Chapter 4

Metallophthalocyanine Nitrogen Dioxide Gas Sensor
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4.1 Introduction

A gas sensor is a device that allows conversion of chemical energy into electrical signal. It gives a response in terms of electrical signal after receiving a stimulus of a chemical nature. In general, it allows the direct conversion of the qualitative and quantitative information of an analyte or gas in a physical signal. Gas sensors using metallophthalocyanine (MPc) materials lead to change in the number of charge carriers when gas molecules come in the vicinity of it, they are referred as electrical sensors.

Phthalocyanine (Pc) is a conjugated heterocyclic 18π electron containing compound. In Pc system, methane-bridges of porphyrin are replaced by azabridges and, therefore, Pcs can be regarded as tetrabenzotetra-azaporphyrins. The family of MPc has been found to be highly sensitive with strong oxidizing gases such as NO₂ [1]. MPcs are coordination compounds in which Pc ring is coordinated with a central metal atom and it exhibits a unique combination of chemical, electrical and optical properties [2] which made it as a versatile organic material. CuPc, CoPc, NiPc, ZnPc, FePc are all belongs to this family of organic molecular solids. Their composition consists of hydrogen, carbon, nitrogen and substituted metal atom. In other words, MPc is a symmetrical 18 π electron aromatic macrocycle. The properties exhibited by MPcs are practically important for dyes, colorants and catalysis [3, 4]. Their semiconducting properties are exploited for photoconducting, solar cells as well as gas sensing applications [5]. One of the most important advantages of MPcs over other organic materials is their thermal and chemical stability. The gas sensing principle is based on the change of conductivity upon the adsorption of gas species at the surface [6, 7]. Suspended gate field effect transistors (FETs) are used for NO₂ detection at room temperature with low power consumption [8]. Nickel phthalocyanine (NiPc) films were deposited by vacuum sublimation for NO₂ gas
sensing. This chapter includes synthesis details, various characterizations and NO$_2$ gas sensing properties of CuPc, CoPc, NiPc, ZnPc, FePc. The samples in the form of pellets were prepared for the gas sensing study.

4.2 Synthesis of Metallophthalocyanine

MPcs were synthesized by chemical method by phthalic anhydride-urea route. Copper phthalocyanine (CuPc), Cobalt Phthalocyanine (CoPc), Nickel phthalocyanine (NiPc), Zinc phthalocyanine (ZnPc) and Iron phthalocyanine (FePc) were synthesized by chemical route which earlier explained in chapter 3 in section 3.2.

Table 4.1: Synthesized MPc materials and yield of the product.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>MPc material</th>
<th>Yield (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuPc</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>CoPc</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>NiPc</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>ZnPc</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>FePc</td>
<td>41</td>
</tr>
</tbody>
</table>

The average yield of the products of MPcs is 42.2 weight %. The synthesized materials were crushed with the help of mortar and pestle to the fine powder. Figure 4.1 shows the photographs of CuPc, NiPc, CoPc, FePc and ZnPc powders respectively. The synthesized MPc material was characterized with X-ray diffraction, absorption spectra, IR spectra and TGA/DTA. The same material was used for sample preparation using different techniques such as press technique, spin coating technique and electrophoretic deposition technique. In this chapter gas sensing characteristics of MPc samples in the form of pellet are discussed.
4.3 Characterisation of synthesised metallophthalocyanines

Synthesized materials of MPcs were characterized by using the characterization techniques such as X-ray diffraction (XRD), UV-Visible absorption spectra, Fourier Transform Infrared spectra (FTIR), Thermogravimetric Analysis and Differential Thermal Analysis (TGA/DTA) and Scanning Electron Microscopy (SEM).

4.3.1 X-ray Diffraction

X-ray diffraction characterization of as synthesised MPc powder was carried out using a Philips X-ray diffractometer (Model PW 1729) with Cu Kα radiation (λ = 1.5406 Å) to analyze synthesized material for crystal structure as well as particle size determination. The results of XRD pattern of CuPc, CoPc, NiPc, ZnPc and FePc are discussed below.

XRD spectra and positions of XRD peaks of CuPc are shown in Figure 4.2. It is found to be in good agreement as in literature and JCPDS number 11-0893. CuPc is found to be in stable β form. The average grain size is 56.42 nm which is calculated using schererer formula.
Figure 4.2: X-ray diffraction pattern of copper phthalocyanine powder.

X-ray pattern given in Figure 4.3 belongs to NiPc powder. The lattice constants are $a = 1.49$ nm, $b = 0.47$ nm, $c = 1.99$ nm and $\beta = 121.15^\circ$. It is found to be in good agreement with data in JCPDS number 11-0744. NiPc is found to be in stable $\beta$ form and the average grain size is 56.42 nm.

Figure 4.3: X-ray diffraction pattern of nickel phthalocyanine powder.

The XRD pattern of synthesised CoPc powder is shown in figure 4.4. The peaks are obtained at 2$\theta$ values of 7.1°, 9.2° and 14° which agree with the JCPDS data file 14-0948. The data obtained for synthesized powder matches with the $\beta$-
cobalt phthalocyanine. The average grain size is calculated for the synthesized material of CoPc and its value is 38.39 nm.

Figure 4.4: X-ray diffraction pattern of cobalt phthalocyanine powder.

The crystal structure of ZnPc powder has been studied by X-ray diffraction. Figure 4.5 shows the X-ray diffraction spectrum of ZnPc in powder form. The experimental peaks were compared to those corresponding to the $\beta$ polymorph of zinc phthalocyanine (JCPDS number 39-1882, monoclinic system; cell parameters $a=14.56$, $b=4.87$, $c=17.27$, $\beta=106.15$). Main peaks of the $\beta$ polymorphs appear in the experimental spectrum showed the presence of these crystals in ZnPc powder. The average crystal size calculated using the Scherrer’s formula is 69.26 nm [9].

Figure 4.5: X-ray diffraction pattern of zinc phthalocyanine powder.
XRD of FePc is shown in Figure 4.6 and it reveals the 2θ peak at 6.2°. The data matches with the α− morphology of FePc. The average grain size is calculated to be 72.69 nm.

![X-ray diffraction pattern of iron phthalocyanine powder.](image)

**Figure 4.6:** X-ray diffraction pattern of iron phthalocyanine powder.

The morphology and grain size of the synthesised MPc materials are summarized in table 4.2.

**Table 4.2:** Morphology and grain size of synthesized MPc materials.

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>MPc material</th>
<th>JCPDS No.</th>
<th>Phase</th>
<th>Average grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuPc</td>
<td>11-0893</td>
<td>β</td>
<td>56.42</td>
</tr>
<tr>
<td>2</td>
<td>NiPc</td>
<td>11-0744</td>
<td>β</td>
<td>29.87</td>
</tr>
<tr>
<td>3</td>
<td>CoPc</td>
<td>14-0948</td>
<td>β</td>
<td>38.39</td>
</tr>
<tr>
<td>4</td>
<td>ZnPc</td>
<td>39-1882</td>
<td>β</td>
<td>69.26</td>
</tr>
<tr>
<td>5</td>
<td>FePc</td>
<td>22-1771</td>
<td>α</td>
<td>72.69</td>
</tr>
</tbody>
</table>
4.3.2 Ultraviolet-Visible Absorption Spectra

The UV-Visible absorption spectrum of MPcs originates from molecular orbitals within the aromatic 18π electron system and from overlapping orbitals within the central atom [10-12]. All spectra display the existence of strong absorption bands in the range of 400 nm and 800 nm caused by the π-π* transitions of the conjugated macrocycle of 18π-electrons [13]. The high-energy side of the absorption spectrum shows a sharp absorption edge. The absorbance spectrum shows sharp increase in absorption at wavelength near the absorption edge of the threshold wavelength of the absorbance spectrum, the energy corresponds to this determines the optical band gap of the semiconductor material [14]. The central metal atom of the phthalocyanines influences the optical absorption spectrum [15].

Figure 4.7 shows the UV-Visible absorption spectra of CuPc, NiPc, CoPc, ZnPc and FePc. The solution of MPcs was prepared in N,N dimethyl formamide. Absorption spectra were obtained using absorption spectrometer JASCO V-607. The absorption peaks observed in Ultra Violet (UV) region from 200 nm to 350 nm reveals three peaks which are termed as soret band [16]. The peak of the Soret band indicates the presence of d band associated with the central metal atom. It is thought that π-d transitions are involved MPcs has partially occupied d-bands. The absorption bands in the region of 275 nm to 210 nm called the S-band, may be due to d-π* transition. The broad absorption band in the UV region is preceded by the UV absorption band edge of the phthalocyanine molecule.

The other band appears in the visible region between 500 nm to 750 nm. This band is named as Q-band. As observed from figure the distinct characterized peaks for MPc in this visible region can be interpreted in terms of π-π* excitation between bonding and antibonding molecular orbital. This band also shows the characteristic splitting called Davydov splitting. Davydov splitting is the splitting of bands in the electronic or vibrational spectra of crystals due to the presence of more than one interacting equivalent molecular entity in the unit cell. The high energy peak of the Q-band can be assigned to the first π-π* transition on the phthalocyanine macrocycle. The low energy peak of the Q-band is assigned to second π-π* transition [17]. Absorption due to π-π* transitions is reported to appear in the visible region at
wavelengths between 500 nm and 750 nm (Q band) exhibiting a doublet due to Davydov splitting [18].

Results obtained from the absorption spectra of MPcs shows the $\lambda_{\text{max}}$ values of CuPc, NiPc, CoPc, ZnPc and FePc as 547 nm, 663 nm, 658 nm, 700 nm and 660 nm respectively.

The absorption coefficient ($\alpha$) is related to the direct band transitions [19, 20]. The variation in absorption coefficient ($\alpha$) with photon energy for direct band-to-band transitions is of the form,
\[ \alpha = \alpha_0 \left( \frac{h \nu - E_g}{E_g} \right)^r \]  

(4.1)

Where,

\( E_g \) = Energy gap

\( h \) = Planck’s constant = 6.623 x 10\(^{-27}\) JS

\( \nu \) = Frequency of radiation.

\( r \) = \( \frac{1}{2} \) for allowed direct transitions and \( \frac{3}{2} \) for forbidden direct transitions.

Hence the absorption coefficient \( \alpha \) related to the photon energy \( h \nu \) can be expressed as,

\[ \alpha = \alpha_0 \left( h \nu - E_g \right)^{1/2} \]  

(4.2)

where, \( E_g \) is the difference between the valance band and conduction band also called as optical band gap. The direct allowed band gap can be determined by plotting \( \alpha^2 \) as a function of photon energy \( h \nu \) (eV). The plot of \( \alpha^2 \) versus \( h \nu \) (eV) yield a straight line for direct transitions as shown in figure 4.8 from which the extrapolation of linear portion to \( \alpha^2 = 0 \) near the absorption edge gives the band gap energy [21].

The plot of \( \alpha^2 \) versus \( h \nu \) near the absorption edge of the Q band of CuPc, NiPc, CoPc, ZnPc and FePc in DMF produce a linear fit over a range of 1.5 eV to 2.0 eV in \( h \nu \) as shown in Figure 4.8. The optical energy gaps of CuPc, NiPc, CoPc, ZnPc and FePc as seen from Figure 4.8 are 1.87 eV, 1.65 eV, 1.8 eV, 1.7 eV and 1.8 eV respectively.

![Figure 4.8](image.png)

\textbf{Figure 4.8:} The plot of \( \alpha^2 \) vs \( h \nu \) for a) CuPc, b) NiPc c) CoPc, d) ZnPc and e) FePc in lower energy band region (Q- band).
UV-Visible absorption spectra of Soret band of CuPc, NiPc, CoPc, ZnPc and FePc in DMF are shown in figure 4.9. The optical energy gaps of synthesized materials of CuPc, NiPc, CoPc, ZnPc and FePc as seen from Figure 4.9 are 3.2 eV, 2.75 eV, 2.9 eV, 5.75 eV and 6.05 eV respectively.

Figure 4.9: The plot of $\alpha^2$ vs $h\nu$ for a) CuPc, b) NiPc c) CoPc, d) ZnPc and e) FePc in higher energy band region (Soret band).

4.3.3 Fourier Transform Infrared Spectroscopy

IR spectra of synthesized powders were performed at room temperature using JASCO FT/IR-6100 type A infrared spectrophotometer in the spectral range 400 cm$^{-1}$ to 2000 cm$^{-1}$. Synthesized material material was mixed with IR-grad Pottassium Bromide (KBr) powder. Figure 4.10 shows IR spectra of CuPc, NiPc, CoPc, ZnPc and FePc. The region between 400 cm$^{-1}$ - 1350 cm$^{-1}$ has same type of nature or similar type of peaks in all MPcs, this is because the region corresponds to the skeleton of MPcs. The change in the spectral range from 1350 cm$^{-1}$ to 1550 cm$^{-1}$ for the Pcs with different metal atoms to be unique for each Pc [22, 23].
A series of weak absorption observed between 1700 cm\(^{-1}\) and 2000 cm\(^{-1}\) is due to the aromatic compound which is also same for all MPcs as expected [24, 25].

The bands appearing at 1166 cm\(^{-1}\), 1270 cm\(^{-1}\), 1290 cm\(^{-1}\) and 1295 cm\(^{-1}\) are assigned to the C-N in isoindiole and in plane band stretching vibration. The peak observed at 1606 cm\(^{-1}\) is due to the benzene ring skeletal stretching vibration. The band corresponding to C-C stretching in isoindole is observed at 1335 cm\(^{-1}\). The bands appearing at 874 cm\(^{-1}\) and 725 cm\(^{-1}\) were assigned to the C-H bending out of plane deformations. The peaks observed in the 700 cm\(^{-1}\) – 400 cm\(^{-1}\) interval originates from the vibrations in the benzene ring in interaction with the pyrrole ring. All MPcs show three strong peaks in the 1000-1200 cm\(^{-1}\) region. The middle band shows the highest intensity as compared to the other two peaks. The middle peak originates from the vibration mode of a pyrrole ring. The other two peaks are of in-plane deformation vibration of C-H bending in the ring [26]. The peak observed at 1333 cm\(^{-1}\) is due to

**Figure 4.10:** FTIR spectra of A) CuPc, B) NiPc, C) CoPc, D) ZnPc and (E) FePc
C-C in isoindole and peak at 1291 cm\(^{-1}\) is C-N in isoindole. Peak at 1093 cm\(^{-1}\) is C-H in plane deformation while C-H out of plane deformation is at 915 cm\(^{-1}\) and 876.4 cm\(^{-1}\). The peak at 781 cm\(^{-1}\) is due to C-N stretching vibration. The peak at 719 cm\(^{-1}\) indicates the macrocycle ring deformation [27].

4.3.4 Thermo Gravimetric Analysis/Differential Thermal Analysis

Thermal studies of MPcs studied to know thermal stability of metal phthalocyanines and decomposition behaviour at different temperatures on the detector DTG-60H. Figure 4.11 shows the thermogram of CuPc and CoPc powders.

![Thermogram of a) CuPc and b) CoPc.](image)

**Figure 4.11**: Thermogram of a) CuPc and b) CoPc.

It is observed from thermograms of different metallophthalocyanines that they do not have sharp melting point. They decompose at elevated temperature. It is observed that cobalt phthalocyanine is stable upto 410°C and starts decomposing at around 425°C. The decomposition products might be hydrocarbon, ammonia and metal oxide and different thermal events were observed. FePc, NiPc and CuPc show similar thermal pattern with slightly lower decomposition temperature for FePc and NiPc.

4.3.5 Scanning Electron Microscope images of synthesized material

SEM images of synthesized powders of CuPc, NiPc, CoPc, ZnPc and FePc are shown in Figure 4.12. SEM images shows the crystalline nature of MPcs.
Figure 4.12: SEM images of a) CuPc, b) NiPc, c) CoPc powders.
4.4 MPc sensor sample preparation in the form of pellets

Sensor samples of the synthesized MPc material were prepared in the pellet form. In order to prepare pellet of the synthesized material the powder was compacted in the form of pellets under the application of pressure for sufficient time to cure it using hydraulic press. The weight (200 mg) of the material used to prepare sensor sample was taken to get sufficient thickness, sturdiness and mechanical strength and kept constant throughout for all samples. Silver paste electrical contacts were made on either side of the pellet and then the pellet was used as a sensor.

Pellets were prepared with optimized pressure and optimized time of application of pressure. The initial resistance of the prepared pellet samples was measured for optimization. Figure 4.13 shows the change in resistance of CuPc pellet with different pressure applied with hydraulic press for a fixed time (2 minutes). It is seen that the resistance of the pellet decreases as pressure applied on the material to
make its compact form (Pellet) increases. The resistance reaches to the constant value of 120 MΩ at and above 8 ton pressure. Hence all the samples were prepared with 8 ton pressure. The samples with 8 ton pressure with different pressure applied were prepared and the resistance is measured.

![Figure 4.13](image1.png)

**Figure 4.13:** Resistance of the pellet with different pressure and constant time (2 minute) of application of pressure.

Figure 4.14 shows the change in resistance of pellet with different time of application of pressure. It is seen that the resistance decreases as the time to cure the material in compact form is increased up to 3 minutes. If applied time is more than 3 minute there is no change in resistance is observed. Hence all the samples were prepared with 8 ton pressure for pressure applied time of 3 minute. All the pellets were prepared at room temperature with the help of hydraulic press and the die set.

![Figure 4.14](image2.png)

**Figure 4.14:** Resistance of the pellet with constant pressure (8 ton) applied for different time duration.
Hence the samples were prepared in the form of pellets under the optimized conditions stated above. Figure 4.15 shows the photograph of the samples prepared in the form of pellets. For electrical measurements, electrodes of copper wires were attached to one of the surfaces of the pellets using silver paste. For the gas sensing properties study, pellets with silver paste electrodes were used. Pellets with silver paste electrodes were suitable for holding the pellets in the pellet holder constructed in the gas testing setup. The samples with copper wire electrodes and the silver paste electrodes are shown in figure 4.15.

![Figure 4.15: MPc pellets with copper wire and silver electrical contacts on the surface.](image)

### 4.5 Resistivity determination of the MPc

Resistivity of the pellet sample of CuPc is determined by measuring physical dimensions such as width (\(l\)), area of cross section (\(A\)) and resistance (\(R\)). Two surfaces of the sample are coated with silver paste and for electrical contacts copper wire electrodes were attached. The resistivity is calculated using formula,

\[
\rho = \frac{RA}{l}
\]  

(4.2)

Where,

- \(R\) = resistance of the sample,
- \(A\) = cross sectional area of the sample and
- \(l\) = width of the sample.
Figure 4.16 shows the pellet coated with silver paste and the attached electrodes. The width of the pellet is considered as the length and the area of one of the faces is considered as area of cross section of the element of which the resistivity is to be determined. The width of the pellet (l) was 0.212 cm and the diameter of the pellet was 1.3 cm. Hence the area of one surface (cross sectional area A) is 1.33 cm$^2$.

![Diagram of CuPc pellet with silver paste coating and attached electrodes.](image)

Figure 4.16: MPc pellet with both the surfaces coated with silver paste.

The resistance of the sample is determined from the I-V characteristics. The resistance of the sample is $170 \times 10^6 \ \Omega$. The resistivity of CuPc is calculated using equation 4.2 is $1.066 \times 10^9 \ \Omega \text{cm}$. 
4.6 Nitrogen dioxide sensing characteristics of MPc sample in pellet form

Nitrogen dioxide sensing properties of CuPc, NiPc, CoPc, ZnPc and FePc were studied in the laboratory by using a special experimental setup constructed in the laboratory. The change in the resistance of the sample in the vicinity of gas was monitored using Keithley- 2000 electrometer. The electrometer was interfaced with the computer and with special software readings were noted in the suitable time interval. Suitable volume of nitrogen dioxide gas was inserted into the chamber by using a syringe.

4.6.1 Nitrogen dioxide sensing properties of CuPc pellet

An evaluation of the gas sensing performance is carried out in a glass chamber maintaining the controlled environment in it at room temperature. CuPc sensor samples in the form of pellets were exposed to different nitrogen dioxide concentrations in atmospheric air in the closed glass chamber with known volume. The typical plot of the variation of sample resistance after insertion of nitrogen dioxide (2 Volume %) gas with the exposing time is shown in Figure 4.18. The resistance was monitored continuously in the time interval of 30 seconds. The sample was allowed to stabilize for 30 minute before the insertion of nitrogen dioxide mixed air into the gas chamber. The pellet sample is allowed to expose to nitrogen dioxide (NO₂) with 2 volume % concentration for 10 minute. Initial resistance of the sample
was 287 Mohm. It is seen that the resistance decreased with exposing time after exposing the sensor to the air mixed with nitrogen dioxide gas (region A-B). The resistance was decreased to 30 MOhm in 10 minute. It is seen from the figure that the resistance of the sensor increases after NO₂ gas was shut off. Recovery starts by removing the mixture of air and nitrogen dioxide surrounded by the sample and exposed it to the air atmosphere. It is seen from Figure 4.18 that the resistance increases in the recovery region. The increased resistance from 30 MOhm within 20 minute in the recovery stage was to 50 MOhm. The recovery region (region B-C) is shown for 20 minute.

![Figure 4.18: Typical response of CuPc pellet exposed to NO₂ gas.](image)

However the resistance of the sensor was not recovered to the original value within 2 hours of the recovery time. The decrease in resistance of the sensor sample that is the increase in the conductivity in presence of NO₂ gas molecules in the surrounding of the sensor sample can be explained as follows.

When the gas molecules are adsorbed on sample surface, MPcs may be donating electrons to gas and holes are created and delocalize it on phthalocyanine ring. The gas molecules contact with π- electron network of phthalocyanine causes the transfer of electrons from phthalocyanine ring to adsorbed gas molecules. Hence the adsorbed gas molecules may act as an acceptor and become negatively charged and
phthalocyanine ring becomes positively charged. These holes contribute the increase in conduction and hence the resistance of the sample decreases [28]. The gas sensing process can be explained into three steps as equations (4.3 - 4.5). First the adsorption of gas on the solid surface, second the charge transfer between the adsorbed gas and the surface and third the charge delocalization [29].

\[
\text{gas + surface} \rightarrow \text{gas - surface} \quad (4.3)
\]

\[
\text{gas-surface} \rightarrow \text{gas}^- \text{surface}^+ \quad (4.4)
\]

\[
\text{gas}^-\text{surface}^+ \rightarrow \text{gas}^- \text{surface} + \text{hole} \quad (4.5)
\]

Different CuPc sensor samples were tested to different NO\textsubscript{2} gas concentrations like 0.05 volume %, 0.1 volume %, 0.5 volume %, 2 volume %, 3 volume % and 5 volume %. The resistance is monitored with 30 seconds interval and the response is plotted. The response of CuPc samples with different NO\textsubscript{2} concentration is shown in Figure 4.19. in terms of instantaneous sensitivity \(S(t)\) given by equation 4.6.

\[
S(t) = \left( \frac{R_a - R_g}{R_a} \right) \times 100\% \quad (4.6)
\]

Where,

- \(S(t)\) = instantaneous sensitivity,
- \(R_a\) = initial resistance of the sample,
- \(R_g\) = sample resistance in the presence of gas at any time \(t\).

**Figure 4.19:** Response of CuPc pellets exposed to various NO\textsubscript{2} concentration.
Sensitivity of CuPc sample to different concentrations of nitrogen dioxide after 50 minute exposure ($S_{50}$) is shown in Figure 4.20. It is seen from the graph that the sensitivity ($S_{50}$) increases with increase in NO$_2$ concentration and remains constant at high NO$_2$ concentration. With increasing the gas concentration, number of holes that is hole concentration increases till the saturation is reached. Hence increase in concentration of gas the conductivity of the sensor increases and finally remains constant.

![Graph showing sensitivity to NO$_2$ concentration](image)

**Figure 4.20:** Sensitivity ($S_{50}$) of CuPc pellets after 50 minute exposure versus NO$_2$ concentration.

The sensor is allowed to expose to NO$_2$ till the saturation is reached. The sensitivity ($S$) after complete exposure is same from low NO$_2$ concentration of 0.05 volume percent to high concentration as 5 volume % which is indicated in Figure 4.21.
Response time of the sensor decreases as concentration of NO$_2$ gas in air surrounding the sample increases. The response time to 0.05 volume % (500 ppm) NO$_2$ concentrations is 95 minute and it decreases to 1 minute for 2 volume % and higher NO$_2$ gas concentrations. The variation of response time with different NO$_2$ gas concentration is shown in Figure 4.22. The small recovery of the sensor is seen after the removal of air containing nitrogen dioxide of the surrounding of the sensor and allowing it to recover in atmospheric air. The average recovery ratio is 0.12 and average recovery time is 21 minute.

The response graphs gives information of the sensitivity and the response time of the pellet samples upon the exposure of pellets to nitrogen dioxide. The other information also can be drawn from it. The careful look to the response graph for various NO$_2$ concentrations sees that the rate of change of sensitivity is different for different concentrations.
It is also seen from the response graph shown in Figure 4.19 that the response rate is different for different NO\textsubscript{2} gas concentrations. The response rate increases with increase in NO\textsubscript{2} gas concentration in the air surrounding of the sample. The variation of sensitivity during the NO\textsubscript{2} sensing period of the CuPc sample shown in Figure 4.19 is derived from the variation of resistance in the doping stage of the sensor. The variation of electric current or resistance during the doping stage of the sensing period is given by kinetic model based on gas adsorption/desorption theory. The derived general form of it is expressed as equation 4.7 [30, 31].

\[ y = a \left(1 - e^{-bt}\right) \]  

(4.7)

Where, \( y \) is the film property which may be the increment in current, increment in sensitivity or surface coverage ratio. In Figure 4.19 it is increment of sensitivity. The parameter \( a \) is the steady state value of the property and the constant \( b \) is a kinetic constant called rate constant in the doping stage. The rate constant \( b \) is related to the rate constant of adsorption (\( k_a \)) and desorption (\( k_d \)) as \( b = k_a C_0 + k_d \). \( C_0 \) represents the bulk concentration of NO\textsubscript{2} in the test chamber. The above equation 4.7 in this study can be written as,

\[ S(t) = S(1 - e^{-bt}) \]  

(4.8)
Where,

\[ S(t) = \text{Instantaneous value of sensitivity}, \]
\[ S = \text{steady state value of sensitivity}, \]
\[ b = \text{rate constant in the doping stage and} \]
\[ t = \text{time}. \]

In order to determine the rate constant \( b \), equation 4.8 can be modified as,

\[ \ln \left( \frac{S}{S - S(t)} \right) = b t \]  \hspace{1cm} (4.9)

The slope of graph of \( \frac{S}{S - S(t)} \) versus \( t \) will give the value of rate constant \( b \).

Table 4.3 shows the rate constants corresponding to the data for different \( \text{NO}_2 \) gas concentrations as of Figure 4.19. It is seen that the rate constant increases with increase of the \( \text{NO}_2 \) gas concentration. The highest value of rate constant is observed at higher \( \text{NO}_2 \) concentration. At higher concentration of 3 volume % or more the rate constant and hence the rate of adsorption of gas molecules is constant and it is 3.1 per minute.

**Table 4.3**: Rate constant in the doping stage of CuPc sensor with different \( \text{NO}_2 \) gas concentrations.

<table>
<thead>
<tr>
<th>( \text{NO}_2 ) concentration (Volume %)</th>
<th>0.05</th>
<th>0.1</th>
<th>0.5</th>
<th>2</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b ) (Min.(^{-1}))</td>
<td>0.024</td>
<td>0.032</td>
<td>0.066</td>
<td>0.765</td>
<td>3.069</td>
<td>3.1</td>
</tr>
</tbody>
</table>

It is seen from figure 4.19 that the rate of change of sensitivity \( S(t) \) is changing with respect to time. At the beginning stage of the exposure the rate of change of sensitivity is large and it slows down as the time progresses. Differentiating equation 4.8 we get,

\[ \frac{dS(t)}{dt} = Sb e^{bt} \]  \hspace{1cm} (4.10)

Where,
\[ \frac{ds(t)}{dt} = \text{rate of change of sensitivity with respective to time}, \]
\[ S = \text{steady state value of sensitivity (S)}, \]
\[ b = \text{rate constant in the doping stage and} \]
\[ t = \text{time}. \]

From equation 4.10 it is clear that the rate of change of sensitivity decreases as time progresses.

As time \( t \to 0 \), \( \frac{dS(t)}{dt} \to Sb \) \hspace{1cm} (4.11)

and \( t \to \infty \), \( \frac{dS(t)}{dt} \to 0 \) \hspace{1cm} (4.12)

Equations 4.11 and 4.12 implies that the rate of change of sensitivity as soon as the gas is inserted in the chamber is large and as time progresses the rate decreases and finally reaches to zero. It is seen from the table that the rate of change of sensitivity in the initial stage of doping is different for different \( \text{NO}_2 \) gas concentrations. It is seen from equation 4.11 that the rate of change of sensitivity depends on the rate constant \( b \), which further depends on concentration of \( \text{NO}_2 \) present in the test chamber because the rate constant is given by following equation 4.13.

\[ b = K_a C_o + K_d \] \hspace{1cm} (4.13)

where,
\[ b = \text{rate constant in the doping stage,} \]
\[ K_a = \text{rate constant of adsorption,} \]
\[ K_d = \text{rate constant of desorption and} \]
\[ C_o = \text{concentration of gas.} \]

The average recovery ratio is 0.12 which is too small to use the sensor repetitively, hence this type of sensor in the pellet form is one time use sensor.

### 4.6.2 Nitrogen dioxide sensing properties of CoPc pellet

The typical response of CoPc to \( \text{NO}_2 \) concentration 0.5 volume % is shown in Figure 4.23. There is decrease in resistance observed upon the exposure to \( \text{NO}_2 \). The sensor was allowed to recover in atmospheric air and it was found that within 30 minute recovery ratio is 0.12.
CoPc sensor samples were studied with exposure to different NO\(_2\) concentrations such as 0.5 volume %, 1 volume %, 3 volume %, 4 volume % and 5 volume %. The response of CoPc samples with different NO\(_2\) concentration is shown in Figure 4.24. Recovery characteristics were not shown, as the recovery of CoPc pellet samples is small and can be used as one time sensors. Though the recovery characteristics are not shown, the recovery ratio and recovery time is calculated for NO\(_2\) concentration 0.5 volume %. Initial resistance that is the resistance before NO\(_2\) doping was 108.6 \(\times\) \(10^6\) \(\Omega\) and the resistance recovered was 13.24 \(\times\) \(10^6\) \(\Omega\). Hence the recovery ratio calculated to be 0.12 and recovery time is 25 minute.

Figure 4.23: Typical response of CoPc pellet exposed to NO\(_2\) gas.

Figure 4.24: Response of CoPc pellets exposed to various NO\(_2\) concentrations.
The sample is saturated at NO\textsubscript{2} gas concentration of 0.5 volume % and reaches to the maximum sensitivity after 60 minutes duration of exposure. The sensitivity is found to be increasing from 0.5 volume % NO\textsubscript{2} concentration to 3 volume % NO\textsubscript{2} concentrations. At high level of gas concentration than 3 volume % there is no further increase in sensitivity. The maximum sensitivity is 99 %. Figure 4.25 shows the sensitivity obtained for CoPc pellet sensor samples for different NO\textsubscript{2} concentrations.

![Sensitivity graph](image)

**Figure 4.25:** Sensitivity of CoPc pellets exposed to various NO\textsubscript{2} concentrations.

The response time of CoPc sample to nitrogen dioxide is calculated for various gas concentrations. The response time for NO\textsubscript{2} gas concentration of 0.5 volume % is found to be of 23 minutes and it decreases with increasing NO\textsubscript{2} gas concentration. The response time reaches to constant value of 2 minute at and high level of NO\textsubscript{2} gas concentration than 5 volume %. Figure 4.26 shows the graph of response time versus NO\textsubscript{2} concentration. Response time decreases as NO\textsubscript{2} concentration increases.
There is increase in rate constant as we go from low concentration to high concentration. The rate constant for 0.5 volume % NO\textsubscript{2} is 0.062 per minute and it increases with increase in concentration. The rate constant finally achieves the steady value indicating that there is no further increase of rate of absorption. For example as shown in Table 4.1, the rate constant for 5 volume % NO\textsubscript{2} is 1.38 per minute and for 6 volume % NO\textsubscript{2}, and for 6 volume % it is 1.4 per minute. This indicates that the rate constant and hence the rate of absorption of gas molecules up to certain gas concentration increases and after this concentration rate of absorption is steady. In case of CoPc this situation is achieved at 5 volume % NO\textsubscript{2} concentration.

Table 4.4: Rate constant in the doping stage of CoPc with different NO\textsubscript{2} gas concentrations.

<table>
<thead>
<tr>
<th>NO\textsubscript{2} concentration (Volume %)</th>
<th>0.5</th>
<th>1</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Min.\textsuperscript{-1})</td>
<td>0.062</td>
<td>0.19</td>
<td>0.27</td>
<td>0.45</td>
<td>1.38</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The sensor was repetitively exposed to NO\textsubscript{2} concentration 5 volume % for comparatively short time of 20 minute and recovery in atmospheric air was studied for 40 minute. Figure 4.27 shows the repetitive response of CoPc sensor to NO\textsubscript{2}.
In case of CoPc the change in resistance goes on decreasing and recovery time goes on increasing in subsequent cycles. This is may be due to the absorbance and holding of NO$_2$ molecules into the bulk of sample.

4.6.3 Nitrogen dioxide sensing properties of NiPc pellet

The response of NiPc pellet samples to NO$_2$ with 0.1 volume % to 0.5 volume % concentrations is shown in Figure 4.28. The sensitivity for NO$_2$ concentration 0.1 volume % is 86 % and it increases with increase in NO$_2$ concentration up to 0.4 volume %. Samples do not show increase in sensitivity for high level concentration than 0.4 volume %. The data presented in Figure 4.26 indicates that the steady value of sensitivity is 99 %.
The conclusion can be made from the above data that there is effect of NO\textsubscript{2} gas concentration on the sensitivity of the samples. Figure 4.29 shows the graph of sensitivity versus NO\textsubscript{2} concentration for NiPc.

![Figure 4.28: Response of NiPc pellets exposed to various NO\textsubscript{2} concentrations.](image)

**Figure 4.28:** Response of NiPc pellets exposed to various NO\textsubscript{2} concentrations.

The response time for different NO\textsubscript{2} gas concentration to which NiPc pellet sample was exposed is shown in figure 4.30. The response time is different for different NO\textsubscript{2} concentration. It has the maximum value of 72 Minute for 0.1 volume % of NO\textsubscript{2} concentration. The response time decreases as gas concentration increases.

![Figure 4.29: Sensitivity of NiPc pellets exposed to various NO\textsubscript{2} concentrations.](image)

**Figure 4.29:** Sensitivity of NiPc pellets exposed to various NO\textsubscript{2} concentrations.
The response time finally achieves steady value for gas concentrations equal to and for more than 0.4 volume %.

![Graph showing response time vs. NO₂ concentration.](image)

**Figure 4.30:** Response time of NiPc pellets exposed to various NO₂ concentrations.

The rate constant in the doping stage for NiPc pellet sensor exposed to different NO₂ concentrations is given in Table 4.5. It is seen that the rate constant increases with increasing NO₂ concentration.

**Table 4.5:** Rate constant in the doping stage of NiPc sensor with different NO₂ gas concentrations.

<table>
<thead>
<tr>
<th>NO₂ concentration (Volume %)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Min⁻¹)</td>
<td>0.03</td>
<td>0.05</td>
<td>0.16</td>
<td>0.50</td>
<td>1.51</td>
</tr>
</tbody>
</table>

The recovery ratio of NiPc was found to be 0.12 with recovery time 29 minutes when exposed to 0.5 volume %. The initial resistance was $8 \times 10^9 \, \Omega$ and resistance recovered was $16 \times 10^6 \, \Omega$. But it is found that the small time exposure to NO₂ causes more recovery of the resistance.

The NiPc sensor sample was exposed to NO₂ concentration of 0.4 volume % repetitively for short time duration of 5 minutes and allowed to recover in atmospheric air for 5 minutes. The corresponding resistance change with respective to time is shown in Figure 4.31. At the beginning change in resistance is different for the same
concentration but in successive cycles. The stability of change in resistance was obtained after 3 exposing cycles. At the first cycle change in resistance is $14 \times 10^9 \Omega$; it decreases in next successive cycles and remains constant to the average value of $30 \times 10^6 \Omega$.

![Figure 4.31: Response of NiPc pellets exposed to NO$_2$ conc. 0.4 volume %.

Figure 4.32 shows the response of NiPc in terms of resistance for successive cycles. The mean value of change in resistance of NiPc upon the exposure of NO$_2$ gas concentration of 0.4 volume % is $30.85 \times 10^6 \Omega$ with the standard deviation of $\pm 0.72 \times 10^6 \Omega$.

![Figure 4.32: Response of NiPc pellets exposed to NO$_2$ concentration 0.4 volume % with successive cycles.](image)
4.6.4 Nitrogen dioxide sensing properties of ZnPc pellet

The response of ZnPc to various nitrogen dioxide concentrations was studied and the response is shown in Figure 4.33. The response is plotted for NO₂ concentrations of 0.1 volume % to 2 volume %. The data represented in this plot is used to find sensitivity and the response time of ZnPc sample to the nitrogen dioxide gas.

![Figure 4.33: Response of ZnPc pellets exposed to various NO₂ concentrations.](image)

The variation of sensitivity and the response time with different NO₂ concentrations is shown in Figure 4.34 and Figure 4.35 respectively. The maximum sensitivity obtained is 66 % for the NO₂ concentrations of 2 volume % and above. It is seen from the Figure 4.33 that the response time decreases as the NO₂ concentration increases. After certain NO₂ concentration steady state value of response time is reached. The minimum response time seen in the study is 21 Minutes.
The recovery ratio of ZnPc was found to be 0.03 with recovery time 32 minute when exposed to 0.5 volume %. The Initial resistance was 284 KΩ and resistance recovered was 90 KΩ.

The rate constant (b) is obtained by fitting the data presented in Figure 4.33 with equation 4.7. The rate constant in the doping stage of ZnPc sample to different NO₂ concentration is shown in Table 4.6. The maximum rate constant is 0.14 per minute. The rate constant is having steady value from 0.5 volume % NO₂ concentration and above.
Table 4.6: Rate constant in the doping stage of ZnPc with different NO2 gas concentrations.

<table>
<thead>
<tr>
<th>O2 concentration (Volume %)</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Min.⁻¹)</td>
<td>0.09</td>
<td>0.14</td>
<td>0.13</td>
<td>0.14</td>
</tr>
</tbody>
</table>

4.6.5 Nitrogen dioxide sensing properties of FePc pellet

Nitrogen dioxide sensing properties of FePc was studied with different NO2 concentrations and the corresponding response is shown in Figure 4.36. The response is plotted for NO2 concentrations of 0.1 volume % to 3 volume %. The data presented in this plot is used to find sensitivity and the response time of FePc sample to the nitrogen dioxide gas.

Figure 4.36: Response of FePc pellets exposed to various NO2 concentrations.

98 % maximum sensitivity is found in case of FePc samples to NO2 and the minimum response time seen from the response curve is 5 minute. The change in sensitivity and the response time with different NO2 concentrations is shown in figure 4.37 and 4.38 respectively. As seen from the figure, the sensitivity increases with increasing concentration at and above 2 volume % NO2 concentration the sensitivity is almost constant.
Figure 4.37: Sensitivity of FePc pellets exposed to various NO$_2$ concentrations.

The large response time is seen for the low NO$_2$ gas concentration and its value decreases as the NO$_2$ gas concentration increases. It has the minimum and steady value above 2 volume % NO$_2$ gas concentration.

Figure 4.38: Response time of FePc pellets exposed to various NO$_2$ concentrations.

The rate constant (b) is obtained for FePc sample by fitting the data presented in Figure 4.36 with equation 4.7. The rate constant in the doping stage of FnPc sample
to different NO₂ concentration is shown in Table 4.7. The maximum rate constant is 1.44 per minute.

Table 4.7: Rate constant in the doping stage of FePc sensor with different NO₂ gas concentrations.

<table>
<thead>
<tr>
<th>NO₂ concentration (Volume %)</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>b (Min.⁻¹)</td>
<td>0.09</td>
<td>0.05</td>
<td>0.12</td>
<td>0.42</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The recovery ratio of FePc was found to be 0.01 with recovery time 30 minute when exposed to 0.5 volume %. The Initial resistance was 19 MΩ and resistance recovered was 90 KΩ.

In order to study the effect of decreasing gas concentration on the conductivity of MPc sample, the NiPc pellet was exposed to decreasing NO₂ gas concentration in the surrounding air of the sample. The NiPc pellet was exposed to different NO₂ concentrations following the decreasing order from 0.4 volume % to 0.005 volume % and response resistances were recorded with respect to time. The plot of response resistance versus time for decreasing NO₂ gas concentrations is shown in Figure 4.39. Each time the gas concentration was changed the sensor was allowed to expose to the gas for the same time interval that is 10 minute. Hence for each NO₂ gas concentration exposing time is constant.

It is seen from Figure 4.39 that the resistance of the sample decreases upon the exposure of sample to the gas (NO₂ ON) and it increases when the sample was open to the atmospheric air (NO₂ OFF). The decrease in resistance when NO₂ was ON is called decrement in resistance denoted by ΔR is given by equation 4.14.

\[ ΔR = R_a - R_g \]  

Where,

\( R_a \) = Resistance of sample before exposure to NO₂,
\( R_g \) = Resistance of sample after exposure to NO₂.

It is seen from Figure 4.39 that, the decrement in resistance (ΔR) is different for different NO₂ gas concentrations to which the NiPc sample was exposed. It is also seen that the value of ΔR decreases with decreasing NO₂ gas concentration. Note that more is the decrement of resistance (ΔR) of the sample less is the resistance offered.
by the sample. As conductivity is inversely proportional to the resistance, we can say that less is the resistance, more is the conductivity offered by the sample. Hence more is the value of \( \Delta R \), more is the conductivity. Decrement of resistance \( \Delta R \) of sample at each NO\(_2\) gas concentration to which it was exposed is tabulated in Table 4.8.

There is decrease in the value of \( \Delta R \) with decrease in NO\(_2\) gas concentration to which the NiPc sample was exposed. As discussed earlier, decrease in the value of \( \Delta R \) implies the decrease in conductivity. Hence decrease in NO\(_2\) gas concentration decreases the value of \( \Delta R \) that is there is decreases the conductivity of the sample.

The graph of \( \Delta R \) (Megaohm) versus NO\(_2\) gas concentration is shown in Figure 4.40.

**Figure 4.39:** Response of NiPc pellet to decreasing NO\(_2\) gas concentration.

**Table 4.8:** NO\(_2\) Gas concentrations and decrement of resistance (\( \Delta R \)) values.

<table>
<thead>
<tr>
<th>Obs. No.</th>
<th>NO(_2) gas concentration (Volume %)</th>
<th>Sensor resistance (M( \Omega ))</th>
<th>Resistance decrement ( \Delta R ) (M( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NO(_2) ON ( R_a )</td>
<td>NO(_2) OFF ( R_b )</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>85</td>
<td>01</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>75</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>73</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
<td>74</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
<td>78</td>
<td>57</td>
</tr>
</tbody>
</table>

The graph of \( \Delta R \) (Megaohm) versus NO\(_2\) gas concentration is shown in Figure 4.40.
It is seen that $\Delta R$ increases with increasing NO$_2$ gas concentration. In other words, conductivity of NiPc sample increases if the NO$_2$ gas concentration in the surrounding air of the sample increases.

![Figure 4.40: Decrement of resistance versus NO$_2$ gas concentration.](image)

The increase in conductance of NiPc sample on the adsorption of the oxidizing molecules such as NO$_2$ may be explained as follows. When the sample is exposed to a certain concentration of NO$_2$ gas, the gas molecules are adsorbed on the surface of sample. The interaction takes place between NiPc molecules and the adsorbed NO$_2$ molecules. The nitrogen dioxide is a strong oxidizing gas. The adsorbed molecules of analyte gas (NO$_2$) on the surface of sample contact with the $\pi$-electron network of MPc which cause the transfer of electrons from MPc ring to adsorbed gas molecules. Consequently, adsorbed gas molecules which act as an acceptor and become negatively charged and the Pc ring act as donor becomes positively charged. Donating electrons to the gas molecules, holes are generated on the sample surface. In this way generation of holes takes place due to the formation of charge transfer complexes in the surface of MPc [32]. These holes transport along the crystal and may leads to a drastic increase in the conductance. The adsorbed NO$_2$ gas
may act as an acceptor in the MPc lattice through the reversible doping process given in equations 4.15 and 4.16 [33].

\[
\text{MPc} + \text{NO}_2 \leftrightarrow \text{MPc}^+ + \text{NO}_2^- \quad (4.15)
\]

\[
\text{MPc}^+ + \text{NO}_2^- \leftrightarrow h^+ + \text{MPc} + \text{NO}_2^- \quad (4.16)
\]

The increase of conductivity of the sample upon the exposure to increasing NO\textsubscript{2} gas concentration may be explained as follows. High concentration of gas in the surrounding of the sample means large number of gas molecules are available in the surrounding of the sample. Hence large number of interactions between gas molecules and MPc molecules may takes place which in turn generate more number of holes in the sensing material. The increase of hole density results in increase of conductivity of the MPcs [34]. Hence the increase in concentration of gas causes the increase of conductivity of the sample.

Change in sensitivity of different MPcs with respect to various NO\textsubscript{2} gas concentrations is plotted in Figure 4.41. It is observed that the sensitivity of each MPc pellet increases with increasing gas concentration. It is also observed that after certain gas concentration, the sensitivity remains constant and does not depend on the gas concentration. This increase in sensitivity with gas concentration may be explained by understanding the interaction between MPc molecules and gas molecules. Increasing concentration of gas, may increase the number of interactions between the gas molecules and MPc molecules which causes increase in hole density as explained before. Increase of hole density causes more decrease in resistance of the MPc pellet in the presence of gas (R\textsubscript{g}). More decrease in R\textsubscript{g}, increases the difference between R\textsubscript{a} and R\textsubscript{g} that is (R\textsubscript{a}-R\textsubscript{g}). The sensitivity is given by the equation 3.6 given bellow.

\[
S = \left( \frac{R_a - R_g}{R_a} \right) \times 100 \% 
\]

The sensitivity S in the above equation is directly proportional to (R\textsubscript{a}-R\textsubscript{g}). Hence the increasing value of (R\textsubscript{a}-R\textsubscript{g}) with increasing gas concentration causes increase in sensitivity. MPc pellet may saturate after certain gas concentration and there may be no further interactions takes between MPc and gas molecules. This may lead to no further increase in number of holes. Hence the resistance of the pellet in air (R\textsubscript{g}) is constant. Constant value of R\textsubscript{g} gives constant difference between R\textsubscript{a} and R\textsubscript{g}. 

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Hence the sensitivity may be independent of gas concentration. The NO$_2$ gas concentration from which sensitivity is constant is different for different MPc pellets. Its values are 0.1 volume % for CuPc, 1 volume % for CoPc, ZnPc and FePc and 0.4 volume % for NiPc.

![Figure 4.41: Sensitivity of CuPc, CoPc, NiPc, ZnPc, FePc with different NO$_2$ gas concentrations.](image)

Response time of the pellets decreases with increasing NO$_2$ gas concentration. The change in response time of MPc pellets with respect to the NO$_2$ gas concentration is plotted in Figure 4.42.

Table 4.9 shows the different parameters such as sensitivity, response time, recovery ratio and recovery time for CuPc, CoPc, NiPc, ZnPc and FePc. From table 4.9 it is seen that the maximum recovery ratio that can be obtained is only 0.14. That is the only 14% of the original resistance can be recovered. Average recovery ratio of studied MPcs exposed to 0.5 volume % NO$_2$ concentration is 0.06. The average recovery time is 29 minutes. The regime values of the resistance or current at a certain gas concentration are reached after several hours which is relevant to the literature [35].
The sensors having much high recovery time cannot be used repetitively; hence these types of sensors based on MPcs in the form of pellets are one time use sensors.

Table 4.9: Sensitivity, response time, recovery ratio and recovery time of MPcs.

<table>
<thead>
<tr>
<th>MPcs</th>
<th>Sensitivity (%)</th>
<th>Response time (Min.)</th>
<th>Recovery ratio</th>
<th>Recovery time (Min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPc</td>
<td>99</td>
<td>1.85</td>
<td>0.12</td>
<td>29</td>
</tr>
<tr>
<td>CoPc</td>
<td>89</td>
<td>23</td>
<td>0.12</td>
<td>30</td>
</tr>
<tr>
<td>ZnPc</td>
<td>55</td>
<td>26</td>
<td>0.03</td>
<td>32</td>
</tr>
<tr>
<td>CuPc</td>
<td>90</td>
<td>35</td>
<td>0.14</td>
<td>23.5</td>
</tr>
<tr>
<td>FePc</td>
<td>68</td>
<td>100</td>
<td>0.01</td>
<td>30</td>
</tr>
</tbody>
</table>

Though these samples were used as one time sensors, the parameters like sensitivity and response time are still important because one time sensors are used in their doping stage only and not in the recovery stage. The sensitivity and response time both are the parameters which are doping stage parameters of the sensor. The material showing short response time and largest sensitivity are found to be better materials for one time sensors. Hence minimum the value of ratio of response time.
(T\(_{\text{res.}}\)) and sensitivity (S) better will be the material. Table 4.10 shows the ratio of response time to sensitivity for CuPc, CoPc, NiPc, ZnPc and FePc.

**Table 4.10:** Response time to sensitivity ratio of CoPc, NiPc, CuPc, ZnPc and FePc.

<table>
<thead>
<tr>
<th>MPcs</th>
<th>T(_{\text{res.}})/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPc</td>
<td>0.02</td>
</tr>
<tr>
<td>CoPc</td>
<td>0.26</td>
</tr>
<tr>
<td>CuPc</td>
<td>0.38</td>
</tr>
<tr>
<td>ZnPc</td>
<td>0.47</td>
</tr>
<tr>
<td>FePc</td>
<td>1.47</td>
</tr>
</tbody>
</table>

From table 4.10 it can be decided that the NiPc is found to be the best material for nitrogen dioxide sensing with respective to response time and sensitivity.

### 4.7 New approach of gas detection and determination of gas concentration

Taking into account the MPc based electrical sensors in the form of pellets; they exhibit slow response and recovery. The regime value of the sensitivity at a fixed concentration of which is reached after several minutes. Some different approach may be used for detection and measurement of analyte gas concentration within a short time of exposure of sample to the gas. The new approach is explained below.

In the new approach, measurement of resistance values are taken within the few tens of seconds immediately after the analyte gas is present in the surrounding of the sample. In the present study, electrical resistances (R\(_g\)) were measured in the interval of 10 seconds for first 30 seconds, immediately after the gas-air mixture is inserted in the chamber. The response of MPc pellet to the analyte gas in terms of S(t) may be plotted with respect to time as shown in Figure 4.43. The response in terms of sensitivity S(t) at any instant of time is calculated by equation 4.6 given below.

\[
S(t) = \frac{(R_a - R_g)}{R_a} \times 100\%
\]

The plot of S(t) versus time may be fitted to the linear equation to find the slope (ds/dt). The slope of the response graph is directly proportional to the rate constant b as given in equation 4.10 that is,
\[
\frac{dS(t)}{dt} = Sb.
\]

Where the rate constant \( b \) is a function of gas concentration and it is given by equation (4.13) that is \( b = k_a C_o + K_d \), where \( C_o \) is the concentration of gas. Hence the slope \( ds/dt \) depends on concentration of the gas. If the graph of \( S(t) \) versus \( t \) is plotted for different gas concentrations, then we will get a set of straight lines. The slope of which may be different corresponding to the different gas concentrations. Moreover the slope of different lines will increase as the gas concentration increases. The concentration of the gas and corresponding slope of the response curve of sensor sample can be standardized by calibrating the given sample with standard analyte gas concentrations. Then the unknown gas concentrations can be derived from the calibration curve or from standard tabulated data within a few seconds. The application of this method to the final sensor device can be performed on the software level.

In this method the change of sensitivity \( \Delta S(t) = S(t) - S(t_0) \) during the first few seconds after the gas is inserted in the chamber is measured and the rate of change of sensitivity \( \Delta S(t)/\Delta t \) is correlated with the standard calibrated curve or data. Only the contribution of adsorption of gas molecules on the surface of sensor samples is taken into account because of the short time exposure of sensor samples to the gas. The diffusion of gas molecules in the bulk of the sensor is very small. In the long time exposure, the longer response time is mainly due to slow diffusion of gas molecules into the bulk of the sensor. When the gas is inserted into the chamber, the gas molecule first adsorbed on the surface of the sensor and then diffuses into the bulk. The limited period of exposure to the gas mixture allows decreasing the recovery time and short time measurements minimizes the effects of possible long-term drifts of the signal baseline.

In this study, the experiment is performed in three sets with the NiPc pellet samples. All the samples were prepared in the same batch. The samples were exposed to the \( \text{NO}_2 \) gas with different gas concentrations. The resulting response in terms of \( S(t) \) is plotted as shown in Figure 4.43.
Figure 4.43: Response in terms of sensitivity versus time within 30 second after the NiPc sample exposed to NO$_2$ gas.

The slope $\frac{dS}{dt}$ of a line corresponding to each concentration is determined from the graph. The slope is nothing but a rate of change of sensitivity. The calibration data of NO$_2$ gas concentration and $\frac{dS}{dt}$ obtained from the data presented in Figure 4.43 is shown in Table 4.11.

Table 4.11: The concentration of gas and the slope of response curve ($dS/dt$).

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>NO$_2$ gas concentration (Volume %)</th>
<th>$dS/dt$ (%/Sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.49</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1.83</td>
</tr>
</tbody>
</table>

The sensor sample calibrated as above was used to determine the unknown concentration. The graphical method could be used to determine the gas concentration. The graphical representation of the data given in table 4.11 is shown in Figure 4.44. It is the calibration curve of CuPc pellet. The unknown concentration of
NO₂ gas to which calibrated CuPc pellet is exposed may be determined using the curve.

On the device level the determination of concentration could be done on software level. If the sensor sample is exposed to unknown gas concentration then the rate of change of sensitivity (dS/dt) could be determined on software level. The concentration of a gas corresponding to determined dS/dt can be obtained by applying interpolation technique and using tabulated data given in Table 4.11.

![Graph](image)

**Figure 4.44:** dS/dt versus NO₂ gas concentration.

### 4.8 Humidity sensing applications of Metallophthalocyanines

Humidity sensing characteristics were studied for CuPc, CoPc, NiPc, ZnPc and FePc. The MPc pellet samples were used as a sensor element to study the humidity response. The change in resistance was monitored using Keithley-model 2000 electrometer. The resistance of pellet of these materials was decreased with increasing humidity in the surrounding of the sensor samples. The humidity in the chamber was controlled by phosphorous pentaoxide kept inside the chamber. The normalized value of the resistance (Rₐ/R₇) was calculated where Rₐ is the resistance of the MPc sample at 20 % relative humidity and R₇ is the resistance of MPc sample at different humidity. Figure 4.45 shows the plot of response of CuPc, CoPc, NiPc, ZnPc and FePc pellets to different humidity values. Maximum sensitivity to humidity was showed by CoPc and minimum sensitivity was showed by NiPc.
The percentage sensitivity for the detection of humidity [36] is defined as:

$$S = \left( \frac{RH_2 - RH_1}{RH_1} \right) \times 100 \%$$  \hspace{1cm} (4.17)

Where,

$RH_1$ = The resistance of the sample for humidity at level 1,

$RH_2$ = The resistance of the sample for humidity at level 2 for a range of humidity considered.

**Figure 4.45:** Humidity response of CuPc, CoPc, NiPc, ZnPc and FePc pellet samples.

The prototype device was constructed, calibrated and tested for humidity measurements. The construction of the device is discussed in section 3.8 of chapter 3. The photograph of constructed prototype device is shown in Figure 4.46 and photograph shown in Figure 4.47 shows the situation at the time of calibration of the device. The sensor is held in the air atmosphere.
4.9 Summary

Different MPc materials such as CuPc, CoPc, NiPc, ZnPc, FePc have been synthesised in the laboratory by using the earlier reported procedure in the literature (phthalic anhydride urea method) to study them for gas sensor material. Synthesised materials were characterized with different techniques such as XRD, UV-Visible absorption spectra, FTIR and TGA-DTA. The XRD data of the synthesized material is
matched with the data in literature and the JCPDS files. The $\lambda_{\text{max}}$ values and energy band gap values were calculated using standard protocol from the UV-Visible absorption spectra. The IR spectra analysis showed that region between 400 cm$^{-1}$ to 1350 cm$^{-1}$ is same for all MPcs and of MPc skeleton. Region between 1350 cm$^{-1}$ and 1550 cm$^{-1}$ is different for different MPc which depends on the metal atom present in the MPc molecule and the peaks between 1700 cm$^{-1}$ and 2000 cm$^{-1}$ are weak and are due to aromatic ring which are again same for all MPcs.

In order to prepare samples of MPc material, the synthesized material was compacted in the form of pellets using press technique. Parameters such as the pressure and time of application of pressure of 8 ton and 3 minute respectively found to give optimized results. Electrical contacts were formed on the surface of pellets for electrical measurement purpose.

The change in resistance was monitored after exposure of samples to NO$_2$ gas. The special gas test setup comprised of closed glass chamber mounted on steel plate, sample holder, gas insertion assembly, keithley-2000 electrometer and computer interface was developed in the laboratory. This setup was used for measuring the performance of sample. The prepared samples were exposed to different NO$_2$ concentrations by inserting known volume of NO$_2$ in the glass chamber and the change in resistance was monitored. The data obtained is analysed to study the performance of sample in terms of response time, sensitivity, recovery time and recovery ratio.

All the materials showed response in terms of change in resistance after the exposure of samples to NO$_2$ gas. Initial resistance that is the resistance of sample in air ($R_a$) of all the samples is high of the order of Mega ohm ($10^6$ ohm) or Giga ohm ($10^9$ Ohm) and after exposure to NO$_2$ it decreases to few Mega Ohm or few KOhm. The samples were exposed to various NO$_2$ gas concentrations and the sensitivity is calculated. It was observed that the sensitivity decreases with increasing NO$_2$ gas concentration in the surrounding air of the samples. NiPc showed the maximum sensitivity (99 %) and ZnPc showed the minimum sensitivity (55 %) to 0.5 volume % concentration of NO$_2$ gas with the samples prepared in the form of pellets. It was found for all the studied MPc pellets that the response time decreases with increasing gas concentration. NiPc showed lowest response time of 1.85 minute, CuPc, CoPc and
ZnPc showed moderate and FePc showed highest response time that is 100 minute for a 0.5 volume % concentration of NO\textsubscript{2} gas. As far as the sensitivity is considered, CuPc, CoPc and NiPc are suitable materials than ZnPc and FePc for NO\textsubscript{2} sensing. But if the response time is taken into consideration only NiPc CoPc and CuPc are suitable materials. If response time and sensitivity both the parameters are simultaneously considered then NiPc was found to be the best choice. The sensors having high response time were exposed to longer time to get considerable measurement. The longer time exposure of sensor sample to the gas ensures the absorption of gas molecules into the bulk of the sample which may not recovered. Average recovery ratio of the samples exposed to 0.5 volume % concentration of NO\textsubscript{2} gas is 0.06. The recovery ratio of CuPc is 0.14 which is the highest value as compared with that of other studied materials. Also the CuPc showed low recovery time (23.5 minute) as compared same with other materials. Above mentioned values of different parameters shows that the NiPc and CuPc materials are suitable materials to use them as NO\textsubscript{2} gas sensing material. Low recovery in ambient conditions and low cost of the materials and preparation of samples in the form of pellets suggest that these sensors can be used for single use applications.

The increasing value of the rate constant in the gas exposing stage (b) of MPc pellets with increasing NO\textsubscript{2} gas concentration revealed that the rate of change of instantaneous sensitivity \(\frac{dS(t)}{dt}\) increases with increasing gas concentration. The dependence of the rate of change of sensitivity on the gas concentration was used to detect and determine the unknown gas concentration in the surrounding air of the sample. The rate was determined within the few seconds as soon as the sensor was exposed to nitrogen dioxide. This approach may be used to the materials having high response time also. In this way one can determine the pollutant gas concentration within a short period of time of the order of few seconds. This technique may be implemented on device level and gas concentration may be determined on the software level. Determination of concentration of simultaneous presence of different gases in the air could be possible by using array of sensors and analyzing the data on the computer and software level. The necessary microcontroller or the computer interfacing with suitable software is needed in this case.
Ample scope remains for the performance improvement of the sensors by using films or nano-structures of MPcs and inter-digited electrodes for sensing which provides high surface area and miniaturization. Hence, the MPc sensor samples in the form of films using spin coating technique were prepared, their NO$_2$ gas sensing performance and improvement of gas sensing performance was studied. In the next chapter spin coated films and their response to NO$_2$ gas is discussed in detail.
References


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