



## Development of An Optical Sensor Based on Sol-gel Doped with 2,6-Dichlorophenol Indophenol for Analysis of Ascorbic Acid

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### ABSTRACT

In this work, an optical sensor for detection of ascorbic acid is described. The sensor is fabricated by casting and spin-coating silica sol-gel doped with 2,6-dichlorophenol indophenol on the glass plates. The sols are in turn obtained by acidic hydrolysis of various precursors such as tetraethoxysilane, triethoxymethylsilane and triethoxyoctylsilane in the presence of 2,6-dichlorophenol indophenol as dopant. Prepared sols then were coated on glass plates to form sol-gel films. UV-Vis spectrophotometric properties of 2,6-dichlorophenol indophenol doped in sol-gel films were studied and compared with in solution. At the optimum conditions the response of film to ascorbic acid is fast and linear in 0.07 – 3.34 mmol L<sup>-1</sup> range. Detection limit and relative standard deviation of presented sensor for determination ascorbic acid were 0.05 mmol L<sup>-1</sup> and 1.32 %, respectively.

**KEYWORDS:** Ascorbic acid; 2,6-Dichlorophenol indophenol; Optical sensor; Sol-gel films.

### 1. INTRODUCTION

The sol-gel process has been widely shown to be a very flexible route for the fabrication of a large variety of photonic materials in various configurations, such as monoliths, coatings, fibers and films for optical device applications. Coatings applied by sol-gel chemistry are used in many lighting applications. The formation of oxide particles in a liquid phase, and the polymerization of the particles make the structure of sol-gel materials inherently porous. Silicon alkoxides generally react slowly with water, but the reaction process, hydrolysis and condensation, can be sped up by the use of acid and base catalysts. In the fabrication of sol-gel films, acid catalysts (most commonly HCl) are generally used with low amounts of water [1-4]. Systems that rely on optical detection for sensing can overcome many of the disadvantages of the electrochemical systems and exhibit shorter response times and lower operating temperatures [5-7]. The silica sol-gel method offers the advantage of tailor-made porosities with low leachability (for solution measurements) of the indicator dye molecule. It also offers an easier fabrication method which allows pre-mixing of the reagent and dye directly into the sol to produce a coating that is sensitive to the analyte in the parts per million region range [8-9]. One of the unique features of the sol-gel process is that the properties of the final network structure, such as hydrophobicity, thickness, porosity, flexibility, reactivity and stability, can be easily tailored by controlling the process conditions, the type and size of precursors and catalysts

[10-11]. In addition, glass materials of various shapes can be easily prepared [12]. Sol-gel thin films have proved to be excellent hosts for organic dyes. Moreover, these new hybrid materials exhibit a high transparency due to the nanometer scale of the organic aggregates [13]. Finally, the amorphous matrix allows the convenient shaping of monolithic pieces and thin films [14-15]. Recently, sol-gel derived inorganic glasses have been described as promising materials in many photonic applications [16]. In comparison with organic polymers, sol-gel glasses have superior transmission behavior in the UV and in the near IR, and higher values of refractive indices [17]. Dye-doped sol-gel materials thus appear to hold promise for application in optical sensors [8-9, 18-20].

This paper describes the incorporation of 2,6-dichlorophenol indophenol (DCPI) in sol-gel thin films in order to obtain an optical sensor for analysis of ascorbic acid (AA) and applied to the determination of AA in pharmaceuticals and real samples.

### 2. EXPERIMENTAL

#### 2.1. Reagents

Analytical grade chemicals were used without further purification, unless stated otherwise. Double-distilled water was used to prepare all solutions throughout this work. Tetraethoxysilane (TES), TEOS (triethoxyoctylsilane), triethoxymethylsilane (TEMS), DCPI, AA, HCl and ethanol were purchased from Merck (Darmstadt, Germany). Solutions were prepared by dissolving 0.2 ml DCPI in a mixture of 0.4 mL of HCl and 2 mL

of precursors and then diluting to 0.4 mL with double-distilled water. Phosphate buffer solutions with pH ranging from 4 to 7 were prepared with analytical grade reagents to final concentration of 0.1 mol L<sup>-1</sup>, from Merck.

## 2.2. Instruments

Absorbance measurements for sensors characterization were performed in a Cintra-6 UV-Vis spectrophotometer. All films were obtained by spin-coating in a home-made spin-coater (1000 rpm, 1 min, 1 ml). The pHs of different solutions were adjusted using a digital pH meter (Model 691, Metrohm). Sol solutions were magnetically stirred by the stirrer model Jenway 1000. Centrifuge model CE 160, Chimifan (500-3000 rpm) was used as a rotating engine for spin-coater. For picking up concentrated solutions, samplers model Hamilton (10, 100, 1000 µl) were used. Analytical scale model AE 160, Mettler (±0.1 mg) was used for weighing solids. An oven model WTC-binder was used for preparing glass slides.

## 2.3. Preparation of sol-gel films doped with DCPI (sensor layers)

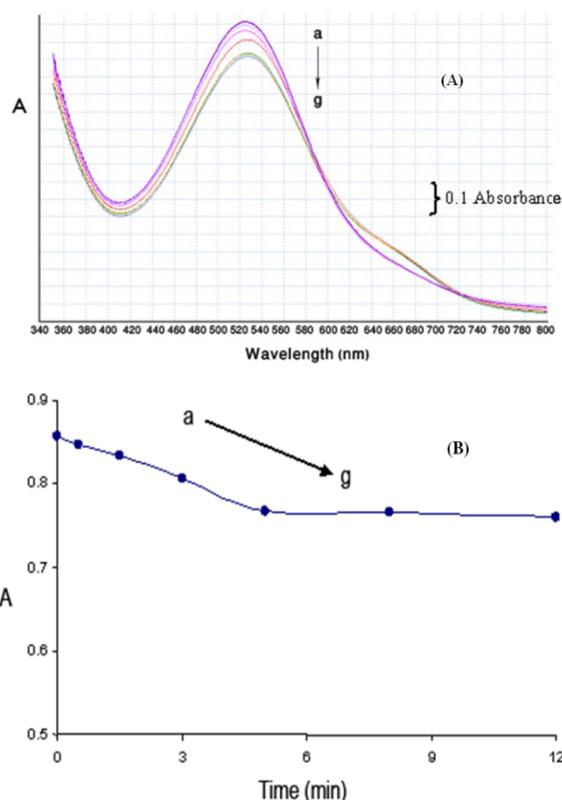
Glass slides (3×1 cm) were used as solid supports onto which the sol-gel was deposited. The silanol groups on the surface of the glass were activated via standard method which involves treatment with a concentrated nitric acid for 5 min and copious amounts of distilled water and ethanol, followed by drying at 100°C for 1 h. Seven different layers were prepared and the composition of their cocktails is summarized in Table 1. Properties and characteristics of sol-gel network depend on various parameters that should be controlled when synthesis of sols. The most important parameters are: acid or base catalyst, precursors and (R) ratio. Due to the application of these films, sol-gel films doped with DCPI should have some characteristics. First, it should stick to the glass slide support so firmly that the result sensor has good enough stability. Secondly, it should not be breakable or cracked. Thirdly, after preparation it should be able to entrap and stabilize DCPI in the network so firmly that the leakage of organic dye out of film be impossible. Finally, the most important object is the response of this film to ascorbic acid. In this work, at first a large number of sol-gel films were prepared and analyzed. Some of these films were very breakable and were easily cracked after drying because of high wall network forces. Some other films, despite of formation of a proper film, did not have good enough response to ascorbic acid. In Table 1 some of these guide directions for preparing sol-gel films are reported. As mentioned in the Table 1, film (7) is the most qualified film that has a good response to ascorbic acid, too. Some of the experiments that have been done on this film are reported in progress. This film was applied for determination of AA in real samples. For all the films reported in Table 1 after preparation of sol-gel, in order to prepare a film, 1 mL of sol-gel solution was measured by sampler and

was cast on glass slide. Then the slide that was fixed on the spin-coater was rotated with the fixed rotation speed of 1000 rpm for 1 min. After formation of a thin homogenous film on the glass slide, it was kept in room temperature for 3 days to dry completely. Then other experiments were done on outcome films.

## 3. RESULTS AND DISCUSSION

### 3.1. Leaching of DCPI from sol-gel network

This sol-gel optical sensor was developed for determination of ascorbic acid. The most important parameter was to choose the appropriate redox indicator that will be sensitive to ascorbic acid. Sol-gel was chosen because of (a) its optical transparency, mechanical stability, chemical inertness and flexibility in terms of shaping sensor configuration and (b) immobilization of the indicator dye by doping is simple and general and leads to much less leaching of the indicator dye than impregnation technique. Leaching of organic dyes from sol-gel matrices is one important handicap which arises when sensors are the final application. In order to examine this parameter, film (7) was immersed into 50 ml phosphate buffer solutions (pH=4) within different intervals. After rinsing in distilled water, the absorbance of the film was recorded by spectrophotometer (Fig. 1). The initial decrease in absorbance shows the leaching of DCPI from sol-gel film and then after 5 min it reaches a fixed absorbance. This experiment shows that this film has



**Fig. 1.** (A) Absorbance spectra of DCPI in film at pH=4. spectra (a) to (g) are for film (7) after dipping in phosphate buffer pH 4 for 0, 0.5, 1.5, 3, 5, 8 and 12 min, respectively. (B) absorbance (in 530 nm) versus dipping time.

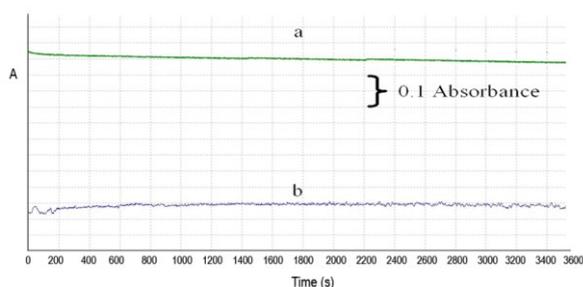
**Table 1.** Composition of sols for preparation of sensor thin films

Film	Precursor (mL)	Acid (mL)	H <sub>2</sub> O (mL)	DCPI (mL)	Time of adding DCPI (h)	Gelation time before coating (h)	Comment
1	TEOS (2)	0.4	0.4	0.2	0	48	Sol-gel layer didn't dry and remained in gel phase.
2	TEMS (2)	0.4	0.4	0.2	0	48	Crumpled layers
3	TES (2)	0.4	0.4	0.2	0	48	Intense cracked sol-gel films
4	TES (1.5) TEOS (0.5)	0.4	0.4	0.2	0	48	Homogenous layers but with no good response to AA
5	TES (1.5) TEMS (0.5)	0.4	0.4	0.2	0	48	Very fragile layers easily broken
6	TES (1.5) TEMS (0.5)	0.4	0.4	0.2	6	48	Leaching of DCPI after immersing the film into the AA solution
7	TES (1.5) TEOS (0.5)	0.4	0.4	0.2	6	48	Homogenous layers with good response to AA

enough stability in leaching DCPI from film. The initial decrease in absorbance may be the result of those DCPIs that were adsorbed on the surface of the film and were not entrapped in the sol-gel network. In the continuation of this work, after preparation of films and before using them as sensors, in order to have a fixed and stable amount of absorbance, the film was immersed into phosphate buffer solution for 5 min and then was used for measurements. Dye doped films were stable all over the pH range at room temperature, showing no leaching of DCPI molecules.

### 3.2. Photostability of sol-gel film

The photostability of DCPI in sensor layer was tested in the spectrophotometer under 520 nm for 1 h. No noticeable decrease was observed in the signal of the layer within 1 h (Fig. 2). As can be seen in Fig. 2, in comparison with DCPI solution, DCPI doped in sol-gel network shows more stability and better photometric behavior.

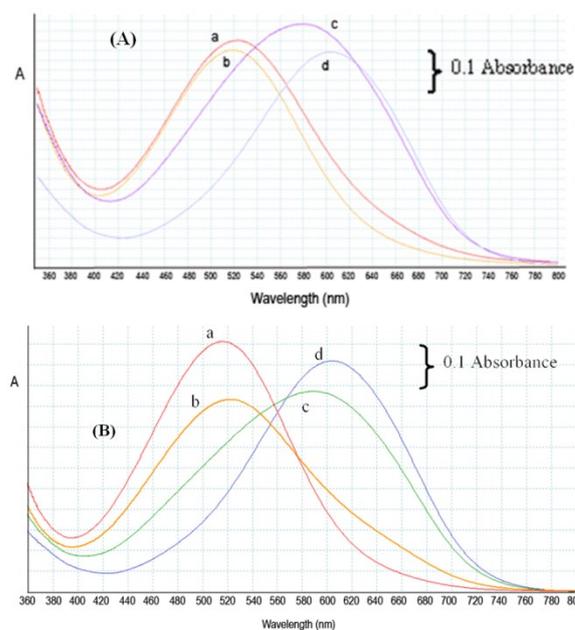


**Fig. 2.** Photostability of (a) sol-gel film 7 and (b) DCPI solution at phosphate buffer pH 4.

### 3.3. Effect of pH on DCPI spectrum in solution and sol-gel film

As well as DCPI acts as a redox indicator; it is also a base and acid indicator. It means that the spectrophotometric behavior of this compound strongly depends on pH. DCPI has acidic properties and has acid and base forms in red and blue colors with maximum wavelength of 520 and 610 nm, respectively. Fig. 3A shows spectrophotometric behavior of DCPI in solution versus pH. As shown, with an increase in pH, absorbance in 520 nm disappears and rises in 610 nm. This is because of a decrease in acidic form and an

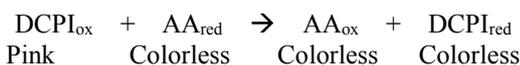
increase in basic form of this compound during increasing of pH. Fig. 3B shows that DCPI doped in sol-gel network has similar behavior to DCPI in solution when pH changes. This means that DCPI in sol-gel network while entrapping on glass substrate, keeps its absorbing and oxidation-reduction properties, too.



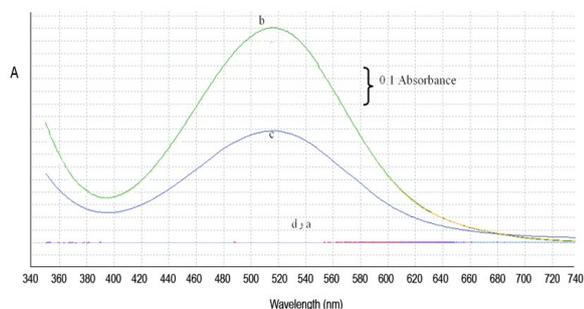
**Fig. 3.** (A) Absorbance spectra of DCPI (300 μmol L<sup>-1</sup>) in phosphate buffer at pHs: (a) 4.0; (b) 4.9; (c) 6.1 and (d) 7.2. (B) Absorbance spectra of film 7 in the same pH conditions.

### 3.4. Spectrophotometric behavior of DCPI in solution with effect of ascorbic acid

As shown in Fig. 4, a solution which only consists of phosphate buffer has no absorbance within the range of 400-800 nm (curve a). In presence of DCPI in the solution a spectrum with maximum wavelength of 520 nm can be observed that is related to this compound, as DCPI is pink in acidic pHs, it will have absorbance in 520 nm (curve b). On the other hand, when ascorbic acid is added to the solution, absorbance of DCPI will decrease. In presence of ascorbic acid the oxidation-reduction reaction occurs and as DCPI reduces the absorbance decreases, too (curve c):



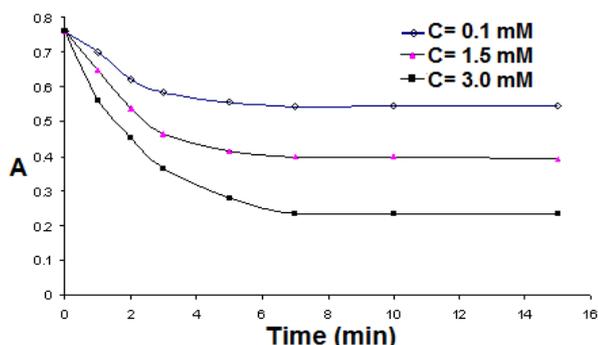
As AA does not have a noticeable absorbance in this range by itself (curve d), it can be shown that as a result of interaction between ascorbic acid and DCPI, absorbance of this dye indicator decreases, and this decrease can be used as a base for measurements of ascorbic acid in solution.



**Fig. 4.** Absorbance spectra of phosphate buffer at pH=4: (a) with no other substance; (b) with  $300 \mu\text{mol L}^{-1}$  DCPI; (c) with  $300 \mu\text{mol L}^{-1}$  DCPI and  $3.0 \mu\text{mol L}^{-1}$  AA and (d) with  $3.0 \mu\text{mol L}^{-1}$  AA.

We can expect that in appropriate conditions, DCPI doped in sol-gel network will also show these characteristics. Although this reaction between ascorbic acid and DCPI is fast in solution, but on the substrate and in sol-gel network this reaction should be tested for purpose of time.

Response time of DCPI doped in sol-gel film to ascorbic acid depends on various parameters that relate to type of sol-gel network. For testing this case, absorbance was measured versus time unit under maximum wavelength of 520 nm, while sol-gel film doped with DCPI was immersed into phosphate buffer solution containing ascorbic acid. The solution was magnetically stirred during this experiment. Fig. 5 shows the response of doped DCPI to ascorbic acid versus time for different concentrations of ascorbic acid. As shown in all concentrations by passing of time, absorbance of DCPI decreases. At first this change is intense but gradually slows down and finally after 7 min becomes fixed and stable. For next further experiments, film was exposed to ascorbic acid solution for 7 min and then the absorbance was measured.

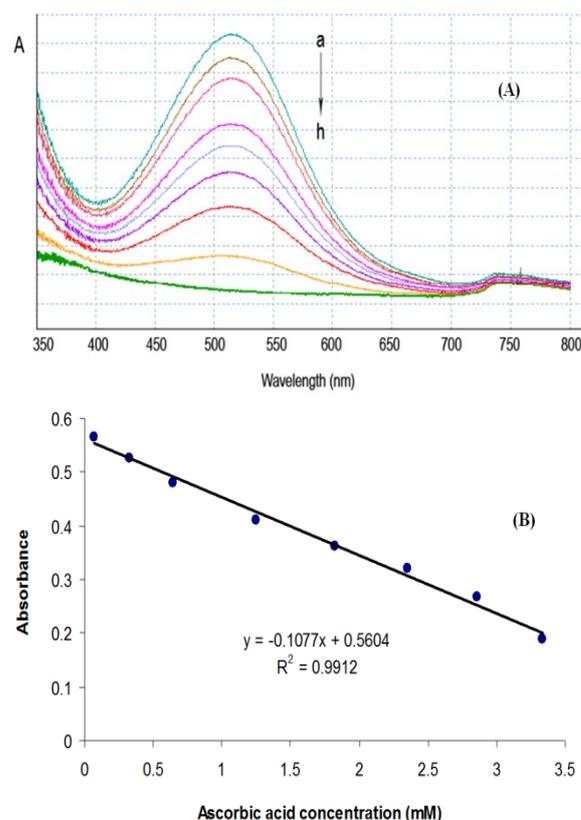


**Fig. 5.** Absorbance (at wavelength of 520 nm) versus time in different concentrations of AA for film 7 at pH=4.

### 3.5. Calibration curve, reproducibility and detection limit

For testing the effect of DCPI doped in sol-gel film on AA, solutions consist of  $0.07$  to  $3.34 \text{ mmol L}^{-1}$  of AA in phosphate buffer (pH=4) were prepared. Then sol-gel films were plunged in these stirring solutions for 7 min. Then, films were rinsed with dioxigen phosphate buffer solution and absorbance of these films was recorded within the range of 350-800 nm by spectrophotometer. Fig. 6A shows the spectra of this experiment in solutions with different concentrations of AA. As shown, with increasing the concentration of AA, absorbance decreases in 520 nm. Fig. 6B shows calibration curve in which absorbance versus concentration of AA is drawn. As can be seen, within this range of AA, there appeared to be a linear relationship between concentration and absorbance.

For testing reproducibility of the sensor, at first, 5 films with the same conditions with film 7 were prepared and after passing developing stages, ascorbic acid ( $1.25 \text{ mmol L}^{-1}$ ) was measured once with each film according to general guide directions. The reproducibility of the manufacturing procedure of the sensor layer was determined by calculating relative standard deviation of absorbance of five sensor layers prepared by the same procedure. The RSD% for these results was 1.32% that shows good reproducibility and precision of the method.



**Fig. 6.** (A) Absorbance spectra of film 7 in different solutions of AA in phosphate buffer at pH=4. Concentrations of AA: (a) 0.07; (b) 0.33; (c) 0.64; (d) 1.25; (e) 1.82; (f) 2.35; (g) 2.86 and (h)  $3.34 \text{ mmol L}^{-1}$ . (B) Calibration curve of absorbance versus AA concentration.

In order to calculate detection limit of the method, film 7 was immersed into the phosphate buffer solution (pH=4) without presence of ascorbic acid (blank solution) for 7 min and then absorbance was measured in 520 nm. Detection limit based on three times of standard deviation of the blank divided by the slope of analytical curve ( $3S_b/m$ ) was  $0.05 \text{ mmol L}^{-1}$ .

### 3.6. Selectivity of method

For evaluating the selectivity of presented sensor, at first absorbance of the film immersed into ascorbic acid solution was measured in 520 nm ( $A_{AA}$ ). Then absorbance of the film immersed into ascorbic acid and interfering compound solution was measured in the same conditions ( $A_{AA+I}$ ). By calculating recovery percents, selectivity of the method was tested. The results in Table 2 show that with some exceptions; none of the tested foreign substances exert any serious interference.

**Table 2.** Effect of foreign substances (interferences  $2 \text{ mmol L}^{-1}$  and AA  $1.25 \text{ mmol L}^{-1}$ )

Interference	Recovery (%)
Epinephrine	92.6
Dopamine	93.9
Glucose	105.8
Cysteine	102.0
Norepinephrine	95.3
Urea	99.1
Uric acid	99.0
Sacharose	100.3

### 3.7. Real sample analysis

To assess the usefulness of sol-gel optical sensor, two pharmaceutical products (effervescent tablet and chewing vitamin C tablet) were selected and the amount of ascorbic acid was measured in each of them. The results given in Table 3, are in good agreement with the obtained results from standard method [21]. The t-test was applied to both sets of results and showed that there was no significant difference at the 95% confidence level.

**Table 3.** Determination of AA in real pharmaceutical samples

sample	AA found (%) <sup>a</sup>	
	Standard method	Proposed method
Effervescent tablet	25.0±0.8	24.1±1.1
Chewing vitamin C tablet	66.0±1.9	65.3±1.8

<sup>a</sup> Average of three determinations±standard deviation

## 4. CONCLUSION

The present study demonstrates a simple encapsulation procedure for the development of an optical sensor by using sol-gel technology to dope DCPI in silica. Prepared silica sol doped with DCPI can be immobilized on the glass plates and produced optical sensor exhibit

good sensitivity towards AA with a linear response in the concentration range of  $0.07\text{-}3.34 \text{ mmol L}^{-1}$ . The response of the sensor to AA was selective and reproducible (RSD = 1.32%). This sensor can be applied to determination of AA pharmaceutical samples.

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## REFERENCES

- [1] P.C. Ricci, C.M. Carbonaro, A. Casu, C. Cannas, R. Corpino, L. Stagi and A. Anedda, Optical and structural characterization of cerium doped LYSO sol-gel polycrystal films: potential application as scintillator panel for X-ray imaging, *J. Mater. Chem.* 21 (2011) 7771-7776.
- [2] T.H. Tran-Thi, R. Dagnelie, S. Crunaire and L. Nicole, Optical chemical sensors based on hybrid organic-inorganic sol-gel nanoreactors, *Chem. Soc. Rev.* 40 (2011) 621-639.
- [3] B. Lebeau and P. Innocenzi, Hybrid materials for optics and photonics, *Chem. Soc. Rev.* 40 (2011) 886-906.
- [4] R.E. Luckham and J.D. Brennan, Bioactive paper dipstick sensors for acetylcholinesterase inhibitors based on sol-gel/enzyme/gold nanoparticle composites, *Analyst* 135 (2010) 2028-2035.
- [5] M.S. Attia and M.M. Aboaly, Highly sensitive and selective spectrofluorimetric determination of metoclopramide hydrochloride in pharmaceutical tablets and serum samples using  $\text{Eu}^{3+}$  ion doped in sol-gel matrix, *Talanta* 82 (2010) 78-84.
- [6] V.S. Tripathi, G. Lakshminarayana and M. Nogami, Optical oxygen sensors based on platinum porphyrin dyes encapsulated in ORMOSILS, *Sens. Actuators B Chem.* 147 (2010) 741-747.
- [7] K. Zhang, H.T. Yan and T. Zhou, Spectrofluorimetric determination of phenylalanine based on fluorescence enhancement of europium ion immobilized with sol-gel method, *Spectrochim. Acta A* 83 (2011) 155-160.
- [8] C.S. Chu and Y.L. Lo, Highly sensitive and linear optical fiber carbon dioxide sensor based on sol-gel matrix doped with silica particles and HPTS, *Sens. Actuators B Chem.* 143 (2009) 205-210.
- [9] C. Chu and Y.L. Lo, Highly sensitive and linear calibration optical fiber oxygen sensor based on Pt(II) complex embedded in sol-gel matrix, *Sens. Actuators B Chem.* 155 (2011) 53-57.
- [10] H. Karsten, Molecularly imprinted polymers in analytical chemistry, *Analyst* 126 (2001) 747-756.

- [11] M. Diaz, E. Garcia and R.B. Liano, Molecular Imprinting in Sol-Gel Materials: Recent Developments and Applications, *Microchim. Acta* 149 (2005) 19-36.
- [12] A. Walcarius, Analytical Applications of Silica-Modified Electrodes –A Comprehensive Review, *Electroanalysis* 10 (1998) 1217–1235.
- [13] M. Sobhani, Sol-gel synthesis of aluminum titanate ( $\text{Al}_2\text{TiO}_5$ ) nano-particles, *J. Mater. Process. Technol.* 206 (2008) 282-285.
- [14] M.A. Villegas, M.A. Garcia and S.E. Paje, Incorporation and optical behaviour of 4-dimethylaminazobenzene in sol-gel silica thin coatings, *J. Eur. Ceram. Soc.* 22 (2002) 1475-1482.
- [15] K. Keiichi and Y. Setsuko, Sol-Gel Modification of pH Electrode Glass Membranes for Sensing Anions and Metal Ions, *Anal. Chem.* 73 (2001) 1605-1609.
- [16] J.I. Zink, B. Dunn, *Sol-Gel Optics: Processing and Applications*, Kluwer Academic Publishers, Norwell (1994).
- [17] N. Sanz, N., P.L. Baldeck and A. Ibanez, Organic nanocrystals embedded in sol-gel glasses for optical applications, *Synt. Met.* 115 (2000) 229-234.
- [18] A. Yari and H.A. Abdoli, Sol-gel derived highly selective optical sensor for sensitive determination of the mercury (II) ion in solution, *J. Hazard. Mater.* 178 (2010) 713-717.
- [19] N.A. Yusof, W.A. Rahman and W.A. Kadir, Optical test strip for trace Hg(II) based on doped sol-gel film, *Spectrochim. Acta A* 72 (2009) 32-35.
- [20] M.S. Attia, Spectrofluorimetric assessment of Ramipril using optical sensor Samarium ion-doxycycline complex doped in sol-gel matrix, *J. Pharm. Biomed. Anal.* 51 (2010) 7-11.
- [21] *AOAC official methods of analysis*, Published in J. of official analytical chemists (1990) pp.1058-1061.