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طراحی یک حسگر نوری برای اندازه‌گیری آلومینیوم(III) بر اساس نشانش اریو کرم سیانین R بر روی تری استیل سلولز

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Design of an Optical Sensor for Aluminium(III) Determination Based on Immobilization of Eriochrome Cyanine R on a Triacetylcellulose

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چکیده

یک حسگر نوری بر پایه نشاندن واکنشگر اریوکروم سیانین‌آر به روی غشاء تری استیل سلولز برای اندازه‌گیری یون آلومینیوم (III) طراحی شد. این حسگر نوری دارای پاسخ برگشت‌پذیر و تکرارپذیر می‌باشد. در اثر بر همکنش انتخابی اریوکروم سیانین‌آر موجود در غشاء با یون آلومینیوم، رنگ غشاء از صورتی به بنفش در pH= ۶/۰ تغییر می‌کند. درشرایط بهینه، روش دارای پاسخ خطی غلظت یون آلومینیوم (III) از $۳/۲۲\times۱۰^{-۸}$ تا $۴/۱۰\times۱۰^{-۵}$ مولار و حد تشخیص آن $۱/۲\times۱۰^{-۸}$ مولار می‌باشد. جزئیات محاسبه خطی، حد تشخیص، حساسیت، گزینش‌پذیری و زمان پاسخ مورد بحث قرار گرفت. پاسخ حسگر وابسته به pH بود. پاسخ غشاء به یون آلومینیوم (III) غیر برگشتی و شامل تغییر رنگ از صورتی به آبی بود. غشاء از طریق گذاشتن در محلول ۰/۱ مولار EDTA در کمتر از ۳۰ ثانیه قابل برگشت برای اندازه‌گیری‌های بیشتر می‌باشد. زمان پاسخ غشاء کمتر از ۱۶ دقیقه بر حسب غلظت آلومینیوم می‌باشد. تکرارپذیری و تکثیرپذیری پاسخ غشاء به ترتیب ۱/۶۲ و ۳ درصد بدست آمد. حسگر پاسخ گزینش‌پذیری را نسبت به آلومینیوم (III) در مقابل کاتیون‌های دیگر نظیر Zn(II)، Cu(II)، Fe(III)، Ni(II) و Co(II) از خود نشان می‌دهد. حسگر برای اندازه‌گیری آلومینیوم (III) در آب‌های شرب و شربت منیزیم-آلومینیوم استفاده شده است.

واژه‌های کلیدی

حسگر نوری؛ تری استیل سلولز؛ اریو کرم سیانین آر؛ آلومینیوم؛ جفت یون لیپوفیلیک.

Abstract

A selective optical sensor based on immobilization of Eriochrome Cyanine R for the determination of Al(III) ions in aqueous solution has been developed. The method is based on the spectrophotometric measurement of complex Eriochrome Cyanine R-aluminium at 537 nm. The sensing membrane is made of a triacetylcellulose film containing Eriochrome Cyanine R colorimetric reagent immobilized as an ion pair with methyltrioctylammonium chloride. The response of the sensor is based on the Eriochrome Cyanine R absorbance decrease by the coordination of Al(III) ions. At pH= 6.0, the linear dynamic rangeis varied from 3.22×10^{-8} to 4.10×10^{-5} mol L^{-1} with a detection limit of 1.2×10^{-8} mol L^{-1}. A dynamic working range, detection limit, sensitivity, selectivity and the response time were discussed in detail. The response was pH dependent. The membrane responds to Al(III) ions irreversibly by changing color from pink to blue. The membrane was regenerated in less than 30 seconds with 0.1 mol L^{-1} EDTA solution and was ready for further measurements. The response time of the sensor was within 16 min depending on the concentration of Al (III) ions. The sensor response was found to have a repeatability and reproducibility of 1.62% and 3%, respectively. The sensor provides appropriate selectivity to Al(III) ions over transition metal cations, including Co(II), Ni(II), Fe(III), Cu(II) and Zn(II). The sensor has been used for the determination of Al(III) ions in potable water and aluminium – magnesium syrup.

Keywords

Optical Sensor; Triacetylcellulose Membrane; Eriochrome Cyanine R; Aluminium; Lipophilic Ion Pairs.

1. INTRODUCTION

Heavy metal ions represent a major environmental problem and their detection and monitoring in waste water outlets, rivers, reservoirs or sources of potable water is necessary [1]. The toxicological effects of metal ions, such

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as aluminum, on living system, especially in human beings, are now well known. Several recent epidemiological studies investigated the correlation between the uptake of aluminum ions, mostly from potable water, on the one hand, and such diseases as Alzheimer, Parkinson, and dialysis-related diseases, on the other [2-6]. Long-term total parenteral nutrition (TPN) patients can inadvertently receive significant amounts of aluminium present as a contaminant in TPN. Many of the solutions for parenteral nutrition have an aluminium content which exceeds the suggested threshold concentration of 25 mg l21 recommended by the American Society for Clinical Nutrition (ASCN) and the American Society for Parenteral and Enteral Nutrition (ASPEN) [7].

Some methods such as graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) [8-9], liquid chromatography [10], flow injection analysis [11] and stripping voltammetry [12] have been used to determine aluminum ions. Although these methods have good sensitivity, well-controlled experimental conditions, and profound sample-preparation [13], time and money consuming, expensive and do not permit real-time or even on-site determinations and the accurate determination of aluminium requires considerable expertise [14-15].

Spectrophotometric methods due to advantages such as accuracy and good precision, acceptable accuracy, low cost and simple operation have been applied for trace metal determination. Several reagents such as xylenol orange, stilbazo, chlorophosphonazo I and methylthymol blue have been reported for the spectrophotometric determination of aluminium [16-17]. ECR is one of the most common spectrophotometric reagents for aluminum determination since it was extensively studied a few decades ago and is a well-known reagent for the trace determination of aluminum that forms a 3:1 complex at a high and 2:1 or 1:1 complex at lower concentrations of the reagent [18-20]. The introduction of more rigorous environmental controls is generating a demand for simple, rapid and sensitive field-based detection instrument for monitoring the presence of environmental pollutants. Optical sensors are particularly suitable to this type of application as they may easily be incorporated into low-cost, easy to use kits, yet at the same time, they can offer the selectivity and sensitivity necessary for environmental monitoring [21] The most optical sensor chemistries for the determination of heavy-metal ions are based on either conventional indicator dyes, neutral ionophore or on the biological recognition component [22]. Over the past two decades, an interest has been increased on the development of optical chemical sensors (known as sensors or optrodes) as viable alternatives compare to electrochemical sensors [23]. These sensors have lower detection limits and high sensitivity [21], do not require internal and external reference devices, long preconditioning time is not a prerequisite, and are not subjected to electrical noise [24].

Herein, we investigate the use of ECR as a colorimetric reagent for developing and designing of the aluminium optical sensor. This sensor has high sensitivity and selectivity in monitoring Al(III) ions and successfully was used to measure Al(III) ions in potable water and aluminium-magnesium syrup samples.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

All stock solution of metal ions was prepared from analytical grade nitrate salts and used without further purifications. ECR, ethylenediamine and MTOACl were purchased from Merck, Darmstadt, Germany. An ammonia-acetic acid buffer solution (pH=6.0) was prepared according to the literature [25]. A Jasco V-570 double beam Uv-vis spectrophotometric (slit width: 1.0 nm, scan rate: 2000 cm/min) was used for absorbance measurements between 350-800 nm. The sensor membranes were fixed in 1 cm × 1 cm of glass cells. The pH measurement was carried out by Metrohm 744 pH-meter with a combined glass electrode. Double-distilled water was used throughout all experiments.

2.2. Sample preparation

2.2.1. Aluminium – Magnesium syrup sample

To prepare Aluminum – Magnesium syrup sample, 1mL of Al–Mg syrup was heated in a furnace to dryness. The remainder was dissolved in nitric acid and diluted to 50 mL [26].

2.2.2. Potable water sample

According to the literature [26], the water sample was acidified with concentrated HNO_3 to pH<2, and the sample was left for five hours at room temperature, and then filtered. Finally, a volume of 25 mL of the prepared water sample was diluted to 50 mL.

2.3. Preparation of the sensor membrane

To prepare the transparent triacetylcellulose membrane, the procedure of reference of [27] was used. According to this procedure, the transparent triacetylcellulose membranes were produced from waste photographic membrane taps and cut into 1 cm × 3 cm and were treated with commercial

sodium hypochlorite for several seconds to remove colored gelatinous layers. Then, washed and dried membrane was placed in the solution containing ECR and MTOACl (1:1) and ethylenediamine for 12 min at room temperature. Then, it was washed with water for removing the extra reagents. The prepared membrane was kept in water when not used.

2.4. Spectrophotometric procedures

All absorption spectra of the sensor were obtained against a without chromoinophore membrane as a reference. To measure the absorbance of the sample, firstly the prepared membrane was immersed in ammonia-acetic acid buffer solution (pH 6.0) for 15 min. Then the membrane was placed in the inner wall of the spectrophotometric cell that contains 3 mL of buffer solution and the titration of solution with Al (III) ions was done, and the absorbance spectrum was recorded (within the wavelength range of 350-800 nm).

The absorbance difference is defined as $\Delta A = A_0 - A$, where A and A_0 are the absorbance of the membrane in the presence and absence of Al (III) ions, respectively at the same wavelength.

3. RESULT AND DISCUSSION

3.1. Mechanism of response

ECR is a spectrophotometric reagent for the determination of Al (III) ions [28, 25]. It was found that the formation of aluminium-ECR complex was more complete in pH range 5.8-6.5 [29]. The reagent ECR has one sulfonic group capable of dissociation, and therefore, it could form an ion pair. ECR is soluble in water due to a sulfonic group in its chemical structure and it cannot be immobilized effect on triacetylcellulose membrane. The water soluble indicator (ECR) was lipophilised in the form of an ion pair with MTOACl (Fig.1), and then immobilized on the membrane. To achieve the best result, the concentration of MTOACl should be optimized. The MTOACl ion pair doesn't form well at the low concentration of MTOACl, and the higher concentration of MTOACl caused the membrane to become opaque. It was found that the additional amount of MTOACl prevents leaching of the dye, by stabilizing the charged form of the indicator [1]. The optimal amount was found to be 1:1 ECR/ MTOACl. The effect of ECR amounts on the sensor response was investigated in the range of 0.01-0.04 gr. The maximum response and sensitivity were used. The immobilization of the ECR/ MTOACl ion pair was effectively performed when using ethylenediamine as solvent. The hydrolyzed cellulose film in ethylenediamine shaped the proposed structure in the polymer, which minimizes barriers of mass transport [30]. To have a membrane with the best response and sensitivity the preparation time of sensing membrane in ethylenediamine and ion pair solution should be optimized. The appropriate time for the maximum response is obtained at 12 min. At the time longer than 12 min, the sensitivity of the membrane was reduced, and the membrane began to degrade.

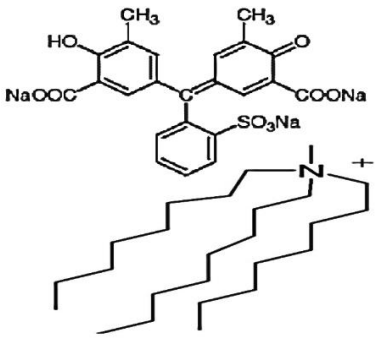

Fig.1. Chemical structure of ECR-MTOACl.

3.2. Spectral characteristics

Fig. 2 shows the absorption spectra of the sensor membrane after being equilibrated in ammonia-acetic acid buffer solution pH 6.0 containing varying concentration of Al (III) ions which are recorded at 350-800 nm.

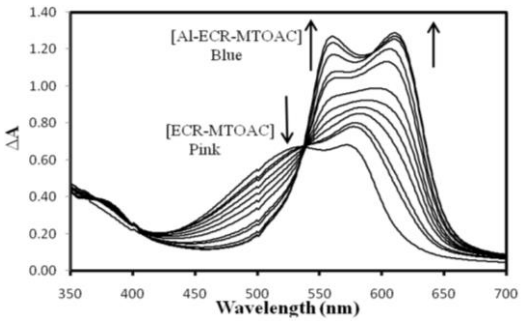

Fig. 2. Absorption spectra of the optode film at pH=6.

The spectrums of ECR–MTOACl ion pair on triacetylcellulose membrane have two absorption maxima at 537 and 576 nm in the buffer solution. The color of the membrane has changed from pink to blue when exposed to Al (III) ions and has reached to absorption maxima at 560 and 611 nm which is due to extraction of Al (III) ions from the bulk solution to the reagent phase was saturated into the membrane and complex formation. The absorption spectra of immobilized indicator on the sensing membrane were shifted in comparison with those of their soluble form. From the above data, it can be suggested, that the structured conformation of the immobilized indicator is planer than that of its soluble analogue [31]. Thus,

the appearance of the characteristic absorption band at 560 and 611 nm are likely to depend on the structure of the complex [32]. Because of the stoichiometries of the complex has a strong influence on the response function of trivalent ions that can be determined by optical measurements [33]. As the data of Fig. 2 show, by increasing the concentration of Al (III) ions, the absorbance of the complex was increased and the wavelength was shifted. For this reason, 537 nm was selected for measuring the response of the sensor when exposed to Al (III) ions.

3.3. Effect of pH

As the response of the membrane depends on the absorbance of the buffer solution, it was necessary to optimize the pH to obtain maximum ΔA [34]. The change in absorbance at 537 nm versus pH plot for the Al (III) sensor shown in Fig. 3, was obtained from investigations on the effect of pH over the range of 4.0-9.0 on exposure to the fixed concentration of the Al (III) ions at 1.3×10^{-5} mol L^{-1} for a fixed time. At lower pH values, the absorbance intensity of the sensor decreased, because of the competition between hydrogen and aluminium ions for the complex formation with reagent and ligand protonation, in high pH values, competition between hydroxyl and organic ligand ions was observed for a complex formation with aluminium ions [35]. In addition, at the pH of high values, the leaching of the reagent from the membrane to a solution is important. Therefore, in general, aluminium-ECR complexation is at a maximum in the acidic to the natural pH range [36]. As it can be seen in Fig. 3, the maximum absorbance intensity was observed at pH=6.0 of ammonia-acetic acid buffer solution. Thus, a solution of pH=6.0 was selected as an ideal experimental condition.

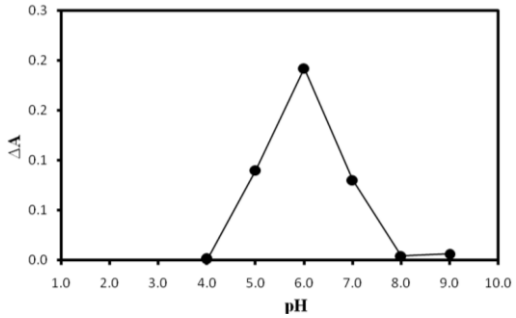

Fig. 3. Effect of pH on the optode response at 537 nm for 1.3×10^{-5} mol L^{-1} Al (III) ions.

3.4. Response time

An important analytical feature of the sensor is its response time. The response time refers to the time required to reach 95% of the equilibrium signal (t_{95}) [33]. To reach an equilibrium state of the absorbance signal, the analyte ion must diffuse through the entire thickness of the membrane, so it depends on the concentration of Al (III) ions [32]. For highly diluted solutions, the sensors show very long response times due to the respective saturation of the membrane with analyte [37- 38]. Because of the response time of the sensor film is governed by three processes: (1) diffusion in the film, (2) the rate of complex formation between the metal ion and ligand, and (3) the rate of complex dissociation [26]. In general, the response time is shorter when proceeding from dilute to the concentrated solution [13]. The response time curve obtained by recording the changes of absorbance from a pure buffer to buffered Al (III) solutions. It takes 16 min to reach the t_{95} value (Fig. 4) when the sensor was exposed to 2.60×10^{-5} mol L^{-1} Al (III) solution at 537 nm. The results were depending on the concentration of Al (III) solution.

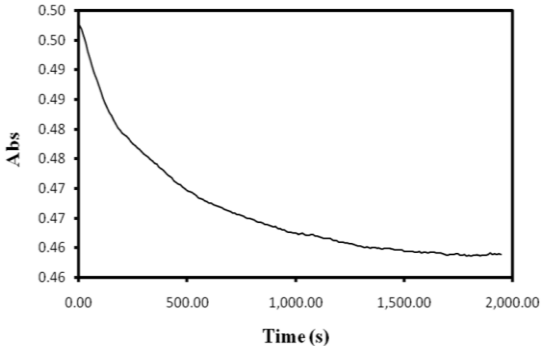

Fig. 4. The response time of the optode at 537 nm when the optode membrane was exposed to 2.60×10^{-5} mol L^{-1} Al (III) ions.

3.5. Regeneration of the sensor

One of the main characteristics of an optical sensor is its regeneration, which allows using the sensor many times leading to the consumption of a small amount of reagent [30]. After the sensor membrane exposed to Al (III) solution, the sensor membrane must be regenerated by using a suitable regenerating reagent. Some reagents, including HCl, HNO_3, H_3PO_4, and EDTA were studied as regenerating reagents in different concentration. Because of the degradation of the membrane and increasing the leaching of the indicator from the membrane, regenerating the membrane by the above acids have no good results. Oppositely, the good regeneration was done by EDTA. The best result was obtained when 0.1 mol L^{-1} EDTA solution was used, which gave short membrane regenerating times (less than 30 seconds) and had no side effect to sensor membrane. Fig. 5 shows the variation of absorbance of the sensor membrane at 537 nm for repetitively exposing it into 1.96×10^{-5} mol L^{-1} Al

(III) solution and a 0.1 mol L^{-1} EDTA solution.

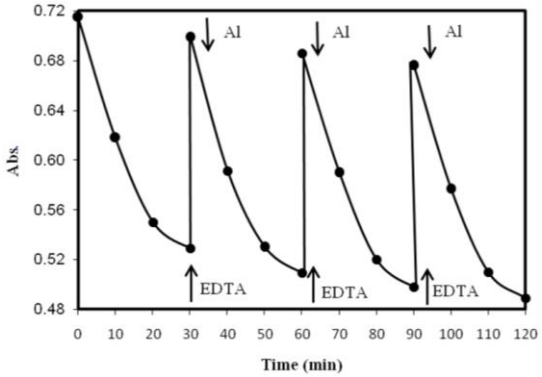

Fig. 5. Variation of absorbance of the optode membrane at 537 nm for repetitively exposing it into 1.96×10^{-5} mol L^{-1} Al (III) solution and a 0.1 mol L^{-1} EDTA solution.

3.6. Repeatability and Reproducibility

The reproducibility and repeatability of the sensor were evaluated by exposing it to 1.96×10^{-5} mol L^{-1} Al (III) solution and ammonia –acetic acid buffer solution (pH=6.0). The repeatability of the membrane response at 537 nm was evaluated by performing five determinations using a single membrane with the same standard solution of Al (III) (1.96×10^{-5} mol L^{-1}). The relative standard deviation (RSD) for these determinations was found to be 3%. The reproducibility of the response of different membranes was also studied. To calculate the reproducibility, five different membranes prepared from the same batch and the same procedure were done all membranes. The RSD for the measurement was 1.62 %.

3.7. Short–term stability and lifetime

To monitor the loss of reagent from the membrane into the buffer solution, the absorbance signal values of the membrane in contact with 1.96×10^{-5} mol L^{-1} Al (III) solution in ammonia – acetic acid buffer solution (pH=6.0) was recorded every 30 minutes over a period of 6 hours and no significant leaching of the indicator arose during this time. The sensor membrane is readily subject to the leaching of the active component of the membrane to the aqueous solution on which the lifetime of the membrane depends [39]. When the sensor was exposed to light or stored in wet condition, the absorbance change was not significant, as a result, it may be concluded, that the indicator was stable in the membrane and has no leaching in contact with water and over the duration of the experiment. Therefore, to keep the membrane from drying up, the membrane could be kept under the water when it is not used. Also, the membrane showed good stability after it was stored in water for more than two weeks.

3.8. Response to Al (III) ions

The dynamic response to Al (III) ions was monitored as a change in absorbance at 537 nm (absorption maximum of ECR) as the membrane was exposed to a buffer solution containing Al (III) ions. Absorption spectra obtained for different concentrations of Al (III) ions are shown in Fig. 6. The calibration graph based on the absorbance of the sensor versus Al (III) ion concentration was linear in the range of 3.22×10^{-8} to 4.10×10^{-5} mol L^{-1} with the detection limit equal to 1.20×10^{-8} mol L^{-1}.

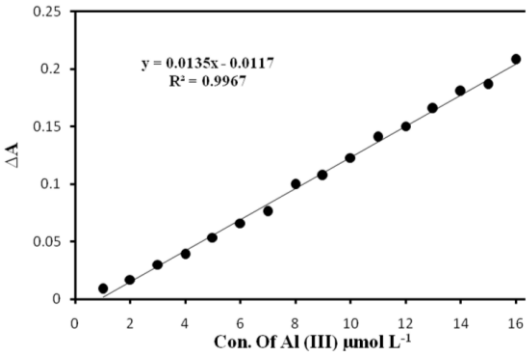

Fig. 6. The optode film response versus Al (III) ion concentrations at pH 6.0.

3.9. Selectivity

Perhaps the most important characteristic of an ion-selective membrane is its selectivity [40]. The tolerance limit is defined as the maximum concentration of a foreign ion, causing, an error of less than ± 5% in the determination of Al (III) ions [30]. The interference for some common species for the absorbance determination of Al (III) was investigated to examine the response of the sensor to other cations and anions. For obtaining the selectivity of the proposed method, the solutions contain a fixed concentration of Al (III) (1.96×10^{-5} mol L^{-1}) and different concentration of interfering species were prepared, and according to the developed method, the absorbance of the membrane was measured. The results, presented in Table 1 and Fig. 7, shows that the proposed sensor has a better selectivity than other ions. However, the interference of Cu^{2+}, Fe^{3+} can be eliminated by using glycine and ascorbic acid respectively.

3.10. Analytical Application

The proposed method was used to evaluate analyzing aluminium in the potable water and aluminium–magnesium syrup samples. The treated samples were spiked with a different amount of aluminium ions and the concentration

was compared with atomic absorption spectroscopy (AAS). As is shown in Table 2, the results of the three real samples were prepared as described in experimental section correlated very well with the value for the same samples determined by AAS.

Table 1. Effect of foreign ions on the determination of Al (III) ions.

Species	Tolerance Limit (Mol Ratio)
Na^+, K^+, La^{3+}, NO_3^-, NH_4^+, CH_3COO^-	1000
Co^{2+}, Ag^+, Cd^{2+}, Ni^{2+}, Zn^{2+}, Tartrate	500
Hg^{2+}, I^-, Br^-, Cl^-	200
Cr^{3+}, Cu^{2+}, Be^{2+}, Phosphate , Citrate, Oxalate	100
Fe^{3+}	20
EDTA	10

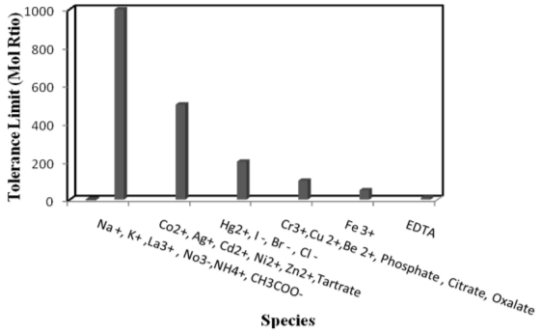

Fig. 7. Effect of foreign ions on the determination of Al (III) ions.

Table 2. Determination of Al (III) in real sample (n=3).

Aluminium concentration ± SD (× 10^5 M)			
Sample	Added	Proposed sensor	(%) Recovery
Al-Mg Syrup	-----	1.23 ± 0.27	-----
Potable water	-----	< D.L[c]	-----
	1.14	1.19 ± 0.20	104.5
	2.25	2.28± 0.14	101.3

[a] Average of three determinations ± S.D.
[b]Aluminium – Magnesium syrup, Soha-jel, cosmetic company, Tehran, Iran.
[c]D.L.: detection limit.

4. CONCLUSION

The selective determination of Al (III) was performed by use of ECR, immobilized on a triacetylcellulose membrane as a lipophilic ion pair with MTOACl. The purposed sensor has been shown to have good operating characteristics such as sensitivity, stability, detection limit and a wide linear working range. The membrane responds to Al (III) by changing color irreversibly from pink to blue, and it is sensitive to Al (III) ions in the 3.22×10^{-8} to 4.10×10^{-5} mol $L^{-1}$with limit of detection 1.2×10^{-8}mol L^{-1}. The determination of Al (III) was performed in a buffer solution at pH=6.0. The optical sensor was successfully applied for the determination of Al(III) ions in potable water and aluminium–magnesium syrup. Therefore, the proposed sensor shows higher performance compared to the several fibers based optic sensors (Table 3).

Table 3. Comparison of the proposed Al (III) sensor with the reported sensor.

Ionophore name	Membrane and used instrument	Linear Range (M)	Detection limit (M)	pH	Ref.
Morin	PVC Absorption spectrophotometry	3.0×10^{-4}- 3.0×10^{-7}	2.0×10^{-7}	4.8	41
Morin	Sol-gel Fluorescence	1.0×10^{-4}-1.0×10^{-6}	-----	3.75	----
Morin	Cellulose powder Fluorescence	1.0×10^{-4}-1×10^{-6}	1.0×10^{-6}	4.8	42
Purpurin	XAD-4 fluorescence	3.2×10^{-3}- 5.0×10^{-5}	3.0×10^{-5}	6.0	43
Quinolin-8-ol-5- sulfonate	Microcrystal cellulose Fluorescence	-----	3.0×10^{-7}	----	44
Chrome Azurol S	XAD-2 Reflectance Spectrophotometry	2.0×10^{-4} -1.3×10^{-5}	1.0×10^{-5}	6.0	35
Lumogallion	Microstructure optical fiber fluorescence	1.0×10^{-4}-1.0×10^{-6}	1.0×10^{-6}	5.0	45
Eriochorome Cyanine R	Triacetylcellulose membrane Absorption spectrophotometry	3.22×10^{-8} - 4.10×10^{-5}	1.2×10^{-8}	6.0	This work

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REFERENCES

[1] I.M. Steinberg, A. Lobnik and O.S. Wolfbeis, Characterisation of an optical sensor

membrane based on the metal ion indicator Pyrocatechol Violet, *Sens. Actuators B* 90 (2003) 230–235.

[2] P.F. Good, C.W. Olanow and D.P. Perl, Neuromelanin-containing neurons of the substantia nigra accumulate iron and aluminum in Parkinson's disease: a LAMMA study, *Brain Res*. 593 (1992) 343-346.

[3] M. Kawahara, K. Muramoto, K. Kobayashi, H. Mori and Y. Kuroda, Aluminum promotes the aggregation of Alzheimer's amyloid beta-protein in vitro, *Biochem. Biophys. Res. Commun*. 198 (1994) 531-535.

[4] J.L. Lin, M.T. Kou and M.L. Leu, Effect of long-term low-dose aluminum-containing agents on hemoglobin synthesis in patients with chronic renal insufficiency, *Nephron* 74 (1996) 33-38.

[5] S.R. Paik, J.H. Lee, D.H. Kim, C.S. Chang and J. Kim, Aluminum-induced structural alterations of the precursor of the non-A beta component of Alzheimer's disease amyloid, *Arch. Biochem. Biophys*. 344 (1997) 325-327.

[6] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, *Brain Res. Bull*. 55 (2001) 187-196.

[7] L. Sombra, M. Luconi, M.F. Silva, R.A. Olsina and L. Fernandez, Spectrophotometric determination of trace aluminium content in parenteral solutions by combined cloud point preconcentration-flow injection analysis, *Analyst* 126 (2001) 1172–1176.

[8] S. Polizzi, E. Pira, M. Ferrara, M. Bugiani, A. Papaleo, R. Albera and S. Palmi, Neurotoxic effects of aluminium among foundry workers and Alzheimer's disease, *Neurotoxicology* 23 (2002) 761-774.

[9] K. Popinska, J. Kierkuo, M. Lyszkowska, J. Socha, E. Pietraszek, W. Kmiotek and J. Ksiazyk, Aluminum contamination of parenteral nutrition additives, amino acid solutions, and lipid emulsions, *Nutrition* 15 (1999) 683-686.

[10] H. Lian, Y. Kang, S. Bi, Y. Arkin, D. Shao, D. Li, Y. Chen, L. Dai, N. Gan and L. Tian, Direct determination of trace aluminum with quercetin by reversed-phase high performance liquid chromatography, *Talanta* 62 (2004) 43-50.

[11] G. Albendin, M.P. Manuel-Vez, C. Moreno and M.R. Garcia-Vargas, Reverse flow-injection manifold for spectrofluorimetric determination of aluminum in drinking water, *Talanta* 60 (2003) 425-431.

[12] A.L. Balbo, V.C.D. Orto, S. Sobral and I. Rezzano, Linear Scan Stripping Voltammetry at Glassy-Carbon Based Thin Mercury Film Electrodes for Determination of Trace Aluminium in Dialysis Fluids, *Anal. Lett.* 31 (1998) 2717-2728.

[13] A. Safavi and M. Sadeghi, Design and evaluation of a thorium (IV) selective optode, *Anal. Chim. Acta* 567 (2006) 184–188.

[14] M. Shamsipur, S. Ershad, A. Yari, H. Sharghi and A.R. Salimi, Hydroxy-thioxanthones as suitable neutral ionophores for the preparation of PVC-membrane potentiometric sensors for Al(III) ion, *Anal. Sci.* 20 (2004) 301-306.

[15] A. Shokrollahi, M. Ghaedi, M.S. Niband and H.R. Rajabi, Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium ion, *J. Hazard. Mater* 151 (2008) 642–648.

[16] Z. Ying-Quan, Z. Lin and L. Jun-Yi, Spectrophotometric determination of aluminium with chlorophosphonazo I, *Talanta* 30 (1983) 291–293.

[17] M. Chamsaz, M.H. Arbab Zavar and M.S. Hosseini, Flotation Spectrophotometric Determination of Aluminium with Alizarin, *Anal. Lett.* 33 (2000) 1625-1633.

[18] U.T. Hill, Direct Photometric Determination of Aluminum in Iron Ores-Corrections, *Anal. Chem.* 28 (1956) 191-191.

[19] U.T. Hill, Direct Photometric Determination of Aluminum in Iron Ores, *Anal. Chem.* 28 (1956) 1419-1424.

[20] U.T. Hill, Direct Spectrophotometric Determination of Aluminum in Steel, Spelter and Iron Ores, *Anal. Chem.* 38 (1966) 654-656.

[21] W.R. Seitz, *Optical Ion Sensing Fiber Optic Chemical Sensors Biosensors II*, in: O.S. Wolfbeis (Ed.), CRC Press, Bocaraton, FL, (1991) pp. 1–19.

[22] I. Oehme and O.S. Wolfbeis, Optical sensors for determination of heavy metal ions, *Microchim. Acta* 126 (1997) 177–192.

[23] M.R. Ganjali, M. Hosseini, M. Hariri, F. Faridbod and P. Norouzi, Novel erbium (III) -selective fluorimetric bulk optode, *Sens. Actuators B* 142 (2009) 90–96.

[24] G. Absalan, M. Asadi, S. Kamran, S. Torabi and L. Sheikhian, Design of a cyanide ion optode based on immobilization of a new Co(III) Schiff base complex on triacetylcellulose membrane using room temperature ionic liquids as modifiers, *Sens. Actuators B* 147 (2010) 31–36.

[25] M. Ahmad and R. Narayanaswamy, A flow-cell optosensor for monitoring aluminium (III) based on immobilised eriochrome cyanine R (ECR) and reflectance

spectrophotometry, *Sci. Total Environ.* 163 (1995) 221-227.
[26] S. Abbasi, A. Farmany, M.B. Gholivand, A. Naghipour, F. Abbasi and H. Khani, Kinetic-spectrophotometry method for determination of ultra trace amounts of aluminum in food samples, *Food Chem.* 116 (2009) 1019-1023.
[27] M.M. Bordbar, H. Khajehsharifi and A. Solhjoo, PC-ANN assisted to the determination of Vanadium (IV) ion using an optical sensor based on immobilization of Eriochorome Cyanine R on a triacetylcellulose, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.* 151 (2015) 225-231.
[28] M. Ahmad and R. Narayanaswamy, Fibre optic reflectance sensor for the determination of aluminium (III) in aqueous environment, *Anal. Chim. Acta* 291 (1994) 255-260.
[29] N. Pourreza and M. Behpour, Column Preconcentration of Aluminum Using Eriochrome Cyanine R and Methyltrioctylammonium Chloride Adsorbent Supported on Naphthalene with Subsequent Spectrophotometric Determination, *Microchem. J*. 63 (1999) 250–256.
[30] S. Rastegarzadeh, N. Pourreza and I. Saeedi, An optical chemical sensor for thorium (IV) determination based on thorin, *J. Hazared. Mater.* 173 (2010) 110–114.
[31] B. Kuswandi and R. Narayanaswamy, Characterisation of a Hg(II) ion optrode based on Nafion®-1-(2-thiazolylazo)-2-naphthol composite thin films, *J. Environ. Monit.* 1 (1999) 109-114.
[32] S. Sadeghi and S. Doosti, Uranyl ion-selective optical test strip, *Dyes Pigments* 80 (2009) 125-129.
[33] M.M.F. Choi, X. Jun Wu and Y. Rong Li, Optode Membrane for Determination of Nicotine via Generation of Its Bromoethane Derivative, *Anal. Chem*. 71 (1999) 1342-1349.
[34] M.K. Amini, T. Momeni-Isfahani, J.H. Khorasani and M. Pourhossein, Development of an optical chemical sensor based on 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol in Nafion for determination of nickel ion, *Talanta* 63 (2004) 713–720.
[35] M. Ahmad and R. Narayanaswamy, Development of an optical fiber Al (III) sensor based on immobilised chrome azurol S, *Talanta* 42 (1995) 1337-1344.
[36] C.T. Driscoll, W.D. Schechler, H. Sigel and A. Sigel, *Metal Ions in Biological Systems*, 24, Marcel Dekker, New York (1978).
[37] M. Lerchi, E. Bakker, B. Rusterholz and W. Simon, Lead-selective bulk optodes based on neutral ionophores with subnanomolar detection limits, *Anal. Chem.* 65 (1992) 1534–1540.
[38] M. Lerchi, E. Reitter and W. Simon, Uranyl ion-selective optode based on neutral ionophores, *Fresenius' J. Anal. Chem.* 348 (1994) 272-276.
[39] O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf and W. Simon, Lifetime of neutral-carrier-based liquid membranes in aqueous samples and blood and the lipophilicity of membrane components, *Anal. Chem.* 63 (1991) 596-603.
[40] F. Abbasitabar, V. Shahabadi, M. Shamsipur and M. Akhond, Development of an optical sensor for determination of zinc by application of PC-ANN, *Sens. Actuators B* 156 (2011) 181-186.
[41] M. Wang-bai and Z. Zhu-jun, The Investigation of a Fiber Optical Aluminum Sensor Using Poly (Vinyl Alcohol) Gel as a Substrate, *Chem. J Chinese U*. 12 (1991) 1304-1307.
[42] L.A. Saari and W.R. Seltz, Immobilized morin as fluorescence sensor for determination of aluminum (III), *Anal. Chem.* 55 (1983) 667-670.
[43] M. Ahmad and R. Narayanaswamy, Optical fibre Al (III) sensor based on solid surface fluorescence measurement, *Sens. Actuators B* 81 (2002) 259-266.
[44] K. Carroll, F.V. Bright and G.M, Hieftje, M. Fiber-optic time-resolved fluorescence sensor for the simultaneous determination of aluminum(III) and gallium(III) or indium(III), *Anal. Chem*. 61 (1989) 1768-1772.
[45] S.C. Warren-Smith, S. Heng, H. Ebendorff-Heidepriem, A.D. Abell and T.M. Monro, Fluorescence-Based Aluminum Ion Sensing Using a Surface-Functionalized Microstructured Optical Fiber, *Langmuir* 27 (2011) 5680–5685.