Ammonia nanostructured sensor to implement a monitoring grid of urban environmental pollutants

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Abstract

The present study is focused on the implementation of a novel, low cost, urban grid of nanostructured sensors (based on carbon nanotubes) for ammonia concentrations monitoring, being NH_3 one of the main precursors of secondary fine particulate. The most significant interfering compounds (NO_2, NO_X and O_3), capable to influence the sensor's selectivity, have been selected by analyzing, in the city of Milan, their atmospheric concentrations collected by the ARPA monitoring network. The same data have also been used to train an Expert System, based on fuzzy logic and neural networks, aimed to extract the atmospheric concentration of ammonia (with a sensitivity of a few ppb) from the output signal of a model chemresistor gas sensor exposed to a gas mixture. In addition to the historical data set, the expert system has been fed with calibration curves (signal vs. concentration) of the gas sensor response to NO_2, O_3, NO_X and NH_3.

Capsule

A nanotechnology-based, neural network operated sensor for ammonia has been constructed and successfully tested as a component of a diffuse urban air monitoring network.

Keywords: carbon nanotubes, air quality control, environmental sensors, ammonia, fuzzy logic, urban environment.

1. Introduction

Continuous monitoring of ammonia atmospheric concentrations in urban areas has been so far widely overlooked, since its average levels are usually low (in the 20-30 ppb range) and not too different from those observed in rural areas [(1)]. Even though ammonia sources may be different for rural and urban areas, the local contribution to ammonia concentrations in the urban environment is mostly ascribed to vehicles emissions [(2)].

A growing body of investigations is highlighting the relevant role played by ammonia as a precursor of secondary fine particulate (PM10 and PM2.5) [(3,4,5)]. As a consequence, the next European regulations, presently under discussion, will possibly include ammonia among the gaseous pollutants to be steadily monitored by air quality stations. Furthermore, with respect to fine particulate, whose concentrations show the dominant contribution of the regional background [(6)], ammonia might be used as a local marker of secondary particulate formation, also acting as an effectiveness indicator of local policies aimed to control specific, even if indirect, PM emission sources.

Diffuse monitoring of air pollutants throughout an urban area requires a large number of monitoring stations, which implies a considerable economic effort if traditional (i.e. light-absorption based) pollutants detectors are used.

Chemresistors gas sensors (CGS) can represent, if properly and steadily calibrated, a valid alternative to the current systems, providing even an extended area with a diffuse monitoring network at low investment and maintenance costs. Among CGS, those based on thin or thick films of semiconducting oxides are presently available on the market even if characterized, in most cases, by a sensitivity of only few ppm.[(7)]. Basic research on this kind of sensors has not produced significant breakthroughs yet, in spite of the capability to test new architectures based on nanowires or nanorods of semiconducting oxides [8]. On the other hand, in recent years [9] carbon nanotubes (CNT)-based gas sensors have been tested, and they soon resulted to be a promising class of materials for the development of gas sensors [10-22].

With respect to commercial electrochemical sensors for environmental monitoring (mostly based on metal oxides like SnO_2, TiO_2, usually doped with Pd, Pt and Au), CNTs show a higher physical and chemical stability, better transport of charge to the electrodes and a wide range of possible architectures and operational features that make them a unique system for gas detection [21,22]. However, both the oxide and CNT-based CGS share a common deficiency, i.e. the inability to reach a sufficient selectivity in the detection of a single gas in presence of other gaseous compounds interfering with the response signal. In this frame, it is of paramount importance the search of novel algorithms for data analysis and signals deconvolution, in order to acquire high-resolution signals from the disturbing background of interfering gases.

Fuzzy logic algorithms represent a promising tool to overcome the problem of CGS selectivity, that might arise in the detection of a specific gas molecule [23, 24] (i.e. NH_3) in the presence of an interfering gas mixture (NO_2, NO_x, O_3) background.

Neural networks and fuzzy algorithms have been previously used only for the detection of alarming concentration values of leaking harmful substances (e.g. explosive gases) [25, 26], during specific tests carried out under known conditions in closed chambers. To bridge this knowledge gap, the present investigation has been focused on the selective detection of ammonia environmental levels in urban areas (where its concentrations are always much lower than 1 ppm).

In this study, we provide the first results concerning the development of a network of CNT-based gas sensors to determine (with a sensitivity of a few ppb) the environmental concentration of ammonia ($[NH_3]$) over the land domain of the city of Milan (Italy). The sensor output signal is related to a gas mixture, containing ammonia (NH_3) and some interfering pollutants, nitrogen dioxide (NO_2) above all. The sensor will be finally integrated into a diffuse grid where NO_2 O_3, C_6H_6, SO_2, CO and PM are independently monitored. It is shown that fuzzy logic algorithms can be regarded as a promising tool to extract the [NH_3] signal from an overall CGS response dominated by [NO_2] and [NO_X].

Both commercial and nanostructured sensors have been tested in parallel to evaluate the resistivity variations due to sensors exposure to NH_3 and NO_2 and specific calibration curves (inside the atmospheric concentration ranges of both parameters) have been obtained. Concerning the signal analysis of a real gas mixture (including ammonia), an Expert System based on neural networks and fuzzy logic has been trained using historical data series (Data Source: ARPA LOMBARDIA (27)) of different gaseous pollutants concentrations monitored in a specific monitoring station in Milan. Within a specific framework called *Fuzzy World* (28), fuzzy applications have been developed in order to evaluate continuous ammonia concentrations using the gas mixture signal and NO_2 continuous concentrations as input data.

The CNT-based CGS developed in the present project is responding to both NH_3 and NO_2, and the NO_2 concentration is also being measured independently, so that the NH_3 concentration can be obtained using fuzzy logic to provide a calibration for NH_3 that uses the known NO_2 concentration to remove the NO_2's contribution to the signal.

2. Materials and methods

2.1 Preliminary characterization of urban pollution in Milan

The preliminary analysis of the relative concentrations of NO_2, O_3 , NO_X and NH_3 was carried out on the basis of experimental data collected with standard certified analyzers based on light absorption principles (in the IR and UV ranges) distributed in the eight monitoring sites of the public air quality network of the Regional Agency for Environment Protection (ARPA Lombardia) . The historical data used to feed the Fuzzy Logic algorithms have been recorded by the same network. As a typical case of fuzzy logic training, the hourly monitoring of NO_2, NO_X O_3, NH_3 during the whole month of March 2008 in a specific monitoring station (Via Pascal, Milan) has been considered (**Fig.1**).

2.2 Chemresistor gas sensor preparation and calibration

CNT thin layers have been deposited by drop casting a solution (water and NaOH) of single wall CNT (CARBOLEX, Inc.) on either plastic or alumina substrates. For electrical measurements, two Ag contacts have been deposited on the plastic substrates at the opposite sides of the films, whereas interdigitated metallic electrodes have been deposited on the alumina substrates. All sensors, including humidity and temperature sensors, were mounted on a specifically designed circuit board (**Fig.2, right panel**) connected to a personal computer through a National Instrument PCIe-6251 data acquisition board.

The measurements have been carried out in air by exposing the sensors to a point-like source of NH_3, or in a controlled N_2 inert atmosphere by exposing the sensor to selected ammonia concentrations. The gas concentration was measured either with a calibrated, commercially available, chemresistor gas sensor (Figaro, Mod. TGS 2602) or with a quadrupole mass spectrometer (Prisma QMS 200, Pfeiffer Vacuum), depending on the [NH_3] range.

The variation R_S/R_0 of sample resistance R_S upon gas exposure with respect to the baseline resistance value R_0 was measured according to the electrical scheme shown in **Fig.2 (left panel)**, by using the following equation (2.2.1):

$$\frac{R_S}{R_0} = \frac{V_C - V_{RL}}{V_{RL}} \frac{V_0}{V_C - V_0} \qquad (2.2.1)$$

where R_L is a load resistance (about 30 KΩ), V_c is a fixed voltage (5 V) , V_{RL} is the measured voltage drop across R_L upon gas exposure, and V_0 is the voltage drop across R_L measured before the gas exposure. Once V_c has been fixed, the measure of V_{RL} and V_0 yields the R_S/R_0 ratio.

2.3 Expert system implementation

In order to determine continuous hourly average ammonia concentrations from the sensor's output signal due to a gas mixture, a selectivity analysis has been carried out by developing two new dedicated applications based on "Fuzzy World (FW)", a data analysis framework [(28)] characterized by the use of neural networks, fuzzy sets [(29)] and genetic algorithms [(30, 31)] .

In this framework, each variable (i.e., ammonia concentration, specific gas signals, the overall signal due to the gas mixture) has been identified as a fuzzy function characterised by proper fuzzy sets. A fuzzy set, F, is described through a membership function μ_F, within the continuous range [0,1] and represents the membership degree to a fuzzy set of values of each fuzzy function. In general, a fuzzy set is represented by trapezoidal or triangular values (see **Fig. 3-a,** which shows the representation of a fuzzy trapezoidal number identified by the membership function μ_F).

The present study approach has been developed through the coupling of two linked Fuzzy Applications (hereafter denoted as Direct and Inverse Applications, respectively). The algorithm that, applied to fuzzy systems, determines the approximated value of the consequent variable follows two successive steps:

- the determination of the membership function of a crisp value of an antecedent variable (e.g., [NH_3], [O_3], …) to one or more fuzzy sets that build up the fuzzy system (fuzzification process);
- the evaluation process of the value of the membership function associated to the fuzzy consequent (defuzzification process).

The defuzzification process that has been used in our case study is based on the centroid method, also known as center of gravity or center of the defuzzification area. This technique, developed by Sugeno in 1985 [(32)] is the most commonly used technique and is very accurate.

It has been demonstrated [(33)] that, when the centroid method is used, a fuzzy system is a neural network composed by an input layer, one internal hidden layer and an output layer (**Fig. 4**). Generally, the neural network is composed by an input signal that enters the network through the synapses that link the first external layer (input layer) and, through the internal connections (from the left to the right, **Fig. 4**) of the hidden layer, ends up with the output layer, generating a signal that is compared to the input one. If the difference between the output signal and the input signal is below a defined fixed value, the algorithm stops and the weights associated to the synapses are used for the deconvolution of successive input signals. If the difference between the output signal and the input signal is higher than the defined fixed value, then the algorithm adjusts the weights moving from the left to the right and the training process goes on till the result becomes acceptable. Training algorithms can then be applied to this neural network. In particular, a one step algorithm, called TLS (Table Look up Scheme) algorithm [(34)] has been adopted in Fuzzy World in our case study. The TLS algorithm is used for the Expert System training, generating $2n_i + 1$ fuzzy sets (neurons) for each literal variable (fuzzy antecedents and fuzzy consequent), where n_i depends on the variability ranges of the numerical values of each specific variable. The Fuzzy World application suggests a possible number of fuzzy sets for each variable (not optimised) that can also be modified by the end user. The TLS algorithm is able to generate the fuzzy rules (that constitute the hidden layer of the neurofuzzy Expert System) automatically on the basis of historical data and learns how to answer to new inputs as the inference engine (i.e. the hidden layer) finds the connections (synapsis) among the antecedent variables and generates several fuzzy rules describing these connections, instead of a manual generation of fuzzy rules by an operator. The approximation of functions with the TLS algorithm is usually good according to literature (35). Nevertheless, the optimisation of the number of fuzzy sets of each literal variable can improve the precision of the Expert System results: a genetic algorithm (36) has then been adopted in order to optimise the number of fuzzy sets associated to each single variable (fuzzy antecedents and fuzzy consequent). The genetic algorithm applied to our case study represents an innovation with respect to standard applications and has improved the Expert System results of about 10-20% with respect to the results obtained only using the TLS algorithm.

Fig.3-b shows a schematic representation of the genetic algorithm applied to our case study. Input data LV_i (represented by the different pollutants concentrations) are elaborated by the Expert System through a genetic algorithm that generates a number of different populations (30 populations globally in our case) represented by specific individuals characterized by a proper genome (each $n_{i,j}$ in **Fig.3-b** represents the fuzzy set of the LV_i variable in the j-th genome). When the measured output data (gas mixture signals V_M) are sufficiently close to the real ones (with a maximum percentage error of about 5%) the genetic algorithm has reached its aim. The difference between the measured and real values of gas mixture signals is called “Fitness coefficient”: the best individuals among the 30 populations created by the genetic algorithm will be then represented by the lower fitness coefficient and the genome associated to this selected individual will be adopted for the defuzzification process since it optimises the TLS algorithm results.

The procedures so far described constitute the “Expert System Training” or “Direct fuzzy Application”. After the Training Session of the Expert System, an Inverse Fuzzy Application reproduces the functionality of the sensor under real working conditions (**Fig. 5**). Actually, starting from the signal of the gas mixture (input variable N.1) and from the continuous concentration of the most interfering pollutant with ammonia (NO_2, as input variable N.2), the Expert System selects, among all the fuzzy rules elaborated during the optimisation of the Direct Application, the only rules containing the data inputs of the Inverse function. Input data of the Inverse function and the selected rules are then elaborated (thus explaining the importance of the linkage with a Direct Application) so that the Expert System calculates the ammonia concentration which approximates best the real ammonia value as final output. The Inversion process can calculate [NH_3] from single gas mixture signals in real time or treat larger datasets and create an output file that lists all [NH_3] results.

3. Results

3.1 Preliminary investigation of gaseous pollutants concentrations in Milan

Both the experimental and modelling parts of this study have started from the analysis of continuous concentrations data of gaseous pollutants already monitored by an existent air quality monitoring station in Milan where ammonia concentrations are monitored along with nitrogen oxides from the same standard certified analyzer. Actually, an historical data series of pollutants monitored in the city of Milan can show their characteristic atmospheric concentration ranges (fundamental for the design of new specific environmental sensors) and represents, at the same time, a validated data set on which an Expert System, based on fuzzy logic and neural networks, can be trained in order to be selective for the determination of single gas concentrations from an overall signal due to a gas mixture. In **Fig.1** an extrapolation of a whole month (March 2008) of concentrations data for different atmospheric pollutants is reproduced. Despite of the low and quite stable concentrations of ammonia and ozone at urban level in Spring (within the range 0-40 ppb), the great instability (remarked by high and narrow peaks) of nitrogen oxides concentrations surely represents the most critical aspect of the study when dealing with the selectivity analysis of the output signals of environmental sensors.

3.2 CNT-based CGS testing

Fig.6 shows a typical resistivity variation obtained by exposing the CNT layer to different concentrations of NH_3, ranging from 1 to 5 ppm. The response of CNTs is compared to that measured for a commercially available chemresistor gas sensor (Figaro, Mod. TGS 2602). For a better comparison with the CNT response, the signal of the latter has been multiplied by (-5). Therefore, while CNTs show an enhancement of resistivity upon NH_3 exposure, the TGS 2602 gas sensor actually shows an increase of conductivity. It should be observed that the response of CNTs is slower than that of the semiconducting metal-oxide layer. However, the CNT sensor is operated basically at room temperature, while the TGS 2602 sensor has an internal heater (280 mW dissipated on 2x2 mm^2 area, approximately). The heating process is required to refresh the sensor surface and avoid poisoning upon exposure to gas molecules. This can be detrimental for the chemical and structural stability of the sensor if it is continuously operated for several months. The response of CNTs is presently good even at low temperatures and this is a promising feature if one does not want to induce any sensing layer degradation through heating elements. The calibration curve of the CNT based sensor, in the 0-10 ppm range of ammonia concentration, is shown in **Fig.7-a**., where different datasets are represented, which distribute along a straight line for $[NH_3]$ ranging from 0 ppm up to about 5 ppm, evidencing a clear linear response of the CNT-based ammonia sensors. **In Fig.7-a**, the vertical axis displays the R_s/R_o-1 values, and therefore the straight line intercepts the axis origin (0,0). The datasets differ from one another because they have been collected at different relative humidity (R.H.) conditions. As each data set displays a linear behaviour of R_S/R_0 vs. $[NH_3]$ (i.e. $R_S/R_0 = \alpha_{R.H.} \cdot [NH_3] - 1$), with different slopes ($\alpha_{R.H.}$) determined by the different R.H. conditions, in order to represent all data in the same plot, the R_s/R_0-1 values have been normalized to the proper slope (see the discussion below on the humidity effects). The first experimental tests results for the CNT-based sensor in the 0-1 ppm range are interesting if compared to the ones resulting from standard certified analyzers where an analogous linear correlation between the output signal and pollutants concentrations is evidenced too. This aspect reinforces the modelling approach used for the Expert System training based on the assumption of a linear correlation between pollutants concentrations and output signals coming out from the sensor. In **Fig.7-a** deviations from a linear behaviour are detectable for $[NH_3]$ values, in agreement with the results presented by Suehiro *et al.* [(37)] **.** Finally, **Fig.7-b** shows the effects of R.H. on the response of CNT-based CGS to $[NH_3]$. This effect is described by plotting the slope $\alpha_{R.H.}$ of the Rs/R_0 vs. $[NH_3]$ curves collected at different R.H. conditions, ranging from 50% to about 65 %. In this range, the $\alpha_{R.H.}$ dependence on R.H. is linear and $\alpha_{R.H.}$ increases with R.H.

3.3 Testing of Expert system algorithms

As mentioned above, the approach followed in the present project for signals elaboration is based on fuzzy logic and neural networks within the Fuzzy World framework. In this framework several applications (both direct and inverse) have been built on the basis of historical data of atmospheric pollutants concentrations over the whole year 2008. The aim of these applications is to support the readout of the [NH_3] by the CGS, providing a tool for extracting this value from the gas mixture signal read by the CGS, once the [NO_2] is independently measured. As an example of the Fuzzy World output, we consider the data measured in about two weeks with a readout of the 4 gas concentrations (NH_3, O_3, NO_X and NO_2) every hour. The total number of the four concentrations readouts is 336. These readouts constitute the dataset for the direct application. Once the system has been trained, the inverse application has been run by feeding the system with a dataset of 605 readouts, each one composed of the [NO_2] and the overall gas mixture signal. These readouts have been created by using hourly values collected in about 25 days different from those used to build the (direct) training dataset.

A typical output of Fuzzy World algorithms is shown in **Fig.8** and summarized in **Table 1**. The top panel of **Fig.8** shows the correlation between the measured [NH_3] values and those calculated by the inverse application. As can be observed, the inverse application has grouped the 605 readouts into 15 distinct [NH_3] values (i.e. 15 horizontal lines in the plot). The points distribution in each line is indicative of the spread of the set of measured [NH_3] values that the inverse application has related to a definite calculated value. In order to evaluate the capability of the inverse application to return a [NH_3] value consistent with the measured values, a 5x3 matrix of plots is shown below the top panel of **Fig.8**. Each of these plots displays the histogram generated for each horizontal line. The height of the histogram bars represents the frequency of measured [NH_3] values in the 5-30 ppb range across each line. Each histogram is labelled by the corresponding calculated value. **Table 1** summarizes the main results of **Fig.8**. In the first column the [NH_3] values calculated by the inverse application are reported, while the second column specifies the number of measured [NH_3] values that have been related to each calculated value. The third column reports the average of the real [NH_3] values, while the fourth column reports the absolute value of the difference, Δ, between the calculated and the average measured values. The fifth column reports the standard deviation of the average measured values (column 3), while in the sixth column the separation between two consecutive calculated [NH_3] values is reported.

Calculated [NH3] [ppb]	Number of measured data	Average neasured [NH_3] [ppb]	Difference between average real and calculated NH_3 values [ppb]	Standard deviation of the average measured [NH_3] [ppb]	Separation between consecutive calculated values [ppb]
6.12	18	8.32	2.2	0.73	
6.88	218	8.93	2.05	1.08	0.76
7.89	50	9.17	1.28	1.56	1.01
8.9	41	9.68	0.78	1.09	1.01
9.91	11	9.18	0.73	1.09	1.01
10.92	129	10.79	0.13	0.91	1.01
11.93	9	11.83	0.10	0.61	1.01
12.95	29	11.89	1.06	1.72	1.02
13.96	8	12.46	1.5	3.33	1.01
15.27	19	14.90	0.37	2.45	1.31
16.73	15	16.14	0.59	3.67	1.46
18.18	16	17.19	0.99	4.1	1.45
19.63	28	20.04	0.41	3.67	1.45
21.09	3	23.50	2.41	0.62	1.46
22.54	11	23.75	1.21	4.40	1.45

Table 1: Main results of the Inverse Fuzzy Application extracted from the data represented in Fig.8

4. Discussion

Air pollution in Milan is actually monitored by the air quality network of ARPA Lombardia (the Environment Protection Agency of Lombardy) composed of 8 monitoring stations, located in areas characterised by different atmospheric pollution conditions. In these monitoring stations continuous gaseous pollutants concentrations (whose monitoring is mandatory according to Italian Regulations) are measured using standard certified analyzers based on light absorption principles. Since certified analyzers are very expensive, each air quality station monitors at least the most critical parameters for each specific area. This means that O_3 is always monitored in background stations or where traffic congestion is not present while C_6H_6 is mainly monitored along streets with high traffic. Nevertheless, average pollutants concentrations over a wide area are not a valid indicator for the evaluation of people exposure to environmental pollution in an urban area. An exposure study must start from a dataset of continuous pollutants concentrations monitored by a high resolution monitoring grid composed by simple and cheap environmental sensors. An intermediate solution is represented by passive samplers but they just measure average concentrations over their whole exposure time. The final solution (supported by the authors) can be represented by the development of a high resolution grid composed of cheap environmental sensors with a high sensibility for continuous monitoring of gaseous pollutants concentrations.

Concerning the neurofuzzy elaborations of air pollutants hourly average concentrations, collected by a specific monitoring station in Milan municipality over the year 2008, the following gases have been analyzed: ammonia (NH_3), ozone (O_3), nitrogen dioxide (NO_2) and nitrogen oxides (NO_X). A direct fuzzy application has been built to obtain the overall electrical signal corresponding to the interaction between the sensitive layer of a sensor and the gas. [NH_3] has then been extrapolated from that overall signal through an inverse fuzzy function with two data inputs, i.e. the signal itself and NO_2 continuous concentrations.

From the data shown in **Fig.8** and **Table 1**, three basic indicators can be identified to evaluate the capability of the Fuzzy Expert System to extract the unknown [NH_3] from the signal of the gas mixture, provided that [NO_2] is measured independently. The first indicator is represented by the spacing among the calculated [NH_3] values. The measured [NH_3] range for the 605 input values was 6.47-29.09 ppb, while the calculated [NH_3] range was 6.12-22.54 ppb. The inverse application places 15 values in the latter range, separated from each other by less than 2 ppb (0.76 to 1.46 ppb,

Table 1, column 6). This set of values is regarded as satisfactory, if one assumes that the resolution of certified analysers is 2 ppb. Furthermore, a second indicator is important in the output evaluation, i.e. the difference between the calculated [NH_3] values and the average value of the corresponding data-set of measured [NH_3] values. As can be observed (**Table 1**, column 4) this difference is usually below 2 ppb, i.e. comparable with the resolution of certified analysers. Finally, it is important to evaluate the spread of the real data related to each histogram with respect to the average values, i.e. the histogram width. As can be observed, the histograms are usually narrow, the spread being much larger for high concentration values (**Table1**, column 5, standard deviation from the average). However, the cases of a high [NH_3] are much less than those of low [NH_3] , and the result is apparently worse because of the lack of a suitable number of counts to properly characterize the distribution.

Therefore, the results represented in **Fig.8** are regarded as a consistent starting point for future implementations of the algorithm, considering that the direct and inverse algorithms have been run on different datasets, therefore reproducing the working conditions of the [NH_3] detection system by the Fuzzy Expert system, that aims at extracting the unknown [NH_3] value from the gas mixture signal. As already remarked, the expert system aims at supporting the measurement of the [NH_3] by CNT-based CGS, especially in the case of relevant interfering effects due to other polluting gases identified in the present study.

As for the implementation of the Fuzzy application with the CNTs data, it has been observed that, in the absence of interfering pollutants, a linear behaviour for the CNTs signal vs [NH_3] curve can be assumed (**Fig.7-a**) for [NH_3] values below 5 ppm. This well compares with the linear response of certified gas analysers that was introduced in the training stage. Therefore it is straightforward to introduce the CNT response curve into the Fuzzy applications. The same linear dependence was assumed also for the interfering pollutants, when the CNTs are exposed to each of them separately. An apparent non linear behaviour of the CNT signal vs [NH_3] can in principle be detected when the

[NH_3] is monitored in the presence of all interfering pollutants: this has motivated the choice to implement the Fuzzy world applications.

It has already been mentioned that when CNTs are used to detect ammonia, the most important interfering gas is NO_2, since on one hand it represents the prevailing pollutant in the urban environment we consider (see comments to **Fig. 1**) and, on the other hand, it is known that CNTs exhibit a remarkable response to NO_2, as well. Furthermore, the response of CNTs to ammonia and NO_2 is opposite, i.e., while upon exposure to NH_3 the CNTs resistivity increases, upon exposure to NO_2 the resistivity decreases. This behaviour will represent a new element for the implementation of Fuzzy Logic, as so far the response to different gases was assumed to yield signals with the same sign. For instance, one may obtain a null signal from the CNTs sensor, but this signal is provided by a suitably balance of non-zero [NH_3] and [NO_2] values.

Another important aspect of monitoring under real conditions is represented by the role of humidity. It has been found that humidity strongly affects the CNTs response, as well as the response of the Figaro reference CGS, as shown in **Fig.7-b** by the dependence of $\alpha_{R.H.}$ on R.H, at least in the R.H. range we have considered (51%-64%). We can not exclude that outside this range the behaviour can deviate from the linear one, expecially in the conditions of very high RH (e.g. 80%) where saturation effects are expected. However, the measure of R.H. can also be independently carried out with a dedicated (and calibrated) humidity sensor. On this basis, the set of measured [NH_3] values can be normalized on the basis of the calibration curve of the sensor response vs. R.H. at fixed [NH_3].

Finally, it is worth observing that the most interesting range for atmospheric [NH_3] monitoring is well below a ppm concentration. In this view an effort is being made to increase the sensitivity of our CNT sensors down to a few ppb detection limit. This can be achieved by a correct balance of the electrical components in the signal readout circuitry, that has already proven to be crucial for noise reduction. More interestingly, the sensitivity can be enhanced by suitable doping or functionalization of the CNT layers with metallic clusters or nanoparticles. It is worth mentioning that the present calibration curve has been extended to sub-ppm range, which is usually neglected in current studies on CNTs (see, e.g., Ref. 38 and Refs therein) which adds further value to the present data in the field of atmospheric monitoring.

5. Conclusions

The present study has been focused on the development of a nanostructured sensor for the detection of atmospheric ammonia concentrations to be implemented in a low cost and diffuse air quality monitoring grid in Milan. On the basis of historical data of pollutants concentrations (including ammonia) of the ARPA air quality monitoring grid, a neurofuzzy Expert System has been trained in order to selectively determine ammonia concentration from the sensor's output signal due to a gas mixture. CNT-based gas sensors have then been developed (sensible to ammonia and to other interfering gases, mainly NO_X) and demonstrated to be a valid and economic solution for diffuse environmental monitoring in urban areas since carbon nanotubes are high sensitive to gaseous pollutants even under environmental temperature and relative humidity conditions. Concerning the selectivity analysis of CNT based sensors output signals, a modelling approach based on fuzzy logic and neural networks has elaborated overall sensors signals for the determination of continuous ammonia concentrations, filtering the interfering pollutants background signals.

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FIGURE CAPTIONS

Fig. 1: Continuous gaseous pollutants concentrations over one week (March 2008). Data source: ARPA LOMBARDIA (monitoring station of Via Pascal, Milan). Public data (with the exception of [NH_3]) available on the website: www.arpalombardia.it

Fig. 2. Right panel: Schematic representation of the electric circuit used to measure the resistance variation R_S/R_0 upon gas exposure. Left panel: Board specifically designed for the location of relative humidity, temperature, and CNT-based ammonia sensors

Fig. 3-a: Trapezoidal fuzzy set described through the membership function μ_F

Fig. 3-b: Genetic algorithm applied to "genomes" represented by populations of fuzzy set numbers associated to each specific literal variable (LV_N) of the direct application. The first individual of the first population created by the genetic algorithm is represented by its specific genome (in red, first row).

Fig. 4: Box diagram representing the Direct Fuzzy Application for the determination of a Gas signal mixture from a known set of pollutants concentrations

Fig. 5: Box diagram representing the Direct and Indirect Fuzzy Applications for the determination of ammonia continuous concentrations

Fig. 6: Example of CNT response to ammonia exposure, compared with the TGS 2602 response to the same gas exposure

Fig. 7-a: Calibration curve (R_S/R_0 -1 vs. ammonia concentration, ppm) for the CNT sensor. The straight line has a slope of $1x10^{-3}$ ppm^{-1} and is drawn to point out the linear dependence of R_S/R_0 on [NH_3] for low ammonia concentrations. The different symbols indicate that the data have been collected at different R.H. conditions.

Fig. 7-b: Dependence of the slope of the (linear) R_s/R_0 vs. [NH_3] calibration curve on R.H. conditions.

Fig. 8: Top panel: Correlation between the measured and the calculated [NH_3]. The straight line represents the ideal 1:1 ratio between calculated and measured values.
Bottom panel: Absolute frequency plots (histograms) of the measured values associated to each calculated value. The plots have been labelled by the corresponding calculated (FW) value.