Discrimination of volatile organic compounds emitted by building materials using an electronic nose

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DISCRIMINATION OF VOLATILE ORGANIC COMPOUNDS EMITTED BY BUILDING MATERIALS USING AN ELECTRONIC NOSE

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ABSTRACT

This work concerns the development of a real time air quality monitoring tool using an electronic nose based on conducting polymer sensors and artificial neural network pattern recognition technique. Eight aromatic Volatile Organic Compounds (VOCs) frequently emitted by the building materials were chosen to assess electronic nose discrimination capability. This discrimination was based on three criteria: carbon chain length (toluene, ethylbenzene and propylbenzene), substituent position on the cycle (o-xylene, m-xylene and p-xylene), and insaturation level of the substituent (ethylbenzene, styrene, phenylacetylene).

An acquisition protocol was defined and a data base constituted. All compounds were evaluated below their saturation vapor pressure limit and with similar response amplitudes for comparison purposes. An optimized neural network performed a good discrimination of the set of samples with a classification rate, for the three criteria, reaching 93 %.

INTRODUCTION

The use of new synthetic materials such as carpets, plastic tiles, paints etc. in residences, commercial or public buildings has been increasing these last decades in relation with comfort improvements, noise reduction, energy savings as well as psychological well being. During the same time, the number of complaints about adverse effects on comfort and health associated with the use of such materials has been increasingly reported and the VOCs emission has been frequently addressed as a possible cause in the debates on indoor air quality problems.

Several physico-chemical techniques (GC/MS, HPLC etc.) have been used in order to evaluate indoor air quality (IAQ) by assessing individual volatile organic compounds (VOCs) emitted by building materials and furnishings [1, 2]. On the other hand, subjective human analysis allowing assessment of odor intensity [3] or acceptability [4,5] has been developed. However, these techniques are time consuming, expensive and not able to perform real time evaluation.

Promising techniques such as multi gas sensor systems (also named electronic noses) have been developed and used in several fields such food, packaging, cosmetic and car industry and, more recently, for some environmental applications such as space, ambient and indoor air. Based on different kind of active materials (sintered metal oxide, phtalocyanines, conducting polymer, quartz

crystals ...), available sensors are used for their broad specificity, and because, when they are used in arrays, they can discriminate complex chemical mixtures without separation of individual compounds. As such, an electronic nose is an instrument trying to mimic the human olfaction [6,7].

The aim of the research conducted at CSTB is the development of a real time air quality monitoring tool using an electronic nose based on conducting polymer sensors and artificial neural network pattern recognition technique. The first part of the work presented here is the evaluation of the discrimination capability of such electronic nose regarding VOCs frequently emitted by the building materials. The experimental methodology as well as the results obtained are presented below.

METHODS

1. Choice of the discrimination parameters

Eight pure compounds frequently emitted by building materials (except for phenylacetylene) were chosen to determine the ability of the system to discriminate slightly different samples. Three criteria were used :

- the length of the carbon chain : Toluene, Ethylbenzene, Propylbenzene.

The three compounds differ according to the number of carbon atoms on the substituted chain (one, two and three atoms of carbon respectively).

- the insaturation level : Ethylbenzene, Styrene, Phenylacetylene.

The three compounds differ by the nature of the carbon-carbon bond in the substituted chain : simple, double or triple (increasing bond reactivity).

- the position of the substituents : Ortho-Xylene, Meta-Xylene, Para-Xylene.

The three compounds differ according to the relative position of the two methyl groups on the benzene core.

The discrimination is based on the different interaction energies between active sites scattered in the conducting polymer film and the volatile compounds giving rise to different levels of variation in the bulk electronic conductivity of each sensor [8]. These molecular interactions are dependent on the nature and structure of sites and compounds alike. The problem is to determine if the system is able to recognize small variations in the nature or the structure of samples. An ideal discrimination power being represented by the recognition of the smallest variation with regard to a reference compound.

2. Experimental protocol

Electronic nose

The work is based on an electronic nose constituted with a layer of 32 conducting polymer sensors, sensitive to a stimulus (volatile compounds) by producing time-dependent electric signals which are processed independently afterwards to produce a multi-dimensional vector. This vector represents the pattern of the stimulus, it is then checked for identification against a database containing similar vectors by pattern recognition techniques which are either statistical methods (principal component analysis, discriminant function analysis being the most used) or artificial neural network techniques.

Methodology

The tests were realized by injection with a syringe of a known volume of the pure liquid compound in a sample bag filled with 700 ml of synthetic air at a relative humidity of 15-20% (at ambient temperature : 20-25°C). Each sample bag was then tested against a blank bag filled with synthetic air after an equilibrium time sufficient to the total liquid -vapor transition (Figure 1). The response obtained is then expressed in percent of relative resistance variation of each sensor (% ΔR/R). After each acquisition the sensors were cleaned with a 98/2 water/n-butanol saturation vapor during 210 seconds and again exposed to clean air.

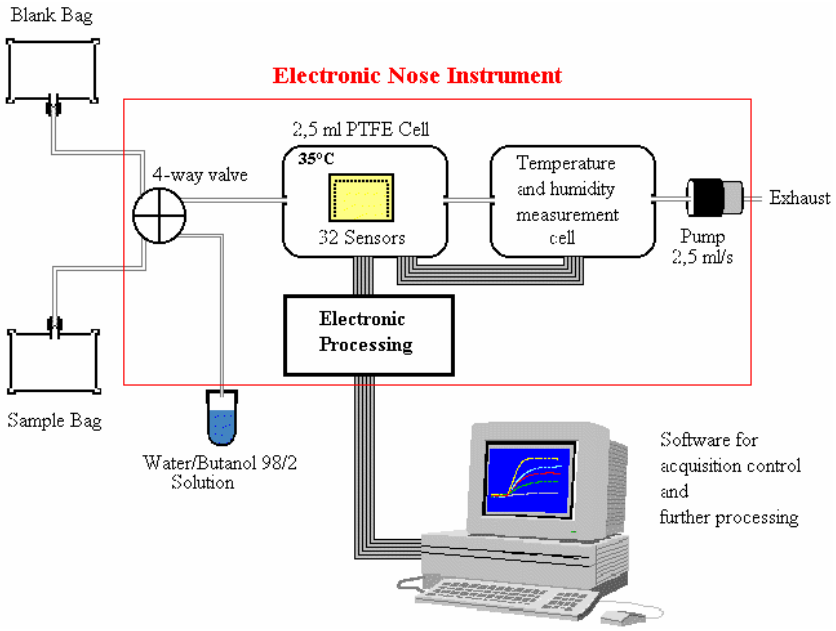


Figure 1 : Experimental schema

For each compound the injected volume is determined by the saturation vapor *pressure and relatively by the other compounds* in order to obtain the same magnitude of the global response (sum of the 32 responses for one test). The last parameter allows to keep the signal/noise ratio constant along the experiments. It gives a same level of noise for all the measurements allowing the comparison of the results even if the concentration used for each compound was different. Ten replicates were realized for each compound. The concentration level used varies from 1920 part per million (ppm) for ethylbenzene to 4300 ppm for styrene. All relative standard deviations were within 2% of the concentration.

Statistical data analysis as well as neural classification were used to analyse the data obtained.

RESULTS

The data acquired comprises 80 samples, representing the eight chemical species (10 samples each) described.

Two examples of electronic nose response (toluene and phenylacetylene) are presented on figure 2. The response observed for phenylacetylene shows both positive responses (increase in the polymer resistance) as well as negative responses (increase in the polymer conductivity). On the other hand, all sensors show a positive slope when exposed to toluene and to the other compounds except styrene which shows an intermediate response type, with sensors that did not respond at all.

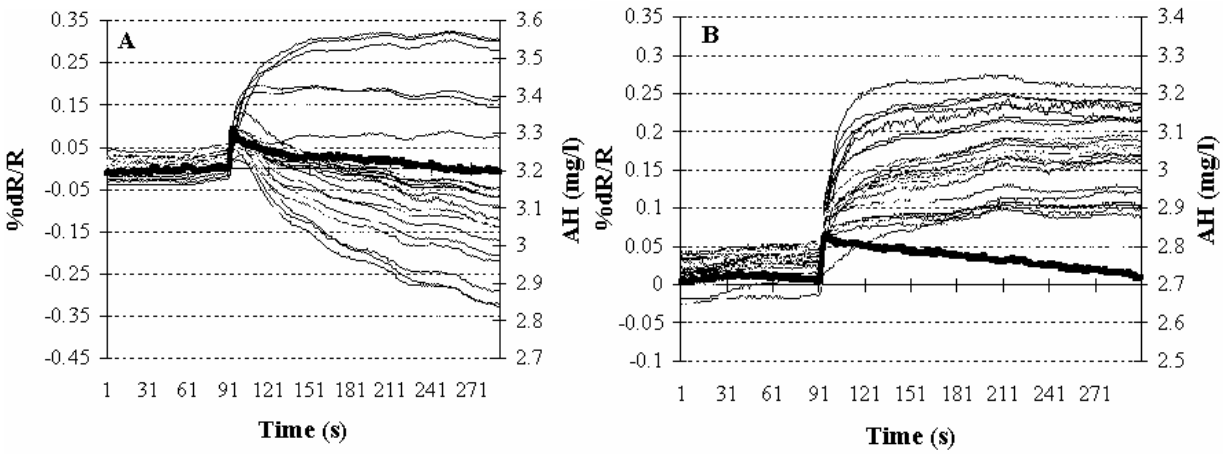


Figure 2 : time dependent response (% DR/R) and absolute humidity variation (AH, in bold) for phenylacetylene (A) and toluene (B).

The response level of the sensors, for the ten replicates of each compound, was within -0,5 and 0,5 % ΔR/R with relative standard deviations of 6 to 50% (observed with sensors giving insignificant responses). These variations of the response were due to ambient temperature variations, atmospheric pressure variations, and absolute humidity differences between blank bag and sample bag (the maximum difference observed was 0,1 mg of water per liter which is equivalent to a difference of 135 ppm at 25°C). Nonetheless, compound concentrations used were sufficiently high to compensate for the variations observed.

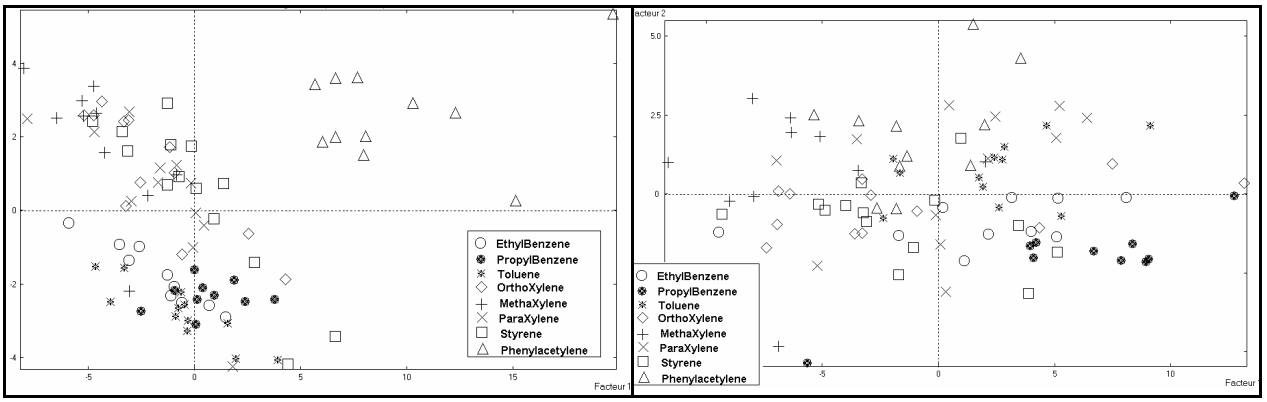
Given the data acquired, we optimised a pattern recognition tool (especially neural network technique) in order to improve the discrimination power of the electronic nose used for recognizing profiles of the compounds. In order to compensate for the drawbacks of the sensors, the pattern recognition techniques have been used for better discriminant, real-time (a few minutes) and perturbing conditions tolerant device. These techniques, applied to the multi dimensionnel signal produced by the acquisition process allowed a unique attribution, to every single gas, of a fingerprint.

The data were analysed by comparing two phases of the signal : a) the dynamic phase, corresponding to the beginning of the adsorption/desorption process giving rise to an important response change; b) the static phase, corresponding to the equilibrium in the adsorption/desorption process with a stabilized response level. The data analysis process was split in two steps:

a- Statistical data analysis

A hierarchichal classification of the whole set of samples was used according to their first factorial coordinates created by a principal components analysis (P.C.A).

The results showed that the samples of the whole set are difficult to discriminate based on their factorial coordinates (except phenylacetylene, see figure 3) and that the relationships that are undergone between the sensors and the chemical species cannot be described using such a technique. The use of static and dynamic information seems to give comparable results.



A **B**

Figure 3 : A) P.C.A : static phase ; B) P.C.A : dynamic phase

O stends for EthylBenzene, ● for PropylBenzene, ✞ for Toluene, ✧ for OrthoXylene, + for MetaXylene, ▯ for ParaXylene, ❑ for Styrene and Δ for PhenylAcetylene.

b- Neural classification of the data

Due to the hardness of obtaining repeatable measures with the electronic nose and the drift over time in its response to the same sample, we decided to use neural network approach to deal with these imperfections.

For neural network learning purposes the samples set was split into two sets : learning set and test set. The type of neural network used was a multi-layered perceptron using the backpropagation learning algorithm to update its weights with random initialisation.

Table 1: Classification rate and error obtained according to every single criterium.

	length of carbon chain criterium			**Position of the substituents criterium**			**Insaturation level criterium**		
Phases		***Static***	***Dynamic***		***Static***	***Dynamic***		***Static***	***Dynamic***
RMS Classif-rate:		0.250	0.189		0.192	0.183		0.115	0.123
	Global	**93 %**	**100 %**	**Global**	**77 %**	**93 %**	**Global**	**93 %**	**90 %**
	EthylBenzene	100 %	100 %	OrthoXylene	83 %	100 %	EthylBenzene	80 %	83 %
	PropylBenzene	80 %	100 %	MetaXylene	80 %	80 %	Styrene	100 %	86 %
	Toluene	100 %	100 %	ParaXylene	67 %	100 %	Phenylacetylene	100 %	100 %

After using the three criteria to classify the different chemical species (results in Table 1) belonging to every sub-set of samples (EthylBenzene, PropylBenzene, Toluene); (OrthoXylene, MetaXylene, ParaXylene), (EthylBenzene, Styrene, Phenylacetylene), a global classification involving the samples of the eight species was tried (results in Table 2).

Table 2: Classification rate and error obtained with the whole set of samples.

	Static phase	***Dynamic phase***
RMS Classification rate	0.130	0.137
Global (eight species)	**79 %**	**81 %**
EthylBenzene	80 %	50 %
Styrene	75 %	71 %
Phenylacetylene	100 %	100 %
OrthoXylene	100 %	83 %
MetaXylene	80 %	80 %
ParaXylene	17 %	67 %
PropylBenzene	100 %	100 %
Toluene	83 %	100 %

RMS holds for the root mean square error on the test set and classif-rate for the classification rate over the test set. The learning process took less than 20.000 cycles (about 10 minutes learning time on a Personal Computer type machine with Pentium 100 Mhz processor).

CONCLUSIONS

The evaluation of the discrimination capability of an electronic nose as regards VOCs frequently emitted by the building materials has been studied.

The statistical approach showed that the relationships between the classes of samples regarding every criterium were so complex that factorial techniques were unable to separate them clearly. The use of neural networks helped to deal with these complex non-linear relationships and to obtain good results. These results confirmed that the electronic nose was sensitive to the criteria chosen and led to good discrimination. As regards the information acquired by the electronic nose, we found that the use of the static information was sufficient to discriminate our samples although the dynamic information led to more accurate classification.

AKNOWLEDGEMENTS

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Chemical sensitivity, instrumentation, odor, perceived air quality, VOC.