schiff's base ligand immobilized agarose membrane optical sensor for selective monitoring of mercury ion. *J Hazard Mater* 186: 1794-1800.
35. Shamsipur M, Alizadeh K, Hosseini M, Caltagirone C, Lippolis V (2006) A selective optode membrane for silver ion based on fluorescence quenching of the dansylamidopropyl pendant arm derivative of 1-aza-4,7,10-trithiacyclododecane ([12]aneNS<sub>3</sub>). *Sens Actuators B* 113: 892-899.
36. Ahmad M, Hamzah H, Sufliza Marsom E (1998) Development of an Hg(II) fibre-optic sensor for aqueous environmental monitoring. *Talanta* 47: 275-283.
37. Kilian K, Pyrzyaska K (2003) Spectrophotometric study of Cd(II), Pb(II), Hg(II) and Zn(II) complexes with 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrin. *Talanta* 60: 669-678.
38. Shamsipur M, Shirmardi Dezaki A, Akhond M, Sharghi H, Pazirae Z, et al. (2009) Novel PVC-membrane potentiometric sensors based on a recently synthesized sulfur-containing macrocyclic diamide for Cd<sup>2+</sup> ion. Application to flow-injection potentiometry. *J Hazard Mater* 172: 566-573.