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Comparative Performance of Two Fiber Optic Ammonia Sensors Employing Different Sensing Materials

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Abstract: The design and fabrication of fiber based ammonia sensors employing Bromothymol blue and Chitosan as sensing elements are presented in this paper. In the presence of ammonia gas the absorption of Bromothymol blue changes while in the case of Chitosan the refractive index changes which in turn modulates the intensity of light propagating through a fiber. *Copyright © 2008 IFSA.*

Keywords: Fiber optic sensor, Evanescent wave, Bromothymol Blue, Chitosan

1. Introduction

Accurate measurement of chemical species in air has acquired great practical significance because of the toxic effects these can cause to humans. The monitoring of ammonia gas has received wide-spread interest with the increase in environmental awareness and stricter regulations for pollution control. Moreover, in industry and clinical analysis, continuous ammonia measurement is desired. Development of simple, sensitive, low cost and portable sensors capable of direct measurement of environmental pollution is of considerable interest in this context. Optical fiber technology offers several advantages for chemical sensing over conventional methods [1] and hence it is worthwhile to investigate the feasibility of this method to the problem of pollution monitoring. The present paper gives a detailed account on the design, fabrication and characterization of two sensitive and low cost fiber optic sensors based on BTB and Chitosan as sensing elements for the measurement of ammonia gas in air.

2. BTB Based Fiber Optic Ammonia Sensor

Bromothymol blue (BTB), also known as dibromo thymo sulfo nephthalein, is a chemical indicator. It is green in neutral solution and appears yellow in acidic and blue in basic solutions. Bromothymol blue is mostly used in measuring pH value of substances that would have relatively low acidic or basic levels.

2.1. Theory

Fiber optic sensors based on evanescent wave are discussed in detail in literature[1-5]. If a part of the cladding is removed from the fiber and is replaced by an absorbing medium then the evanescent field interacts with the medium and hence the power transmitted by the fiber will decrease. This is the basis of the absorption sensors utilizing evanescent wave in an optical fiber.

Consider a step index multimode optical fiber of normalized frequency V for which the cladding has been replaced locally by an absorbing medium. If P_0 is the power transmitted by the fiber in the absence of an absorbing medium, then the power transmitted in the presence of the medium is given by:

$$P(L) = P_0 \exp(-\gamma CL), \tag{1}$$

where L is the length of the lossy cladding or unclad portion of the fiber, C is the concentration of the absorbing medium and γ is the evanescent wave absorption coefficient of the medium which can be written as:

$$\gamma = \eta\alpha, \tag{2}$$

where α is the bulk absorption coefficient of the medium at the propagating wavelength λ of the light source used and η is the fraction of the power transmitted through the cladding and is given by:

$$\eta = \frac{4}{3\sqrt{N}}, \tag{3}$$

where $N = V^2/2$ is the total number of modes propagating through the fiber.

2.2. Experimental Setup

The optical fiber used for the sensor element fabrication is a multimode plastic clad silica fiber (F MBC, Newport make). A suitable length of the cladding is removed from the middle portion of the fiber. The ends of the fiber are polished well. To avoid vulnerability of the exposed silica to surface cracking and other damaging phenomena, the removal of the cladding is performed carefully with acetone. The sensing portion of the fiber is kept clean and free from dust and dirt [4].

Fig.1 shows the absorption spectra of BTB solution recorded using a spectrophotometer (Jasco, V-570) under two different environments viz before and after ammonia gas exposure. During exposure of ammonia gas, depending on the concentration of ammonia, the ammonia sensitive dye changes its colour from yellow to blue. It is also seen that the absorbance increases by large levels in the

500-750 nm range. The change in absorbance leads to an attenuation of the guided light at this wavelength or near to this wavelength. The maximum absorption is in the 600-750 nm range. Therefore a red LED is used to power the present sensor [6].

Experimental setup is as shown in Fig. 2. This consists of a red LED having a peak emission wavelength at 632 nm, prepared fiber, a glass cell, which contains the solution, and a power meter to measure the output from the detector. Bromothymol blue solution is prepared by dissolving 1 gram of Bromothymol blue powder in 1 litre of methanol. The NH_3 gas for the experimental investigation is obtained by heating liquor ammonia (25% solution) in a round bottom flask at a temperature of 45 ^{0}C. The liberated NH_3 gas is passed on to the sensing cell.

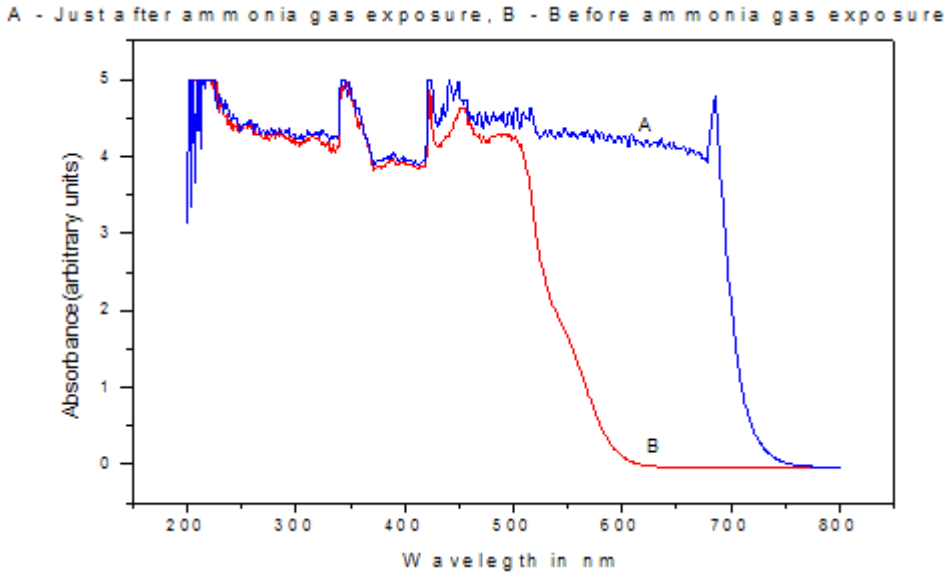

Fig. 1. Absorption spectrum of BTB solution before and after ammonia gas exposure.

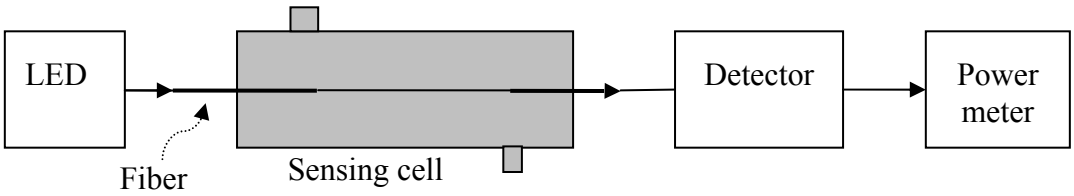

Fig. 2. Block diagram of the experimental setup.

2.3. Results and Discussion

When light from red LED is launched into the fiber placed in the sensor cell, the evanescent wave penetrates and interacts with the surrounding medium. Depending on the concentration of ammonia, evanescent wave absorption increases at the propagating wavelength.

The variation of the sensor output with different concentrations of ammonia gas is shown in Fig. 3. As the amount of ammonia in the BTB solution increases, more of the indicator dye will be in the non-protonated form. The non- protonated form of the indicator is detected by the absorption of light. The absorption of light in the solution increases as the concentration of ammonia increases.

$$NH_3 + Dye \longrightarrow NH_4^+ Dye^- \quad (4)$$

The dynamic range of the sensor is within the range of gas concentration liberated from 15 ml to 100 ml of liquor ammonia. Sensitivity of the sensor is found to be 0.02 μW/ml. Fig. 4. shows the time response of the sensor element to ammonia gas liberated from 100 ml of liquor ammonia.

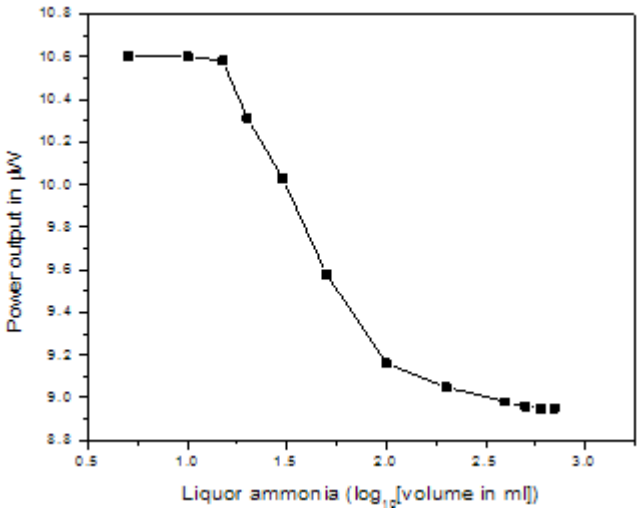

Fig. 3. Variation of ammonia sensor output with different concentrations of ammonia gas.

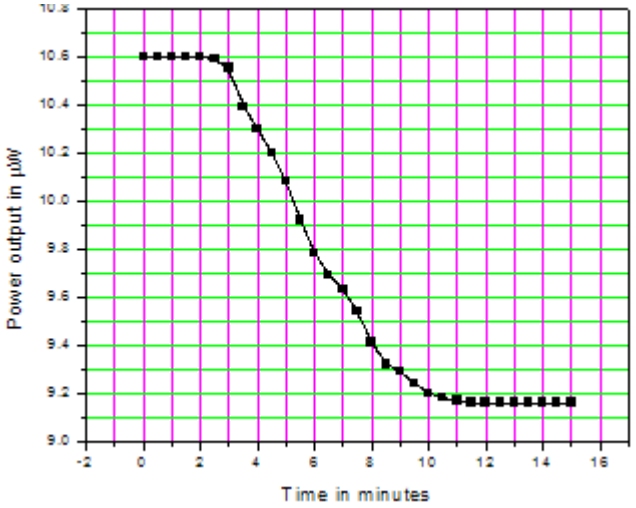

Fig. 4. Response of sensor element to ammonia gas liberated from 100 ml of liquor ammonia.

3. Chitosan Based Fiber Optic Ammonia Sensor

Chitosan is a fiber-like substance derived from chitin. Chitin is the second most abundant organic compound in nature after cellulose. Chitin is widely distributed in marine invertebrates, insects, fungi, and yeast. Generally, the shell of selected crustaceans consists of 30-40% protein, 30-50% calcium carbonate and calcium phosphate, and 20-30% chitin. Chitin is widely available from a variety of sources among which, the principal source is shellfish waste such as shrimps, crabs, and crawfish. It also exists naturally in a few species of fungi.

With regard to their chemical structure, chitin and chitosan have similar chemical structure. Chitin is made up of a linear chain of acetylglucosamine groups while chitosan is obtained by removing enough acetyl groups (CH_3-CO) for the molecule to be soluble in most diluted acids. This process is called deacetylation. The actual difference between chitin and chitosan is the acetyl content of the polymer. Chitosan having a free amino group is the most useful derivative of chitin [7, 8].

3.1. Theory

In this method the refractive index of the cladding changes in accordance with its reaction with the analyte [1]. Sensor head is fabricated by coating the uncladded portion of a fiber with chitosan solution. Chitosan possess positive ionic charges which give it the ability to chemically bind with fats, lipids, ammonia and metal ions. When it is exposed to ammonia gas, the refractive index of the cladding layer begins to change in proportion to the concentration of ammonia gas present. Hence the intensity of the transmitted light also changes in proportion to change in refractive index. Thus the relative trace gas concentration can be determined by measuring the output intensity of the light passing through the sensing region.

A schematic model of the sensor head is shown in Fig. 5. [9]. On the basis of the above-mentioned principle, the output light intensity passing through the sensor head is calculated theoretically using a ray tracing method.

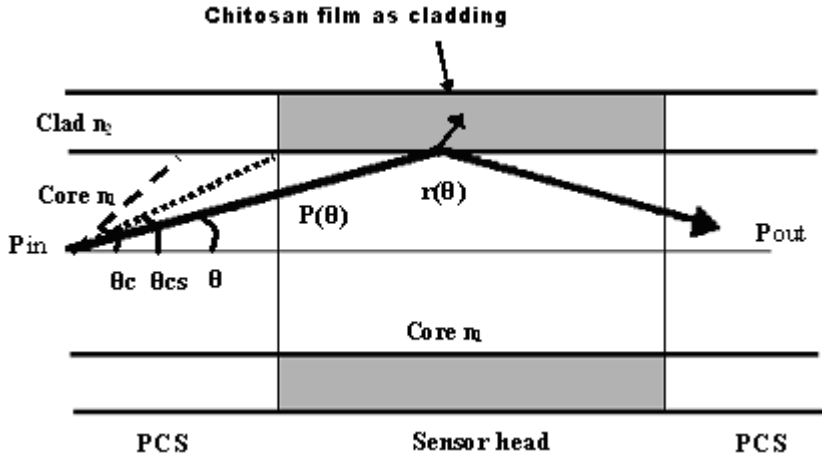

Fig. 5. Leaky and guided modes of the sensor head.

For the leaky sensor head in Fig. 5, P_{out} is given by:

$$P_{out} = \sum_{\theta=0}^{\theta cs} P(\theta) + \sum_{\theta=\theta cs}^{\theta c} P(\theta) r^{m} \tag{4}$$

where θc is the critical angle in the input-side of PCS fiber, $r(\theta)$ is the reflection coefficient and m is the number of reflections for the sensor head and θcs is the critical angle in the sensor head [9].

3.2. The Experiment

The sensor element fabrication includes fiber preparation and deposition of the chitosan film on the prepared fiber. The fiber preparation is already discussed in section 2. The chitosan sensor head is fabricated by dip coating the uncladded portion of the fiber in chitosan solution prepared by dissolving 1% chitosan in 4% acetic acid solution. The dip-coated fiber is kept 24 hours at room temperature for drying. The water and the acetic acid in the polymer layer is evaporated off while drying and an equilibrium with the room humidity is achieved [9, 10]. Experimental set up, which is similar to the earlier case, consists of a green LED having a peak emission wavelength at 523 nm, a glass cell which contains the uncladded fiber coated with chitosan and a power meter to measure the output from the detector. A finite amount of liquor ammonia (25% solution) taken in a round bottom flask is gently heated to a temperature of 45^{o}C. The ammonia gas released is passed onto the sensing cell.

3.3. Results and Discussions

When the sensor head coated with chitosan solution is exposed to ammonia gas, the refractive index of the cladding layer begins to change. Hence the intensity of the transmitted light also changes in proportion to changes in the refractive index. Thus the relative trace gas concentration can be determined by measuring the output intensity of the light passing through the sensing region. The variation of the sensor output with different concentrations of ammonia gas liberated from various

amount of liquor ammonia is shown in Fig. 6. The dynamic range of the sensor is within the range of gas concentration liberated from 10 ml to 400 ml of liquor ammonia. Sensitivity of the sensor is found to be 0.002 μW/ml.

The reversible nature of the sensing element is also studied and is shown in Fig. 7. In this figure, the graph corresponding to each concentration of ammonia gas has three regions; A, B and C. Regions A and C correspond to the sensor output before and after ammonia gas exposure whereas region B represents the sensor output during ammonia gas exposure.

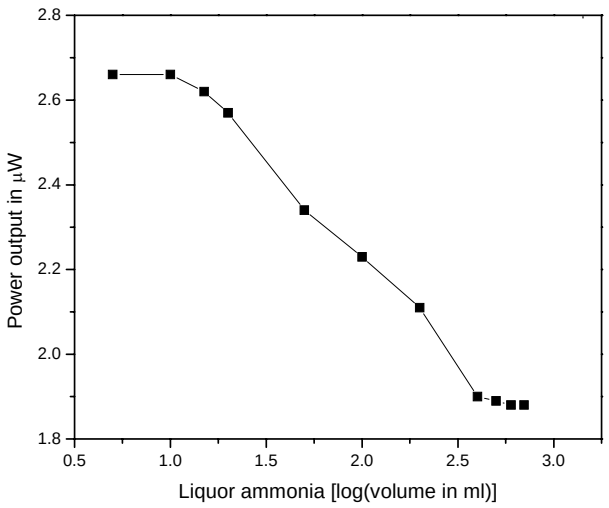

Fig. 6. Variation of ammonia sensor output with various concentrations of ammonia gas liberated from liquor ammonia.

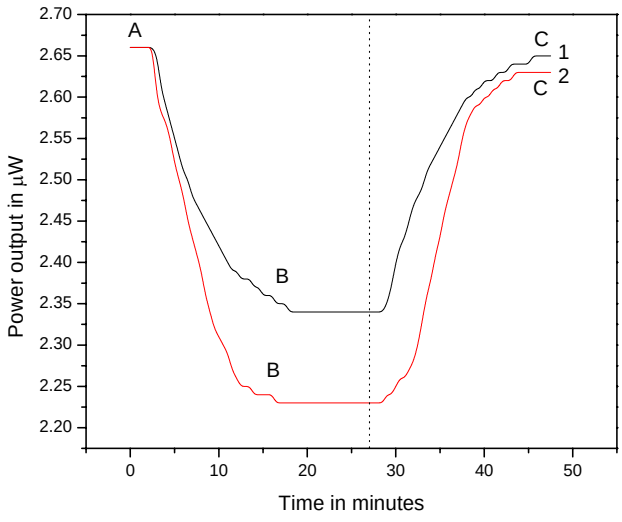

Fig. 7. Traces1 and 2 correspond to ammonia gas liberated from 50 ml and 100 ml of liquor ammonia respectively.

From the response curve of the ammonia sensor it is seen that for each concentration of ammonia gas the sensor output decreases from region A during ammonia gas exposure and reaches a steady state region B after a few minutes. Then if we stop the ammonia flow, the sensor output increases and reaches almost the starting region A, which is due to the reversible behavior of the sensor head. This reversible nature of the sensing element eliminates the difficulty of replacing the sensing fiber after each measurement. Comparison between fiber optic ammonia sensors employing BTB and Chitosan as sensing materials is shown in the Table 1.

Table 1. Comparison between BTB and Chitosan based fiber optic ammonia sensors.

	BTB	**Chitosan**
Sensitivity (μW/ml)	0.02	0.002
Dynamic range (gas liberated from liquor ammonia(ml))	15 - 100	10 - 400
Response time(in minutes)	6	8

4. Conclusions

Two fiber optic sensors for the determination of ammonia concentration have been studied. The first one uses an indicator dye BTB and works on the principle of evanescent wave absorption of light propagating through the fiber. The second one uses a thin film of bio polymer chitosan as cladding of

the sensor head and works on the principle of refractive index variation and subsequent changes in the local numerical aperture of the fiber. From the results it is clear that these sensors can be used for the detection and measurement of ammonia gas after proper calibration of the sensor. The sensors are also cost effective, easy to fabricate and maintain.

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