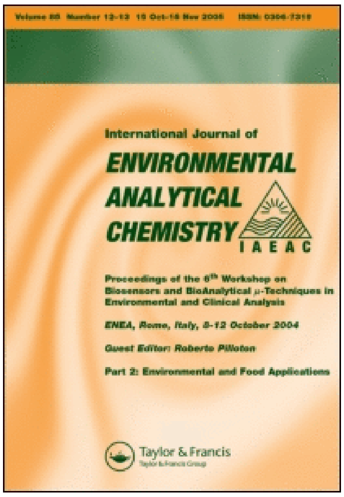

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A. Szczurek[a]; K. Lorenz[a]
[a] Institute of Environment Protection Engineering, Technical University of Wroclaw, Wroclaw, Poland

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An Organic Semiconductor as Gas Detector

A. SZCZUREK and K. LORENZ

Institute of Environment Protection Engineering, Technical University of Wrocław, Pl. Grunwaldzki 9, 50 377 Wrocław, Poland

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The objective was to investigate the application of copper phthalocyanine (CuPc) films to the detection of air-borne NH_3. The phenomenon of gas adsorption on the available surface area of an organic semiconductor was studied. Repeatable results can be obtained relatively quickly provided that a certain state of the semiconductor (which may be adopted as a reference system) will be re-established prior to each measurement of air-borne NH_3. The development of an appropriate method for the regeneration of the CuPc film following completion of the detection procedure is described. A linear relation between minimum current intensity and partial pressure (concentration) of NH_3 in the gas sample is obtained. The method proposed in this study for the measurement of atmospheric NH_3 has analytical potential.

KEY WORDS: Air-borne NH_3, organic semiconductor, gas detector, copper phthalocyanine film.

INTRODUCTION

In the past decade, the utility of organic semiconductors for the detection of gases has increasingly been studied in various research centres.[1–4] Among the variety of organic semiconductors, copper phthalocyanine (CuPc) of the structural formula $C_{32}H_{16}N_8Cu$ raises particular interest.[2] Owing to its planar structure, CuPc readily forms strong out-of-plane bonds and weak in-plane bonds. Bonds of that kind enable interaction with various gas particles. In most instances, this interaction proceeds via physical adsorption, i.e., weak van der Waals forces are involved. In spite of this, the molecules of some adsorbed gases have a distinct influence on the density of the electric charge carriers included in CuPc.[5] Depending on the donor-acceptor properties of the gas particles, the intensity of the electric current flowing through the adsorbent either increases or drops. In the case of CuPc, the holes act as charge carriers. As a result electron-acceptor gases, e.g. oxygen or nitric oxides, effect an increase in current intensity, whereas electron-donor gases, e.g. hydrogen or ammonia, account for a decrease. Changes occurring in the electric conduction of CuPc are influenced by the concentration of the gas which gets in touch with the surface of the adsorbent. Most of those changes, however, are at least partly reversible.

These above-mentioned properties of CuPc suggest that the semiconductor may be employed for measuring the concentration of gases. In this paper, a method for the direct measurement of airborne NH_3 is developed.

EXPERIMENTAL

The change in the intensity of the current flowing through the semiconductor which is in touch with the gas depends on the number of particles adsorbed on the adsorbent surface; therefore, CuPc has been deposited in the form of a thin film. A film like that is characterized by the presence of numerous active centres which are responsible for the adsorption phenomenon. CuPc films, about 10 μm thick, were deposited by sublimation onto glass substrates kept at room temperature. Prior to deposition the glass slide was equipped with concentric gold electrodes (Figure 1), because gold forms an ohmic contact to copper phthalocyanine and is resistant to the action of NH_3. The distance between the electrodes was 1 mm. During measurements a voltage was applied to the outer ring electrode and the resulting current was measured with an electrometer. The response of the CuPc film to the action of gases was measured by applying a voltage of 100 V. As the intensity of the current flowing through an organic semiconductor is temperature-

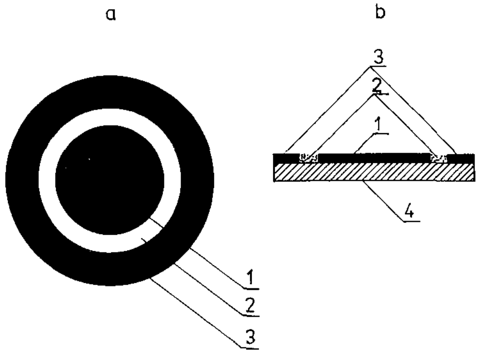

FIGURE 1 CuPc film deposited onto a glass plate. 1, 3, gold electrodes; 2, CuPc film; 4, glass plate.

dependent, it was necessary to keep the CuPc film at constant temperature conditions throughout the measurements.

RESULTS AND DISCUSSION

Preliminary experiments

Before exposure to the air–NH_3 mixture, the CuPc film was prepared as follows. The aim of the preparation procedure was both the ageing of the layer and the removal of weakly adsorbed molecules of other gases from its surface, since their desorption may have a substantial influence on the current intensity flowing through the semiconductor film. The preparation procedure consisted of repeated annealing and cooling of the CuPc film in atmospheric air and vacuum. The layer is annealed and cooled until the $\log R$ vs. $1000\,T^{-1}$ relationship becomes linear (here R denotes the CuPc film resistance and T stands for the CuPc film temperature). This is an indication that the weakly adsorbed molecules of other gases—the desorption of which may exert a strong influence on the current intensity—have been removed.

The CuPc film, which has been prepared via the above route and is kept at constant temperature, and was subjected to a 10-min exposure to 10^{-3} Torr vacuum and then exposed to atmospheric air, shows no significant change in electric conductivity. On the contrary, a mixture of air and NH_3 reduced the conductivity of the layer. This mixture makes the electric current flowing through the adsorbent drop to a minimum value. The time required to reach this minimum depends on the temperature at which the organic semiconductor has been kept (e.g. 323 K) whereas the time required to achieve the minimum value of current intensity is about 2 min. After the current flowing through the CuPc film had reached the minimum value its intensity increased slowly up to a constant value. In this situation, it was impossible to determine the concentration of air-borne NH_3 in terms of the measured stabilized maximum intensity value of the electric current flowing through the CuPc film exposed to the given gas mixture. Hence, attempts were made to involve the minimum current intensity value.

To make the CuPc film fit for re-use the adsorbent should be regenerated following exposure to the given gas mixture. In our investigations, the assumption was made that the regenerating procedure had to be relatively short and the organic semiconductor had to be stored under decreased pressure. A treatment like that accounted for the desorption of NH_3 particles which had been adsorbed on the CuPc film surface, and this led to the increase in the intensity of the current flowing through the film. However, the proposed regeneration method did not bring about a complete removal of all the NH_3 molecules adsorbed on the surface, so that the original current intensity value could not be obtained, either. Long-term exposure of the CuPc film to vacuum also failed to be successful. A non-complete removal of NH_3 molecules adsorbed on the CuPc film surface made it impossible to obtain a repeatable value of the measured minimum intensity of the current flowing through the adsorbent during successive exposures to the same gaseous mixture.

Final procedure

For the purpose of obtaining reproducible results, a special method of measurement and regeneration of the sensing element was developed.[6,7] The method consists of the following steps.

1) Prior to the measuring procedure, it is necessary to select the maximum concentration of air-borne NH_3 which can be measured with the given CuPc film.

2) Then, a state of dynamic equilibrium should be established between the adsorbent and the air–NH_3 mixture to which the film is alternatively exposed and from which it is also alternatively removed. In this mixture, the partial pressure of NH_3 has the same value as the selected maximum concentration of air-borne NH_3. The procedure of establishing the dynamic equilibrium must be started by removing the gases that are present in the measuring cell. Then the film should be exposed to the air–NH_3 mixture until the intensity of the current flowing through the adsorbent reaches its minimum value. Once this has been achieved, the gas mixture should be evacuated, and the film should be kept under decreased pressure, e.g. for 10 min. A longer time of regeneration would make the method inapplicable. After the chosen time of regeneration has elapsed, the film is again subjected to exposure and evacuation of an identical gaseous mixture. The procedure should be continued until repeatable minimum intensity values for the current flowing through the adsorbent during several successive exposures are achieved. The minimum intensity value obtained via this route is an indicator characterizing the state of the semiconductor film which is regarded as a reference system. When the dynamic equilibrium between the CuPc film and the selected gaseous mixture has been reached, it is necessary to measure the intensity value for the electric current flowing through the adsorbent immediately following completion of storage (for a given period of time) under decreased pressure. It was anticipated that this measured current intensity value would every time indicate the moment at which the storage of the CuPc film under decreased pressure was completed.

3) After having obtained the desired state of the semiconductor film, the system is ready for the measurement of air-borne NH_3 concentrations. Thus, the gas under study should be introduced into the environment of the CuPc film immediately after completion of storage in vacuum, when the intensity of the electric current had already reached the anticipated value. Influenced by the presence of NH_3, the intensity value will drop to reach a certain minimum. From this minimum it is possible to determine the concentration of NH_3 in the influent air. After having measured the minimum current intensity value during exposure, the gases must be evacuated from the environment of the CuPc film.

4) Evacuation should be discontinued after the current intensity

has reached the value which has been assumed to be the moment of completion for the storage of the semiconductor film under decreased pressure.

5) When this value has been achieved, it is necessary to re-establish the state of the CuPc film which is regarded as the reference state. This state may be re-established by exposure of the organic semiconductor to a mixture of air and NH_3, in which the NH_3 concentration has the maximum value that can be measured by means of the given CuPc film. Exposure should take 2–3 min.

6) The adsorbent should be placed again in vacuum until the current intensity achieves the value required.

7) Then, the NH_3 concentration in the successive gas samples can be measured.

One should realise that the system has to be recalibrated after each series of measurements, that is, after each apparatus switch-off.

EVALUATION

The proposed method of measuring air-borne concentrations of NH_3 was tested for mixtures in which the partial pressure of NH_3 ranged from 0.02 to 0.20 Torr (18.1 mg/m^3–181.0 mg/m^3). The repeatability of results for the measurement of NH_3 concentrations expressed in terms of partial pressure, which amounted to 0.02 Torr, was also examined. The results are shown in Figure 2. In this figure, points marked + in Region I indicate the minimum intensities of the electric current flowing through the adsorbent during exposure to an air and NH_3 mixture in which the partial pressure of NH_3 is 0.2 Torr. Points marked + in Region II incorporate the minimum current intensity values for a mixture with partial pressure of NH_3 amounting to 0.02 Torr. Points marked ● denote intensities of the current flowing through the adsorbent immediately before exposure to a given gas mixture. The data given in Figure 2 (points marked + in Region II) indicate that the measuring method proposed is able to ensure the repeatability of results. The mean standard deviation in this method was about 1%.

The data of Figure 3 show that in the investigated range of partial NH_3 pressures a linear relationship exists between the measured

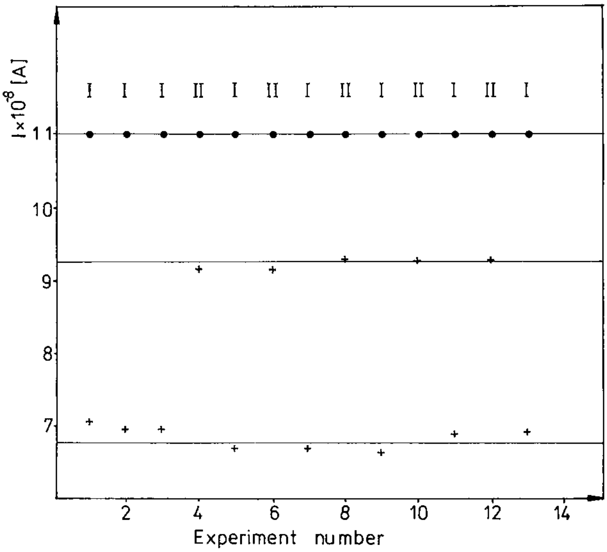

FIGURE 2 Repeatability of measurements at partial NH_3 pressure of 2×10^{-2} Torr (Region II) after regeneration of the film at partial pressure of 2×10^{-1} Torr (Region I). + Minimum intensities of the electric current flowing through the adsorbent during exposure to a given gas mixture. ● Intensities of the current flowing through the adsorbent immediately before the exposure to a given gas mixture.

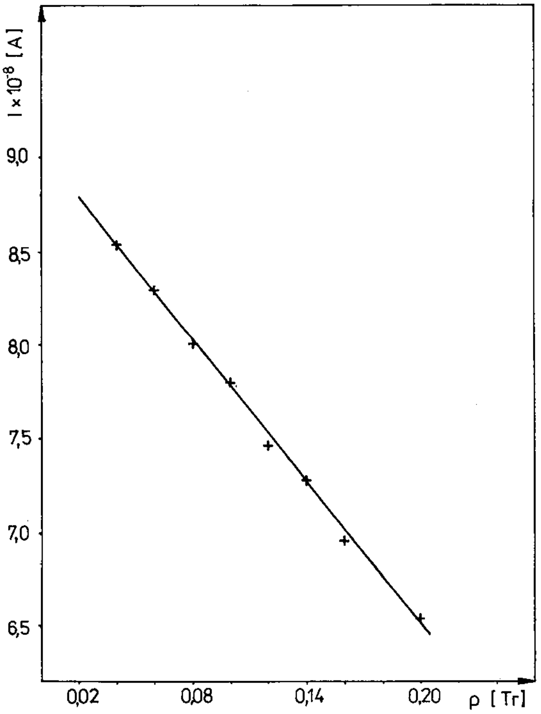

FIGURE 3 Relationship between intensity of current flowing through the CuPc film and the atmospheric NH_3 concentration.

intensities of the electric current flowing through the adsorbent during exposure to a selected air–NH_3 mixture and the partial NH_3 pressure.

The method proposed for the measurement of atmospheric NH_3 can be applied in analytical chemistry. The method may also be of utility in detecting other gases, e.g. NO_x. Still, the results reported here should be treated as the first step leading to the application of organic semiconductors to analytical techniques. Investigations into the problem of interest are under way. They include the selectivity of the method.

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