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Humidity effect on ammonia sensing properties of substituted and unsubstituted cobalt phthalocyanines

Thibaut Sizun, Marcel Bouvet*, Jean-Moïse Suisse

Institut de Chimie Moléculaire de l'Université de Bourgogne, CNRS UMR 6302, Université de Bourgogne, 21078 Dijon, France

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ABSTRACT

In this paper, we studied the effect of humidity on the response of cobalt phthalocyanine—containing resistors to ammonia, in the ppm range. We pointed out the fact that, when alternating exposure periods with recovery periods, the humidity effect had to be carefully studied, in correlation with the flow variation. Thus, for a sulfonated cobalt phthalocyanine, the effect of NH_3 was totally screened as soon as the relative humidity (RH) was above 10%. On the contrary, when using unsubstituted cobalt phthalocyanine (CoPc) as sensing material, the sensors' response to NH_3 appears to be quite stable in a wide RH range, allowing a discrimination between 12, 25 and 50 ppm of NH_3 over the 10–70% RH range. Finally, CoPc offers a promising perspective as sensing material for air quality control applications, even at relatively high humidity levels.

1. Introduction

Most people know of the dangers CO_2 poses for the environment, being a green house gas and of the negative role played by ozone in our cities, being responsible for pollution peaks. But, for a full air quality awareness, the impact of many other gases on environment and/or health has to be considered. Air quality should be monitored outdoors as well as indoors and compounds such as BTEX (benzene, toluene, ethylbenzene and xylene), VOC (Volatile Organic Compounds) and also NH_3 [1,2] must be kept in check. This latter gas is encountered most of the time in industry because of its use as refrigerant gas and in raw materials as fertilizer. As a result, it is important to monitor NH_3 concentrations in air as a safety measure to protect industrial employees. In order to do so, European air quality labor legislation for NH_3 sets a daily exposure limit at 20 ppm. Many detectors that cover this range are available for sale. However, those sensors, which are often used as alarm or leakage detectors, could be improved to be much more compact, more simple and less sensitive to other gaseous species. The main drawback of such devices is indeed their lack of selectivity towards NH_3, which makes them prone to the influence of other species. Moreover, within an industrial environment the effect of humidity is not very well known. In literature, many solutions for NH_3 sensing are available. Those are based on various kinds of transducers, namely electrochemical, acoustic, optical or conductimetric [3–9]. However, articles which deal specifically with cross sensitivity between NH_3 and humidity are quite rare [10–15]. Most of the time, when necessary, humidity sensors are combined with NH_3 sensors. This kind of setup using multiple sensing devices is rather expensive because of the supplementary sensors and electronics, and because of computer generally added for *in situ* data processing, especially for principal component analysis or neural network [5,8,10]. Moreover, many sensors such as catalytic sensors, are equipped with a heating component that consumes a lot of power. This is the reason why new materials must be studied to address these issues. Materials with a simple processability are needed, associated with a transduction principle suitable for simple electronic design and data processing. They should also be able to work at room temperature. All these conditions must be fulfilled to allow a cost effective device for this application. In this study, we decided to use molecular materials commonly found in organic electronics [16,17]. Phthalocyanines are interesting candidates for the development of conductimetric sensors [18–21]. These compounds offer a large variation of molecular properties, which can be tuned by introducing various chemical moieties. Thus, it is possible to introduce hydrophilic and/or hydrophobic substituents, which opens the door to low cost deposition methods like aqueous solution processing, Langmuir–Blodgett [22,23], Langmuir–Schäfer [24] and related deposition

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* Corresponding author. Tel.: +33 380396086; fax: +33 380396098.
E-mail address: marcel.bouvet@u-bourgogne.fr (M. Bouvet).

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techniques [25]. In this study, we did conduct a survey of combined NH_3 and humidity effects, with sulfonated cobalt phthalocyanines (s-CoPc) and neat cobalt phthalocyanine (CoPc) as sensitive molecular materials. Those materials, whose properties are well defined in a recent review [26], used in resistors, allow us to simply determine the NH_3 concentration. The conductivity of cobalt phthalocyanines is of p-type, so, when a donating species such as NH_3 is adsorbed on the surface, charge carriers are trapped and the conductivity decreases [20]. These materials were studied in a previous work on cross-sensitivity to O_3 and NH_3, in the ppb and ppm range, respectively [27]. Regarding the effect of O_3, it is important to keep in mind that O_3 induces an increase in conductivity while NH_3 induces a decrease in conductivity, as the nitrogen dioxide [23], so we cannot fail to find the nature of these different gases. In addition, O_3 sensors will be mainly used in big cities for air quality monitoring where the main interfering species is the nitrogen dioxide, whereas ammonia sensors are needed in manure industries, on the breeding sites or inside food plants where the concentration of O_3 will be considerably lower than outdoors. Finally, the lifespan of O_3 is shorter and O_3 is easily destroyed by filters such as those developed by Pauly and co-workers to get rid of the cross sensitivity issue [28–30]. Surprisingly, s-CoPc was insensitive to O_3, but sensitive to NH_3, a much sought-after advantage [27]. The aim of the present work was to clarify the effect of humidity on a transducer in the presence of a target gas, NH_3 in our case. Humidity can indeed induce a dramatic variation of gas sensor responses and can affect the devices lifespan. We will show how the response depends on the relative humidity (RH). This study highlights the effect of moisture on the sensor's response and the feasibility of operating NH_3 sensors in humid area. This also pinpoints the exact role played by the experimental set-up, particularly the effect of gas flow variations on the actual RH in the measurement cell. In the literature, most of the experimental data available about the effect of humidity on gas sensing are quite hard to compare to each other. Obviously, most of the reported studies involve, in their experimental setup, an additional flow injected right after the humidity regulation system, but the authors do not mention that effect or even a method to estimate it. In the present study, the applied protocol was divided into four successive steps. Firstly, the effect of NH_3 on the sensors was studied in dry argon (Ar). This step of the protocol was put in place only to assert the sensitivity of our sensors to NH_3. Secondly, a study of the humidity effect was performed, for at least two reasons: in one hand, in order to know whether or not the sensing element could sustain high humidity levels and, in the other hand, to get informations about the conductivity drift upon each humidity variation. Then, we investigated the injected flow effect. The last step was the study of the response of sensors to NH_3 at several controlled RH levels.

2. Experiments, materials and data processing

The sensing principle is similar for both phthalocyanine samples, namely a resistor constituted of a molecular material deposited on the surface of interdigitated electrodes (IDEs). All experiments were carried out in the same measurement chamber using the same workbench.

2.1. Samples processing

The IDE arrays were made of Indium Tin Oxide (ITO) deposited on a floated glass substrate. They were composed of ten pairs of digits matching the following metrics: 125 μm electrode width, 75 μm spacing, 5850 μm overlapping length, and 20 nm electrode thickness. Prior to the molecular material deposition, IDEs substrates were washed in dichloromethane, then in ethanol for 30 s with sonic waves and dried in air. Then, the sensing material was deposited, metallic connectors were clipped on the IDEs and sticked on with silver paint. Both molecular materials were deposited on IDEs by two different deposition methods. s-CoPc is an industrial product, supplied by the Europhtal company as additive 8020, consisting of a mixture of sulfonated cobalt phthalocyanines, with a mean substitution ratio of 2.3 per macrocycle (formula $Co[(SO_3Na)_{2.3}Pc]$). This product is soluble into water and was deposited via solution processing. The mother solution was diluted to a concentration of 4.4×10^{-4} mol L^{-1} and deposited directly on the surface of the IDEs with a micro syringe. The sample was heated in a desiccator during 1 h at 60 °C and then annealed at 100 °C for at least 15 h, leading to *ca.* 100 nm-thick films. CoPc was deposited onto IDEs by means of classical thermal evaporation (using a VEECO 770 system) at *ca.* 10^{-6} mbar and at a 2 Å s^{-1} rate. The thickness (100 nm) was controlled by means of a quartz micro-balance.

2.2. Ammonia workbench with controlled humidity

This ammonia workbench performs the usual conductivity measurements and monitors NH_3 concentration exposure cycles while regulating humidity levels. Argon and Ar/NH_3 cylinder were purchased from Air Liquid. All the flow rates were regulated by 5850S Brooks mass flow controllers (MFCs). The fluidic system can be depicted as two gas injection lines (Fig. 1): a primary line, which provides Ar gas charged with controlled RH at a steady flow rate of 500 mL min^{-1} and a secondary line that supplies a dry NH_3/Ar mixture containing 1000 ppm of NH_3 at variable rate in the range of 0 to 50 mL min^{-1}. The RH control in the primary Ar line is achieved by a humidity generator developed by Serv'Instrumentation, through the balance of two Ar flows (dry Ar and Ar charged with humidity) using two MFCs and monitored by a Vaisala HMT100 humidity sensor. NH_3 concentration is regulated using a MFC on the secondary line. This allowed us to conduct our survey in the 0–91 ppm range. All measurements were carried out in a cylindrical Teflon sensor chamber (*ca.* 10 cm^3 internal volume). A Keithley K6517A multimeter equipped with an internal voltage supply was used to measure the current through the sensor, which allowed us to survey conductivity of the studied materials as a function of time. All experiments were carried out at a working temperature in the range 18–22 °C. All apparatus, namely MFCs, K6517 and humidity sensor were monitored by a computer. In particular, this automation allowed us to control the samples polarization, an important point to manage in order to avoid a possible perturbation of the electronic transport by ionic conductivity, as previously reported [27]. In order to counteract this effect, we biased samples positively for 1 s and then carried out the current measurement, then we inverted the sample's polarization, also for 1 s, before switching back to 0 V during 5 s.

2.3. Specific setups

In order to depict the effects of the flow variation and of the RH variation on the sensors response, devoted protocols were designed. We used the previously described workbench (see Section 2.2).

2.3.1. Study of humidity effect

In this study, the dry and humid lines were used without any additional NH_3 injected flow (Fig. 1). The conductivity was measured as a function of time by setting a humidity level during

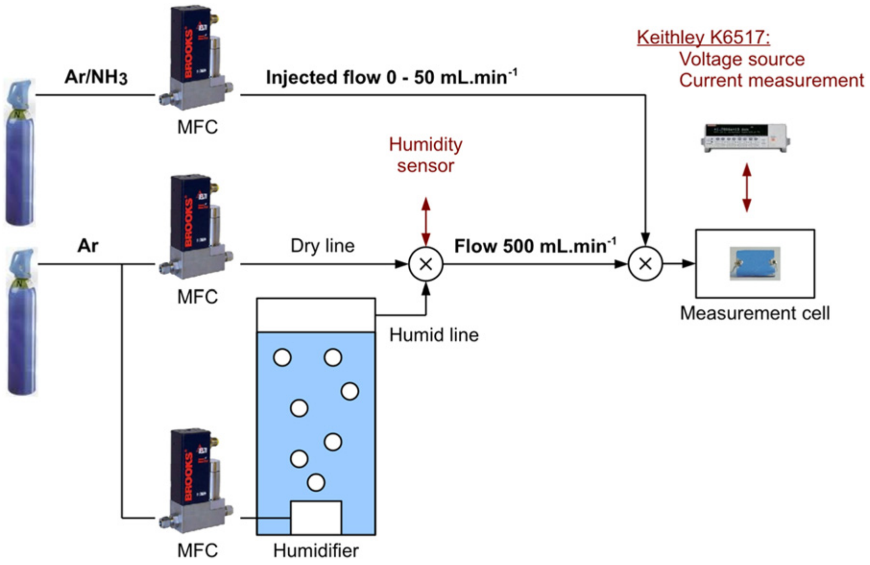

Fig. 1. Ammonia workbench with controlled humidity.

15 min and then changing the value. RH values were alternatively increased and decreased by step of 10% in the 0–80% range when possible (see Section 3.2).

2.3.2. *Study of a supplementary flow*

In this study, the Ar/NH_3 cylinder was replaced by an Ar cylinder (Fig. 1). Using this setup, experiments were conducted in the same flow conditions as ammonia workbench and could be compared. Rest periods at a flow of 500 mL min^{-1} alternate with 1 min-long periods during which an additional flow of Ar in the 0–50 mL min^{-1} range was added. The additional dry Ar flow is injected after the RH regulation of the 500 mL min^{-1} main flow. Thus, the actual RH value of the total flow injected in the measurement cell is slightly lower than the value read on the humidity sensor.

2.4. *Data processing*

Data processing was achieved using a custom-made software. The conductivity and relative response (RR) were computed and plotted *versus* time. The RR to NH_3 at a fixed humidity level was obtained after alternating of exposure and recovery periods. The exposure and recovery durations were set to 1 and 4 min, respectively. The RR was calculated using the formula (1).

$$\frac{\Delta\sigma}{\sigma_0} = \frac{\sigma_f - \sigma_0}{\sigma_0}. \qquad (1)$$

where σ_0 is the conductivity value at the beginning of an exposure/recovery cycle and σ_f the conductivity value at the end of the same cycle.

This relative variation gives the trend of sensors during a period of time. A positive variation means that the $\sigma(t)$ curve increases and reciprocally, a negative variation means that the $\sigma(t)$ curve decreases. The RR indicates the maximal conductivity variation during a cycle since the conductivity is strictly increasing or decreasing throughout a period. We studied the effects of NH_3 concentration and RH value on the different molecular materials using this metrological parameter.

3. Results and discussion

3.1. *Effect of ammonia on gas sensor*

This study has been reported in a previous publication [27]. Relative responses of the sensors were studied when exposed to different concentrations of NH_3 and O_3. Both samples showed a decrease in conductivity during exposure to NH_3 gas flow. Interestingly, s-CoPc exhibited a lack of sensitivity towards O_3 while the conductivity of CoPc increased under O_3 [27].

3.2. *Effect of humidity on gas sensor*

Prior to studying the effect of NH_3 and humidity, sensors were exposed to high RH atmospheres. CoPc is not soluble in water and thus was expected to be stable at several humidity levels. On the contrary, s-CoPc is soluble in water due to its ionic substituents. The conductivity was measured as a function of time when sensors were exposed to humidity as developed in the experimental section (see Section 2.3.1).

The measurement of the conductivity as a function of time established that s-CoPc conductivity increased when humidity levels were rising (Fig. 2). This effect can be explained by the ionic nature of the phthalocyanine substituents. Water enhances ionic charge carrier mobility thus inducing the observed increase in conductivity. However, the operating range of a s-CoPc sensor was limited to 40% RH. At higher RH values, the conductivity exhibits a sharp increase then an important decrease, without any stabilization. Observations through an optical microscope allowed us to conclude that s-CoPc had migrated on the surface of the substrate due to the presence of water vapor. The sensor was irreversibly altered.

In general, CoPc was less affected by humidity (Fig. 3). It is worth noting than the full scale in conductivity is smaller than for s-CoPc (Fig. 2). No sign of alteration of the sensing layer was observed in the 0–80% RH range. The conductivity variation at each new RH value was smaller than for s-CoPc. However, when the RH dropped below 20% the increase in conductivity became quite large, +30% from 20 to 10% and a sharp increase, +100%, was observed when lowering the humidity level from 10% to 0% RH. Such a dramatic effect can be attributed to the drying of material. Contrary to our previous observations on s-CoPc, we can conclude that CoPc conductivity highly increases only for very low RH levels.

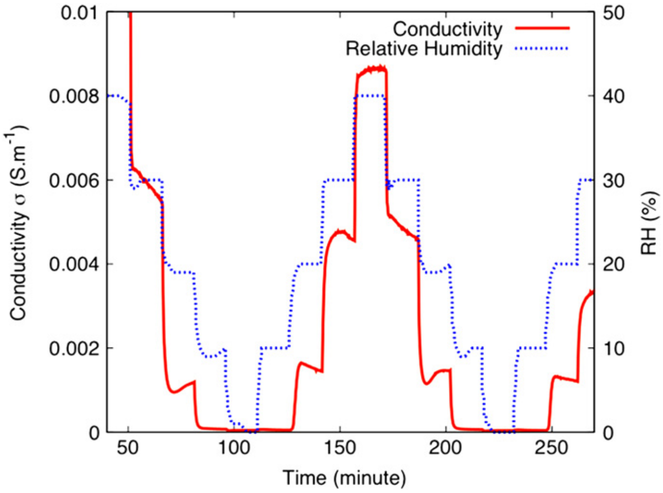

Fig. 2. Conductivity (solid line) as a function of time of a s-CoPc resistor exposed to different humidity levels (dotted line).

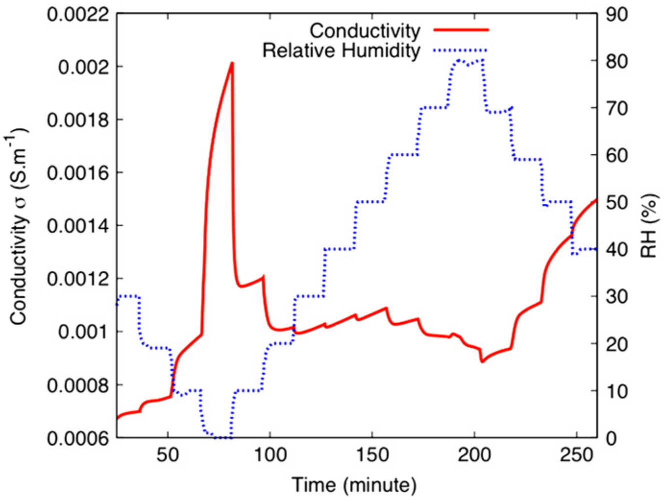

Fig. 3. Conductivity (solid line) as a function of time of a CoPc resistor exposed to different humidity levels (dotted line).

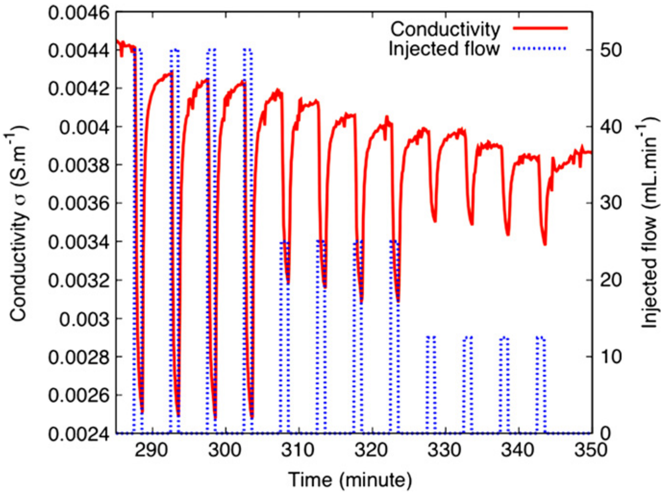

Fig. 4. Conductivity (solid line) as a function of time of a s-CoPc resistor exposed to supplementary flow of Ar for 1 min-long periods spaced by a 4 min-long static rest period. This measurement was realized at 30% RH level with 4 exposure/recovery cycles at each supplementary Ar flow of 50, 25 and 12.5 mL min^{-1} (dotted line).

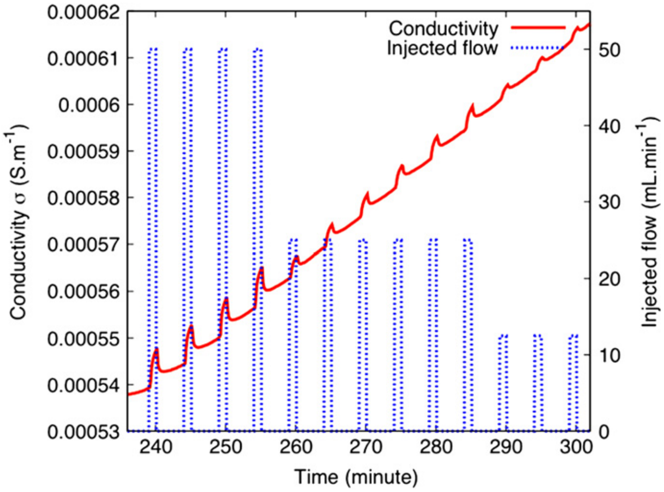

Fig. 5. Conductivity (solid line) as a function of time of a CoPc resistor exposed to supplementary flow of Ar for 1 min-long periods spaced by a 4 min-long static rest period. This measurement was realized at 60% RH level with 4, 6 and 3 exposure/recovery cycles at each supplementary argon flow of 50, 25 and 12.5 mL min^{-1}, respectively (dotted line).

3.3. Effect of flow on gas sensor

The flow effect is an important issue in gas sensing domain that has to be depicted in order to distinguish it from the actual target gases effects. Throughout the experiments performed using the protocol described in Section 2.3.2, we did observe the variations of conductivity induced by a supplementary flow. When injecting an additional flow of Ar on the s-CoPc surface, a decrease in conductivity was observed as shown at a RH value of 30% (Fig. 4). Thus, a decrease of 1.8×10^{-3} S m^{-1} was observed for an additional flow of 50 mL min^{-1}, which corresponds to a variation of 40%. Stopping the flow for a recovery period leads to an increase in the measured conductivity allowing the conductivity to return to its usual drift. Reversely, in the case of CoPc, the additional Ar flow induces a slight sensor conductivity increase as shown at a RH value of 60% (Fig. 5). The apparent dramatic drift is mainly due to a "scale effect" but has no real basis. Indeed, introducing an additional Ar flow of 50 mL min^{-1} increases the measured conductivity by less than 1.10^{-5} S m^{-1}. This corresponds to a RR of 1.5%, which is the maximum value observed. Again, stopping the flow during a recovery period allows the conductivity to decrease and return to its usual drift. These phenomena were related to a drying effect of the surface achieved by injecting the supplementary flow. As mentioned in the study of the humidity effect (see Section 3.2), in the case of s-CoPc, conductivity variations follow that of humidity. On the contrary, CoPc's conductivity increases in response to a decrease in the RH levels (Fig. 5).This is the reason why, for s-CoPc, we depicted the results for each RH value, data are summarized in Table 1a. The negative RR values show the decrease in conductivity upon each exposure. The higher the supplementary Ar flow and the humidity level, the lower the RR. At a given RH value, doubling the additional flow is followed by an identical variation of the RR. This is true for all humidity levels. However, at a given flow, the RR variation changes dramatically with the RH value. From 10 to 20% RH, the RR value is multiplied by *ca.* 17, whereas it is only increased by a factor of 1.3 when rising humidity levels from 20 to 30% RH. Clearly, the strongest effect is observed from 10 to 20% RH. However, the main point is that the higher the RH value is the more important

Table 1
s-CoPc relative response as a function of relative humidity and complementary injected flow: (a) Ar, (b) Ar/NH3 mixture.

(a) s-CoPc exposition to an Ar flow

RH (%)	12.5 mL min^{-1}	25 mL min^{-1}	50 mL min^{-1}
10	−0,49%	−0,96%	−1,86%
20	−8,69%	−17,00%	−31,71%
30	−11,36%	−22,62%	−40,50%

(b) s-CoPc exposition to Ar/NH3 flow

	23 ppm	45 ppm	87 ppm
RH (%)	12.5 mL min^{-1}	25 mL min^{-1}	50 mL min^{-1}
10	−24,01%	−31,23%	−40,63%
20	−23,30%	−33,58%	−47,92%
30	−22,17%	−33,43%	−50,84%
40	−18,68%	−30,18%	−48,43%

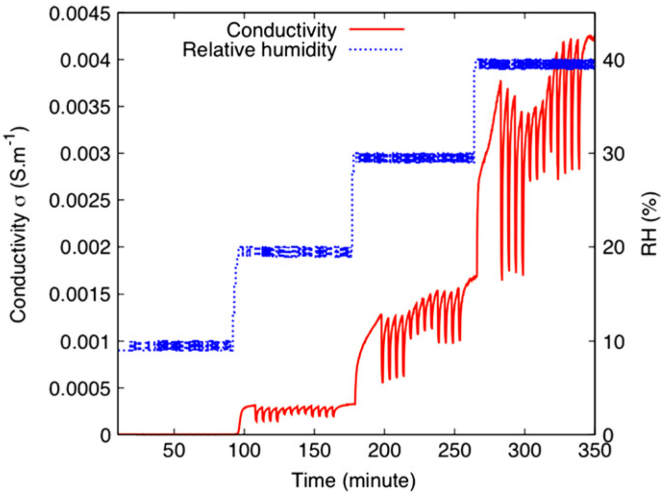

Fig. 6. Conductivity (solid line) as a function of time of a s-CoPc resistor exposed to NH_3 diluted in Ar at different concentrations for 1 min-long periods spaced by a 4 min-long rest period. This measurement was realized for 4 different humidity levels (dotted line), at 10, 20, 30 and 40% RH, respectively and for 4 exposure/recovery cycles for 3 different supplementary flows of 50, 25 and 12.5 mL min^{-1} (87, 45 and 23 ppm NH_3).

will be the drying effect of the supplementary flow. We can then conclude that s-CoPc is so sensitive to humidity that the drying effect of an additional flow, even limited to 10% of the total flow, has to be taken into account in gas sensing studies, whereas it could be neglected for CoPc.

3.4. *Effect of ammonia at controlled RH values*

Following studies on the effects of NH_3, humidity and flow, we studied the response to NH_3 at controlled humidity levels. In this study, a s-CoPc resistor was exposed to NH_3 using 3 successive injected supplementary flow of 50, 25 and 12.5 mL min^{-1} of Ar/NH_3 mixture, thus setting the concentration of NH_3 in the measurement cell at 87, 45 and 23 ppm, respectively. This measurement was carried out for four humidity levels, namely 10, 20, 30 and 40% RH. As shown in Fig. 6, the conductivity baseline of the signal was dramatically altered by each new humidity level, and the response to NH_3 highly increased with the RH value. Once more, the conductivity variation depends on the NH_3 concentration. In Table 1, these results were compared with those obtained without NH_3, as detailed in Section 3.3. At a first glance, Table 1b shows that the RR to a given NH_3 concentration remains in the same range whatever the RH value is. Thus, at 45 ppm, the RR slightly varied around 32%. Moreover, at a given RH value, the variation of the RR was proportional to the injected flow. It was then observed that when the flow was multiplied by 2 the RR was multiplied by 1.3, 1.4, 1.5 and 1.6 at 10, 20, 30 and 40% RH, respectively. However, we have to keep in mind the effect of the additional flow, as depicted in Section 3.3. The apparent NH_3 effect was mainly due to the additional flow, which is different for each NH_3 concentration (see Table 1a). Thus, at 30% RH, the effect of NH_3 remains constant at *ca.* 10%, after deducting the flow effect from the RR values. The same observation can be made at 20%, with a response to NH_3 of about 16%. Actually, except for very low humidity levels, *e.g.* 10% RH, the apparent response of the sensor was totally overshadowed by the effect of the additional flow. If this study had not been performed we would have missed the effect of the extra flow.

The CoPc resistor was exposed to NH_3 diluted in Ar using the same concentrations as for s-CoPc. Each concentration was tested for four exposure/recovery cycles. This measurement was conducted under six different humidity levels, namely 10, 20, 30, 50, 60 and 70% RH. In Fig. 7, conductivity and RH were plotted as functions of time. The drift of the baseline appears to be very small compared to the variation of conductivity associated with the exposure to NH_3. This indicates a good reversibility of the NH_3 effect during the recovery periods, and a negligible effect of the humidity variation. At each new humidity level, the recovery period was maintained longer in order to obtain the stabilization of the RH value. The associated increase in conductivity is due to the extended rest period after exposure to NH_3, while at any given RH value, the conductivity variation depends solely on the NH_3 concentration (Fig. 7). The present decrease in conductivity is very high compared to the variation due to the flow effect (see Section 3.3). For example, at a 60% RH value, at 50 mL min^{-1}, the variation is 55%, compared to a variation of only 1.5% for the flow effect, *i.e.* about 35 times higher.

In addition, the RR to NH_3 during the exposure as a function of the RH was also plotted for the three different concentrations (Fig. 8). The three curves remain quasi-horizontal for the RH values in the 20–60% range. At 10 and 70% RH, the RR starts to vary, but remain different from one NH_3 concentration to another one. From those two figures, we can conclude that the response of CoPc to NH_3 is stable in the studied humidity range and that the sensitivity appears good enough for air quality monitoring applications. Thus, no matter the RH value, the responses to 12.5, 25 and 50 ppm NH_3 remain in the 23–32%, 38–43% and 46–56% ranges, respectively (Fig. 8).

4. Conclusion

This study of the effect of humidity on NH_3 sensor response allows us to conclude that CoPc is a better sensing material for air quality monitoring applications in ambient conditions than s-CoPc. CoPc resistor exhibits a low detection level around 10 ppm and a humidity operating range from 10 to 70% RH. It is worth noting that the CoPc sensor does require neither a heating set up nor a complementary humidity sensor. The next step will be to study the response of CoPc to NH_3 diluted in air. Keeping constant the air flow, and so the oxygen concentration, but adding NH_3 during the exposure periods, we will measure the effect of NH_3. Obviously, the absolute conductivity may be different, since oxygen enhances conductivity of p-type molecular materials, but

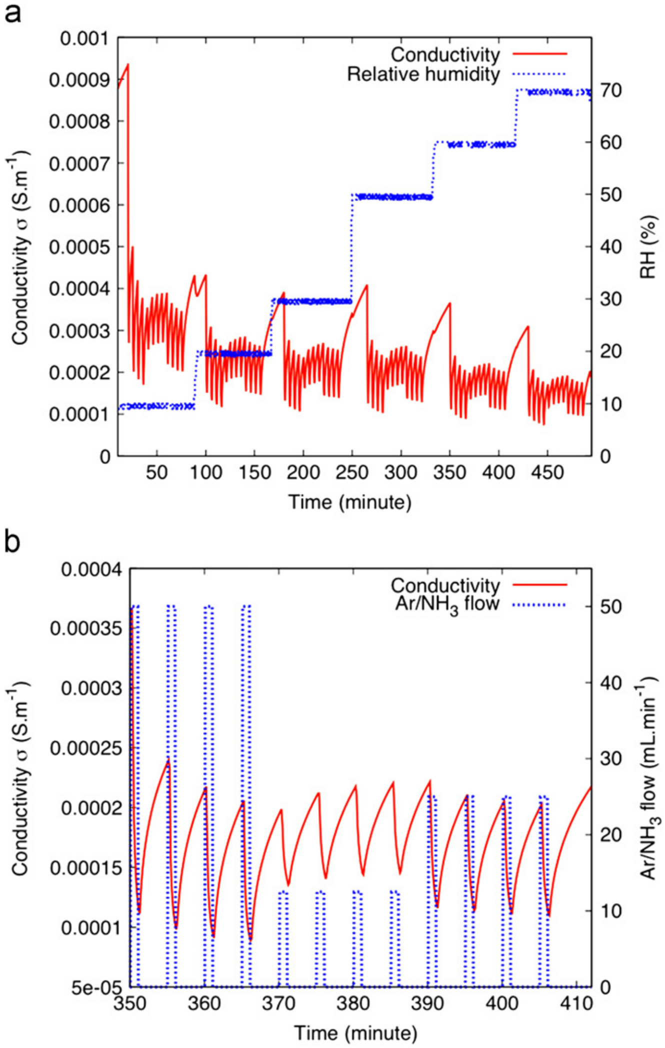

Fig. 7. (a) Conductivity (solid line) as a function of time of a CoPc resistor exposed to NH_3 diluted in Ar at different concentrations for 1 min-long periods spaced by a 4 min-long static rest period. This measurement was realized for 4 different humidity levels (dotted line) 10, 20, 30, 40, 60 and 70% RH, respectively and for 4 exposure/recovery cycles at 3 different supplementary flow of 50, 25 and 12.5 mL min^{-1}, (87, 45 and 23 ppm NH_3); (b) zoom of the curve 7a at a RH value of 60%; the Ar/NH_3 flow at each cycle was indicated (dotted line).

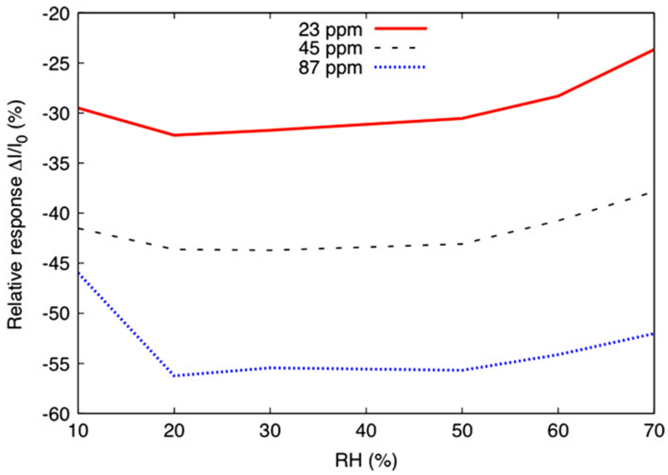

Fig. 8. Relative response to NH_3, for the exposure period, as a function of relative humidity of a CoPc resistor, at 23 ppm (solid line), 45 ppm (dashed line) and 87 ppm (dotted line).

CoPc will remain sensitive in the 20–100 ppm range of NH_3 and capable to operate in a broad range of relative humidity. We applied a dynamic methodology, with exposure periods separated by rest periods. So, the response results from a differential measurement. Another important point is the study of the supplementary injected flow that modifies the response of sensors. We demonstrated that, when the humidity level is regulated, it is important to check whether the sensor is sensitive or not to the effect of small humidity variations, especially when switching between exposure and recovery periods. Such a study should be performed each time a sensing material is used with similar fluidic setup. The s-CoPc looks unusable as sensing material for NH_3 sensors. However, another film processing with this molecule incorporated in a hybrid material did exhibit astonishing performance for high humidity level [31]. On the contrary, CoPc exhibits a response to NH_3 mainly insensitive to humidity, opening the door to a promising future for air quality monitoring applications.

Acknowledgments

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