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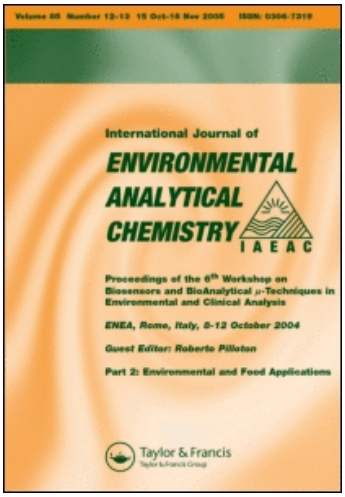


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# COPPER PHTHALOCYANINE LAYER AS AN ORGANIC SEMICONDUCTOR SENSOR OF $NO_2$ IN AIR

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The applicability of copper phthalocyanine (CuPc) as an organic semiconductor gas sensor for the detection of high concentrations of $NO_2$ in air is the aim of this study. Thin films of CuPc were deposited by sublimation. Measurements were carried out to determine the effect of $NO_2$ on the conductivity of a CuPc film. A detection method for $NO_2$ in air is proposed.

KEY WORDS: Sensor, organic semiconduetor, phthalocyanine, nitrogen dioxide.

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## INTRODUCTION

One of the most promising areas which can provide sensors for environmental analytical chemistry is the field of solid-state chemical sensors employing organic semiconductors, for example phthalocyanines. Detection of gases by measuring electric conductivity variations in phthalocyanine crystals,[1–5] thin films[6–12] or L-B[13–15] layers has been the aim of many investigations. Published data show that electrical conductivity changes in metal-free and lead phthalocyanines at temperatures over 423 K (150 °C) can provide a convenient means for the selective detection of $NO_2$ and halogens over a wide range of low concentrations in air (max., 10 mg/m$^3$).[8,9] The thickness of the phthalocyanine layers was 300–1000 nm.

The main aim of the present study was to investigate the potential of thin copper phthalocyanine (CuPc) films (thickness less than 65 nm) when applied to the measurement of airborne $NO_2$ concentrations higher than the industrial hygiene level (ca. 5 mg/m$^3$). The recovery process should be more effective for the thin films, especially in the case of high concentrations of $NO_2$ in air.

## EXPERIMENTAL

### *Materials*

$NO_2$ gas was prepared by thermal decomposition of $Pb(NO_3)_2$. Copper phthalocyanine (CuPc) was synthesised and kindly supplied by the Institute of Organic and Physical Chemistry, Technical University of Wrocław.

CuPc films were deposited by means of vacuum sublimation at $10^{-5}$ Torr over an interdigitated gold electrode system. The substrate was made of smooth glass

(Corning 7059). The thickness of the semiconductor layer was measured by concurrent coating of a reference slide and by measuring this coating with the help of an optical method. In this study, the CuPc films thickness varied between 40 and 64 nm.

The connecting wires leading to the heater and those leading to the electrode system were made from silver and platinum. The contacts were prepared using a silver paste (Electrodag 915, Acheson Colloids Co., Prince Rock, Plymouth).

*Apparatus*

The measuring system has been designed and constructed for the purpose of this study, and has enabled the following: adjustment of the gas mixture composition, control and measurement of the semiconductor temperature and monitoring of the strength of the electric current. The main part of the experimental system was a measuring cell (a cylindrical vessel made of glass). There were two major reasons to prefer glass, viz. the aggressiveness of the immediate chemical environment and the readiness of $NO_2$ to adsorb on solid surfaces of other materials.

The measuring cell contained the substrate with a deposited CuPc layer. The substrate and the CuPc film were attached to a ceramic plate. The back of this plate was provided with a thick film resistor in order to heat the sensor. The substrate temperature was adjusted by varying the electric current through the heater. Since the semiconductor–film conductivity varies with temperature, it is necessary to maintain the temperature of the substrate at a constant level. The temperature was measured with a Cu-constantan thermocouple and was stabilized in the range of 293–450 K with an accuracy of 0.5 K.

The voltage fed to the electrode varied from 0 to 100 V. The resulting electric current was measured with an electrometer.

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*Procedures*

In each experiment the CuPc films were inserted into a gas stream (air or $NO_2$–air mixture). The semiconductor layer was placed against a gas nozzle so as to enable carrier gas injections directly to the surface of the CuPc film. The carrier gas was the air circulating in the measuring system at a constant flow of $100\,dm^3\,h^{-1}$. Before being used as the carrier gas, atmospheric air had been passed through a 0.1 M NaOH solution for purification, and had been dried over silica.

High concentrations of $NO_2$ in air were generated by injecting a portion of $NO_2$ into the air stream. The circulating gases were sampled after each exposure to $NO_2$; the concentration of $NO_2$ in air was determined by colorimetry (Saltzman method).

## RESULTS AND DISCUSSION

Generally, the conductivity change for a given film varies as the film ages. That is, the history of the semiconductor layer can influence the response towards gases. It

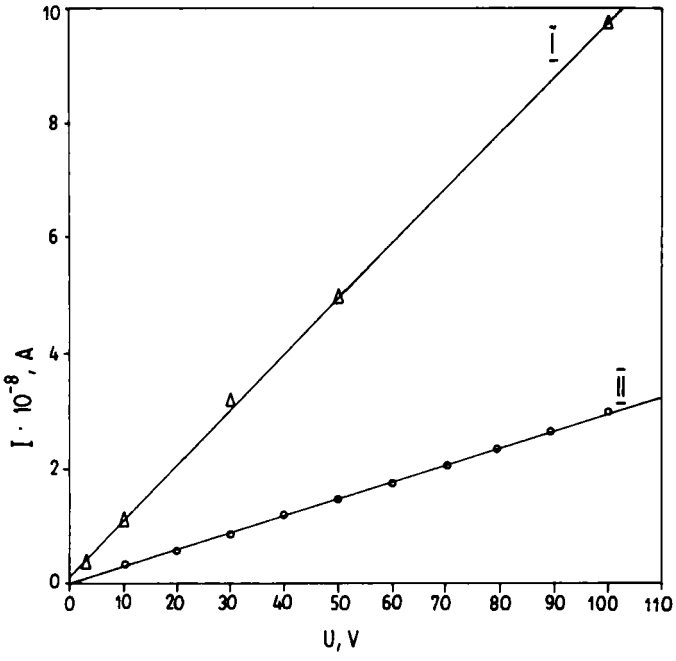


**Figure 1** Strength of electric current, $I$, through CuPc film versus applied voltage, $U$, for two layers of thickness, 61.4 nm (curve I) and 46.8 nm (curve II). Temperature, 432 K.

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is possible to achieve good repeatability of the chemical and electrical characteristics of the CuPc layer.[10–12] In this study, a fresh film was alternately heated to 432 K and cooled down to room temperature during the ageing process. The heating and cooling operations were done several times.

After completion of the ageing process, current-voltage characteristics were measured in the range of 1–100 V for all the experimental films. In each case, the conductivity followed Ohm's law for the range of voltages applied, i.e. a linear dependence of the electric current intensity on the voltage was observed. An example is shown in Figure 1. The thicknesses of the films I and II were 61.4 and 46.8 nm, respectively. The experiments were run at a temperature of CuPc equal to 432 K.

Attention was also given to the temperature dependence of the conductivity. The measurements were performed at temperatures between 300 and 432 K. The results are described by the relationship

$$\sigma = \sigma_0 \exp(-E/2kT) \tag{1}$$

where $\sigma$ is the surface conductivity, $\sigma_0$ is a constant, $E$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature. Figure 2 displays temperature variations of $\log \sigma$ for a CuPc film of 61.4 nm thickness. The results of curve I were obtained for the CuPc film during its heating to 432 K. After heating, the CuPc

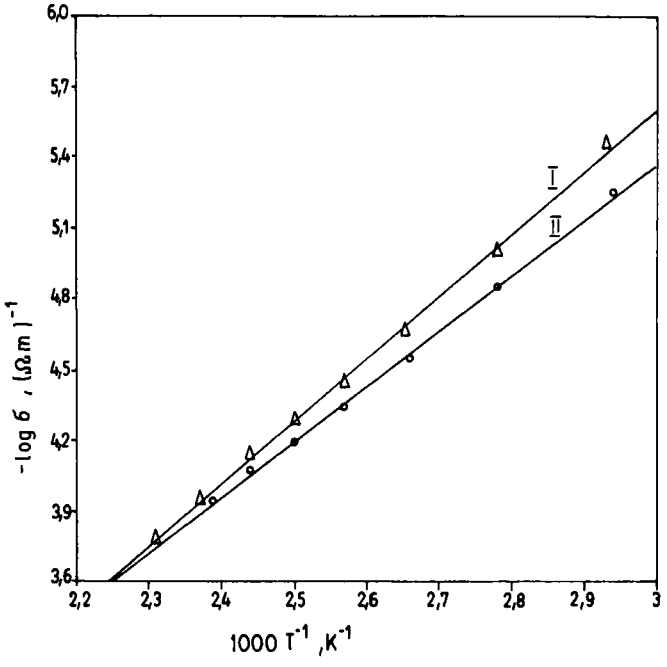


**Figure 2** Variations of surface conductivity, $\sigma$, with temperature $T$. CuPc film thickness 61.4 nm. Curve I: CuPc layer heated to 432 K. Curve II: CuPc layer cooled down to room temperature after heating.

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layer was cooled down to room temperature; the pertinent results are shown by curve II. The plots of $\log\sigma$ versus $T^{-1}$ are linear, but the curves I and II show a different slope. We assume that the hysteresis during a heating-cooling cycle must be attributed to adsorption/desorption, especially of water.

The physical and chemical processes that occur on the semiconductor layer are complex. It is, therefore, difficult to describe the sensor in a model form. Therefore, the parameters characterizing the working of the sensor should be established experimentally.

One of these parameters is the temperature of the CuPc layer, which should be optimized for the detection of $NO_2$ in air. The effect of the gas on the conductivity of the semiconductor film was investigated over the temperature range of 373–432 K. This temperature was low enough to ensure stability of the material and high enough to eliminate the effect of physisorption of water vapour. In this temperature range, no chemical reaction occurred. We observed re-evaporation of the semiconductor layer inserted into an air stream at a temperature around 473 K.

Exposure of the CuPc film to an $NO_2$–air mixture immediately after completion of the ageing process led to a rapid increase in the conductivity of the CuPc layer. The strength of the electric current through the semiconductor at 381 K changed $\sim 1000\%$ in the stream of $NO_2$ in air. The concentration of $NO_2$ was 40 mg/m$^3$.

This effect was completely reversible, but it took a long time ($\sim 10$ h) for the film to obtain its original conductivity following removal of the $NO_2$–air mixture. The reversibility was achieved by heating the CuPc film at 381 K in a stream of dry air in the open system. When the $NO_2$ concentration in the stream of air surrounding the semiconductor decreased, so did the enhancement of the CuPc films conductivity. The regeneration time was shorter, but was still far from acceptable for practical measurements.

The effect of $NO_2$ on the conductivity of the semiconductor was reversible, but only slowly so, especially at high concentrations of $NO_2$ in air; therefore we tried to devise a method for $NO_2$ detection without the need for a complete regeneration of the CuPc layer. The method proposed in this paper consists of two stages: (i) the exposure to a given gas mixture and (ii) the regeneration of the characteristic conductivity in the shortest possible time. This characteristic conductivity was treated as the reference point in the regeneration process.

After introduction of the $NO_2$–air mixture to the surroundings of the semiconductor, several minutes were allowed before the strength of the current was measured. Within this time span, the gas concentration surrounding the sensor reached a constant value. Variations in the strength of the electric current in the presence of $NO_2$ were measured as the conductivity of the semiconductor had reached its constant value. It was quite difficult to establish the exact response time of the sensor because of the relatively large volume of our measuring system. We postulate that the response time of the sensor typically falls between 1 and 2 min. The response and regeneration time also depended on the $NO_2$ concentration in the air sample.

The regeneration of the CuPc layer was started immediately after its being exposed to a particular gas concentration. The $NO_2$–air sample that circulated in the measuring cell during the exposure was expelled from the system into the atmosphere. The measurement system was then purged with clean, dry air. The purging air was allowed to vent to the atmosphere continuously. In the course of the purging process, the CuPc film was heated at 423 K. This led to the release of $NO_2$ from the semiconductor layer. As a result, the conductivity of the CuPc film decreased. The desorption process was slow and it was difficult to make the film's conductivity obtain its original level. For the sensing procedure, it was interesting to know if $NO_2$ concentrations in air can be measured without a complete regeneration of the semiconductor layer. It was also of interest to determine the minimum time of regeneration. In this study, we assumed that the purging and heating processes should be discontinued as soon as the strength of the electric current reached an arbitrarily chosen value. This is the strength of the electric current after 20–30 min heating of the layer in an air stream at the temperature of 423 K after its exposure to the highest concentration of $NO_2$ measured, 50 mg/m$^3$. When this value had been reached, the temperature was reduced to the initial level (the temperature of the first stage) and the purging air stream was allowed to vent to the atmosphere. The CuPc layer was then ready for the next exposure to $NO_2$ in the air.

The described method was tested over a wide concentration range (1–50 mg/m$^3$). The thickness of the CuPc film was 51 nm. The results are plotted in Figure 3,

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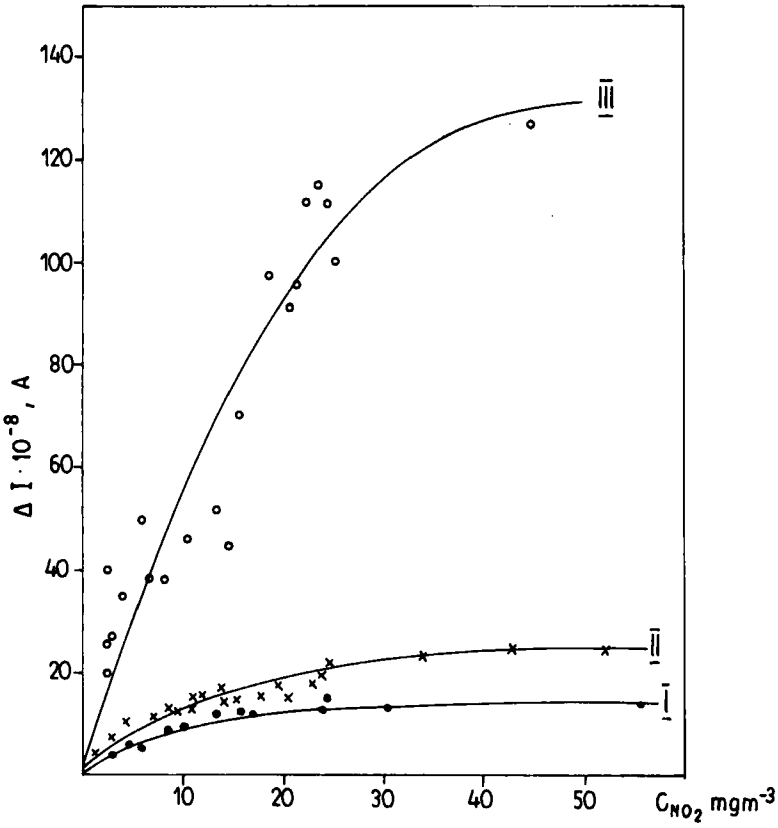


**Figure 3** Intensity variations ($\Delta I$) in electric current through a CuPc film of thickness 51 nm versus $NO_2$ concentration in air (C). Curves I, II, and III were measured at 379, 403, and 423 K, respectively.

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wherein the changes in the current ($\Delta I$) are plotted as a function of the $NO_2$ concentrations (C) in the air sample. The measurements were conducted at 379 K (curve I), 403 K (curve II), and 423 K (curve III). The regeneration process was carried out at 423 K in each instance.

The curves I, II, and III are remarkably similar in shape and they can be described by the following functions: $\Delta I = 3.5\,C^{0.4}$, $\Delta I = 4.4\,C^{0.5}$, and $\Delta I = 16.4\,C^{0.6}$, respectively. It can be seen from Figure 3 that the saturation level occurs at different concentrations. Figure 3 also shows that sensitivity for $NO_2$ is higher at higher temperatures. Although $NO_2$ was not completely desorbed from the semiconductor layer during the regeneration process, it was possible to determine $NO_2$ concentration in the air sample. However, it should be noted that fast changes from high to low concentrations cannot be measured with high accuracy. Due to this, the measurement points exhibit some scattering (curve III).

## CONCLUSIONS

The electrical and chemical characteristics of the investigated CuPc film were

stable following completion of the ageing process. In each instance, conductivity fulfilled Ohm's law for the applied voltage. The relationship log (surface conductivity) versus $T^{-1}$ for the heating and cooling processes shows some hysteresis, which may be attributed to gas adsorption on, and gas desorption from, the semiconductor surface.

Exposure of CuPc to the $NO_2$–air mixture led to a rapid conductivity increase of the semiconductor layer. This effect was reversible, but it took a long time for the layer again to obtain its original conductivity, especially at high concentrations of $NO_2$.

We studied a method for measuring $NO_2$ concentrations in air. In this method, a complete release of $NO_2$ from CuPc after its exposure to $NO_2$ was not necessary. The regeneration process was discontinued after the strength of the electric current had reached a fixed value. The method was tested over a wide concentration range (1–50 mg/m$^3$) at 379, 403, and 423 K. The relationship between current changes ($\Delta I$) and the concentration of $NO_2$ in an air sample (C) can be described by

$$I = aC^b \tag{2}$$

where $a$ and $b$ are constants. The best sensitivity for $NO_2$ was achieved at 423 K.

The analysis of the obtained data sets substantiates the suitability of CuPc films for the detection and semiquantitative determination of high $NO_2$ concentrations in air, viz. of up to about 30 mg/m$^3$.

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