Chapter 5

EVANESCENT WAVE FIBRE OPTIC SENSOR TO DETECT
NITROGEN DIOXIDE

Abstract
A novel method for the detection of pollutant and highly toxic nitrogen
dioxide gas is described in this chapter. This fibre optic gas sensor works on
the principle of evanescent wave absorption phenomenon. Here, an NO₂
sensitive material, metal phthalocyanine, incorporated along with an
optical fibre acts as the sensing element. Investigations on the sensitivity of
this device with different metal phthalocyanines were carried out and the
reusability of the device was also verified.

5.1 Introduction:

The tri-atomic molecule NO₂ is a highly reactive gas and it combines with ambient
oxygen to form mixture of various oxides of nitrogen. This toxic gas has a major
contribution in the atmospheric pollution process. The presence of NO₂ in atmosphere is
injurious to the plants, animals and human beings. It reduces the growth process of
plants and enhances the illness rate of animals and human beings. Its affinity to water is
the main cause for formation of acid rain. There are many different methods for the
quantitative detection of nitrogen dioxide in a gaseous sample. Various NO₂ estimation
techniques depend on photometric (absorption, fluorescence, etc), calorimetric,
adsorption and chemiluminescence measurements. Apart from these conventional
techniques, recently a new method involving certain organometallic materials, viz.
metal phthalocyanines, is coming up for the effective detection of NO₂ gas. The
electrical, optical and mass addition properties of metal phthalocyanines have been
utilised for the design of a class of NO₂ sensing devices.
Metal phthalocyanines have attracted a great deal of attention for a long time because of their unique properties such as semiconductivity, photoconductivity etc. Another important feature of metal phthalocyanine is its chemical and thermal stability. As a result they have drawn attention in many potential applications like semiconductor devices, optical data storage, etc. Metal phthalocyanines exhibit large and fast nonresonant optical nonlinear response owing to the presence of delocalised two dimensional \( \pi \) electrons. Their nonlinear properties have been well investigated using techniques like degenerate fourwave mixing (DFWM), Z-scan etc. Also phthalocyanines are good optical limiters as they show excited state absorption (ESA). Apart from these, MPcs were extensively used in gas sensing applications. Due to their high sensitivity to NO\(_2\) and their superior thermal and chemical stability, they offer good potentiality for NO\(_2\) detection. Phthalocyanines allow incorporation of different metal atoms and a number of modifications can be achieved by substituting side groups in the molecular structure and thus we can influence its physical and chemical properties. Reversibility of this material makes them more attractive as a good gas sensing material. Also, many of these metal substituted phthalocyanines can be vacuum sublimed without much difficulties to give stable films and hence possess technological easiness to incorporate them in different sensing designs.

Many groups of workers have studied the electrical conductivity of metal phthalocyanines in the presence of NO\(_2\) gas and developed different amperometric gas sensors based on MPC. Since MPcs are p type organic semiconductors, they exhibit excellent sensitivity to electron acceptor gases such as NO\(_2\) even at low concentrations. Gas adsorption on the surface of these MPC thin films follow charge transfer reactions which induce the generation of charge carriers and hence enhances the conductivity and in principle provides the basis for the development of a sensing system for NO\(_2\). Though this technique has certain limitations, the possibility of using organic semiconducting materials for the sensing purpose is due to the following two reasons. One thing is that the electrical conductivity of organic semiconductors can change by many orders of magnitude when a gas adsorbs on their surface, which make them ideal for detecting very low concentrations of pollutants. The second thing is that the organic molecules...
may be structurally modified which may increase their selectivity to particular gaseous species. We can find from the literature that a variety of metal substituted phthalocyanines were studied for NO₂ detection by different researchers by exploiting its electrical conductivity property. A Krier et al studied the electrical behaviour of Chloro-Aluminium-Phthalocyanine (ClAlPc) thin films in the presence of NO₂. They measured the changes in the dark conductivity of these films on exposure to NO₂ gas at different temperatures. S Dogo et al have reported their results on the electrical conductivity studies of copper phthalocyanine (CuPc) thin film in the presence of NO₂. C Haman et al have analysed the NO₂ sensitivity on monoclinic and triclinic modifications of lead phthalocyanines. Y Sadaoka et al investigated the influence of the changes in topography and structure of film on the electrical properties of MPc film and also on the sensitivity of the same to NO₂ gas.

Another widely accepted method of detection of NO₂ is by using Quartz Crystal Microbalance (QCM). This is achieved by forming either Langmuir-Blodgett (LB) films or thin films of MPc on a quartz crystal microbalance, which is oscillating at a particular frequency. NO₂, an electron acceptor gas, forms a donor-acceptor complex with MPc and the resulting mass increase can be measured by the frequency shift of the QCM. Thus sensing principle of QCM is the mass loading by adsorption of NO₂ on the MPc surface and the resulting change in the oscillation frequency. S R Kim et al synthesised a bulky alkyl-group-substituted MPc and stacked it as a LB multilayer on a QCM. They measured the adsorption capacity of NO₂ by different metal substituted phthalocyanines. A complete regeneration of the sensor is not possible in this method. It is observed that prolonged heat treatment at elevated temperatures gave some recovery. But in the repeated adsorption tests of NO₂, the sensor could not reproduce its initial frequency change satisfactorily. This is one of the major limitations of this method.

Surface Plasmon Resonance (SPR) technique is another approach utilising MPc for the detection of NO₂. Very thin layers of metallophthalocyanines are used in this technique for the detection of NO₂, which is formed on a thin metal layer. In this
case, the change in the optical properties of the active layer in response to external ambients are measured by monitoring the coupling of photons to surface plasmons at the interface between a metal and an active layer. There will be a shift in the SPR curve to higher angles on exposure to NO₂ and also we can see a small decrease in the depth of the SPR curve. The effect is partially reversible although the time required is very large.

The optical properties of metal substituted phthalocyanines in an NO₂ environment forms one of the major parametric studies undertaken by different research groups. D Campbell et al conducted electrical conductivity and optical absorption studies simultaneously for lead phthalocyanines (PbPc) thin films exposed to NO₂. In another paper D Campbell et al investigated the spectral response of monoclinic and triclinic phases of PbPc thin films in the presence of NO₂. They observed that visible and IR spectra of both phases are significantly affected by the presence of NO₂.

The above mentioned methods have numerous disadvantages and limitations. In amperometric NO₂ sensors, the detected signal is affected by electromagnetic as well as radio frequency interference. The regeneration possibility of this device is very poor and the signal response is also influenced by temperature. In the case of quartz crystal microbalance (QCM), a complete regeneration of the sensor is not possible. Repeated adsorption tests of this device limits its reproducibility.

In the coming sections, we discuss a novel method for NO₂ detection that eliminates most of the difficulties and disadvantages of the conventional techniques.

5.2 Optical fibre based sensor design:

An optical fibre based NO₂ sensing system is designed and fabricated during the course of our investigation. In this fibre optic sensor, we have incorporated metallophthalocyanines into a multimode cylindrical waveguide structure by replacing a portion of the cladding region. A uniform coating of highly purified MPc is deposited
by thermal evaporation at a reduced pressure of the order of $10^{-5}$ mbar. The structure of the sensor element is as shown in figure 5.1.

![Figure 5.1 The structure of the fibre optic gas sensor element](image)

Metal substituted phthalocyanines are widely accepted for their strong affinity to nitrogen dioxide and optical absorption behaviour at NO$_2$ atmosphere. Here, in the fibre optic sensor, the evanescent waves at the sensor region get affected by the change in the optical property of the MPc cladding in the presence of NO$_2$ gas. This is utilised for the characterisation of this novel optical fibre sensor design. Besides its simple structure, this fibre optic NO$_2$ sensing device offers numerous advantages. Using this sensor it is possible for in-situ detection of NO$_2$, which is highly useful in mines and industries. These evanescent wave fibre optic sensors are also immune to electromagnetic interference, possess multiplexing capability etc.

5.3 Experimental details:

The schematic of the experimental set-up is as shown in figure 5.2. Light from a diode laser emitting at 670 nm (4.25 mW) is focussed at one end of a multimode plastic clad silica fibre (200/380 μm) and the guided waves are detected using a fibre optic powermeter (Meggar OTP 510) at the other end of the fibre. The sensor head is placed in a chamber that can be evacuated to lower pressures. Nitrogen dioxide gas is allowed to flow through an inlet port provided in the chamber. The investigations have been carried out for different NO$_2$ gas concentrations in the chamber that is evacuated to
rotary vacuum \((10^{-3} \text{ mbar})\) and by employing different metal substituted phthalocyanine at the sensor head.

![Figure 5.2 Schematic of the experimental set-up for the nitrogen dioxide detection](image)

**Figure 5.2** Schematic of the experimental set-up for the nitrogen dioxide detection

A length of 0.04 m of the cladding of the multimode plastic clad silica fibre is replaced with uniform coating of a metal phthalocyanine. The thickness of the MPc coating is about 140 nm. The structure of the MPc is as shown in figure 5.3 and its synthesis and purification procedures are discussed elsewhere.\(^{103}\)

![Figure 5.3 Molecular structure of the metal phthalocyanine. \(M - \text{Cu, Pb}\)](image)
We have carried out experiments with different metal substituted phthalocyanines as the sensor element. Investigations have been carried out with Copper phthalocyanine (CuPc), Lead phthlocyanine (PbPc) and Samarium diphthalocyanine (SmPc) coated at the uncladded region of the fibre to form efficient gas sensing system for the detection of NO$_2$ gas.

5.3.1 FOS with CuPc sensing element:

Copper phthalocyanine shows very good affinity to NO$_2$ and it provides a very rapid response. The absorption spectrum of CuPc thin film is as shown in figure 5.4(a) and the peak wavelengths are at 620 nm and at 697 nm.

![Absorption spectrum of Copper phthalocyanine thin film shows blue shift after exposure to NO$_2$ gas. (a) Spectrum before NO$_2$ exposure (b) Spectrum after NO$_2$ exposure](image)

**Figure 5.4** Absorption spectrum of Copper phthalocyanine thin film shows blue shift after exposure to NO$_2$ gas. (a) Spectrum before NO$_2$ exposure (b) Spectrum after NO$_2$ exposure
The flow of NO$_2$ gas through the sensor chamber is maintained steady and the interrogating wavelength is 670 nm from a 4.25 mW diode laser. As soon as NO$_2$ molecules reach the sensor element, it gets adsorbed on the surface of the MPc. Adsorption of NO$_2$ molecules on CuPc leads to a decrease in intensity and a shift in the 697 nm absorption peak towards 670 nm. This leads to a variation of the output power through the fibre due to change in the evanescent wave absorption. At the interface of the SiO$_2$ core and CuPc cladding in the sensor region, attenuated total internal reflection (ATR) takes place. The variation of the output power with time for this sensor is given in figure 5.5.

![Graph showing the variation of output power with time for CuPc coated fibre optic sensor at three different concentrations of NO$_2$.](image)

**Figure 5.5** Variation of the output power with time for CuPc coated fibre optic sensor at three different concentrations of NO$_2$.

The plots show the sensor response to three different nitrogen dioxide concentrations. The variation of output is attributed to the blue shift in the absorption peak of CuPc on NO$_2$ adsorption (figure 5.4). S R Kim et al observed a similar shift for the CuPc
Langmuir-Blodget film exposed to NO₂ gas. They found that the strong absorbance at 690 nm and at 630 nm decreased in intensity and new absorbance at 580 nm appeared. These changes are characteristic of the formation of MPC radical cation. D Campbell et al in their paper studied the spectral response of monoclinic and triclinic lead phthalocyanines in the presence of NO₂. In the NO₂ environment, they have also observed a decrease in intensity of the absorption peak.

5.3.2 FOS with PbPc sensing element:

Different groups have carried out extensive research on electrical and optical properties of lead phthalocyanine (PbPc) thin films in the presence of NO₂ gas. In our investigation, we have examined the role and characteristics of PbPc in the optical fibre sensor design.

![Figure 5.6 Variation of the output power with time for lead phthalocyanine coated fibre optic sensor at two different NO₂ concentrations.](image-url)}
The variation of the output power of the light propagating in the fibre optic sensor system with time using PbPc thin film coating on the sensor element is as shown in figure 5.6. The plot clearly reveals the NO₂ affinity of lead phthalocyanine deposited on the sensor region and the response of the device at two different gas concentrations. It is observed that the variation is small at low concentrations of NO₂. At higher concentrations, fast response followed by a saturation behaviour is observed.

5.3.3 FOS with SmPc sensing element:

We have also characterised the Samarium diphthalocyanine coated evanescent wave fibre optic sensor for NO₂ detection during the course of our investigations. SmPc has a sandwich structure as shown in figure 5.7 and shows very good response to NO₂ gas. Two phthalocyanine clouds sandwich samarium atom and hence it is influenced by higher π electron contribution.

![Molecular structure of Samarium diphthlocyanine](image)

**Figure 5.7** Molecular structure of Samarium diphthlocyanine

A uniform coating of SmPc is deposited on the uncladded region of a multimode optical fibre by thermal evaporation procedure under reduced pressure. The absorption peak of SmPc thin film is at 653 nm and in the NO₂ environment (2 mbar) the peak shifts to 679 nm as shown in figure 5.8.
Figure 5.8 The spectral response of Samarium diphthalocyanine (a) Before NO₂ exposure (b) After NO₂ exposure

This spectral response has been exploited in the design of an evanescent wave fibre optic sensor. The response of this SmPc coated fibre optic evanescent wave sensor is observed for three different NO₂ environments and the variation of the output power with time is recorded and analysed. The output power variation with time at different NO₂ concentrations is as shown in figure 5.9. Even in this case the response is faster at higher concentrations.
Figure 5.9 Variation of the output power with time for SmPc coated fibre optic sensor at three different NO₂ concentrations

S R Kim et al have investigated the regeneration capability of NO₂ sensors based on quartz crystal microbalance (QCM) by forming mono and multilayer LB films of Metallophthalocyanines. At room temperature they have observed that the regeneration of the sensor is not satisfactory. But satisfactory regeneration was found when QCM was treated in vacuum at 170°C for 30 minutes. We have also checked the SmPc coated fibre optic sensor for its regeneration capability. This is achieved by helically winding a kandal wire across the sensor head and applying an ac voltage across it. The temperature (≈140°C) was measured at the sensing region using a thermocouple. The reversibility of the sensor is illustrated in figure 5.10. It has been observed that the response of the device keeps on changing on repeated regeneration trials. It was also seen that the response becomes faster after repeated NO₂ exposures.
and subsequent heating. This suggests that the method adopted for regeneration is not completely satisfactory.

![Graph showing the response of Samarium diphthalocyanine coated fibre optic sensor under repeated NO₂ exposure and heating.](image)

**Figure 5.10** Plot showing the response of Samarium diphthalocyanine coated fibre optic sensor under repeated NO₂ exposure and heating.

5.4 Comparative analysis:

S R Kim et al investigated the NO₂ response of different metal substituted phthalocyanines, which are stacked in a multilayered form on a quartz crystal microbalance (QCM) by Lagmuir-Blodgett (LB) method. They tried with four different phthalocyanines like H₂Pc, PbPc, CuPc, and CoPc. They found that the central metal atom has a profound effect on the response pattern, rate of adsorption of NO₂ molecule, adsorption capacity and adsorption kinetics. We have also carried out a comparison of the response of the fibre optic sensors developed using PbPc, CuPc and SmPc. Figure 5.11 shows the variation of the output power with time in the case of
these three sensors carried out at a pressure of 2 mbar NO₂ environment. Even though the response of these devices remain more or less the same, it is seen that the fibre optic sensor system using SmPc gets saturated only after prolonged exposure to NO₂. This suggests that SmPc has a greater capacity to adsorb NO₂. Reversibility of the sensor was tried in the case of CuPc and SmPc. It was seen that CuPc does not get regenerated back to its initial condition on heating (≈140°C) whereas SmPc exhibits partial recovery.

Figure 5.12 Variation of the output power with time for three different metal phthlocyanine-coated optical fibre sensors at an NO₂ concentration of 2 mbar.

5.5 Conclusion:

We have designed and developed a new technique based on evanescent wave absorption in optical fibre for the NO₂ detection using MPc. It was observed that effective and
sensitive detection of NO₂ can be done by this method. It has been established that the response of fibre optic sensors developed using SmPc, PbPc and CuPc shows more or less similar response. But, fibre optic sensors based on SmPc exhibit saturation only after prolonged exposure to NO₂. Even though SmPc based sensor exhibits regenerative capability, the performance is not fully satisfactory.