

Investigation of Fiber Optics Sensor for Monitoring of Chemical Contaminants

Sistla S Shastry, Abdeq M. Abdi, A. G. Agwu Nnanna and Nabil Ibrahim
Purdue Calumet Water Institute
Purdue University Calumet, Hammond, IN 46323
Phone: 219 989-2071; Fax: 219 989 2898
Email: nnanna@calumet.purdue.edu

Abstract

Detection and characterization of chemical contaminants in water streams is paramount for water quality and water security. The current trend of monitoring the presence of contaminants is the batch sampling technique, where sample of water is collected and analyzed in the laboratory this method is not practical in case of disasters. A modified cladding Polyaniline based sensor is developed that can detect ammonia and hydrochloric acid. The sensor developed showed a rapid reversible color change when exposed to ammonia and hydrochloric acid. The change in intensity caused by the modified cladding is studied parametrically which will help in formulation of a correlation between response time, concentration of chemical contaminant and change in optical intensity.

1. Introduction

Sensors constitute one of the most important part of any system be it mechanical or electrical. Many systems utilize information from sensors to determine various quantities which can be used for proper functioning. For example, mobile robots use information from various sensors to determine their position with respect to surroundings. Out of the various types of sensors available very few can be used for detecting chemicals, commonly known as chemical sensors. Of the chemical sensors (viz. Enzyme sensors, Catalytic sensors, CHEMFETS, Chemiresistors, Optical Sensors) Optical Chemical Sensors and CHEMFETs are the most commonly used sensor technologies. Fiber-Optic sensors represent an exciting class of devices because of their lightweight, small size, low cost, immunity to electromagnetic interference, and ability to be embedded into other structures. The basic operation principle of the fiber-optic sensor is that when it is exposed to a chemical or physical stimulus, the characteristics of light signal traveling through an optical fiber changes. Therefore, fiber-optic sensors provide a means whereby light guided within an optical fiber can be modified in response to external physical, chemical, biological, or other influences [2]–[5]. Optical Chemical Sensors are based on the interaction of electromagnetic radiation with matter, which results in altering some property of the radiation. Examples of such modulations are variation in intensity, polarization, and velocity of light in the medium [1]. In the recent years, Fiber Optics based sensors are being preferred over conventional chemical sensors, such as Chemiresistors and Transistor based sensors, because of their large dynamic range, selectivity, sensitivity, simplicity and cost effectiveness [1]–[4]. Fiber optics based sensors can be used to respond to external physical, chemical, biological changes [5]–[9]. Denise Wilson et.al, in their study “Chemical Sensors for Portable, Handheld Field Instruments”[10], state that UV/VIS spectroscopy is simple to construct and requires little power but lacks the sensitivity and selectivity for direct measurements, hence indicating that an indirect way of measurement must be utilized. A fiber optics based sensor can be formed in many ways. Among the number of architectures, in the last few years, some intrinsic sensors based on modified cladding sensing elements have been proposed due to simple theoretical background and the low complexity of the resulting structure in addition to good performance with reasonable prices. In this type of sensor a variation in the measuring quantity causes a change in the optical properties of the electromagnetic wave passing through the core area of fiber optic cable which can be measured. Although

core modification technique, where the core is costume made, is another attractive way for forming a fiber optic sensor. Rajeev Jindal et.al, in their work “Optical-Fiber Sensor Using Tailored Porous Sol-Gel Fiber Core” [11], state that an optical-fiber chemical sensor based on evanescent wave interaction is simple in structure, compact in size, less sensitive to stray light noises but is also less sensitive because of the limited path length. The main drawback with this sensor is that it has very high signal to noise ratio, because of which the signal received at the other end is not the same as that was sent. Sunil Khijwania et.al, in their work “An Evanescent wave optical fiber relative humidity sensor with enhanced sensitivity” [12], answer to the point raised by the previous paper. According to them the sensitivity can be enhanced by using fiber optic cables that are “bent”. Bending the fiber cable increases the path length of light flowing hence increasing the sensitivity. In all such sensor systems, although methods like measurement of phase angle change can be employed, intensity change is the preferred way of detecting the contaminants because of the simplicity and less cost. In cladding modification technique, the fiber optic sensing element is prepared by replacing the original cladding material with a chemical sensing fiber. Light intensity modulation is achieved by this modified optical fiber structure based on the refractive index change of the cladding material when it is exposed to a chemical vapor. Various polymers have been utilized in this method such as Polyaniline which can be used in detecting Ammonia and Hydrochloric Acid, reversibly. The main goal of this research is to develop a sensor which can detect ammonia and hydrochloric acid in air.

2. Experimental Setup and Procedure:

2.1. Reagents and materials:

All chemicals were obtained from Acros Organics (New Jersey, USA). Chemicals were used without any purification. All aqueous solutions were prepared with Deionized water. Concentrated Ammonium hydroxide and Hydrochloric acid were used, and based on the requirement the concentration was diluted.

2.2. Sensor Design:

The Setup consists of a light source and the spectrometer which are connected by a fiber cable with a small modified cladding portion which acts as the sensing region as shown in Fig.1.

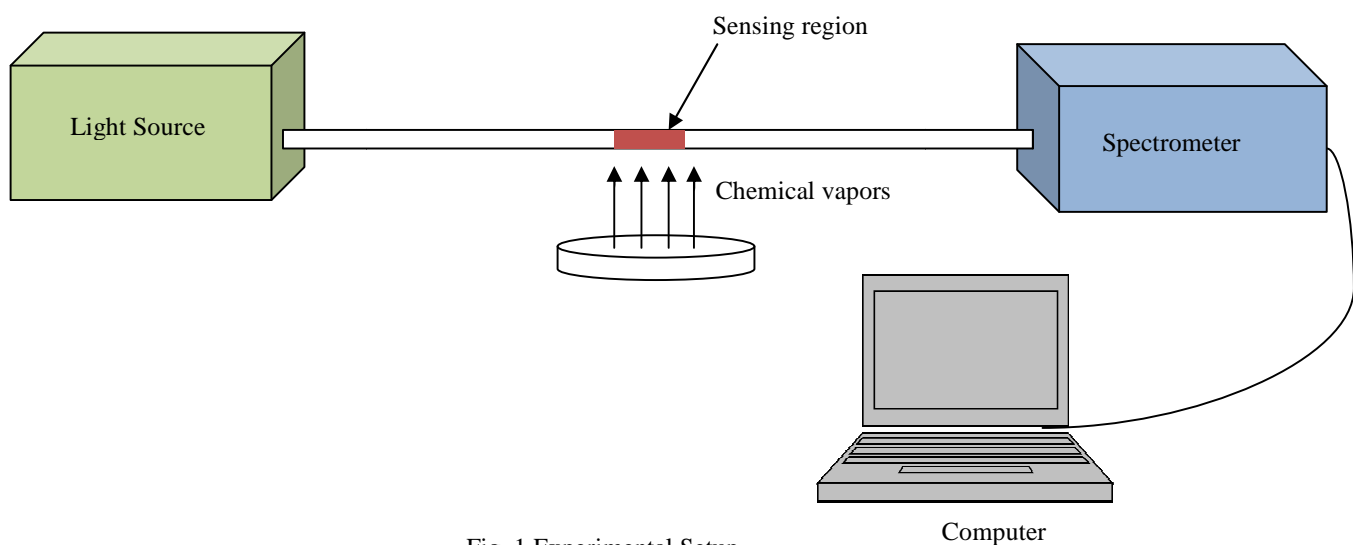


Fig. 1 Experimental Setup

All the above parts were obtained from Ocean Optics Inc. The spectroscopic data was processed with Spectrasuite, software provided by Ocean Optics. The sensing region is made on the fiber cable by replacing a small portion, typically 2 to 3 cm of the glass cladding with the Polyaniline layer. To replace the glass cladding a 50% Sodium Hydroxide solution is used as the etching agent. The rate of reaction increases by increasing the temperature. The temperature of Sodium Hydroxide solution is maintained at 240F, by doing so an etch rate of 660 nm/min is achieved. Using the above solution was found to be much easier to work with when compared to HF solution. The Polyaniline solutions were made as mentioned in [13]. Dip coating technique was used to apply a thin coating of Polyaniline onto the etched portion of the fiber cable. It was observed that by dipping the fiber cable in the solution for 15 minutes, uniform thin films of thickness less than $1 \mu m$ is obtained. Any further exposure of the fiber cable to Polyaniline caused a non-uniform coating. The configuration of the fiber-optic sensor is created on the fiber itself, as shown in Fig. 2, using the cladding modification methodology.

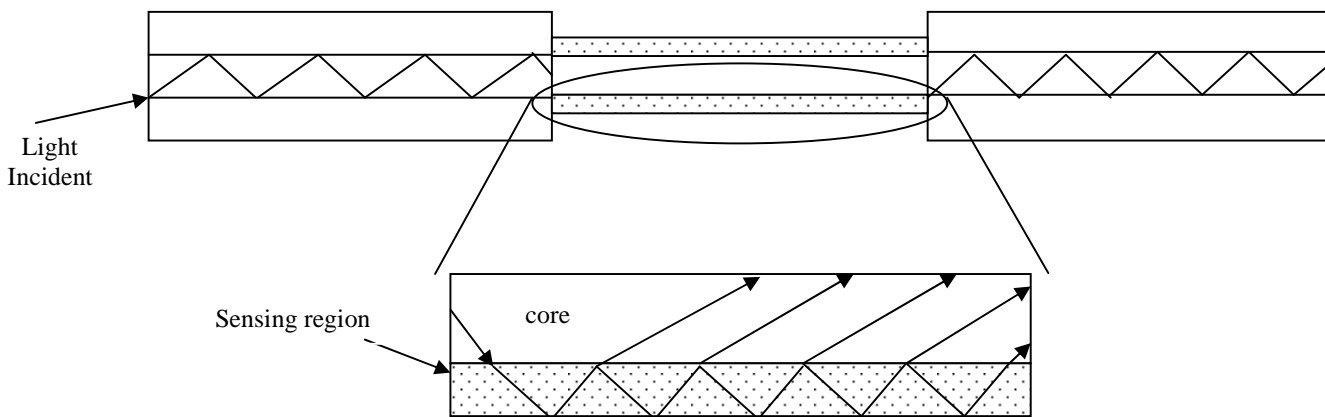


Fig.2 Structure of a modified cladding Polyaniline sensor

3. Theory and Simulation

The sensing takes place due to two reasons in Polyaniline based sensors (i) Evanescent field (ii) Multiple reflections. In evanescent field based sensor the modified cladding, which was exposed to contaminant, interacts with the evanescent field thus absorbing energy at a specific wavelength from it and causing a decrease in the output of the signal. In case of multiple reflections, the modified cladding has higher Refractive Index (RI) compared to core hence light refracts into the cladding region but gets reflected at the cladding-air interface as shown in Fig.2. Polyaniline in its acidic form known as Emeraldine salt has a refractive index of 2.43 and in basic form known as Emeraldine base has a refractive index of 1.94 [14]. Both the values are more than RI of water. Hence the Polyaniline based cladding modified sensor (PCMS) senses contaminants due to both evanescent field and multiple reflections. In order to gain a qualitative knowledge of the thickness of the coating and the length of the sensing region a five point finite difference waveguide analysis was conducted for the evanescent sensor for the Polyaniline sensor region. Maxwell's wave equation in cylindrical form [15, 16] was used to conduct mode analysis and beam propagation:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial E_z}{\partial r} \right) + \left(k^2 n^2(x) - \beta^2 - \frac{\eta^2}{r^2} \right) E_z = -j2\beta \frac{\partial E_z}{\partial z} \quad (1)$$

To determine the modes of the optical fiber, we set the right side of (1) to zero and expand using finite difference and solve the resulting Eigen system:

$$[A] \begin{bmatrix} u_1 \\ u_2 \\ u_{N-2} \\ u_{N-1} \end{bmatrix} = \beta^2 \begin{bmatrix} u_1 \\ u_2 \\ u_{N-2} \\ u_{N-1} \end{bmatrix} \quad (2)$$

Where β (Eigen value), u_i (Eigen vector) and $[A]$ are the effective propagation constant, field sampling points, and characteristic matrix. For the case of five point difference, the FD results in the following:

$$\begin{aligned} A(i,i) &= -\frac{15r(i+1)+15r(i)}{12r_a\Delta r^2} + k^2 n^2 - \frac{m}{r_a^2} \\ A(i,i+1) &= \frac{r(i+2)+15r(i+1)}{12r_a\Delta r^2} \\ A(i,i-1) &= \frac{15r(i)+r(i-1)}{12r_a\Delta r^2} \\ A(i,i+2) &= -\frac{r(i+2)}{12r_a\Delta r^2} \\ A(i,i-2) &= -\frac{r(i-1)}{12r_a\Delta r^2} \end{aligned} \quad (3)$$

To reduce the effects of sharp edges and null point at the center of the optical fiber for case of $r=0$, r_a and n were set to the average radial distance and average refractive index, respectively giving $n=0.5*(n(i)+n(i+1))$ and $r_a=0.5*(r(i)+r(i+1))$. In addition, only TM modes were examined with $m=0$. We solved (2) with Matlab Eigen solver routines and simultaneously determined the effective propagation constant and field values. We used Neumann boundary conditions at the edges of the waveguide. In the mode simulation, the operating wavelength was 600 nm, the core diameter was 200 μm , clad thickness was 20 μm , and the radial step size was set to 0.25 mm. In addition, we estimated the core (n_c) and clad refractive index (n_d) of the optical fiber to be around 1.458 and 1.439 assuming a 0.2 NA and with a pure silica core. Figure 2 shows the penetration depth of the evanescent field into cladding as a function of the angle of the beam with respect to core/clad interference. In this case, the angle is extracted from the effective propagation constant: $\cos(\text{Angle})=\beta/kn_c$. The penetration depth is defined as the point where the field drops by e^{-1} from the peak.

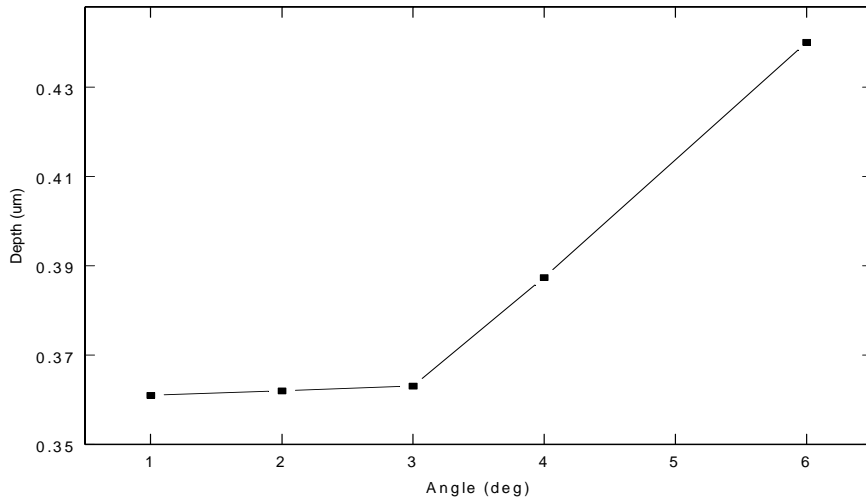


Fig. 3 Penetration depth of the evanescent field into the cladding for the case of higher order modes.

Until the point where the incident angle is 3 degrees the penetration depth is very small but increases to a large value beyond it hence suggesting that for higher order modes which typically have a higher incident angle the penetration depth of the evanescent field into the cladding increases. Using the previous data given in the literature [17], it was estimated that the minimum and maximum absorption coefficient of Polyaniline to be around $0.3 \text{ } \mu\text{m}^{-1}$ when exposed to HCl and $0.6 \text{ } \mu\text{m}^{-1}$ when exposed to concentrated ammonia gas, respectively. Four lengths of the sensing region were examined: 5 mm, 10 mm, 20 mm, and 50 mm. The core diameter was set to 200 μm , the sensing thickness was set to 20 μm , and the step size was set to 0.5 μm . In addition, two parameters were of interest: Percent change in transmittance and Absorbance. The percent change in transmittance is the change in transmittance when the sensor is exposed HCl and then Ammonia:

$$\%T = 100 * \left(1 - \frac{T_{NH_3}}{T_{HCl}} \right) \quad (6)$$

Likewise, the absorbance is given by:

$$A = \log_{10} \left(\frac{T_{HCl}}{T_{NH_3}} \right) \quad (7)$$

Figure 3 shows the absorbance of sensor when the exposed to HCl and Ammonia for the four lengths of the sensor as the angle set to 2, 3, 4, and 6 degrees.

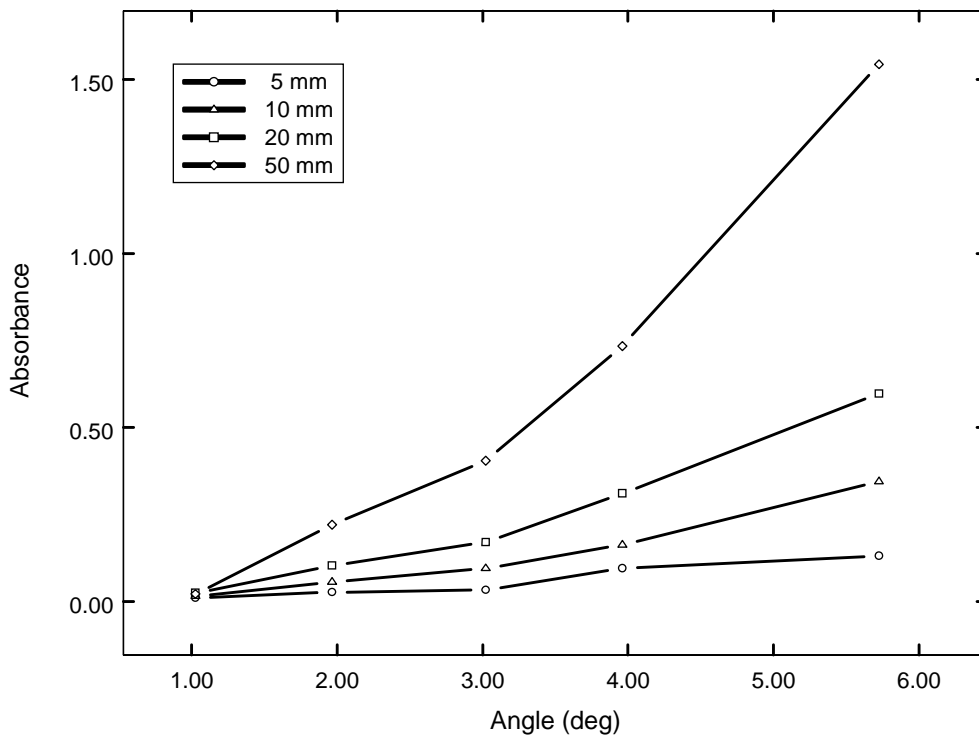


Fig.4 Variation of Absorbance with angle.

As shown in Figure 4, the absorbance increases as the angle of the beam and the length of the sensor increases. At 4 degrees, the absorbance is 0.0625, 0.125, 0.27, and 0.625 for sensing length of 5 mm, 10 mm, 20 mm, and 50 mm, respectively. Since the angle is derived from the effective propagation constant, smaller angles correspond to lower order modes and larger angles correspond to higher order modes.

Higher order modes will result in larger absorbance and percent change in transmittance compared to lower order modes. From the mode analysis we can estimate an optimum thickness and optimum length for the sensing region. We can estimate the optimum thickness to around 0.4 μm or at the midpoint between 0.38 μm and 0.44 μm as shown in Fig. 3. For the length, it was estimated to be 35 mm or the midpoint between 20 mm and 50 mm. When beam propagates through the sensing the region, the penetration depth will slightly reduce due to the high contrast in refractive index between the core and sensing region for the Polyaniline evanescent sensor. In addition, part of the power in the core will be transmitted to the sensing region since the sensing region has a higher refractive index than the core, where it will be absorbed due to the high absorption coefficient of Polyaniline. Since we only examined TM modes, we expect differences in the experimental data for the Polyaniline evanescent sensor. We expect TE modes to have similar sensitivity compared to TM modes. However, skew rays will reduce the overall sensitivity.

4. Experimental Results and Discussion

4.1. Optical property of Polyaniline

Polyaniline polymers are usually prepared by chemical [13-14, 17-18] oxidation of aniline hydrochloride by ammonium persulphate. Most common form of Polyaniline is the Emeraldine Base (EB) form which can be protonated to Emeraldine salt (ES). Of interest for development of optical sensor is the reversible protonation and deprotonation reaction between the base and salt as seen in Fig.5. This change from base to salt and back is accompanied by a shift in λ_{max} from 900nm for HCl to 785nm for ammonia as seen from Fig. 6, where Friedman's statistical smoothing is done for clarity of the plot. The change in UV-VIS spectrum characteristics of Polyaniline when exposed to ammonia and HCl is being used for detection.

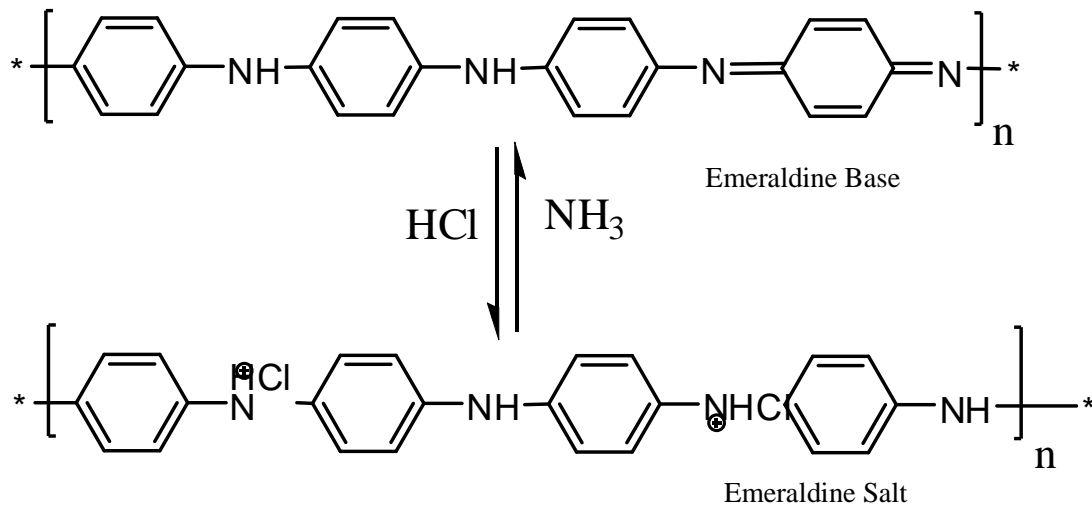


Fig. 5 Polyaniline in Emeraldine Base and Emeraldine salt forms

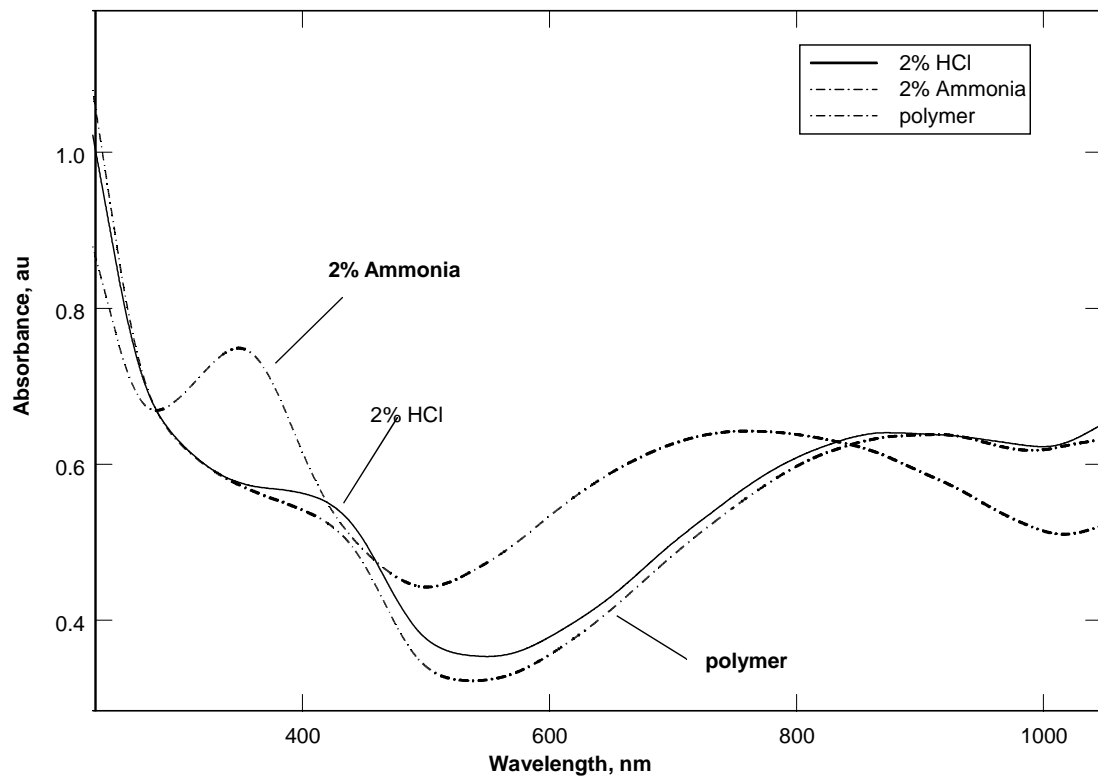


Fig. 6 Characteristic plot of Absorbance as a function of Wavelength for Polyaniline

Polyaniline in basic medium has a characteristic blue color which when exposed to acid changes to green [17]. This change in color of Polyaniline can be used to detect the presence of Ammonia and Hydrochloric acid. From the above graph it can be observed that Polyaniline when exposed to 2% ammonia solution shows a dip at 490 nm which changes to 540nm when exposed to acidic conditions. It is well known that a material of a particular color will not absorb light of wavelength corresponding to that color. The same observation can be made from the above graph where the dips at 490 nm for basic medium (blue in color) and 540 nm for acidic conditions (green in color) are seen. Also to be noticed is the absorbance plot for the dip coated polymer which almost matches the one with HCl solution. This proximity was a result of the acidic conditions used to prepare the Polyaniline coating which improve the various properties of the deposited coating [17].

4.2. Effect of concentration

The effect of varying the concentration on the absorbance-wavelength plot is as shown in Fig.7. and Fig. 8, where Friedman's statistical smoothing is done for clarity of the plot.

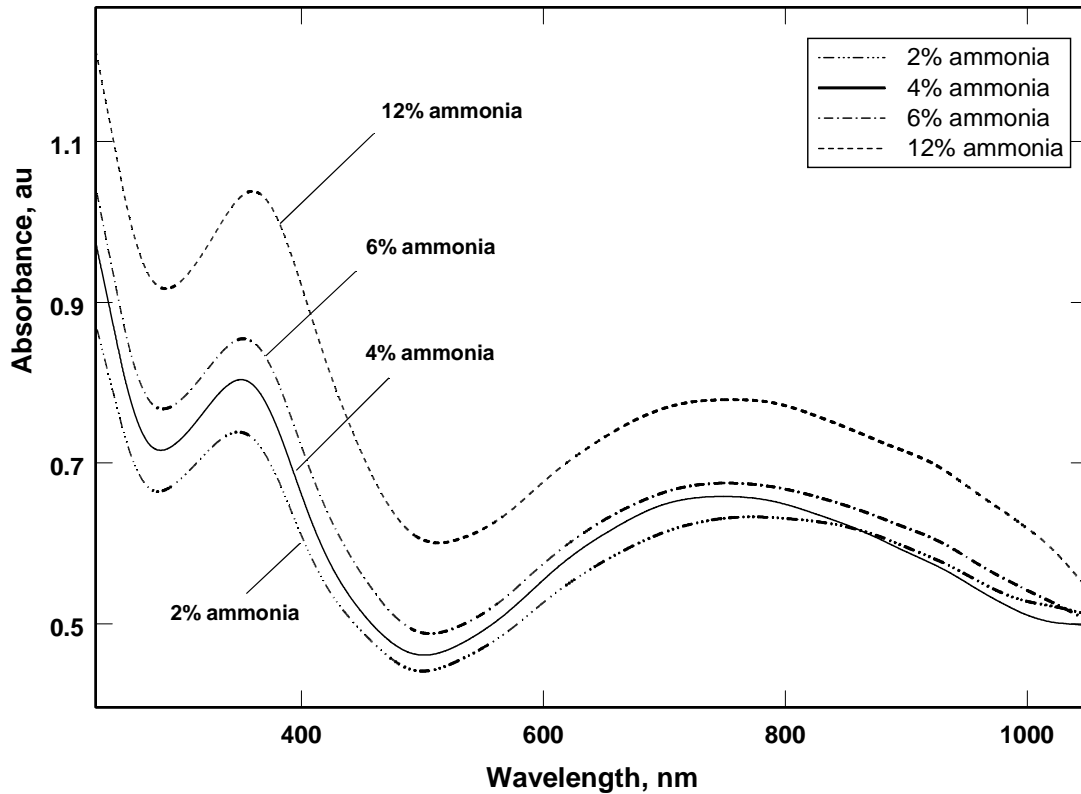


Fig. 7 Absorbance as a function of wavelength for various concentrations of Ammonia

From Fig.7 and Fig.8 it is observed that the minimum absorbance in case of ammonia are observed at 490 nm, 495 nm, 498 nm and 505 nm for 2%, 4%, 6% and 12% Ammonia solutions, respectively. A similar trend of shift in absorbance minima is also observed in case of HCl where the values of wavelengths are 536nm, 540nm, 548nm and 557nm for 2%, 4%, 6%, 12% HCl solutions, respectively. It is concluded from the above graphs that as the concentration of HCl/Ammonia increases the initial greenish-blue/bluish-green color of Polyaniline is converted into pure blue when exposed to ammonia or pure green when exposed to HCl. Based on the wavelength range in which the Absorbance minimum is observed, the contaminant can be observed as either HCl or Ammonia and based on the specific value of the wavelength at which absorbance minimum is observed, the contaminant with the concentration level is identified.

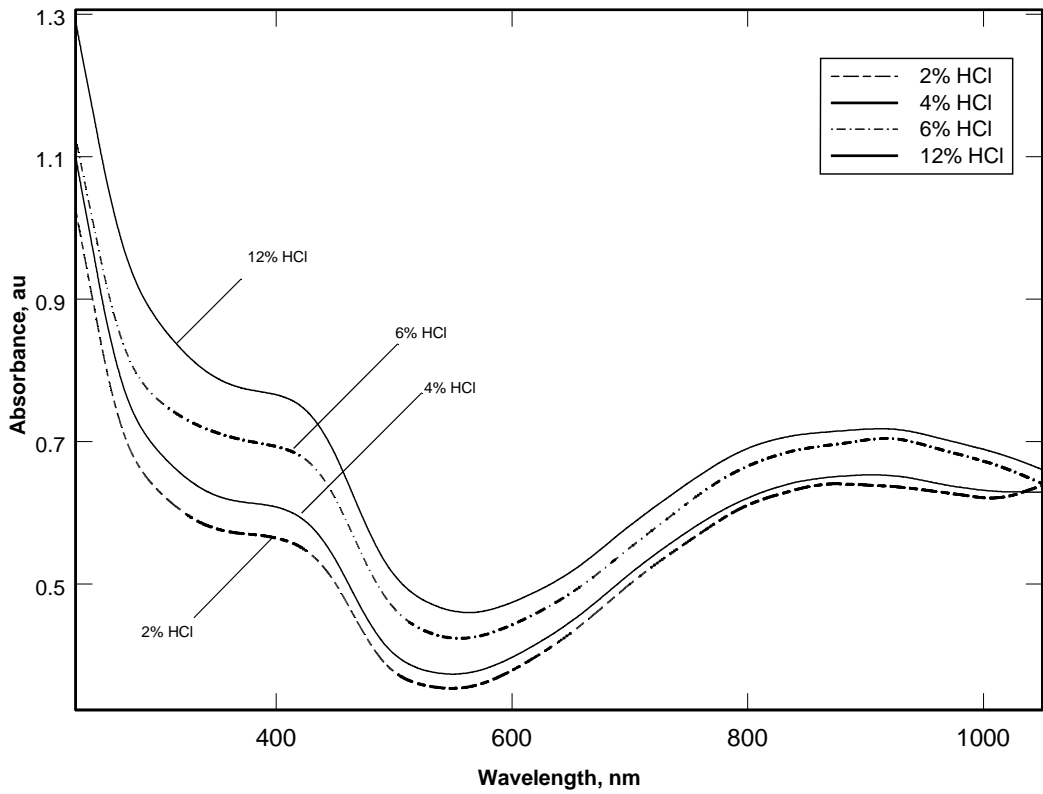


Fig. 8 Absorbance as a function of wavelength for various concentrations of HCl

4.3. Response time

Fig. 9 shows a graph between Absorbance and time for 2, 4, 6 and 12% ammonia solutions.

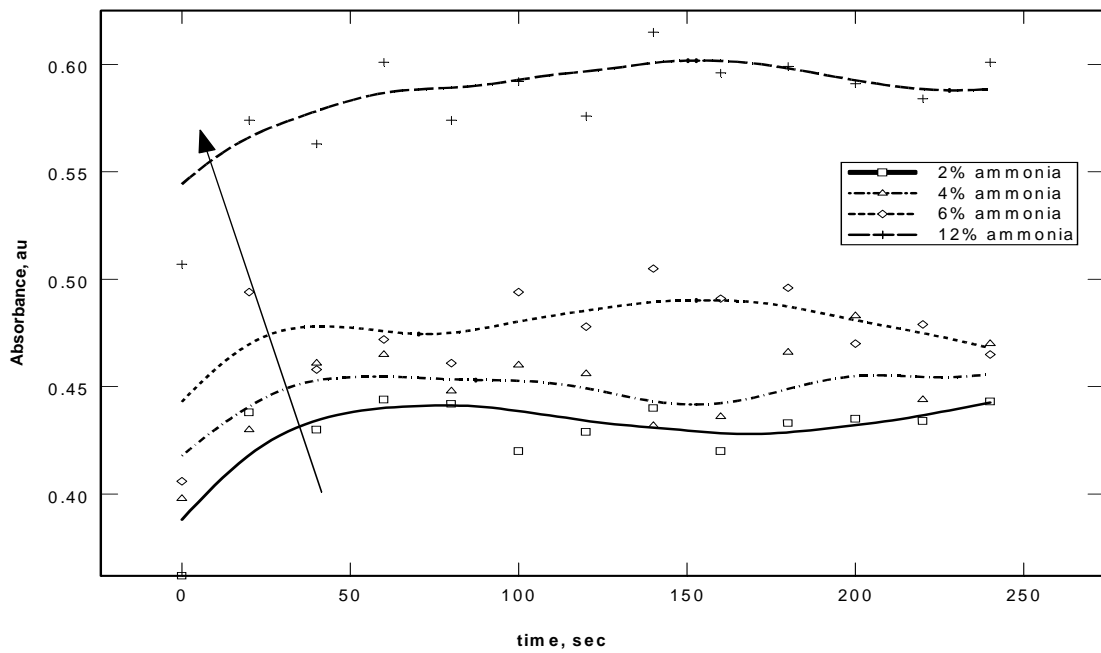


Fig. 9 Absorbance as a function of time

For a given thickness of the sensing region, the response time or rise time which is defined as the time taken by the signal to attain 90% of the steady state value, is a function of concentration of ammonia. Increase in concentration decreases the response time which can be observed from Fig. 9 where the response time for concentration of 2, 4, 6 and 12% ammonia solutions can be observed to be 36, 32, 27 and 8.5 seconds, respectively. This is useful information which can be used for field deployment of the sensor. The settling time defined as the time required for the output to reach 2 to 3% of the steady state value can be observed to be approximately 200 seconds.

5. Conclusions

A clad modified Polyaniline based optic sensor was developed which can detect ammonia and HCl to a concentration level of 2% in air. Based on the simulations a sensing region length between 20 to 50 mm and thickness of less than 1 μm was prepared. By monitoring the absorbance at a fixed wavelength or λ_{min} the concentration and contaminant can be identified. The response time for the sensor developed was observed to be between 36 to 8.5 seconds based on the concentration.

References

1. M. A. El-Sherif, "An Apparatus and a Method Comprising an Optical Fiber Modulator, Coupler, Switch, Sensor, and Distribution System," U.S. Patent 5 060 307, Oct. 22, 1991.
2. J. Yuan, "Development of Smart Structures Utilizing Chromogenic Materials for Optical Fiber Sensor," M.S. thesis, Drexel Univ., Philadelphia, PA, 1997.
3. M. A. El-Sherif, "On-Fiber sensor and modulator," IEEE Trans. Instrum. Meas., vol. 38, pp. 595–598, Apr. 1989.
4. M. A. El-Sherif and J. Yuan, "Development of a novel class of fiber optic sensors for environmental field measurements," in International Conference on Agropoles and Agro-industrial Technological Parks, Barretos, Sao Paulo, Brazil, Nov. 15–21, 1999.
5. A. D. Kersey, "A review of recent developments in fiber optic sensor technology," Opt. Fiber Technol., vol. 2, pp. 291–317, 1996.
6. T. G. Giallorenzi, J. A. Bucaro, A. Dandridge, G. H. Sigel, J. H. Cole Jr, and S. C. Rashleigh, "Optical fiber sensor technology," J. Quantum Electron., vol. QE-18-4, pp. 626–665, 1982.
7. R. Narayanaswamy, "Current developments in optical biochemical sensors," Biosens. Bioelectron., vol. 6, pp. 467–475, 1991.
8. Xiaojing Liu and Weihong Tan, "A Fiber-Optic Evanescent Wave DNA Biosensor Based on Novel Molecular Beacons", Anal. Chem. 1999, 71, 5054-5059.
9. M. A. El-Sherif, J. Yuan, and A. G. MacDiarmid, "Fiber optic sensors and smart fabrics," J. Intell. Mater. Syst. Structures, vol. II, no. 5, pp. 407–414, May 2000.
10. Denise Michele Wilson, Sean Hoyt, Jiri Janata, Karl Booksh, and Louis Obando, "Chemical Sensors for Portable, Handheld Field Instruments", IEEE Sensors Journal, Vol. 1, No. 4, December 2001.
11. Shiquan Tao, Christopher B. Winstead, Rajeev Jindal, and Jagdish P. Singh, "Optical-Fiber Sensor Using Tailored Porous Sol-Gel Fiber Core", IEEE Sensors Journal, Vol. 4, No. 3, June-2004.
12. Sunil K. Khijwania, Kirthi L. Srinivasan, Jagdish P. Singh, "An evanescent-wave optical fiber relative humidity sensor with enhanced sensitivity", Sensors and Actuators B 104 (2005) 217–222.
13. Zhe Jin, Yongxuan Su, Yixiang Duan, "An improved optical pH sensor based on Polyaniline", Sensors and Actuators B 71 (2000) 118-122.
14. J. Yuan and Mahmoud A. El-Sherif, "Fiber-Optic Chemical Sensor Using Polyaniline as Modified Cladding Material", IEEE sensors journal, Vol.3, No.1, February 2003.

15. Okamoto, Katsunari, "Fundamentals of Optical Waveguides", Academic press, San Diego, CA, 2000.
16. Ghatak, A. and Thyagarajan, K., "Introduction of Fiber Optics", Cambridge University Press, Cambridge, U.K., 1998.
17. Jaroslav Stejskal, Irina Sapurina, "Polyaniline: Thin Films and Colloidal Dispersions", Pure and Applied Chemistry, Vol.77, No.5, pp. 815-826, 2005.
18. Stejskal J.; Sapurina I.; Prokes J.; Zemek J., "In-Situ Polymerized Polyaniline films", Synthetic Metal, Vol.105, No.3, Sep. 1999, pp.195-202.