

Sol-gel Film Doped with Bromopyrogallol Red as a Highly Sensitive Sensing Element for a new pH Optical Sensor

A. Yari* and M. Dinarvand

Department of Chemistry, Faculty of Science, Lorestan University, Falakalafak Street, Khorramabad 68178-17133, Iran

(Received 18 February 2011, Accepted 26 May 2011)

Bromopyrogallol red (BPR) pH-indicator was incorporated into a sol-gel silica matrix and used for sensing pH as a solid indicator. Entrapment of BPR into silica matrix was performed by the acid-catalyzed sol-gel reaction of tetraethylorthosilicate (TEOS) and the BPR indicator. The immobilized BPR shows better behavior than its solvated form in solution. No leaching was observed during the repetitive experiments, indicating that BPR molecules were strongly trapped into the silica matrix. At optimal condition, the sensor responded rapidly to pH changes in a range of 2.33-9.42 with the response time about a minute. The equation $A = 0.081 + 0.038 \text{ pH}$ with $R^2 = 0.992$ was obtained by regression of linear portion of the calibration curve plot of the sensor responses at various pH values. This sensor was highly sensitive, quite reversible and had a long lifetime of over 10 months.

Keywords: Bromopyrogallol red, Optical sensor, pH, Sol-gel, Tetraethylorthosilicate (TEOS)

INTRODUCTION

Sol-gel chemistry offers an alternative method for preparing chemical sensors that requires low temperatures to construct sensing elements of chemosensors. Compared with organic polymer coatings, sol-gel films have advantages such as optical transparency, tunability of physical characteristics, low chemical reactivity and high mechanical stability as well as good compatibility with different substrates to be coated [1-6]. Sol-gel technique involves a complex reaction in which a metal alkoxide such as tetraethoxysilane (TEOS), water and a second solvent are mixed thoroughly to achieve homogeneity on a molecular scale. The particles develop in the colloidal sol cross-link to form a gel, which is subsequently dried to form a three-dimensional porous glass. Sol-gel materials doped with organic or biological molecules have been widely studied and have shown interesting and unique properties [6-16].

pH has a significant effect on chemical reactions; therefore, its measurement and control is of major importance in many industrial, medical, chemical and environmental applications. In recent years, sol-gel technology has been developed for optical sensing of pH [17-20].

In the present work, we describe the production and characterization of a highly sensitive thin film for precise measurement of pH values in aqueous solutions. In this respect, we have used chemical doping method for the entrapment of the indicator dye bromopyrogallol red (BPR) into a sol-gel glass layer by which the pH of the solutions can be measured in a wide range with good and reasonable responses.

EXPERIMENTAL

Materials and Reagents

All reagents were of analytical reagent grade and used as purchased without further purification, except for vacuum

*Corresponding author. E-mail: a.yari@ymail.com

drying. The selected sensing material was BPR (Fig. 1), as a sodium salt (NaR). TEOS (98%) was purchased from Aldrich and was used as the liquid precursor. Absolute ethanol (EtOH), Triton X-100, hydrochloric acid (HCl), hydrofluoric acid (HF), standard buffer solutions (pHs 4.0, 7.0 and 10.0) for pH-meter calibration, glass slides ($2 \times 2 \text{ cm}^2$) and potassium hydroxide (KOH) were also purchased from Merck. Test solutions were buffered with citric acid/sodium citrate system (0.1 M) and concentrated HCl and NaOH were used to adjust the pH at the desired value. The metal cations tested were of their nitrate salts (Merck). Aqueous solutions were prepared from doubly distilled and deionized water.

Apparatus

Spectroscopic measurements were made using a Shimadzu 1650 PC double-beam UV-Vis spectrophotometer (Japan) with 1.0-cm quartz cells. A Jenway 3020 (UK) pH-meter with a combined glass electrode was used for pH measurements.

Fabrication of the pH Optical Sensor

We prepared the sol-gel thin film according to the general procedure described in literature [21]. A sol-gel stock solution was prepared from a mixture of 2 ml of TEOS, 1.5 ml of absolute EtOH, 0.5 ml of deionized water, 0.7 ml of 0.1 M HCl, 2-3 drops of Triton-X 100 and 20 mg (3.47×10^{-2} mmol) of BPR in a polyethylene vial. Films were obtained by casting the surface of microscope glass slides ($2 \times 2 \text{ cm}^2$) with the sol-gel solution, *via* spin coating process by using a spinning device (rpm \sim 600), in a duration time of 30 s. Prior to film deposition, the glass slide surfaces were roughened and washed with concentrated HCl and HF (1 M) then immersed in a KOH-EtOH solution for 6 h. The surfaces were then rinsed with water, acetone, 2-propanol, and finally with deionized water and dried at 100 °C for 1 h. This procedure activates the silanol groups on the surface of the glasses. After coating, the coated glasses were dried at room temperature for 10 days and then at 60 °C for 1 h. The coated films were immersed in distilled water and then in diluted HCl (0.1 M) to allow the excess and unbound dyes to be removed from the film. After the coating and drying, the glass slides were cut into appropriate sizes to be mounted in a 1.0 cm quartz cell for absorbance measurements.

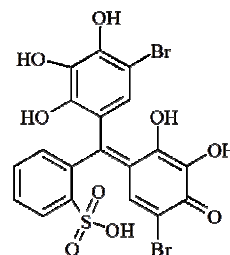


Fig. 1. The chemical structure of BPR.

General Procedure

The glass slide was mounted in the diameter direction of a photometric measuring cell. The volume capacity of the cell was ca. 4 ml. Standard pH solutions were prepared and the absorbance data were recorded at $\lambda_{\text{max}} = 574 \text{ nm}$. By plotting the calibration curve of the absorbance signal values versus the logarithmic concentration of H_3O^+ ion (pH), unknown pHs (in the measurable range) were read easily. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Spectral Characteristics

The spectral behavior of BPR indicator in aqueous solution and in the film was compared by recording its light absorption in both media in the buffer solutions with pH values from 1.0 to 11.0. The results are demonstrated in Figs. 2 and 3, respectively. As can be seen from these figures, the spectral pattern of the indicator BPR undergoes no considerable difference in both media. There is only a slight red shift of the produced peak ($\lambda_{\text{max}} = 574 \text{ nm}$) in the sol-gel compared to the aqueous solution ($\lambda_{\text{max}} = 562 \text{ nm}$). This could be due to the reduced polarity of the environment of the dye in the film and raising the energy levels of the frontier absorbing valance electrons and lowering the magnitude of the energy needed to be absorbed. A plot of absorbance versus pH values of BPR in solution at different pHs is shown in Fig. 4. The output signal varies almost linearly (in average) in a pH range from 3.12 to 6.35 at $\lambda_{\text{max}} = 562 \text{ nm}$.

Performance Characteristics

As shown in Eq. (1), the extraction of H_3O^+ ion from the aqueous sample solution into the membrane phase and its interaction with the indicator dye molecule proceeds with the

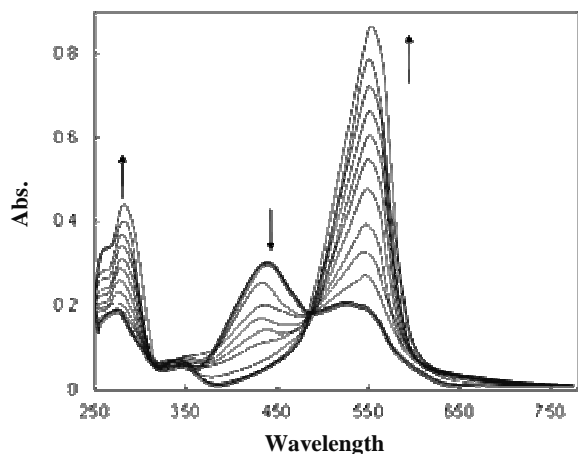


Fig. 2. Absorbance spectra of BPR (2.0×10^{-5} M) in solution at different pH values (1.0 to 8.0).

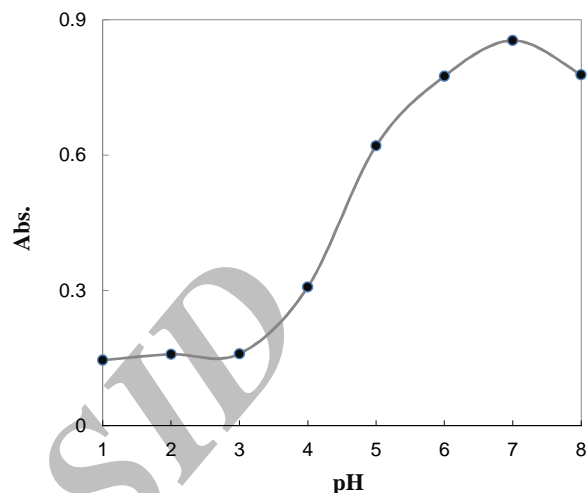


Fig. 4. Absorbance/pH plot of BPR in solution (2.0×10^{-5} M, at $\lambda_{\text{Max}} = 562$ nm) at different pH values (1.0 to 8.0).

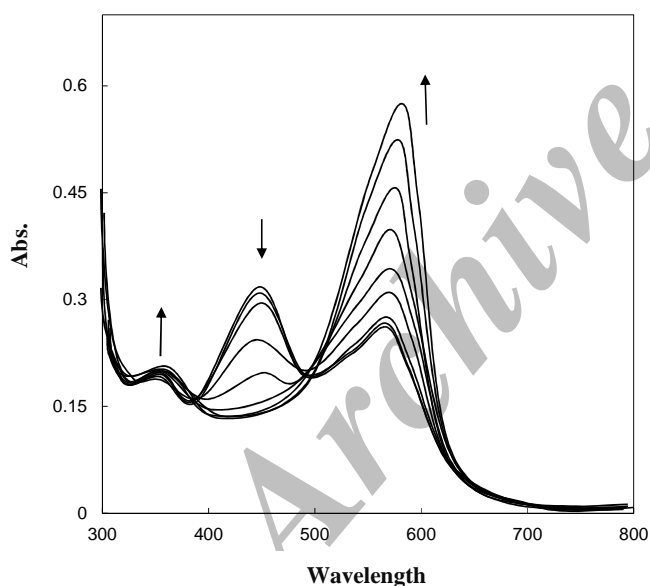


Fig. 3. Absorbance spectra of BPR in the membrane (prepared from the coating solution according to Section 2.3) in solutions with different pH values (1.0 to 11.0).

exchange of a Na^+ from the organic phase. This typical ionic-exchange process is determined by the electroneutrality in the organic membrane phase. When an H_3O^+ ion is extracted into the optical membrane, it protonates the indicator molecule and increases its acidic form ($\lambda_{\text{max}} = 438$ nm) considerably.

Increasing pH results in increasing the basic form ($\lambda_{\text{max}} = 574$ nm). This illustrates that the proposed sol-gel derived optode membrane can be used for the assay of H_3O^+ in aqueous sample solutions.



Effect of BPR concentration. Some films including different concentrations of the trapped BPR (from solutions containing 2.0 to 30.0 mg of BPR) were prepared and examined to obtain the optimum conditions in which the film shows the best response toward the pH of the solution. From the results depicted in Fig. 5, although the absorbance increases continuously by increasing the concentration of BPR, 20 mg of this reagent was selected as the optimum for preparing the coating solution as described in Section 2.3. Higher concentrations of BPR do not allow of the uniform distribution of the indicator within the silica matrix.

Time-dependence response characteristics of the film. The time required for the response of a sensor to reach 95% of its steady state signal is one of the main parameters that must be determined experimentally [22]. The response time of the pH sensor was determined from the absorbance profiles of BPR-doped film in the solution of pH 6.0 at 574 nm. The results are shown in Fig. 6 in which the absorption of the

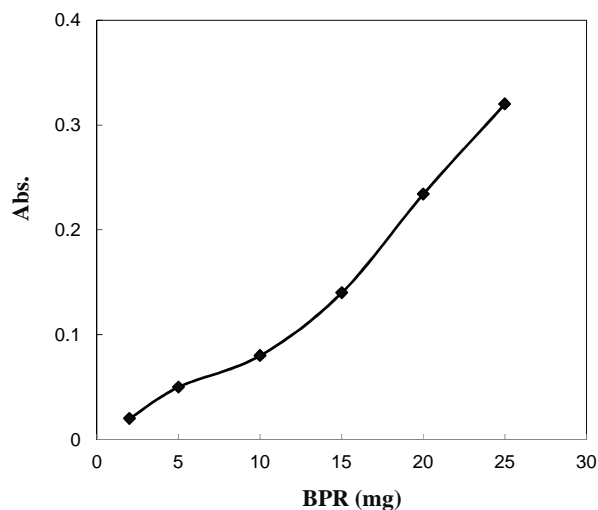


Fig. 5. The relationship between the concentrations of BPR (mg), used for preparation of the sensing element (Sec. 2.3), and the optical response of the film (at λ_{Max} 574 nm) at pH = 6.0.

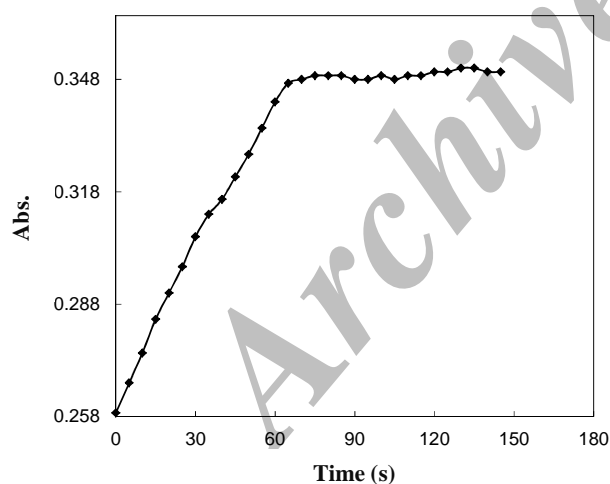


Fig. 6. Response curve of the sensor as a function of time at λ_{max} 574 nm (at pH = 6.0).

sensing film experiences no change after 50 s. The response time of 1 min was used in subsequent signal measurements as a practical response time of the film.

Calibration curve. A plot of absorbance values of the film versus the pH of the test solutions is shown in Fig. 7. Clearly,

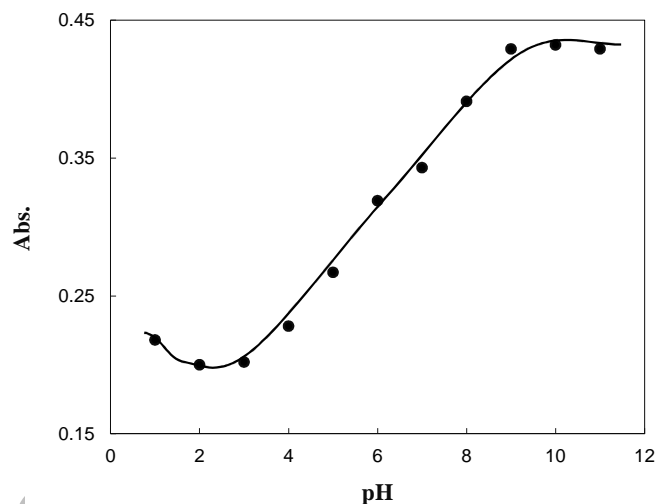


Fig. 7. Response calibration curve of the sensor (absorbance as a function of pH) at $\lambda_{\text{max}} = 574$ nm when pH of the test solution varied from 1.0 to 11.0.

the output signal varies almost linearly in a pH range from 2.33 to 9.42, which is much wider than the range obtained for the indicator in solution (Fig. 4). The linear portion of the calibration curve plot of the sensor responses at various pH values was used to construct a linear regression curve to extract the corresponding pH-dependent equation. The equation, $A = 0.081 + 0.038 \text{ pH}$ with $R^2 = 0.992$, was used to determine the pH values of the solutions through absorbance measurements.

Stability, reversibility, reproducibility and lifetime. One of the main performance parameters of chemical sensors is repeatability of their responses. The reusability of the optode was investigated by performing four cycle measurements in solutions of pH 3.0 to 6.0 to 9.0. These measurements were carried out by alternatively changing the pH values and were repeated several times. The results are shown in Fig. 8. As can be seen from this figure, the system was highly reversible. The evaluated %RSDs was ± 0.03 , ± 0.02 and ± 0.01 for buffer solutions of pH 3, 6 and 9, respectively. These experiments demonstrate that the response of the pH sensor is fully repeatable within the pH range 2.33-9.42.

Reproducibility of the system was tested when several optodes with the same compositions (see Sec. 2.3) were immersed in the same standard buffer solutions. Their

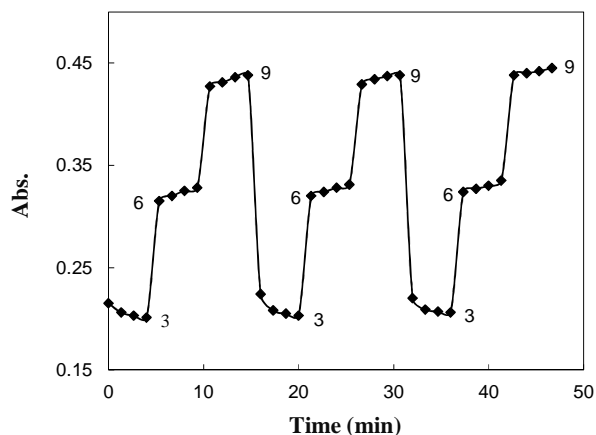


Fig. 8. Evaluation of reversibility of the optical film from alternative absorbance measurements (at λ_{\max} 574 nm) in solutions of pH 3.0, 6.0 and 9.0, respectively.

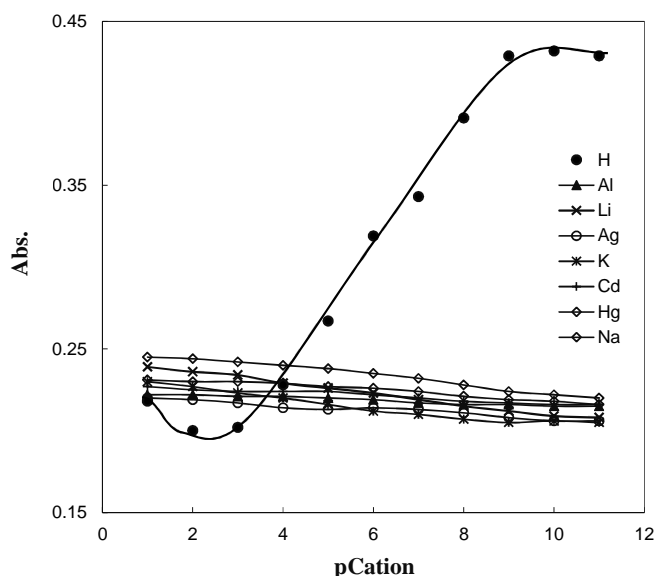


Fig. 9. The optode responses in the presence of cations H_3O^+ , Al(III) , Li^+ , K^+ , Ag(I) , Cd(II) , Hg(II) and Na^+ .

responses were nearly the same (within ± 0.01 absorbance unit) which indicate that there is a good reproducibility. The film was used periodically over a period of 10 months. Over this period, deviation of absorbance signal of the optical film from its normal function was less than 5% and no considerable

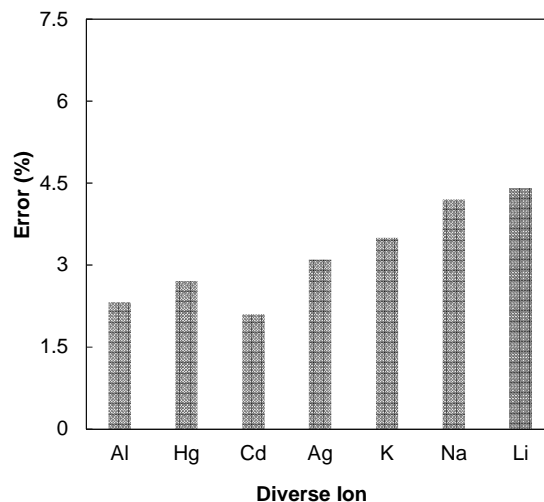


Fig. 10. The optode selectivity with respect to hydrogen ion in the presence of fixed concentrations (0.01 M) of diverse ions Al(III) , Li^+ , K^+ , Ag(I) , Cd(II) , Hg(II) and Na^+ .

leach of the incorporated reagent dye into the solution was detected during the pH measurements in buffer solutions. No drifts were observed in the sensor responses, indicating that there were no obvious changes in sensitivity, response time and absorption signal. These findings reveal that the sensor is highly stable and could be used for at least 10 months without any considerable deviation from its initial performances. These are also good evidences that both sensitivity and reversibility of this pH sensor are reasonable.

Effect of diverse ions and selectivity of the sensor. The optode optical responses were examined in the presence of some diverse ions such as Al(III) , Li^+ , K^+ , Ag(I) , Cd(II) , Hg(II) and Na^+ . As shown in Fig. 9, the optode responses toward these ions are negligible. Furthermore, the optode selectivity with respect to hydrogen ion was investigated in the presence of fixed concentrations of these diverse ions. The results are demonstrated in Fig. 10. This figure shows that deviation of the optode responses in the presence of 0.01 M of each cation is less than 5% which could be evaluated as tolerable.

Analytical Application

The previously derived equation, $A = 0.081 + 0.038 \text{ pH}$

Table 1. Determination the pH of some Water Samples by the Proposed Sensor

Sample	Proposed sensor	Glass electrode
Waste water	5.97 ± 0.05	6.04 ± 0.10
Distilled water	6.44 ± 0.04	6.51 ± 0.10
Mineral water	6.94 ± 0.04	7.03 ± 0.10
Lemon juice	3.69 ± 0.06	3.79 ± 0.10

with $R^2 = 0.992$, was used to determine pH values of a variety of samples through absorbance measurements. The results for some common water samples including wastewater, distilled water, mineral water and the lemon juice are presented in Table 1. The analytical results of the sol-gel-derived sensor were compared with those of a commercial glass electrode. As Table 1 shows, the results obtained from both methods are the same within the reasonable RSD values evaluated for each sample.

The sensor has important characteristics compared with other optical pH sensors reported so far. This sensor offers advantages over many existing sol-gel-based optical pH sensors including wider dynamic pH range, ease of fabrication, good reversibility and stability [23-25].

CONCLUSIONS

It was experimentally demonstrated that sol-gel coating containing BPR is highly useful in constructing a sensitive and durable optical sensor for the pH measurement of aqueous solutions. The sensor demonstrated good response characteristics such as wide linearity, reversibility and repeatability over a wide pH range 2.33-9.42. The proposed optical pH sensor has a relatively fast response and long lifetime, and could be easily fabricated with sol-gel technology through simple procedure.

REFERENCES

- [1] Y. Dimitriev, Y. Ivanova, R. Iordanova, J. Univ. Chem. Technol. Metall. 43 (2008) 181.
- [2] Y. Tang, E.C. Tehan, Z. Tao, F.V. Bright, Anal. Chem. 75 (2003) 2407.
- [3] L. Shapiro, S. Max, D. Mandler, Thin Solid Films 515 (2007) 4624.
- [4] R. Buestrich, F. Kahlenberg, M. Popall, P. Dannberg, R.M. Fiedler, O. Rösch, J. Sol-gel Sci. Technol. 20 (2001) 181.
- [5] B. Kuswandi, J. Ilmu. Dasar. 1 (2000) 18.
- [6] J.P. Desvergne, A.W. Czarnik (Eds.), Chemosensors of Ion and Molecule Recognition, Kluwer Academic Publishers, Boston, 1997.
- [7] R. Narayanaswamy, O.S. Wolbeis (Eds.), Optical Sensors: Industrial, Environmental and Diagnostic Applications, Springer, Germany, 2004.
- [8] M. Shamsipur, M. Hosseini, K. Alizadeh, N. Alizadeh, A. Yari, C. Caltagirone, V. Lippolis, Anal. Chim. Acta 533 (2005) 17.
- [9] D. Saha, S. Das, K. Sengupta, Sens. Actuators B 128 (2008) 383.
- [10] A.M. Massari, I.J. Finkelstein, M.D. Fayer, J. Am. Chem. Soc. 128 (2006) 3990.
- [11] J.M. Nedelec, J. Nanomater. 2007 (2007) 1.
- [12] E. Droghetti, G. Smulevich, J. Biol. Inorg. Chem. 10 (2005) 696.
- [13] S. Fardindoost, A. Irajizad, F. Rahimi, R. Ghasempour, Int. J. Hydrogen Energy 35 (2010) 854.
- [14] A. Yari, H.A. Abdoli, J. Hazard. Mater. 178 (2010) 713.
- [15] Kazemzadeh, R. Kashanaki, M.R. Hassanzadeh, Sens. Transduc. J. 113 (2010) 56.
- [16] G.C. Carramolino, M.D.P. Dominguez, Anal. Chim. Acta 614 (2008) 103.
- [17] S. Dong, M. Luo, G. Peng, W. Cheng, Sens. Actuators B 129 (2008) 94.
- [18] J. Ferreira, E.M. Girotto, Sens. Actuators B 137 (2009)

Sol-gel Film Doped with Bromopyrogallol Red

- 426.
- [19] H.M.R. Gonclaves, C.D. Maule, P.A.S. Jorge, J.C.G.E. da Silva, *Anal. Chim. Acta* 626 (2008) 62.
- [20] K.T.V. Grattan, B.T. Meggitt, *Optical Fiber Sensor Technology: Chemical and Environmental Sensing*, Kluwer Academic Publishers, the Netherlands, 1997.
- [21] C.M. Donagh, F. Sheridan, T. Butler, B.D.M. Craith, *J. Non-Cryst. Solids* 194 (1996) 72.
- [22] K. Farrington, F. Regan, *Talanta* 78 (2009) 653.
- [23] M. Noroozifar, M.K. Motlagh, S. Bahmanzadeh, S. Boroon, *Turk J. Chem.* 34 (2010) 719.
- [24] E. Wang, K.F. Chow, V. Kwan, T. Chin, C. Wong, A. Bocarsly, *Anal. Chim. Acta* 495 (2003) 45.
- [25] Y. Hiruta, Y. Ando, D. Citterio, K. Suzuki, *Anal. Sci.* 26 (2010) 297.

Archive of SID