The developed dual wavelength evanescent fiber optic sensing method is employed for trace analysis of Ammonia, Phosphate and Iron in water.

3.1. Introduction

Accurate measurement of chemical species in water is of great practical significance in water treatment plants and other similar industries. The water quality analysis at different locations of the plant is usually carried out by spectrophotometric methods. Water samples from different locations are subjected to chemical reactions and are analysed for different chemical species like ammonia, phosphate, iron etc. The final analysis using spectrophotometer is costly and the device is bulky too. Use of optical fiber based sensors provides an easy, quick and accurate method to measure the water quality.
Interest in opto-chemical sensors has been growing rapidly in recent times. The direct spectroscopy measures the characteristic absorption spectra of the analyte, whereas chemically mediated spectroscopy indirectly measures the spectral changes of the solution when interacting with the analyte under investigation. Chemically mediated spectroscopy provides better sensitivity and selectivity than direct technique [1]. Using a fibre optic evanescent wave sensing technique the bulky spectrophotometers can be replaced with simpler interrogators with narrow band optical sources. Compared to other sensing methods, evanescent wave sensing technique provides several advantages [2, 3]. The evanescent wave fiber optic chemical sensors reported in literature mostly employ single wavelength probing [4-7]. In the present system with dual wavelength probing, the distortion of the signal, due to fiber bending and source fluctuations are reduced using a reference signal. A non-absorbing narrow band source is used for the compensation of other contributing losses like turbidity and refractive index which will enhance the repeatability aspect of the sensor [8].

We have used a fiber optic evanescent wave sensor with dual wavelength probing for better selectivity, sensitivity and repeatability in chemical sensing. The developed sensor is employed for the measurement of concentration of Iron, Ammonia and Phosphate in water.
3.2 Theory

In evanescent wave based fiber optic sensors the sensing region is developed by either completely or partly removing the cladding for a short length. The light radiation that leaves the core at the sensing region can undergo several modifications. It can produce attenuated total internal reflection (ATIR) depending on the refractive index of the medium surrounding the exposed region. The radiation may get absorbed by the surrounding species if the operating wavelength is same as that of the peak absorption wavelength called analytical wavelength of the species. The absorption and scattering due to other contributing losses like interferences and turbidity. The effects mentioned above are responsible for the modulation of light intensity through an evanescent wave sensor. The first and third effect is present in all evanescent wave sensors and the second effect will come into play only if the operating wavelength is the analytical one for the given species.

So whenever an evanescent wave based fibre optic sensor is employed for chemical sensing, it is always advisable to use an analytical wavelength as the probing tool.

The power through the core of the fiber after the sensing region is [10, 11]

\[ P_{\text{core}} = P_T - P_T \frac{0.3}{a(n_1^2 - n_2^2)} - P_T \cdot A \]  

(3.1)
Where ‘P$_{\text{core}}$’ is the power through the core, ‘P$_T$’ is the total power injected into the fiber. ‘$\lambda$’ is the probing wavelength, ‘a’ is the core radius and ‘n$_1$’ and ‘n$_2$’ are the refractive indices of the core and cladding of the fiber used. ‘A’ is the absorbance of the species surrounding the exposed region of the sensor, which can be explained with the help of Beer’s law for absorbing solutions. It states that the absorbance is directly proportional to concentration of the solution and the path length for light travel through the species is as given in equation:

$$A \propto b.C$$

Where ‘b’ is the path length of light travel and ‘C’ is the concentration of the species. Absorbance can be written as

$$A = \varepsilon b. C,$$  \hspace{1cm} (3.2)

‘$\varepsilon$’ is the absorptivity, a constant that does not depend on concentration.

In a fibre optic sensor, if equal amount of samples are added for every measurement, the value of ‘b’ can be kept constant. Hence $A \propto C$

Since we are taking the differential signal of the same source, source fluctuations can be eliminated. From expression (3.1), the second term corresponds to the contribution of index dependant power variation, which will be the same for absorbing and reference wavelength as explained in chapter 2. The contribution due to turbidity and interferences will also be the same for both wavelengths.
It is possible to select analytical wavelength and non-absorbing reference wavelength from the absorption spectrum of the solution under study. The analytical wavelength is selected in such a way that it corresponds to the absorption peak of the solution. The non-absorbing reference wavelength is chosen to be sufficiently away from the absorption peak, ensuring that it has very little absorption in comparison with analytical wavelength. In order to take the reference signal a 3db coupler is used.

To have a quantitative analysis of concentration / chemical content level, it is better to have a system capable of dual wavelength probing arrangement. In this scheme, one wavelength should be the analytical wavelength for the species under consideration and the second wavelength should be a non-absorbing one. The difference of output power in absorbing and non-absorbing wavelengths will be the contribution due to the absorption of the given chemical content in water. However in the case of mixtures with overlapping absorption bands the present approach cannot be used in a manner that will distinguish the contaminants.

### 3.3 Experimental Details

The experimental setup is as shown in figure 3.1, which consists of different LED sources, a 3dB fibre optic coupler and a pair of source to fibre coupler. The exposed area of the sensor (contact area) is 2 cm long. Light injected into the sensor is measured at the receiving end by two PIN photodiodes. The plastic multimode fibre used for the present study is a step index with core diameter of 980
μm and NA of 0.5. The refractive indices of the core and the cladding are 1.49 and 1.41 respectively. The core is made up of polymethacrylate and a thin layer of fluorinated polymer serves as the cladding material. A detailed discussion of experimental details is given in section 2.5.2.

Figure 3.1 Experimental setup for dual wavelength probing to estimate the traces of ammonia, phosphate and iron in water.

3.3.1 Measurement Method

For the quantitative analysis, the source corresponding to analytical wavelength is switched on and the output of the analog to digital converter (PD₁-PD₂)₁ is recorded. This corresponds to the power loss due to refractive index, spectral absorption, and other contributing losses. This data is stored and the LED is switched off. The source corresponding to the non-absorbing reference wavelength is then switched on and the output data (PD₁-PD₂)₂ is taken. This reading will be the power loss due to refractive index variation, and other contributing losses. (PD₁-PD₂)₁ - (PD₁-PD₂)₂ is calculated to get the contribution due the absorbance of the given species in water. The power loss due to refractive index and other contributing losses like
interferences and turbidity will be almost same for both the wavelengths. Hence \((PD_1-PD_2)_1 - (PD1-PD2)_2\) will be proportional to the power due to spectral absorption of the given species in water.

### 3.3.2. Preparation of reagents and standard solutions

An intermediate reagent which reacts with the analyte forms an absorbing solution. The preparation of the reagents is detailed below.

**Iron:** Soluble iron in ground water is usually in the ferrous state. On exposure to air, ferrous iron is oxidised in to the ferric state \((\text{Fe}^{3+})\) and may hydrolyse to form red, insoluble hydrated oxide. Elevated iron levels in water can cause stains in plumbing, laundry and cooking utensils and can impart objectionable tastes and colour to food. The United Nations Food and Agriculture Organisation recommended the level for irrigation waters is 5mg/L. The U.S EPA drinking water standard MCL is 0.3mg/L.

To study the iron content, water sample is reduced with hydroxylamine hydrochloride and then reacted with bathophenanthroline (4.7-diphenyl-1,10phenanthroline). The red ferrous complex is extracted with n-hexly or isoamly alcohol [12].

**Reagent preparation for Iron**

**Bathophenanthroline Solution** (0.835gm/L): Dissolve 0.835 gm of Bathophenanthroline in 100ml of ethyl alcohol.

**Hydrochloric Acid:** Mix equal volumes of hydrochloric acid (sp.gr.1.19) and water.
Iron standard solution: Dissolve 0.1 gm of pure iron in 10ml of hydrochloric acid and 1ml of bromine water. Boil to remove excess bromine. Add 200ml of hydrochloric acid, cool and dilute to 1 litre with water. Add 10 ml of this solution to 12ml of hydrochloric acid and dilute to 1 litre with water. In order to prepare standard solution of 1ppm, dissolve 0.1g of pure iron in10 ml of hydrochloric acid and 1 ml of bromine water. The solution is boiled to remove excess bromine and add 200 ml of hydrochloric acid. Allow the solution to cool and dilute to 1 litre with water. Take 10 ml of this solution and add 12 ml of hydrochloric acid and dilute to 1 litre with water. Add sufficient quantity of water to prepare solutions of desired concentrations.

Phosphate

Phosphorus occurs in natural waters and waste waters as phosphates. These are classified as orthophosphates, condensed phosphates, and organically bound phosphates. Here the concentration of dissolved orthophosphates in water is determined. To estimate the phosphate content Sample water is reacted with ammonium molybdate in an acidic medium and the resulting phosphomolybdate is reduced to molybdenum blue complex with amino-naphthol–sulphonic–acid [13].

Reagent Preparation for phosphate

ANSA solution: Dissolve 3.7 g of sodium sulphate (Na₂SO₃ )in 100ml of water. Add 0.1 g of 1-amino-2-napthol-4 sulphonic acid and 6.2 g of sodium metabisulphite(Na₂S₂O₅).
**Ammonium Molybdate Solution**: Dissolve 48g of ammonium molybdate in 800ml of water. Add 25ml of ammonium hydroxide (sp. Gr. 0.9) and dilute to 1 litre with water. In order to prepare Phosphate stock solution of 100ppm, dissolve 0.1433 g of potassium dihydrogen phosphate (KH$_2$PO$_4$), dried at 105°C for 1 hour, in water and dilute it to 1 litre. Dilute 10ml of this stock solution with 100 ml of water to prepare standard solution of 10ppm. The absorbing wavelength and the non-absorbing wavelength are determined to be 645 nm and 815 nm respectively from the absorption spectrum of sample solutions.

**Ammonia**

Ammonia is present naturally in surface and waste waters. The Nessler’s reagent is employed for the determination of Ammonia in water [14]. To study the ammonia content, the water sample is reacted with Nessler’s reagent (K$_2$HgI$_4$) to produce a reddish brown colloidal compound. In order to prepare the standard solution of 10 ppm, dissolve 4.718 g of ammonium sulphate [(NH$_4$)$_2$SO$_4$] in water and dilute to 1 litre. Dilute 10 ml of this solution to 1 litre. The absorbing wavelength and the non-absorbing wavelength are determined to be 425 nm and 640 nm respectively from the absorption spectrum of sample solutions.

**Reagent Preparation Ammonia**

Dissolve 100g of anhydrous mercuric iodide (HgI$_2$) and 70g of anhydrous potassium iodide (KI) in small volume of water. Add this mixture slowly with stirring, to a cooled solution of 160g of sodium hydroxide in 500ml of water. Dilute the mixture to 1 litre. Store the
solution in dark for 5 days and filter twice before using. This has a shelf life of one year.

3.4 Results and discussions

The reagents and standard solutions of iron, phosphate and ammonia are prepared and the dual wavelength evanescent wave sensor is utilised for sensing the traces of these components in standard solutions as well as in the boiler feed water of a power plant. The probing wavelengths are selected from the absorption spectrum of each species.

3.4.1 Iron

![Absorption of Iron in water (1000 ppb and 500 ppb)](image)

Figure 3.2 Absorption of Iron in water (1000 ppb and 500 ppb)

The absorption spectrum of Iron is shown in figure. 3.2. The probing wavelengths are selected from the absorption spectrum. 510 nm corresponding to the absorption peak is selected as the analytical
wavelength and 640 nm is selected as the non-absorbing reference wavelength since the absorption at this particular wavelength is very small. The sensor output corresponding to Iron concentration in water from 100 ppb to 1000 ppb is given in the figure. 3.3. The respective result obtained using spectrophotometer is also shown in figure. The sensor showed good repeatable, linear results in the measurement of iron concentration in water from 100 ppb to 1000 ppb as shown and the sensitivity of measurement is 5.8 μV/ppb. Water samples from a power plant is collected and checked with the developed sensor. The results are found matching with the spectrophotometer results and it is depicted in table 3.1.

![Figure 3.3 The response of spectrophotometer and sensor for different concentration of Iron in water](image-url)
Chapter 3

Table 3.1 The comparison of spectrophotometer and the concentration estimated from dual wavelength evanescent wave sensor for iron

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Concentration estimated with spectrophotometer (ppm)</th>
<th>Concentration estimated from the developed instrument (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP Drum 1</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>LP Drum 2</td>
<td>0.19</td>
<td>0.20</td>
</tr>
<tr>
<td>Hp Drum 1</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>Hp Drum 2</td>
<td>0.25</td>
<td>0.26</td>
</tr>
</tbody>
</table>

3.4.2 Phosphate

From the absorption spectrum of phosphate solution the absorbing wavelength is chosen as 645 nm and a non-absorbing wavelength as 815 nm is selected.

![Figure 3.4](image)

**Figure 3.4** The response of spectrophotometer and sensor for different concentration of Phosphate in water.

Spectrophotometric and sensor response of Phosphate sample for a concentration range of 1ppm to 20ppm are given in figure, 3.4. Absorption of the sample increases from 0.039 to 0.65 as the
Concentration measurements of ammonia, phosphate and iron in water concentration varies from 1 ppm to 20 ppm. At the same time as the concentration varies from 1 ppm to 20 ppm, the sensor output increases from 1.37 mV to 14.9 mV. The sensitivity observed is 0.72 mV/ppm. The spectrophotometric results and the sensor output have one to one correspondence and they are linear within the range. The water samples from the different locations of a power plant are collected to evaluate the performance of the developed sensor and it is depicted in the table 3.2.

Table 3.2 The comparison of spectrophotometer and the concentration estimated from dual wavelength evanescent wave sensor for phosphate

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Concentration estimated with spectrophotometer (ppm)</th>
<th>Concentration estimated from the developed instrument (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP Drum 1</td>
<td>17.5</td>
<td>17.48</td>
</tr>
<tr>
<td>LP Drum 2</td>
<td>20</td>
<td>19.5</td>
</tr>
<tr>
<td>Hp Drum 1</td>
<td>6.5</td>
<td>6.52</td>
</tr>
<tr>
<td>Hp Drum 2</td>
<td>6.4</td>
<td>6.38</td>
</tr>
</tbody>
</table>

3.4.3 Ammonia

From the absorption spectrum of the ammonia solution, 425 nm and 640 nm are selected as the absorbing and non-absorbing wavelengths respectively. Figure. 3.5 represents the spectrophotometric and sensor response for Ammonia sample. Here as the concentration increases from 100 ppb to 600 ppb, the absorption of the sample increases from 0.025 to 0.090. Since the absorption is very low, the response of the fiber optic sensor is found to vary from 0.9 mV to 3.2 mV. From this graph it is evident that as the concentration of the sample increases from 100
From ppb to 600 ppb, the output of the sensor and the spectrophotometer is almost matching and shows linear response. The sensitivity of the sensor is 5.6 μV/ppb. The water samples from different locations of a power plant is collected and estimated the concentration of the sample using the spectrophotometer and the developed sensor. The results obtained are shown in table 3.3.

**Figure 3.5** The response of spectrophotometer and Sensor for different concentration of Ammonia in water.

**Table 3.3** The comparison of spectrophotometer and the concentration estimated from dual wavelength evanescent wave sensor for ammonia

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Concentration estimated with spectrophotometer (ppm)</th>
<th>Concentration estimated from the developed instrument (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP Drum 1</td>
<td>0.45</td>
<td>0.455</td>
</tr>
<tr>
<td>LP Drum 2</td>
<td>0.55</td>
<td>0.552</td>
</tr>
<tr>
<td>Hp Drum 1</td>
<td>0.32</td>
<td>0.324</td>
</tr>
<tr>
<td>Hp Drum 2</td>
<td>0.38</td>
<td>0.379</td>
</tr>
</tbody>
</table>
3.5 Conclusion

A sensitive and useful design of dual wavelength probing scheme for evanescent wave based FOS has been developed. The developed sensor is used for the measurement of traces of dissolved iron, ammonia and phosphate in water. The use of dual wavelength probing scheme for fiber optic evanescent wave sensor enhanced selectivity and repeatability. Moreover this design makes use of low cost components which makes the system cost effective, simple and portable. The comparative evaluation between the sensor output and spectrophotometric analysis bears a one to one correspondence. Hence this system can be employed for water sample analysis at a much simpler and cheaper manner in such needy environments.

References


concentration of silica in water with dual wavelength probing, Rev. Sci. Instrum., 81, 035111-1-5, 2010


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