

Polypyrrole Based Aroma Sensor*

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Abstract

The change in conductivity of conducting polymers when exposed to volatile gases can be exploited for the construction of aroma sensors. In this communication we report the preliminary tests of two versions of an aroma sensor based on arrays of doped polypyrrole films. We have used these prototypes for the identification of simple organic vapors and complex aromas. The input signal was the fractional change in the resistance of the films and the data acquisition was performed automatically. The pattern recognition process was implemented by a multivariate analysis and by neural network processing. The discriminating power among different odorants was better than 90%.

Keywords: electrochemical polymerization, polypyrrole and derivatives, gas sensors

1. Introduction

After exposure to a vapor of volatile substances, conducting polymer samples can have their conductivity altered in a reproducible manner. If slightly different polymeric films are used as an ensemble, the combined pattern of variation of the individual conductivities can be treated as a specific “signature” of the volatile compound. This is the operation principle of the conducting polymer based “electronic noses” [1] currently in development in different laboratories. Those equipments could find an appropriate niche in industrial and commercial applications, since aroma analysis and classification continues to be a very subjective matter, mostly dependent on the judgement of human panels.

In this communication we present initial results of a polypyrrole (PPY) based gas sensor, in which an array of differently doped PPY films was used to identify odorant substances. The calibration tests of the equipment were performed using simple odors (such as those of specific chemical compounds) and complex aromas (e.g. those of different types of wine).

Several important steps have to be followed to assure a good reliability of the instrument. First, it is essential that the polymeric films be prepared in a very controlled manner. Second, the data acquisition process must be automatic to allow for the collection of a large amount of input data (i.e. the change in the conductivity of the films as a function of the exposure time) with minimum noise. Finally, the key to a good performance of the device rests in the use of an adequate algorithm of pattern recognition.

In each case considered, we have examined the discriminating features of a Principal Component Analysis (PCA) - a chemometric technique [2, 3] - and of the Multi Layer Perceptron (MLP) model of neural network [4]. In these preliminary analyses, the instruments were able to discriminate among the odorant substances tested with a success rate of the order of 90%.

2. Experimental

2.1 Materials and Methods

Pyrrole (Aldrich, USA) was freshly distilled under reduced pressure before use. As doping agents we have used *p*-toluenesulfonic acid sodium salt (*p*-TSA(Na)), tetrabutylammonium tetrafluoroborate (TBATFB), *p*-toluene-sulfonic acid monohydrate (*p*TSA), octanesulfonic acid (OA) and lithium perchlorate (all of them from Aldrich, USA). Water, acetonitrile (AcCN) (Aldrich, USA) and propylene carbonate (PC) (Janssen, USA) were used as solvents. All reagents had analytical grade and were used as received.

2.2 Preparation of Sensors

Two different types of sensors were prepared, determining the two versions of the instrument (P-1 and P-2, respectively) used in this work. In the first prototype, the sensors were composed by two steel needles fixed in a V-shape on top of a rigid insulating support. The doped PPY films were galvanostatically prepared using a current density of 2.5 mA/cm² and would grow to bridge the ~40 μm gap between the needles. The electrical resistance of the films was measured using a model 195A digital multimeter (Keithley, USA) with a GPIB interface and the data were automatically collected every 30s and stored in a personal

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computer for posterior analysis. Three sensors, identified respectively as P1-S1 (PPy-pTSA (water)), P1-S2 (PPy-TBATFB (PC)), and P1-S3 (PPy-LiClO₄ (AcCN)), were used.

On the other hand, the sensors used in prototype P-2 were doped PPy films electrochemically grown on top of commercially available 300 nm thick gold 4-probe electrodes (MB-4000, Smart Microsystems, UK). The 10 μm wide colinear probes had a 10 μm separation and offered an active length of 2.0 mm for the polymer deposition. All electrochemical procedures were carried out using a three-electrode cell, controlled by a model AFRDE4 bipotentiostat (Pine, USA). (The reference electrode was Ag-AgCl and the counter electrode was a platinum plate.) Before deposition, the gold working electrodes were cleaned by cyclic voltammetry in 2 mol.dm⁻³ sulfuric acid and subsequent immersion in water; they were kept under pure water until the moment of use. All films were prepared at a constant potential V_0 using a mixed solution of pyrrole (0.05M) and of the doping agent (0.1M). In Table 1 the six sensors prepared in this manner are identified.

Table 1

Doped PPy films used as sensors in P2 prototype

Sensor	Composition (nature of solution)	V_0 (Volts)
P2-S1	PPy -pTSA (water)	0.9
P2-S2	PPy -LiClO ₄ (AcCN)	1.10
P2-S3	PPy - TBATFB (PC)	1.20
P2-S4	PPy- OA (water)	0.85
P2-S5	PPy- pTSA(Na) (water)	0.95
P2-S6	PPy -pTSA(Na) (water)	0.95

For this prototype the 4-points probe method [5] can be used to determine the film conductivity during exposure to the volatile compounds. A 30 μA constant current was injected through the two more external probes, while the potential difference V_{23} between the two more internal probes was measured. Typical values of V_{23} were in the (200 μV - 2.00 mV) range, as this potential difference would depend on the polymer resistivity. With this method metal-polymer contact resistance effects were eliminated, and the sensors had an ohmic behavior for currents in the (10 μA - 200 μA) range.

2.3 Sensor arrangement and test chamber

While for prototype P-1 each individual sensor was successively placed directly on the top of an Erlenmeyer containing the volatile substance of interest, in version P-2 of the equipment a 6-sensor array was fixed on the top part of a sealed chamber (see Fig. 1). Special fixtures allowed the controlled entrance of a N₂ flow, used both to purge the system after data acquisition and to collect the baseline. If necessary, the sample could be heated and agitated prior or during measurement.

2.4 Electronic circuit and data acquisition system

For the prototype P-2 a specific electronic circuit was designed to control the current in each individual sensor (Fig. 1). A single CI-741 and a adjustable resistor (trimpot) were used as a current source so that V_{in} , the input tension on the CI, was the same for all sensors.

For all sensors, the values of V_{23} were acquired via a differential voltage input of a Data Acquisition Processor (DAP) interface (Microstar Laboratories, USA), capable of digital filtering to eliminate most of the noise characteristic of DC

measurements and amplify the input signals. Although only six sensors were used in these preliminary tests, 16 single ended or 8 differential input were available in the interface (2 per sensor, in a total of 8 possible simultaneous input data).

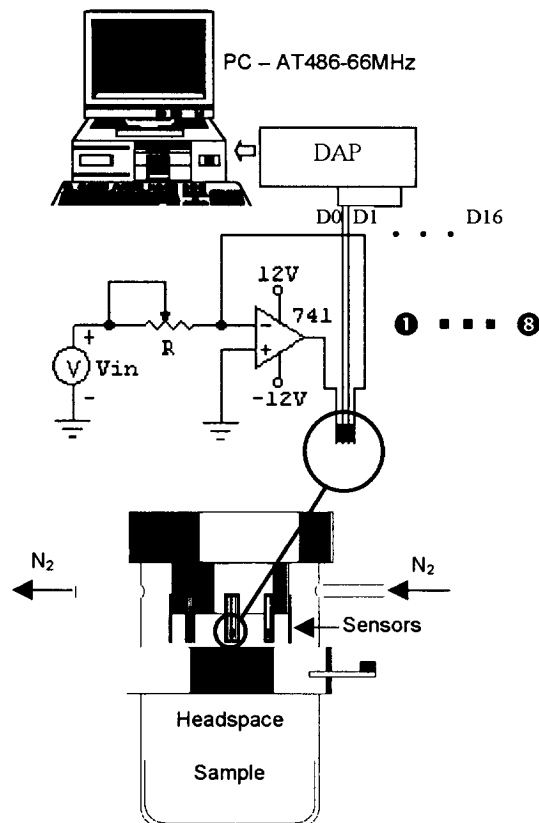


Fig. 1: Diagram of the P-2 prototype, with an indication of the current source for one of sensor units.

2.5 Systems analyzed

The P-1 system was calibrated by exposing the sensors to ethanol (ET), carbon tetrachloride (CT), and methanol (MET) vapors, and the fractional change of the electrical resistance of the films measured. In Fig. 2 the normalized value of this quantity for each sensor is shown after exposure to these substances.

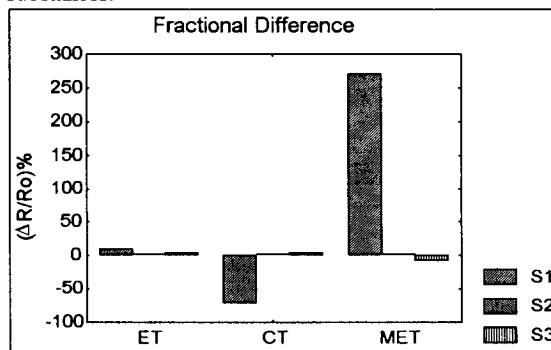


Fig. 2: Fractional change of the electrical resistance of P-1 sensors after exposure to the volatile compounds.

Complex aromas were analyzed with the P-2 prototype. Since sensors S5 and S6 were lost before the end of the tests, complete

data sets were available only for the remaining ones. In Fig. 3 we present the fractional change of the input voltage on these sensors after exposure to different types of wine.

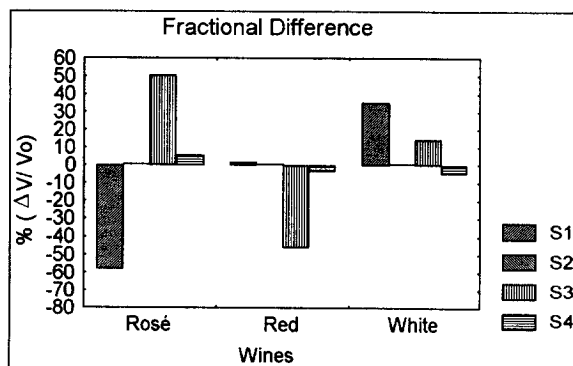


Fig. 3: Fractional change of V_{23} in four of the P-2 sensors after exposure to rosé, red and white wines.

In Fig. 4 we show the corresponding results for the P-2 sensors after exposure to red wines of different vintage.

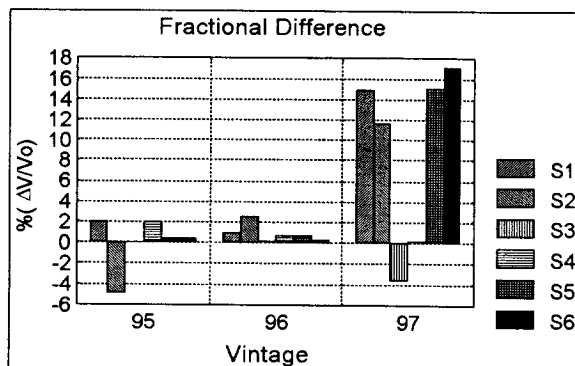


Fig. 4: Fractional change of V_{23} in the P-2 sensors after exposure to red wines of different vintages.

3. Pattern Recognition Procedures

The data were examined by Principal Components Analysis (PCA) and by an artificial neural network procedure to discriminate characteristic patterns of the odorant substances.

3.1 Principal Component Analysis (PCA)

PCA is a powerful linear supervised pattern recognition technique that has been widely used for extracting information from complex multidimensional input patterns. It is a data reduction technique based on the projection of the data set on the basis formed by the principal components (PC) of the covariance matrix. The first principal component (PC1) contains the maximum information available into a single dimension, PC2 (the second PC) is orthogonal to the first one and contains as much of the remaining information projected in that second direction, and so on [2,3].

3.2 Neural Networks

Artificial neural network (ANN) is an artificial intelligence procedure specially suited for the recognition of complex patterns, and as such the method has been applied in different

fields [4]. From the several alternative models of ANN, in this work we have chosen to implement a Multi Layer Perceptron (MLP) scheme [6], composed by an input layer, an intermediate (hidden) layer, and an output layer of artificial neurons. The network is optimized by a backpropagation "learning algorithm" consisting of *i*) a forward step in which the input data is applied to the network and the resulting error is estimated by comparing the output to the desired answer, and *ii*) a retropropagation step in which the estimated errors are used in the backward direction to adjust the weights and operating conditions of the different layers.

4. Results

While prototype P-1 was used to identify simple odors of pure chemical compounds, the version P-2 of the equipment was tested in the more complex task of identifying aromas of different types of wines.

4.1 Simple odors

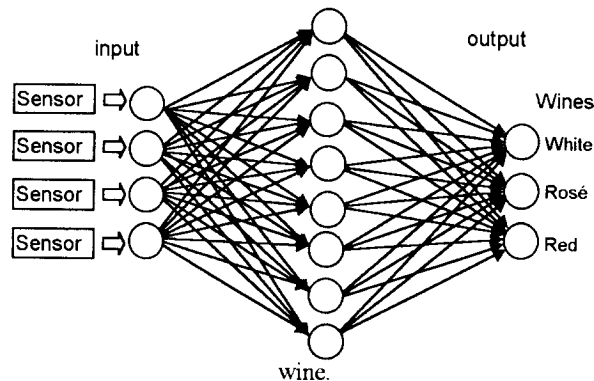
The system was calibrated by exposing the sensors to ethanol, carbon tetrachloride, and methanol (Fig. 2). While the variance explained by the PCA was 100% for the two principal components (PC1: 76%; PC2: 24%), the recognition percentage in the ANN analysis was 100% for both alcohols and 94% for CT. (The ANN configuration was 3:6:3 – i.e. the number of neurons in the input, hidden and output layers were respectively equal to 3, 6 and 3 – and from the total data available, 191 were used for the training of the ANN, and the remaining 64 were used for testing.)

4.2 Complex aromas

We have tested the reliability of the P-2 prototype to discriminate amongst complex aromas in two separate experiments: *i*) identification of different types of wine (rosé, red and white), and *ii*) recognition of different vintages (1995, 1996 and 1997) of red wine. All wines were of Brazilian origin (Almadén, Santana do Livramento).

For the type identification experiment, the explained variance by PC1 and PC2 was respectively equal to 66% and 34%. In the ANN analysis the configuration was 4:8:3 (see Fig. 5), and from the 372 V_{23} input data, 279 were used in the training step and 93 reserved for testing. The recognition was complete (i.e. 100%).

Fig. 5: ANN architecture for the analysis of different types of wine.



Since the vintage identification experiments were of a more complex nature, five repetitions of the data acquisition were performed for each vintage. (During the analysis one of the six

sensors became unreliable and the corresponding input data were discarded in the following analysis.)

From the 180 data points, the variance explained by the first two principal components in PCA was above 77% (and as high as 86% if PC3 was included). In Fig. 6 we present the corresponding plot for the PC1 and PC2 scores.

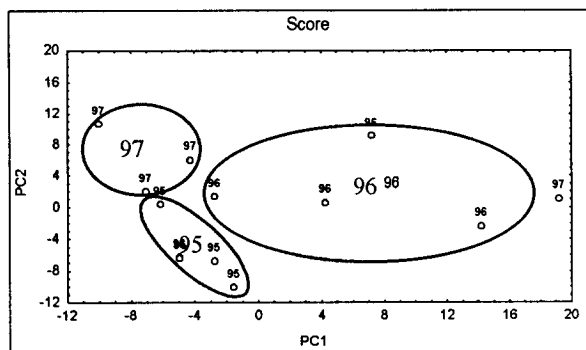


Fig. 6: Scores for the first two PCs for an analysis of red wines of different vintages (5 repetitions; 180 data points).

The ANN had a 7:14:3 configuration for the successive layers, and from the total of 1800 data points, 1350 were used for training and 450 reserved for testing. The average recognition percentage for the years 1995, 1996 and 1997 was 96%, 96% and 97%, respectively.

5. Conclusion

In this work we present preliminary results of the development work of an aroma sensor based on doped PPY films. The changes in conductivity of the polymeric films after exposure to different odors were automatically collected and a pattern recognition algorithm is used to discriminate among different odorant species.

In two different versions of the instrument, the electrical resistance of the polymeric films was determined using either two- or four-probe measurements. In this manner we have been able to establish that the contact resistance is very large (~30% of the total resistance effectively measured), but also that its value changes much less after exposure to the odorants than the

resistance of the film itself. Hence, although the use of four-probe type of sensor is desirable (because in this case the resistivity of the film would be the single varying parameter), simpler two-probe sensors can still be adopted [7].

Acquisition times varying from 30 s to 5 min were examined. Although the discriminating power of the instrument was not severely affected by the amount of input data, in operational terms the convergence of the recognition pattern algorithms becomes progressively more difficult as the shorter is the acquisition period of time. This is an important consideration for the development of real-time instruments.

At present, we plan to continue extensive tests of prototype P2 to better estimate its reliability under different operating conditions. At the same time, there are several points being considered for improvement of the performance of the instrument. For instance, all measurements have been performed under ambient conditions with no control of humidity. Through an alternative design, the spatial arrangement of the sensors could also be varied to assure a better homogeneity of the headspace, the data collection volume.

Likewise, ANN procedures other than MLP (such as cascade correlation and radial basis function [8]) are also under consideration to optimize the pattern recognition step.

Finally, use of thin organic films produced by different techniques (such as self-assembly) could add more flexibility to the instrument and smaller response times.

References

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