In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

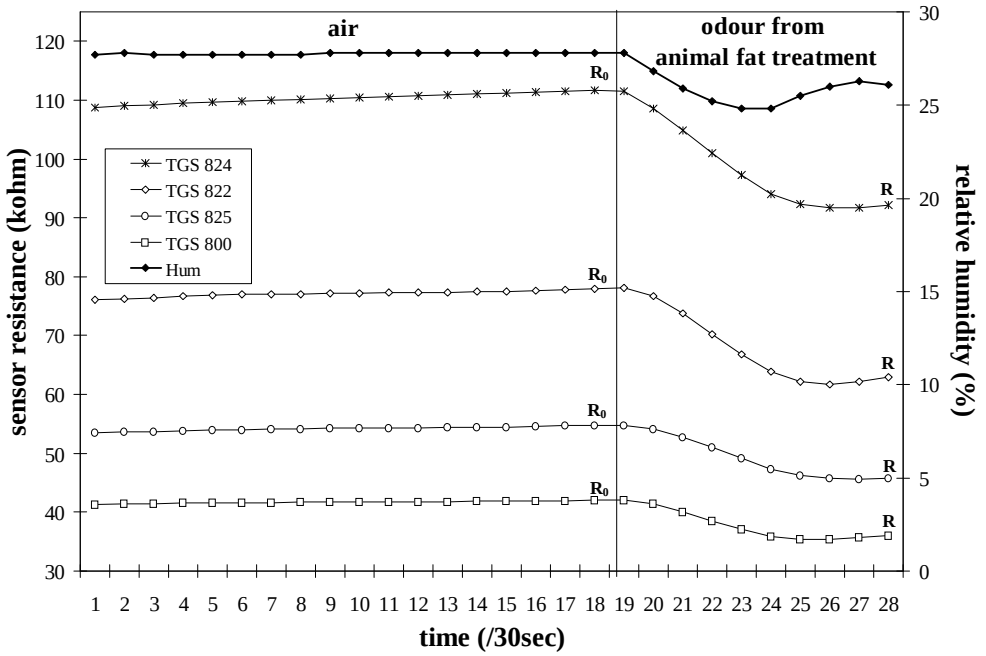


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

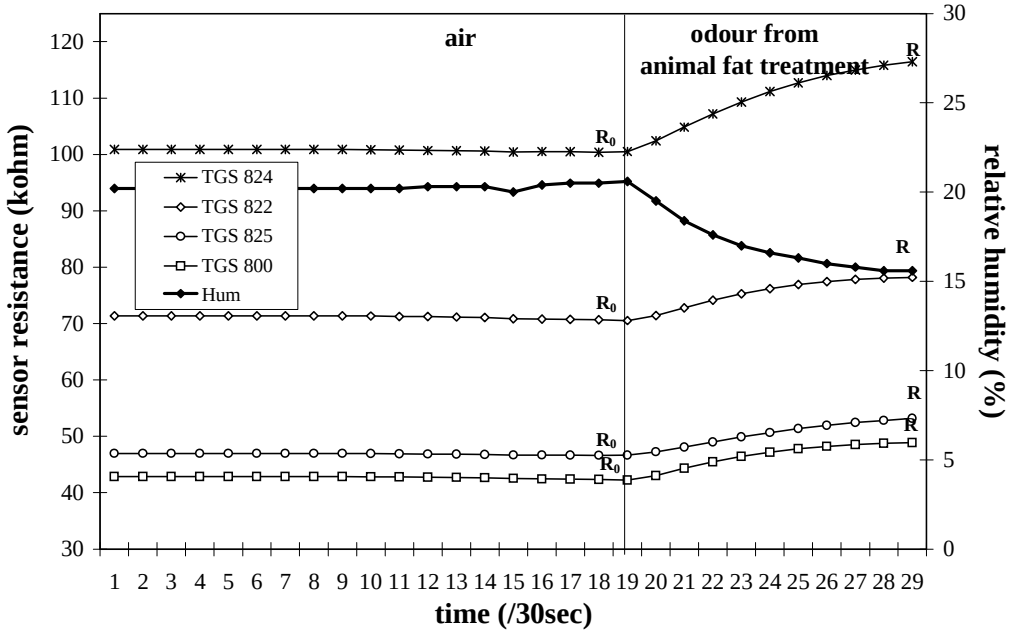

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

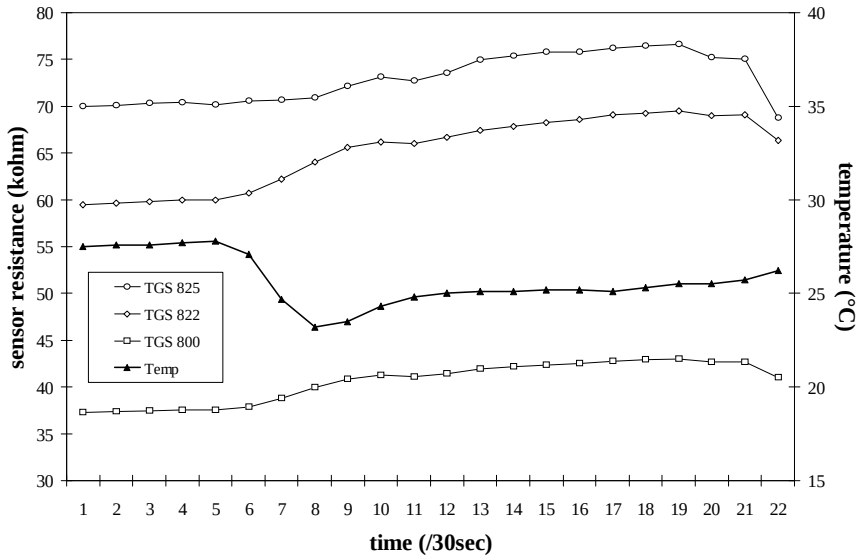
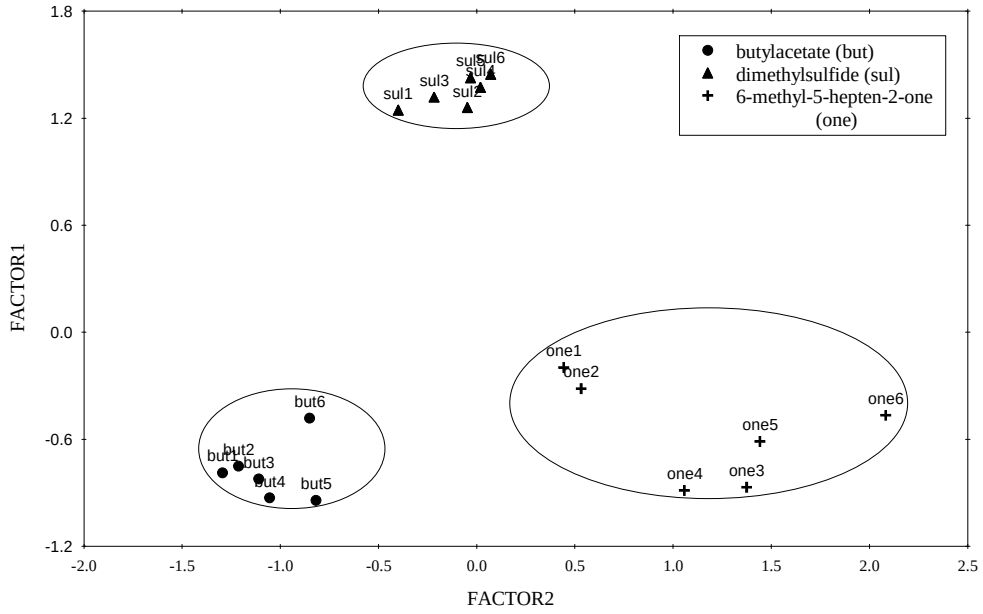

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

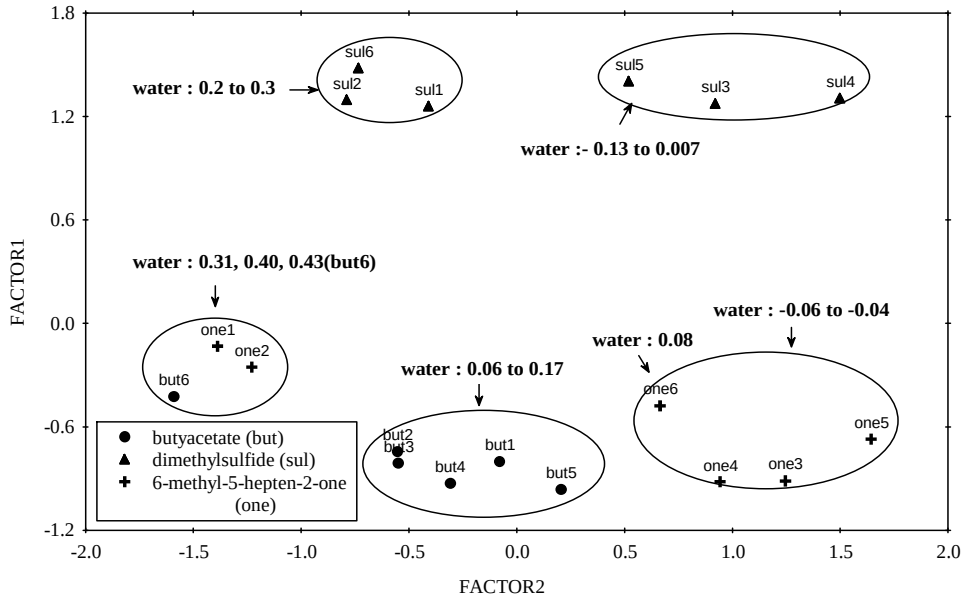

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

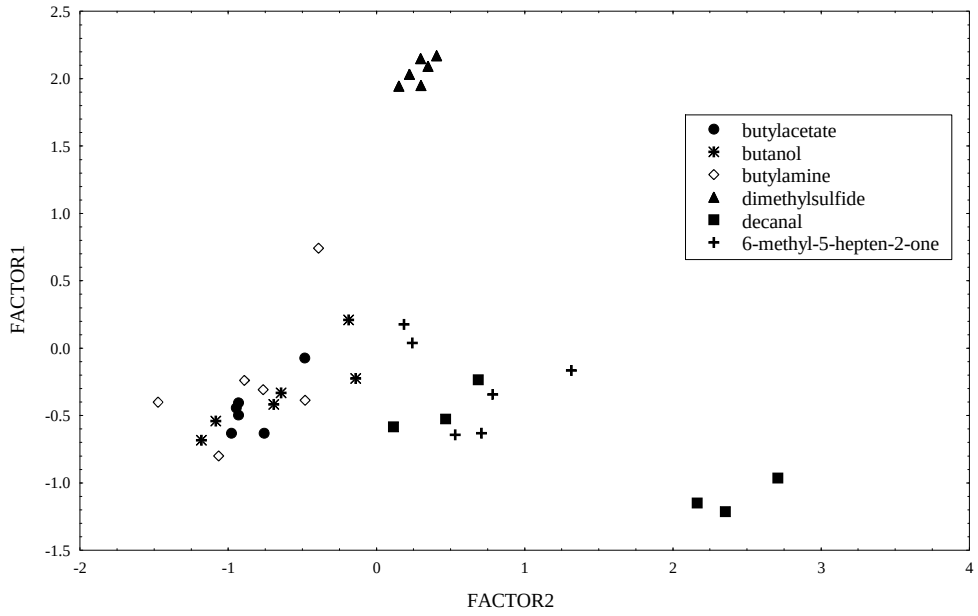

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

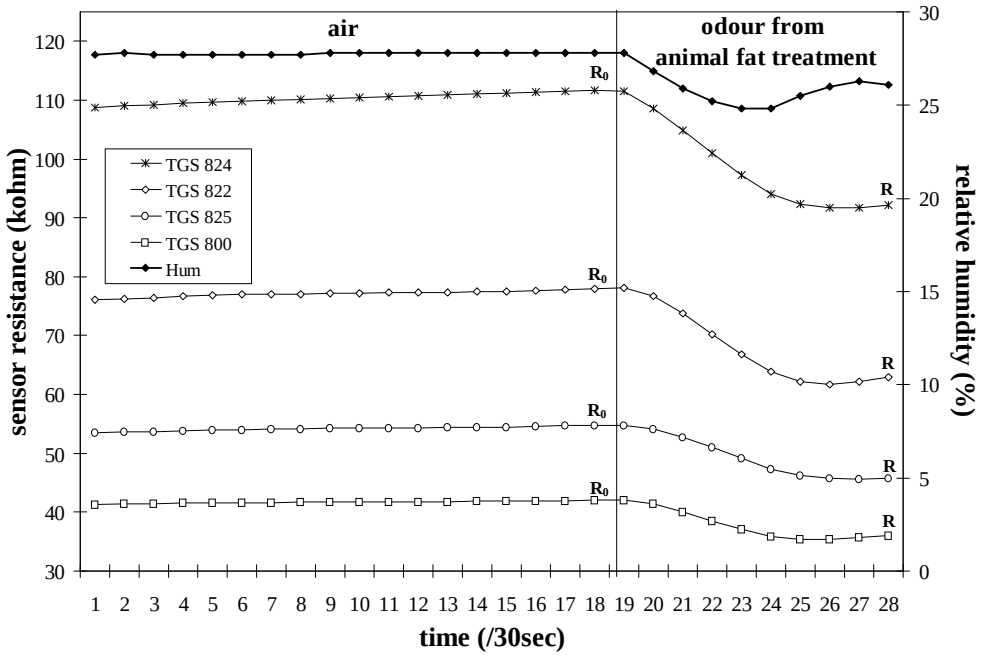


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

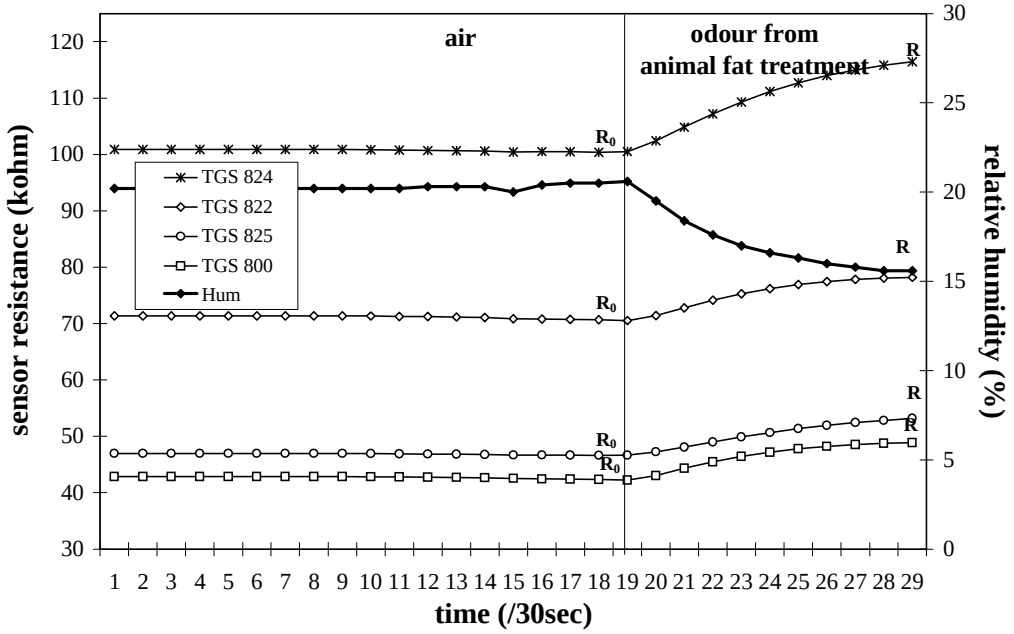

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

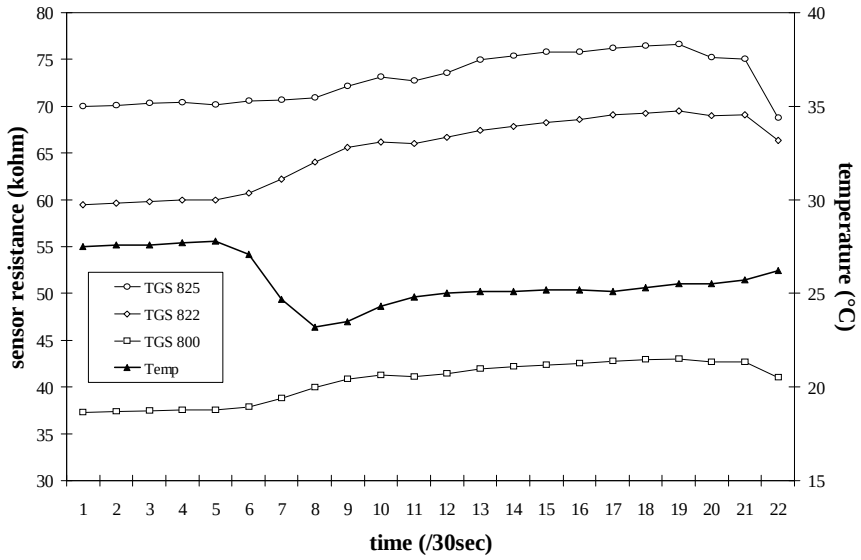
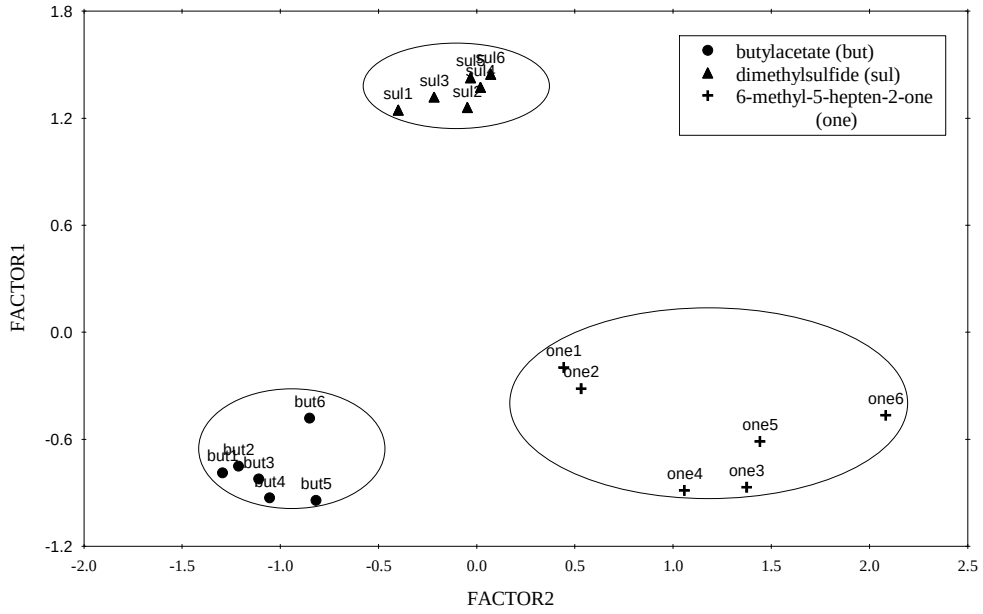

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

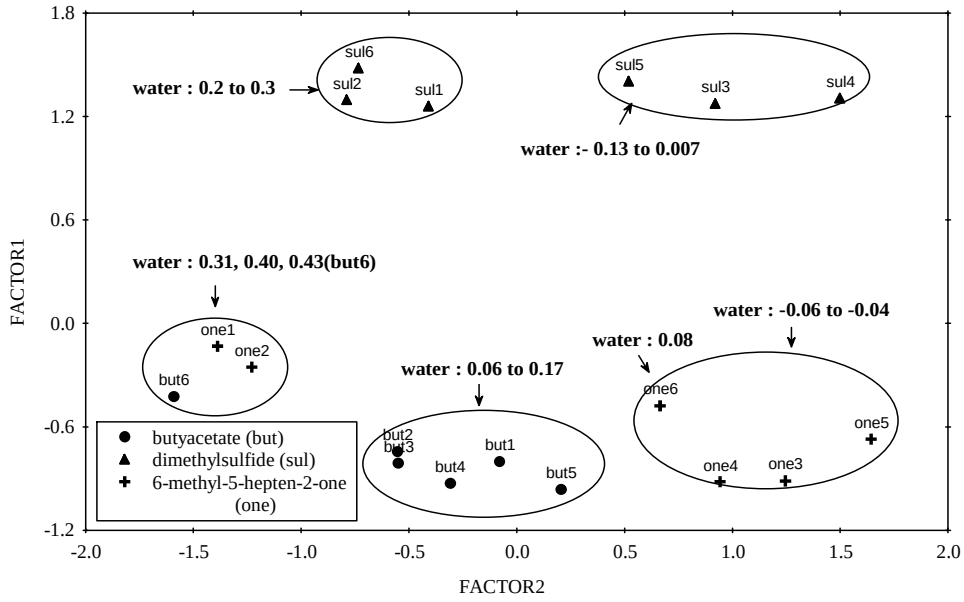

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

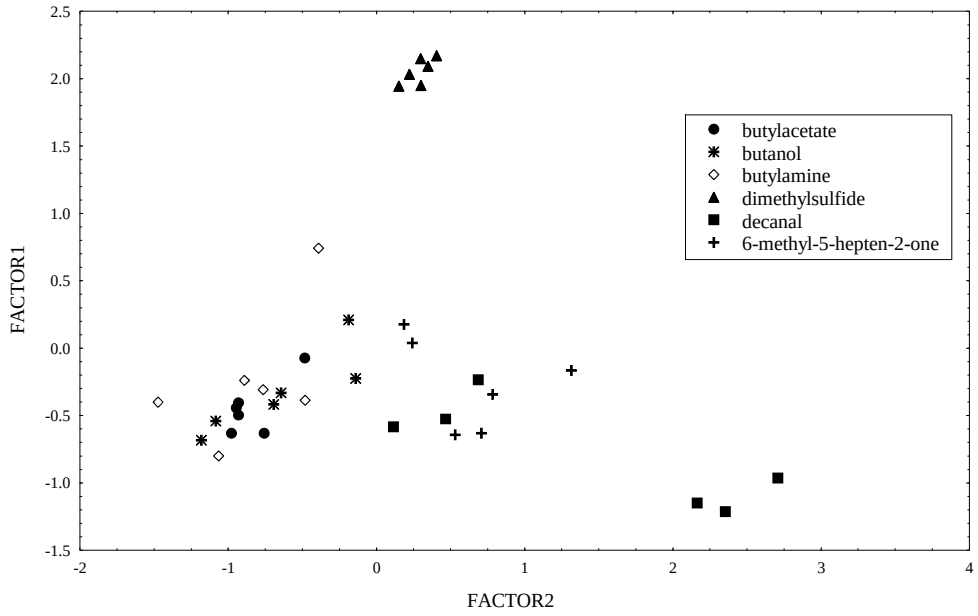

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

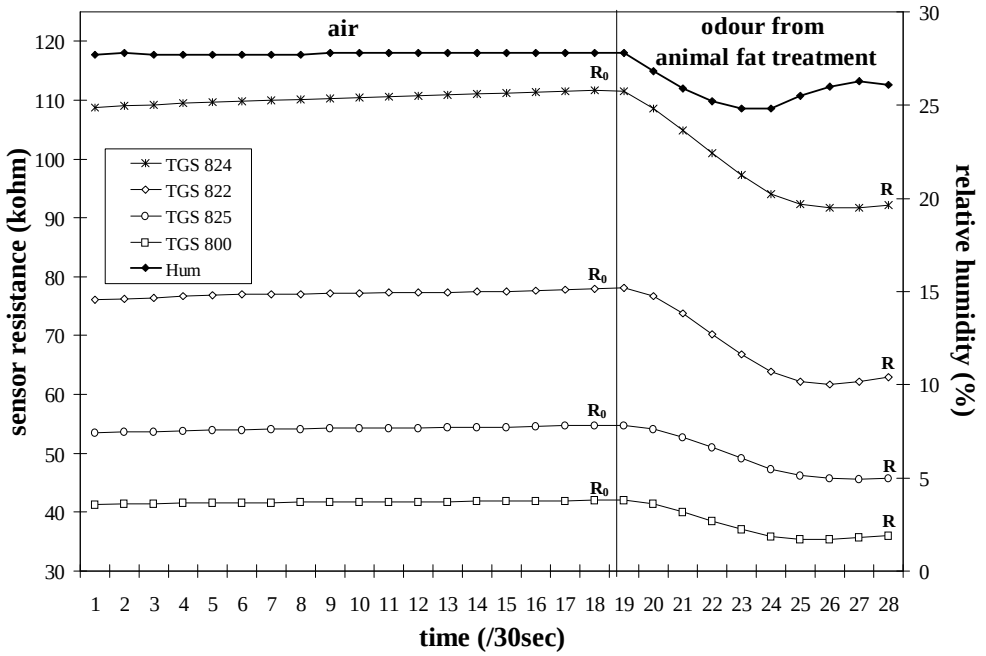


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

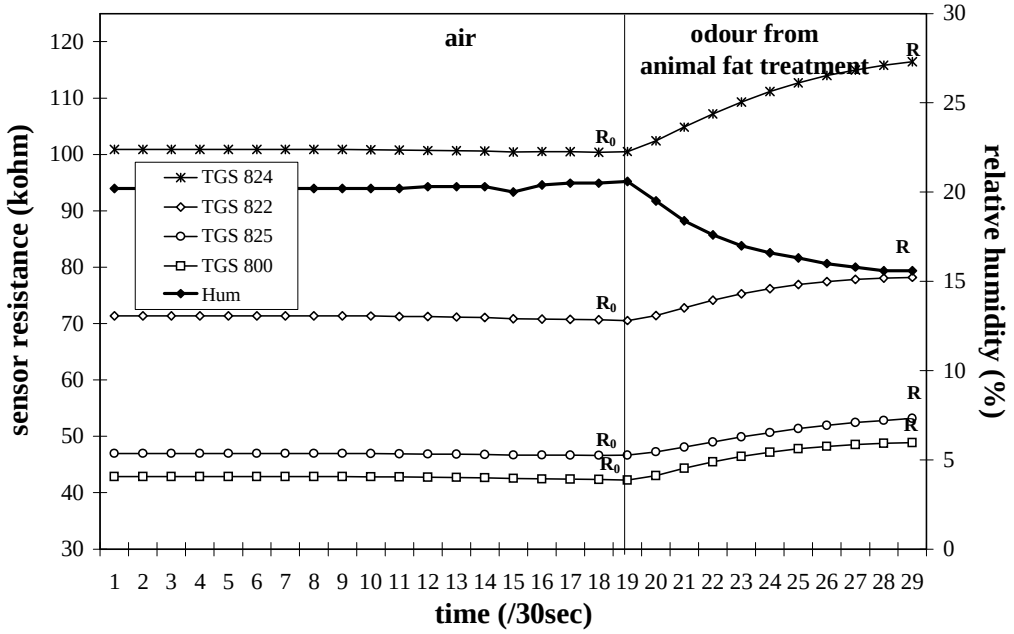

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

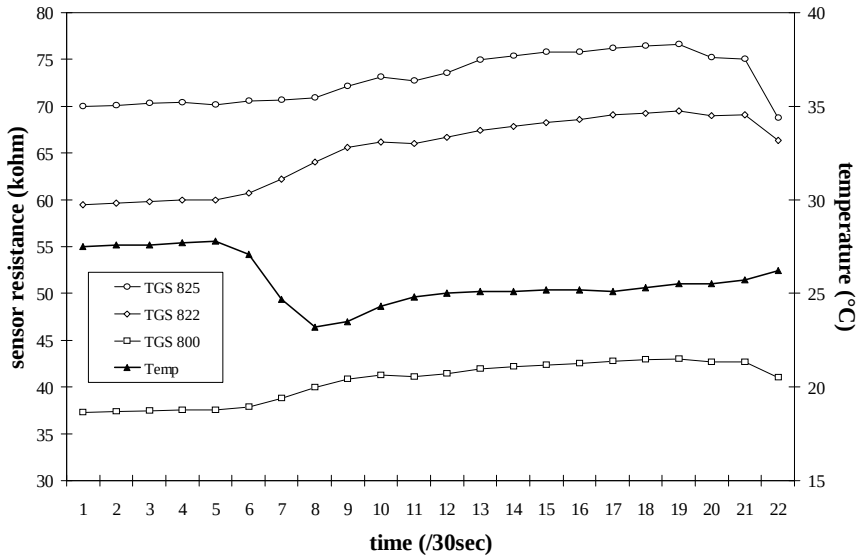
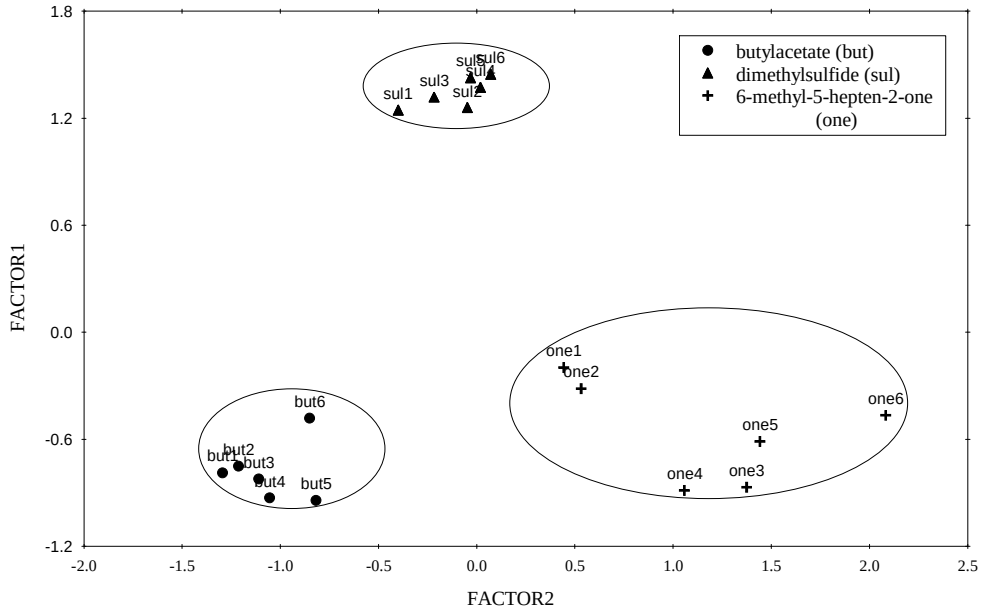

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

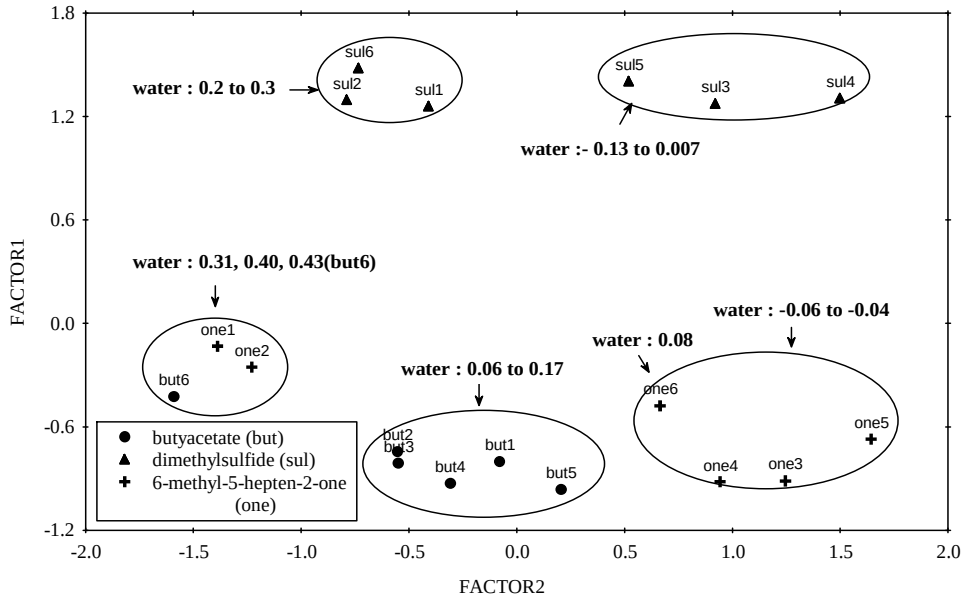

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

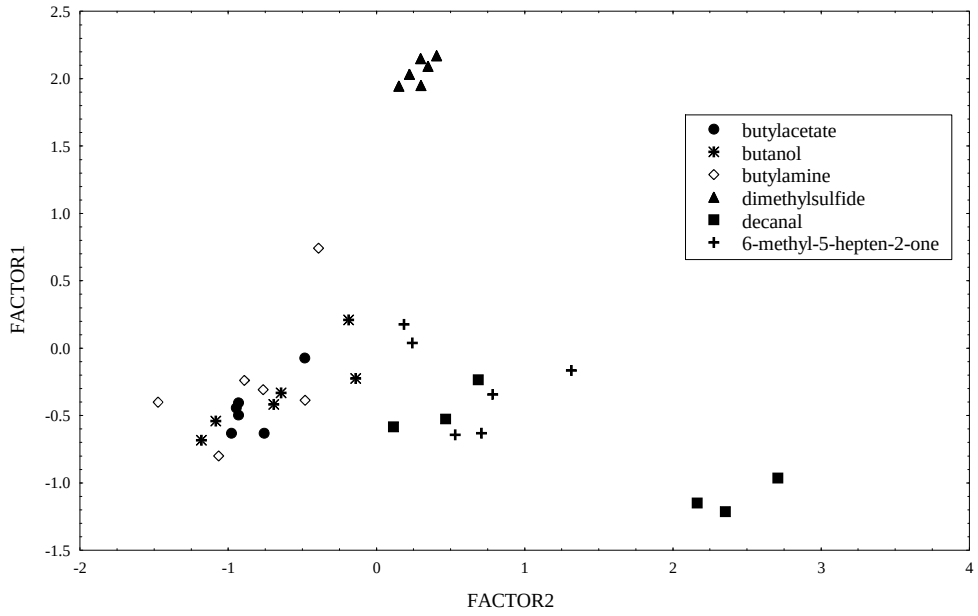

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

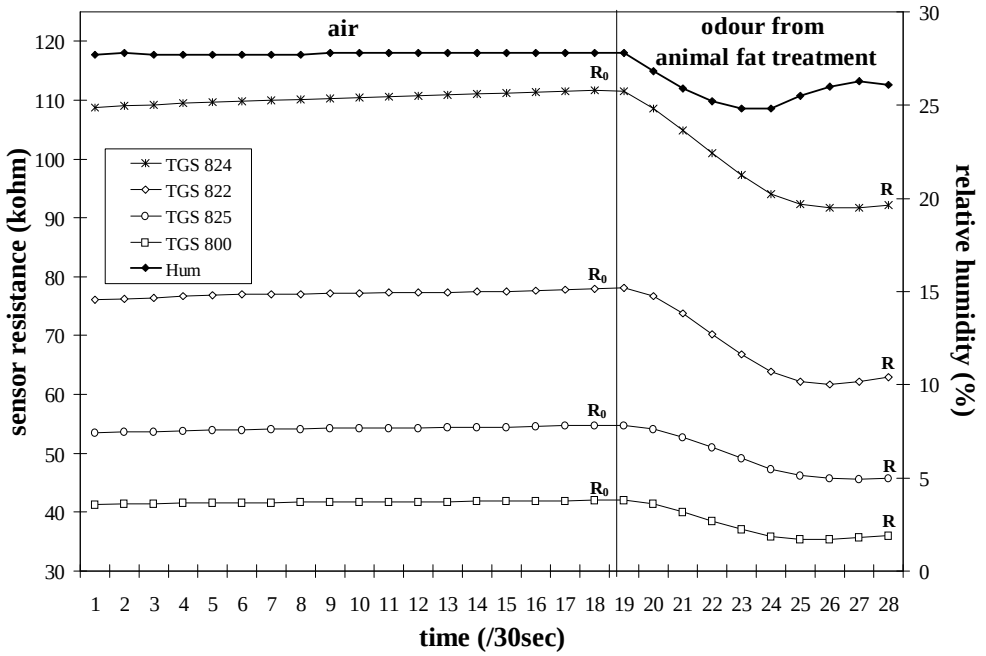


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

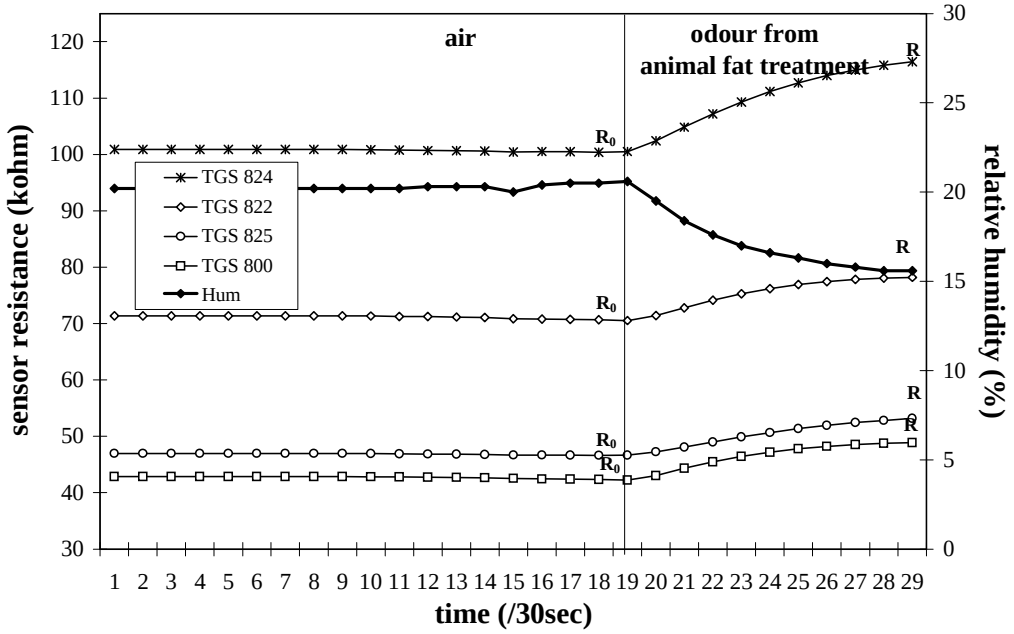

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

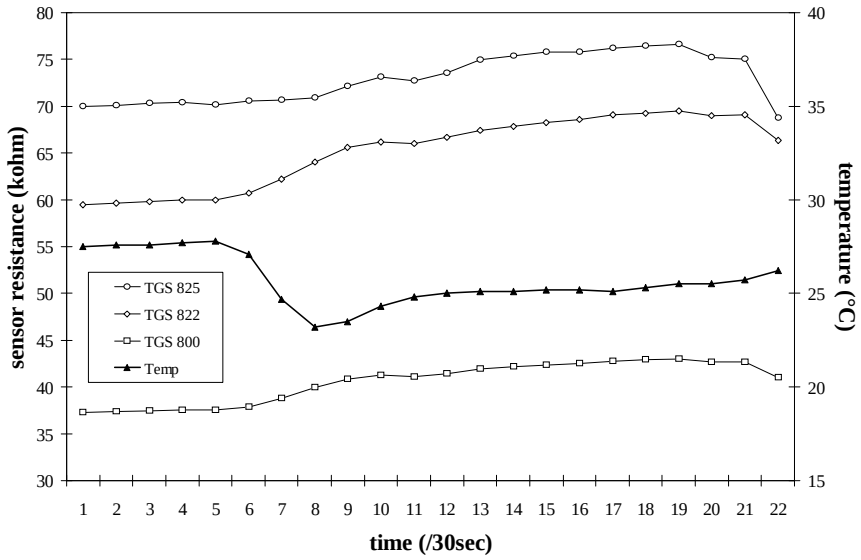
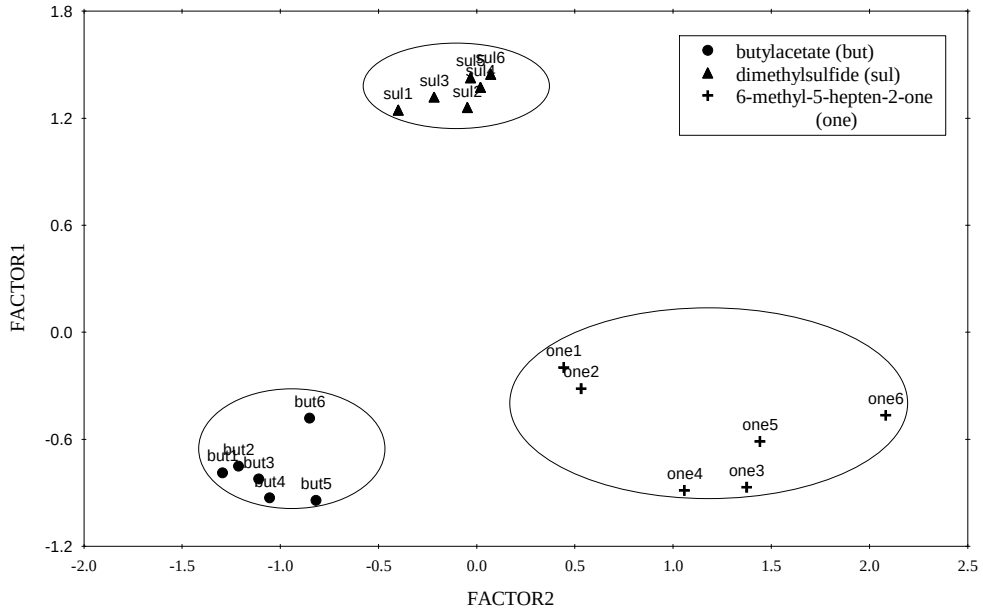

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

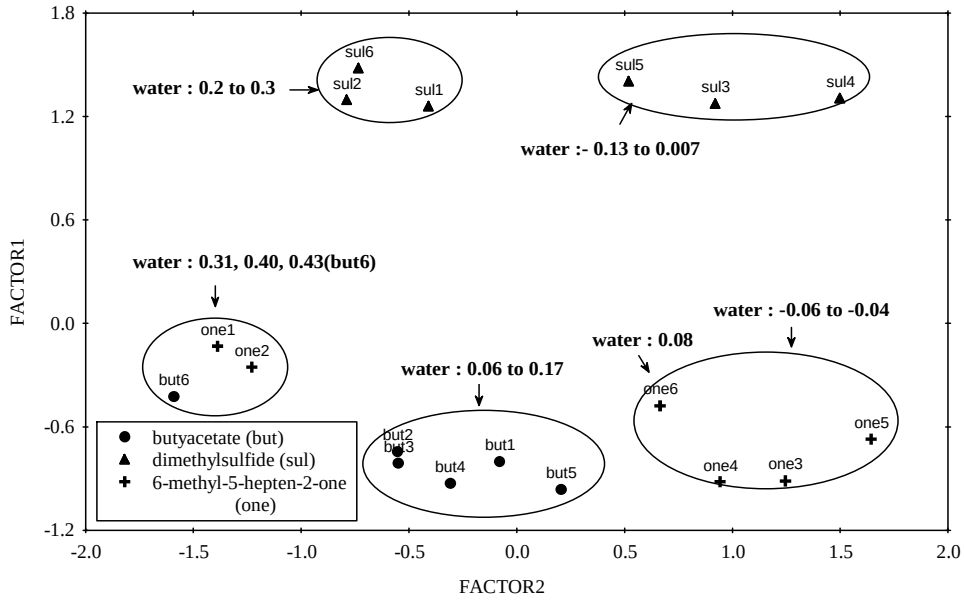

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

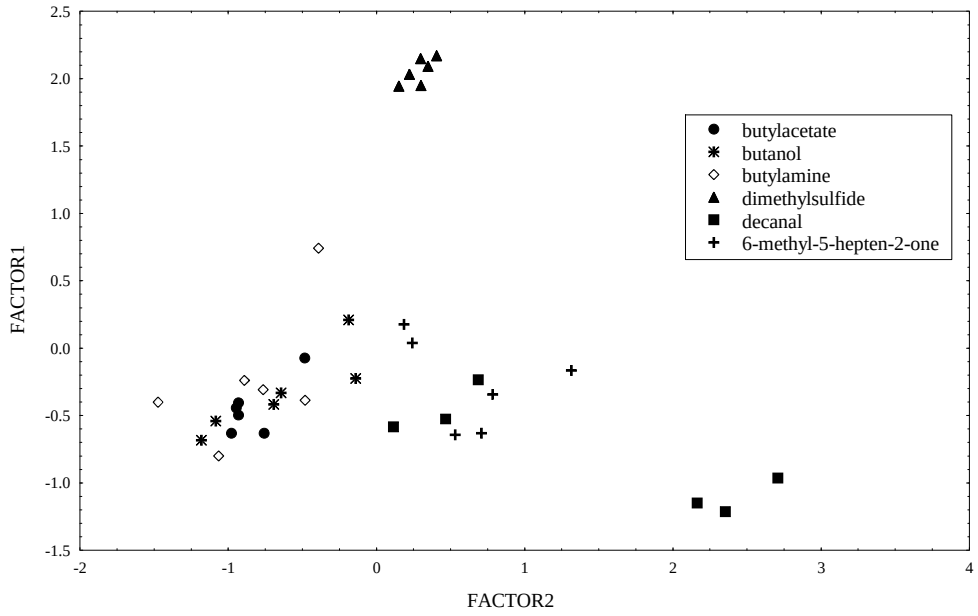

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

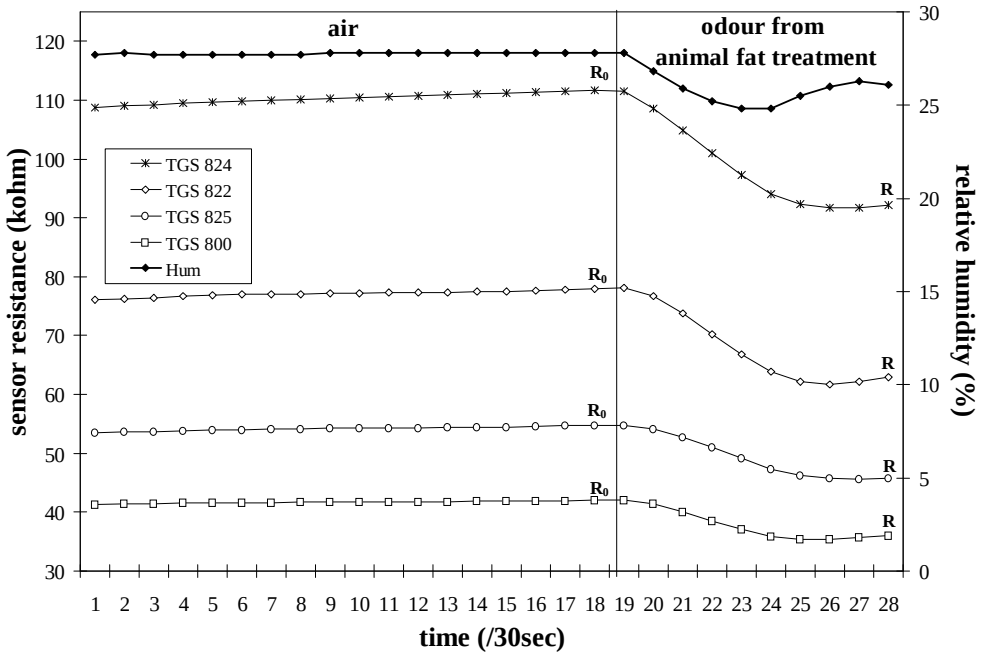


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

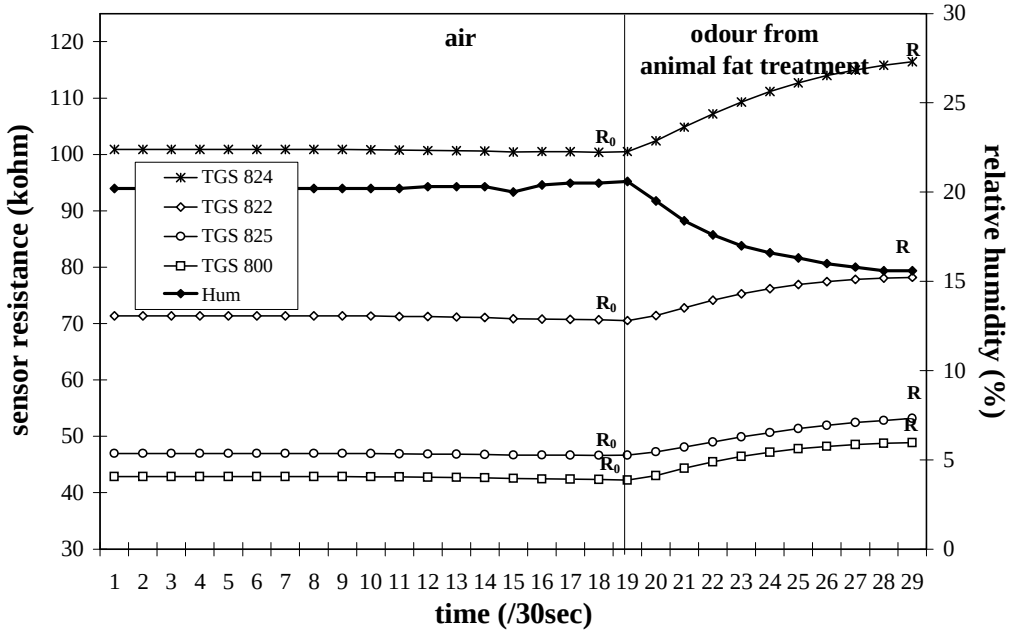

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

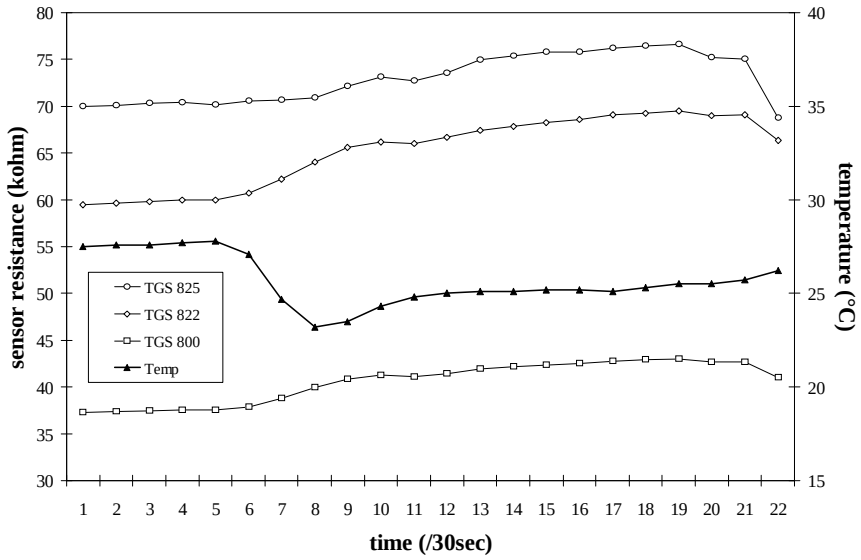
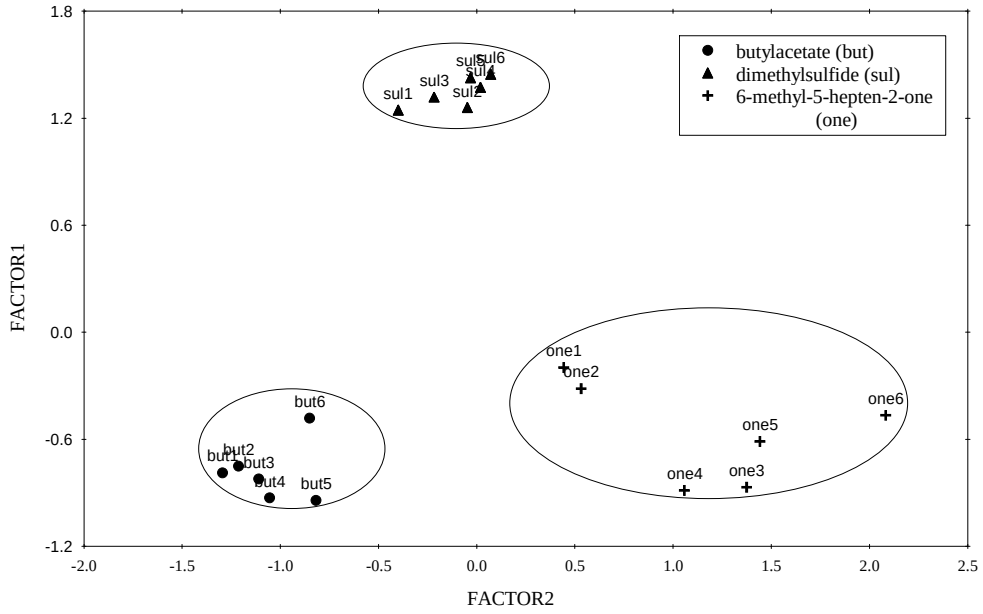

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

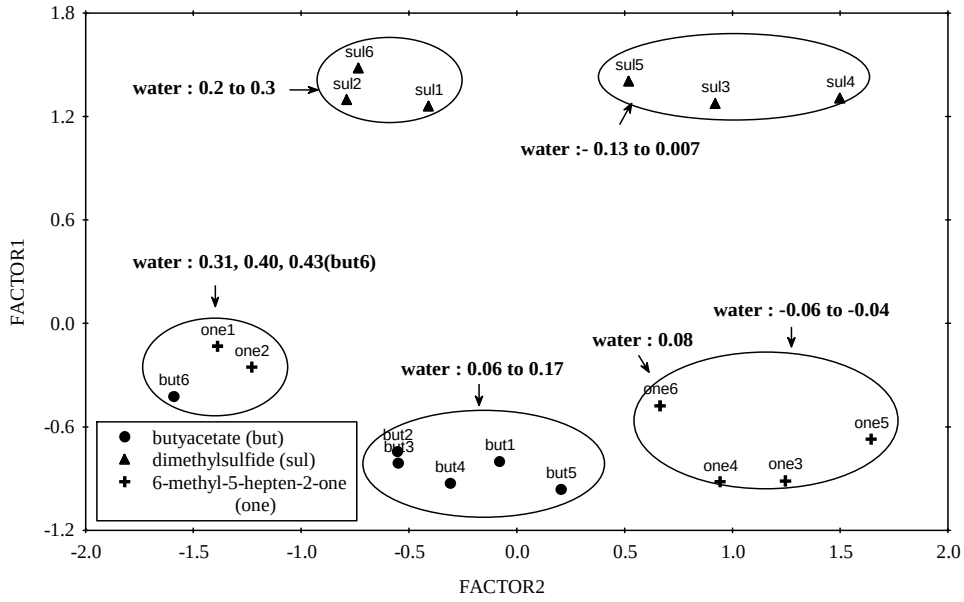

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

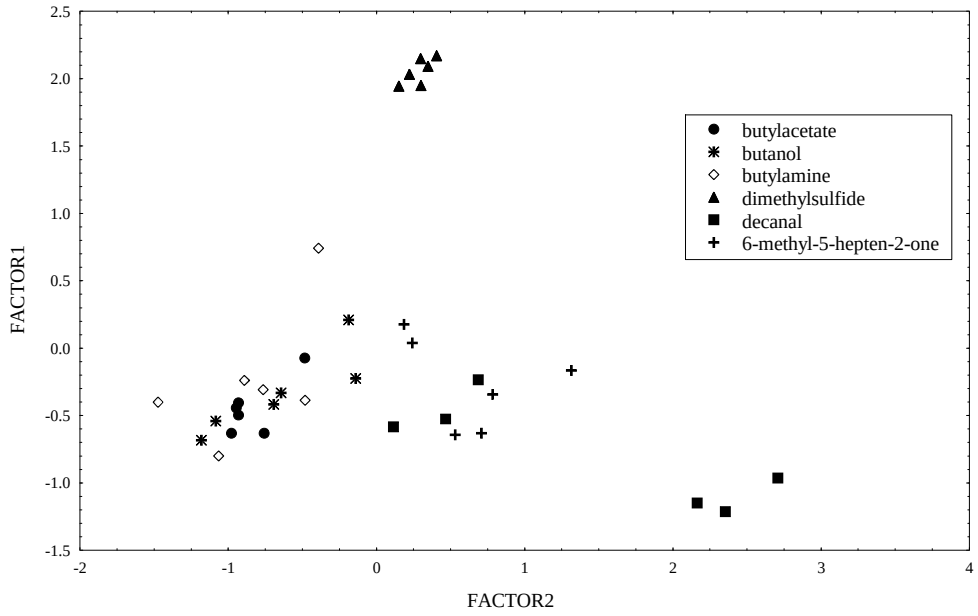

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

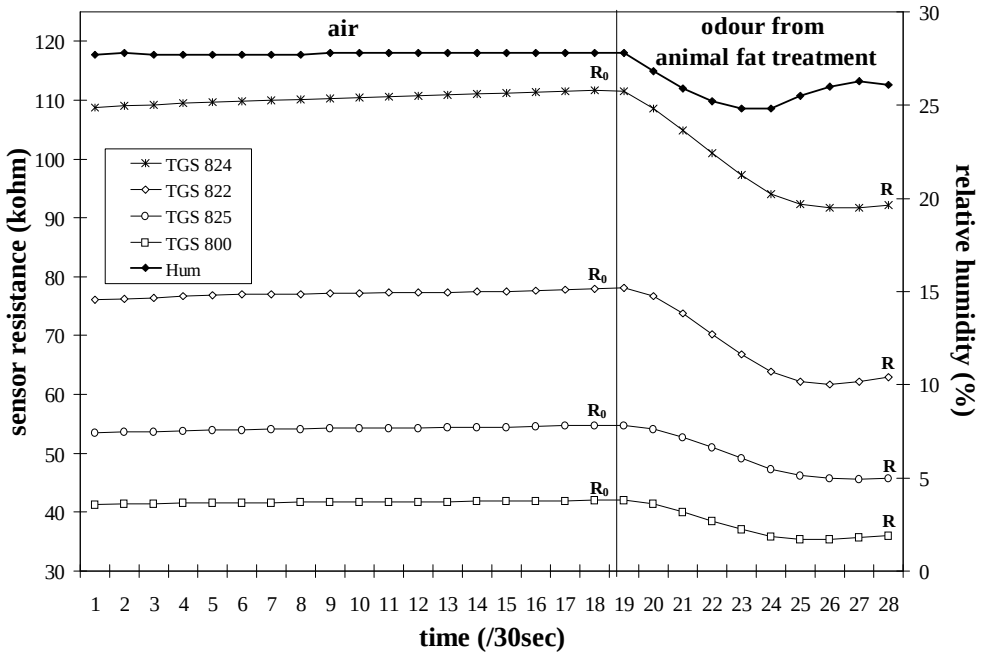


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

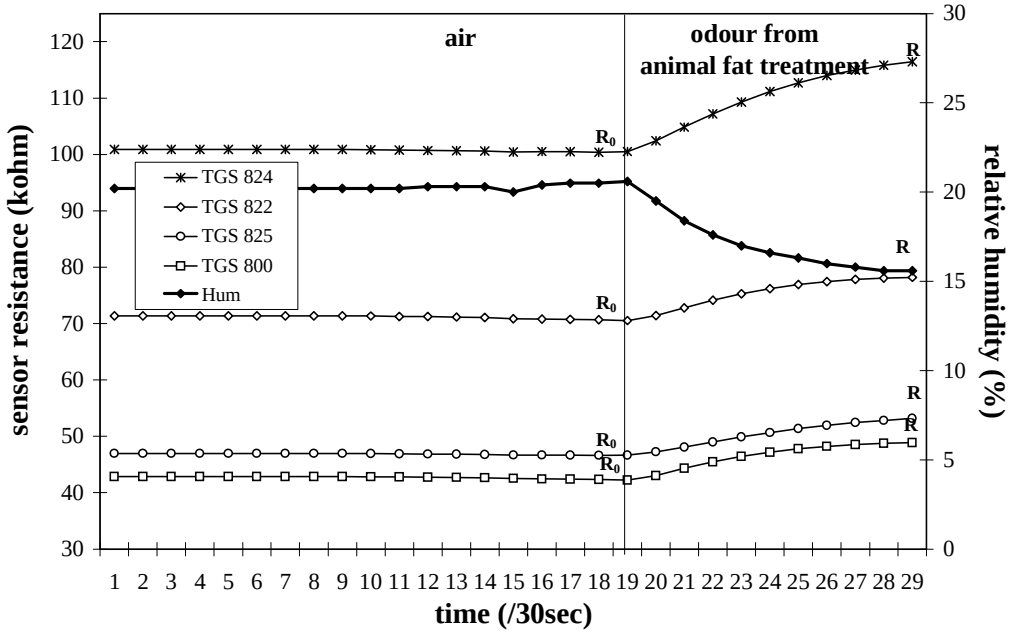

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

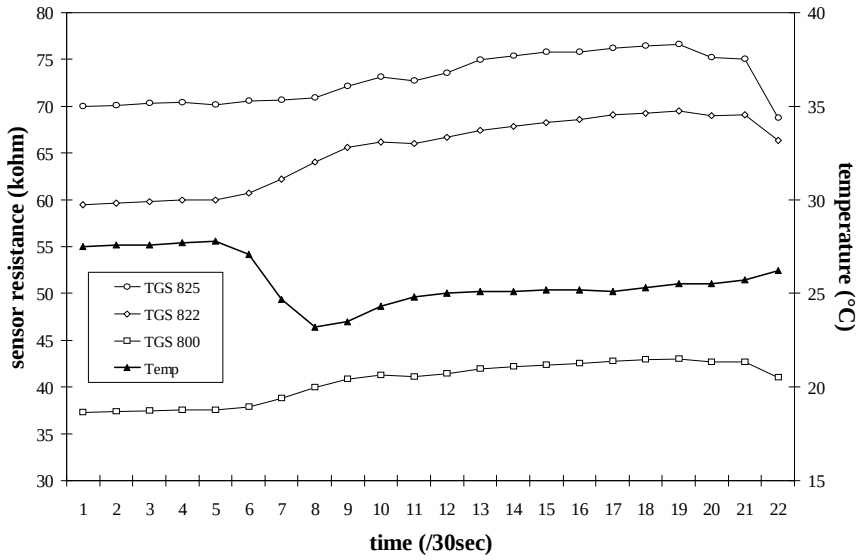
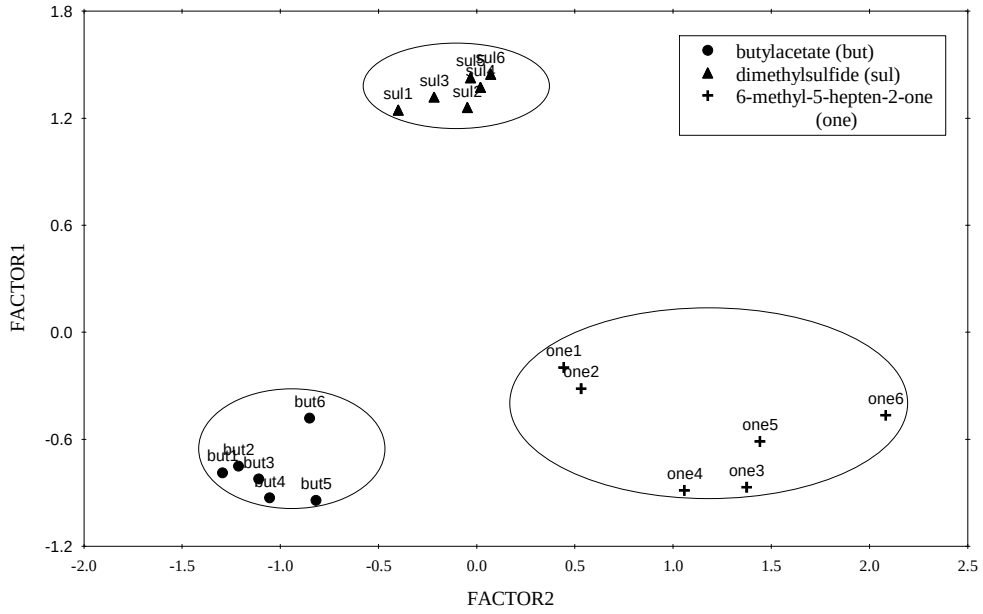

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

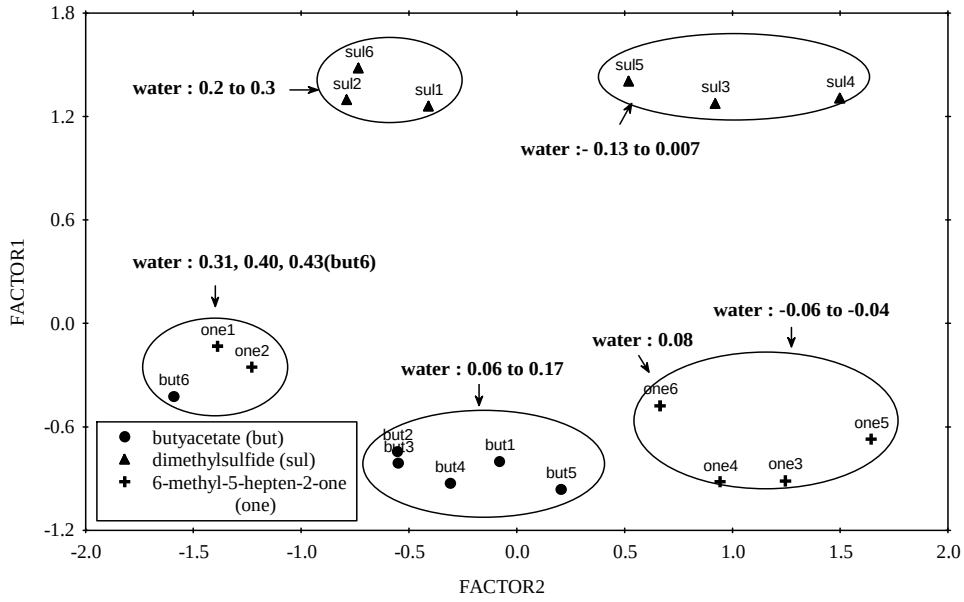

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

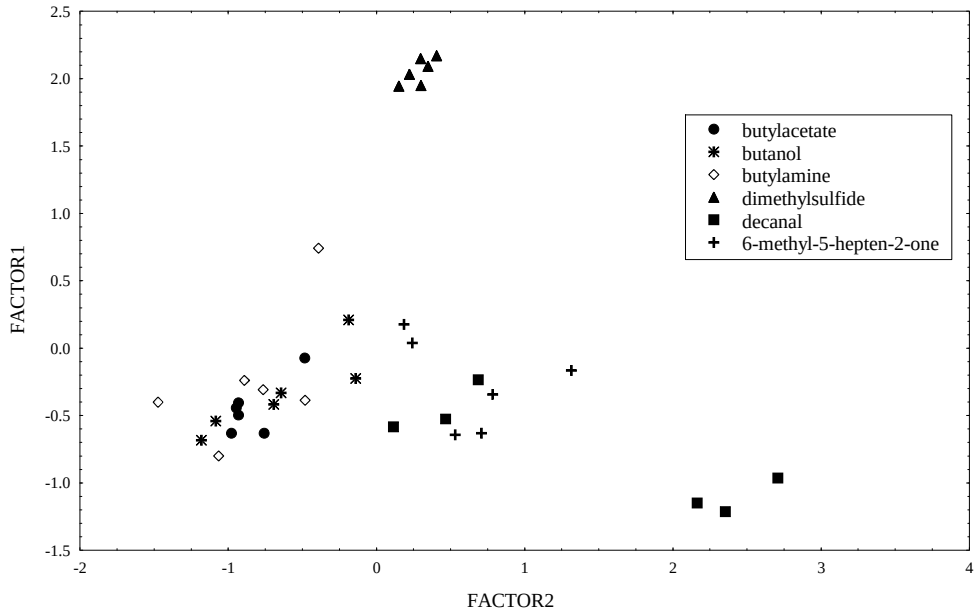

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.

In situ measurement of olfactive pollution with inorganic semiconductors: Limitations due to humidity and temperature influence

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Abstract

Synthetic mixtures, as well as real industrial emissions sampled in Tedlar® bags, are passed through a 12 inorganic semiconductors array (Figaro trademark). The experiments are performed in the laboratory in nearly field conditions. The influence of external factors, such as humidity content of the malodorous, on the sensors signals have been pointed out. Humidity disturbs the results of the pattern recognition techniques. Principal component analysis and artificial neural network (ANN) with back-propagation model have been tested. ANN allows a good recognition of 6 "test" chemicals even if water content of the mixtures don't remained constant during the experiments. The use of SnO_2 multisensors for in situ olfactive pollution assessment is still a challenge but these results give hope and motivation for intended investigations.

keywords : olfactive pollution detector, tin oxide semiconductor, pattern recognition

1. Introduction

The growing public concern about nasty odors near industrial plants, agricultural installations, landfill sites or wastewater facilities gives rise to the implementation of environmental policies in various countries, with the aim of safeguarding or restoring the quality of the natural surroundings. In order to assess and to monitor the state of the environment in this field, and also to suggest odor abatement techniques, it is important to have at one's disposal suitable means of objective measurement and inspection of environmental odors.
Since a few years, an intermediate and very attractive technique is more and more used to identify and to monitor odor phenomena : the "electronic nose". Actually, environment is often mentioned among the numerous applications of e-noses. However, this type of measurement of odor annoyance in the field remains exceptional.
Applications of this technique are almost restricted to food and agricultural emissions [Nexyad, 1995]
To date, the running studies related to the use of electronic noses in the environment are focused on the detection of some specific compounds, such as carbon monoxide in ambient air, or for domestic use [Patissier, 1996] or hydrogen sulfide [Falconer et al., 1990].
Most of these studies however concern the sensing devices able to detect the specific compound (sometimes non odorous, such as CO), but not really an electronic nose, with an array of sensors, and a pattern recognition engine.
Some other research works involve the use of e-nose for the measurement of a group of compounds, such as VOC's [Lorans, 1995] or hazardous organic vapours [Hierlemann et al., 1995], but the authors unanimously admit that the problem is complex.
Finally, very few studies are devoted to environmental applications in the field. All of them are restricted to the identification of very specific odors, chiefly at the emission, just near the source. The majority of them apply the electronic nose to the detection of hazardous compounds or of olfactive nuisance in the agricultural and the breeding sectors [Elliott-Martin, 1994; Persaud et al., 1996].
To become a reality, the use of e-nose to assess the odor directly in the environment has first to overcome two obstacles, at least : the improvement of sensors sensitivity in order to be able to detect

the very low concentration levels of odorous compounds in the atmosphere, and the understanding and the control of the ambient parameters influence, mainly temperature and humidity.
The purpose of the present work, indeed, is to examine the potential of e-nose technology for in situ monitoring of olfactive pollution in the vicinity of industrial plants. Although being an attractive and convenient solution, the use of commercially available electronic noses was discarded for the reason that they are not adapted to environmental constraints. More particularly, actual e-nose instruments are dedicated to lab applications, and they aren't portable; most of the time, they involve a sample preparation technique, such as headspace, but very few are adapted to the handling of gaseous atmospheres, on line or by sampling the air directly from the environment; and lastly, although measuring external parameters variations (temperature and humidity), they do not take them into account in the discrimination procedure.

This paper wonders whether a multisensor array system is able to approach in situ odor assessment, in spite of limitations due to ambient humidity and temperature.

2. Materials and methods

Artificial odors are prepared by injection 4 µl of volatile chemicals through the septum of a Tedlar® bag filled with 40 l of ambient air. After the evaporation of the liquids (Aldrich®, purity between 95% and 99.5%), the gaseous mixture is drawn across the sensors chamber by a mini-pump. Compounds found in typical olfactive pollution (determined by GC-MS) have been tested. Six chemical families are represented : alcohol (n-butanol), ester (butyl acetate), amine (n-butylamine), aldehyde (decanal), cetone (6-methyl-5-hepten-2-one) and sulfide (methyl sulfide).
Real atmosphere from the environment (in this case from animal fat treatment) are sampled in Tedlar® bag without direct contact of pumping.
As the purpose of this experiments is to point out the external parameters influence on the sensors signals and on the PARC, we don't control the experimental conditions :
- mixtures prepared with outside air with humidity content depending on meteorological conditions,
- laboratory atmosphere close to the real milieu's one (opened windows, no constant room temperature),
- no temperature regulation of the sensors chamber.

Only the reference air is a bit more controlled : dry air bubbling into saturated salt water (KCl, in melted ice).
A sensor array consisting of 12 commercial tin oxide gas sensors (Figaro Engineering Inc.) are sealed in 6 dm^3 perspex cubic chamber. Like the other chemical sensors (conductor polymers [Persaud, 1992], SAW and BAW with polymer or lipids active films, electrochemical fuel cells...), tin oxide sensors have a lot of disadvantages : poor stability, low sensitivity, short life time, temperature and humidity sensitivity, drift, poisoning effects, slow response times... The more important one for environmental measurement is the high sensitivity to humidity.
The choice of the SnO_2 sensors results of the best compromise. Their great power consumption is a bad point but they are easily available, robust and industrially produced (better interchangeability). Among this twelve sensors, two are specific to the humidity sensing (TGS 883 and TGS 2180).
Moreover, a temperature sensor and a capacitive humidity sensor are mounted into the chamber.
The sensor resistance is measured by a computer controlled multiplexed system (HP 3421A). A constant power voltage is supplied to the sensors heaters. A home-made software written in Labwindows provides the data acquisition and display (real time graphic). Two commercial software package (Statistica and Matlab) are used to process the data.
The experimental procedure generally consists in leading alternatively the reference air and the gaseous sample into the sensors using a three-way valve, keeping a constant 2000ml/min flow rate.
The samples were presented in random order during three weeks and at least six replicates were done for each compounds.

3. Results and discussion

3.1.Humidity and ambient temperature influence on the sensor signals

The presence of water vapour is known to cause a dramatic decrease of the SnO_2 sensors resistance. Two mechanisms could explain this influence : the dissociation of the water molecule into hydroxyl species which act as electron donors [McAleer et al, 1987 and 1988] and the creation of lattice vacancies by the reaction of the hydrogen atoms, produced from the water dissociation, with oxygen lattice atoms [Vlachos, 1995].
Our goal is not to understand the theory of those mechanisms but only to show the consequences of the water influence on an environmental odor response and how to take this effect into account.
The odorous mixture generated by any industrial source may exhibit a water content ranging from near zero to about saturation. Consequently, the semiconductor resistance variation is modified or even reversed. Figure 1 and 2 show time - response curves for four sensors for animal fat treatment odor. The right scale indicates the relative humidity value. The odor, in the two figures, comes from the same source but the sampling date is different and the external conditions as well.
In this case, the reference air is the lab ambient air.
With a 28% to 25% relative humidity variation, as shown in figure 1, the signal exhibit a decrease due to the animal fat odor, like usual with reducing gases. But with a 20% to 15% relative humidity variation (figure 2), the sensors resistance variation for the same odor (same olfactive perception) and with same temperature and flow conditions are reversed. This unexpected increase can be explain by the humidity value.
Indeed, in the absence of an odor, a diminution of adsorbed water on the SnO_2 ceramics is known to increase its resistance. Its appears that the adsorbed moisture can dominate the resistivity behaviour of the sensors [Vlachos, 1993]. Precisely, the humidity has a higher negative variation and the final value is lower. This experiment proves that it is absolutely necessary to take the water content of the samples into account when interpreting the sensors responses data.

The sensors signals are also strongly dependent of the temperature. This parameter is involved in the kinetics of the chemical processes on the oxide [Moseley, 1991 ; McAleer et al, 1988]. That's why a voltage is applied to a inside heater resistance to keep the sensor at a high fixed temperature (around 400°C). A change of the gas flow or of the surrounding atmosphere temperature can disturb the temperature of the semiconductor surface and hence the conductance value.
Figure 3 shows the sensors signals fluctuations due to the change of the array chamber temperature. However, this parameter is not so important than humidity. The temperature control is easier [Jonda, 1996] than the humidity one because it is a parameter which doesn't depend on the odor quality but only to the external conditions.
For the further experiments, the gas flow is kept at the same fixed level before and during the odor sensing. Though, the temperature in the laboratory hangs on the weather.

3.2. Effect of humidity on PARC results

Data preprocessing

The selection of the data preprocessing algorithms is an important stage. Various algorithms have been investigated (resistance difference, R_0-R, fractional resistance change, (R_0-R)/R_0, normalised fractional resistance change), where R_0, R are the resistance's in air or gas respectively. The best classification results are obtained with the normalised fractional resistance change :

$$\frac{\frac{\Delta R}{R_0}}{\sqrt{\sum_{i=1}^{n}\left(\frac{\Delta R}{R_0}\right)^2}}$$

where *n* is the number of sensors.

This choice was foreseeable since this parameter is known to nearly remove the gas concentration linear dependence [Gardner, 1991; Gardner, 1992]. For the olfactive annoyance recognition, the sensors array must be able to differentiate specific emission mixtures even over a range of concentrations. However, for most of the odors, the concentration-response curves are non-linear and therefore the patterns for individual chemicals may change with concentration [Persaud, 1996].
Here, the injection of 4µl of liquid chemicals in 40 l bag don't produce the same gaseous concentration for each component (various volatility and liquid density) and for the six same samples (various lab temperature, injected volume and bag volume errors).
Furthermore, to perform the pattern recognition, the previous values are scaled (Y-Ymin/Ymax-Ymin) so that the response of each sensor has a value between 0 and 1.

Principal component analysis (PCA)

PCA is a well-known linear unsupervised pattern recognition technique [Everitt, 1994]. Due to the use of dilute individual components, the assumption of a linear concentration-dependent response can be made. The purpose is to reduce the multidimensionality of a problem into two or so dimensions. The 12 original variables (sensors responses) are combined to find a new group of variables called the principal components.

Figures 4a and 4b show the plot of the first two principal components (factor 1 and factor 2) for the sensors responses to 3 sets of compounds. 90 % of the variance within the data is contained in the first two principal components.
Plot 4a shows a good separation of data into three distinct groups that corresponds to each of the three set of compounds.
In the next plot b, two other sensors data have been added, namely the responses of TGS 883 and TGS 2180. This sensors are excessively sensitive to water vapour. In this case the obtained separation does not match the expected one. Five groups can be discerned. The previous "sul" group is splitted and a new one is formed by "but6-one1-one2".
In fact, further investigations show that the two additional clusters are due to distinct water conditions. The water content is represented by the fractional absolute humidity change ($[AH-AH_0]/AH_0$ where AH, AH_0 are the asolute humidity in the array chamber with the odor or with the reference air respectively).
One sul group has a water range between 0.2 and 0.3 then the other one has a lower water range. The three data of the new group (but6-one1-one2) has the same water value. Within the "one3-4-5-6" group, one 6 has a positive water value and it is more separated from the three other ones.
In the end, factor 2 could describe the water parameter : o.1 to the left, 0 in the middle and negative value to the right. Although factor 1 (here vertically represented) reflects well the composition heterogeneity of samples, the scatter along factor2 seems more due to water content : the water parameter varying from 0.1 to negative values from the left to the right of the axis. Indeed, the addition of two water sensitive sensors has pointed out the importance of the external conditions on the PCA results.
Consequently, the data separation is not only due to the nature of compounds but also to the range of humidity.

An other example proving that the variability of the experimental conditions disturbs the PCA classification results is shown in figure 5. Indeed, the PCA on six samples of six compounds (without the data of TGS 2180 and TGS 883) under various humidity levels reveals the difficulties in separating out the six classes of compounds.
This expected result is still due to the change of the sensor signal pattern of a given compound when external conditions varies.

Artificial neural network (ANN)

Unlike PCA, the neural network is a non linear supervised pattern recognition technique [Baughman et al, 1995]. The major advantage of a non linear classification technique is that the data can be non-linear. It is commonly the case of environmental odors. Furthermore, the second fundamental difference is that there is an supervised learning stage.
A three layer network, using back-propagation of errors learning rule, is built. There are 12 elements in the input layer (12 sensors signals), 4 elements in the hidden layer and six elements in the output layer representing the six odor classes. The non linear transfer function is log sigmoïd. Training time is lowered thanks to an adaptive learning rate of 0.05, a learning increase of 1.05, a learning decrease of 0.7 and a momentum term of 0.95.
A batching operation (all the input vectors simultaneously presented to the network) is applied. For the training, there are a maximum of 5 input vectors for each of the six compounds.

During the training stage, the data from known compounds are trained onto target outputs, coded such that a "1" is present on a given output only when the corresponding compound is presented to the network (e.g. output 1=[1 0 0 0 0 0]) (see table1). The process is continually repeated until the final error (the error goal) between the target values and the actual values is less then 0.001.

Table 2a shows the outputs of the network after the training with all 30 input vectors (6 compounds x 5). In fact, these 30 vectors represent 30 experiments done under uncontrolled external conditions and thus under various humidity levels.
After the network learning step, with a training set of odors signals under any humidity levels, the network should be able to recognise new or "test" compounds (6 compounds x 1), this is the validation step. Table 2b shows that the compounds are well identified.

The same operation is performed with the previous compound, but this time, the training was done only with some of the thirty input vectors (table 3a) : those with an absolute humidity level (AH) below 3.
The "test" compounds are the ones obtained with an humidity level above 3. Table 3b shows the unfortunate results of the recognition. A training with a set of odor data obtained in a particular condition don't allow a good classification of new odor data obtained in an other particular condition.
Thus in this case the ANN results are disturbed by the water content. But it worth to be noticed (tables 2a and 2b) that if the network learns the same odors under a lot of various situations (drift, humidity, temperature,...) it can easy recognise an odor under a specific state. This pattern recognition technique is more able than the PCA to classify and to recognise odorous mixtures under various external conditions. Therefore, ANN seems more suitable for olfactive pollution recognition. But the network training with odor from different industrial sources and under various conditions takes a considerable amount of time. Furthermore, it assumes that the SnO_2 sensors array remains unchanged!

4. Conclusions

These results confirm the bad effect of the humidity and temperature fluctuations on the tin oxide sensors responses. Despite this well-known constatation, the consequences for in situ olfactive annoyance measurement is not so dramatic then previous suppose. Even with non fixed experimental conditions, near the ambient atmosphere, a discrimination of various single odors is possible. Furthermore, the six single compounds may be discriminated from each other even if their own concentration varies.
Indeed, we pointed out the importance of using an adapted pattern recognition engine as well as a previous data pre-processing. A supervised non-linear technique (ANN, backpropagation) is able to classify all the test samples for any experimental conditions. In this case, a good recognition is realised despite the humidity influence on the sensors signals.
However, the in situ olfactive pollution assessment with an SnO_2 sensors array and a PARC remains a challenge.
The nature, the number and the concentration of each compounds making up a complex mixture such as olfactive pollution can change from day to day depending, for example, of the industrial process.

But, even if the mixture changes, the source is the same and the annoyance perceived always comes from this typical source! How could the sensors array recognise this source? Maybe with a very intensive supervised training of the data recognition. Furthermore, for an objective olfactive annoyance measurement, they are still other limitations due to the SnO_2 sensors itself, e.g. low sensitivity compared to the human nose one and the short life time. Nevertheless, these results are promising for in situ objective malodors recognition. Further investigations are underway to improve in situ measurement always by keeping sensors limitations in mind. There are focused on the data analysis (e.g. training with real malodors under various ambient conditions, testing other techniques like nonsupervised non-linear techniques Sammon map) and on the experimental conditions (e.g. improvement of the temperature regulations).

References :

Baughman, D.R. and Liu, Y.A. (1995) Neural networks in bioprocessing and chemical engineering. Academic Press.

Elliott-Martin, R.J. (1994) Monitoring of Breath odor in Dairy Cattle : the Fox 2000 intelligent nose in the field. Presented at the Symposium on Olfaction and Electronic nose - Toulouse (France) 26-27 sept 1994.

Everitt, B.S. (1994) Statistical methods for medical investigations. Halsted Press

Falconer, R.S., Xu, Z., Vetelino, J.F., Lec, R.M., Smith, D.J. (1990) Detection of H_2S using a surface acoustic wave gas sensor, Proc. 3rd Meeting on Chemical Sensors - Clevland - 354-357.

Gardner, J.W. (1991) Detection of vapours and odors from a multisensor array using pattern recognition Part 1. Principal Component and Cluster Analysis, Sensors and Actuators B 4, 109-115.

Gardner, J.W. (1992) Detection of vapours and odors from a multisensor array using pattern recognition techniques Part 2. Artificial neural networks, Sensors and Actuators B 9, 9-15.

Gardner, J.W., Pike, A., de Rooij, N.F., Koudelka-Hep, M. , Hierlemann, A., Göpel, W. (1995) Integrated array sensor for detecting organic solvents, Eurosensors VIII, Toulouse Sept 1994 and Sensors and actuators B 26-27, 135-139.

Hierlemann, A., Weimar, U., Kraus, G., Schweizer-Berberich, M., Göpel, W. (1995) Polymer-based sensor array and multicomponent analysis for the detection of hazardous organic vapours in the environment. Conf. Proc. Eurosensors VIII - Toulouse - and Sensors and actuators B 26-27, 126.

Jonda, S., Fleisher, M. and Meixner, H. (1996) Temperature control of semiconductor metal-oxide gas sensors by means of fuzzy logic, Sensors and actuators B 34, 396-400.

Lorans, E. (1995) Identification of volatile compounds in the Paris underground. Application of the electronic nose in this complex atmosphere. 2nd Symp. on Olfaction and Electronic Nose - Toulouse -.

McAleer, J.F., Moseley, P.T., Norris, J.O.W. and Williams, D.E. (1987) Tin dioxide gas sensors, part 1.Aspects of the surface chemistry revealed by electrical conductance variations, J.Chem.Soc., Faraday Trans. 1, 83, 1323-1346.

McAleer, J.F., Moseley, P.T., Norris, J.O.W., Williams, D.E. and Tofield, B.C. (1988) Tin dioxide gas sensors, part 2. The role of surface additives, J.Chem.Soc., Faraday Trans. 1, 84(2), 441-457.

Moseley, P.T. and Williams, D.E. (1991) Oxygen surface species on semiconducting oxides. Techniques and mechanisms in gas sensing (P.T. Moseley et al, ed.) pp.46-60. IOP-Bristol.

Neotronics (1996) Detection of low levels of organic pollutants in water using the e-nose 4000, Sense (the neotronics olfactory sensing equipment newsletter) 1, 5.

Nexyad (1995) Le point sur les capteurs d'odeurs. Rapport de veille technologique pp.113-115.

Patissier, B. (1996) Gas sensor for CO detection in domestic use, Odors & VOC's Journal, Special Issue June 96-56.

Persaud, K., Khaffaf, S.M., Hobbs, P.J., Sneath, R.W. (1996) Assessment of conducting polymer odor sensors for agricultural malodor measurements, Chemical Senses 21, 495-505.

Persaud, K.C., Pelosi, P. (1992) Sensor arrays using conducting polymers for an artificial nose, Sensors and Sensory Systems for an Electronic Nose (Gardner & Bartlett, ed.) pp. 237-256. KlUWER-Dordrecht.

Vlachos, D.S., Skafidas, P.D. and Avaritsiotis, J.N. (1993) Transient effects of tin oxide CO sensors in the presence of water vapor, Appl. Phys. Lett. 63 (13), 1760-1761.

Vlachos, D.S., Skafidas, P.D., Avaritsiotis, J.N. (1995) The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases, Sensors and actuators B 24-25, 491-494.

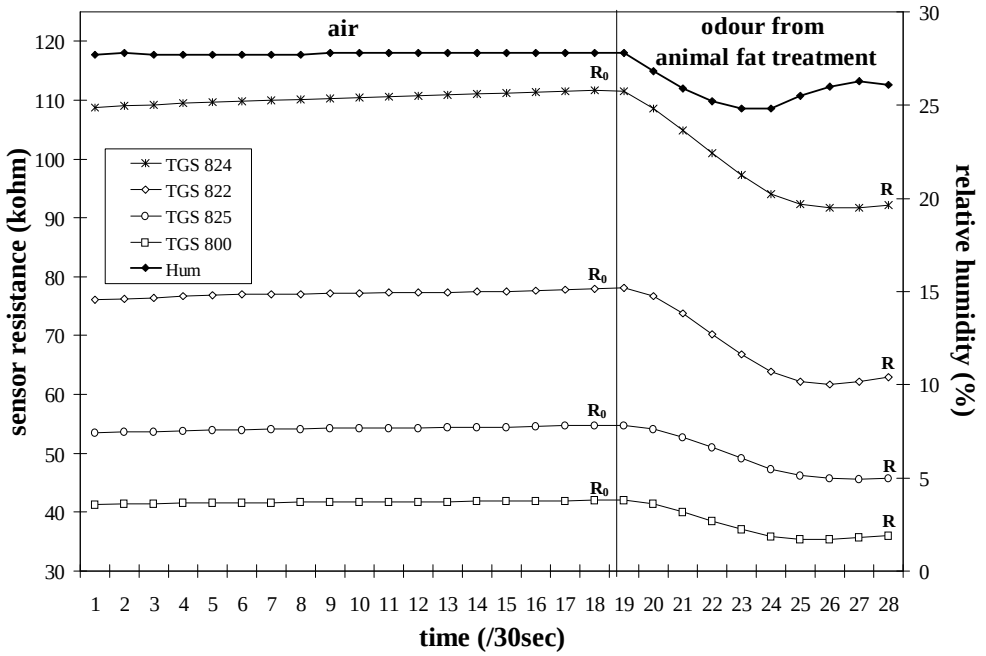


Fig. 1. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale) and relative humidity variation from 28% to 25% (right scale).

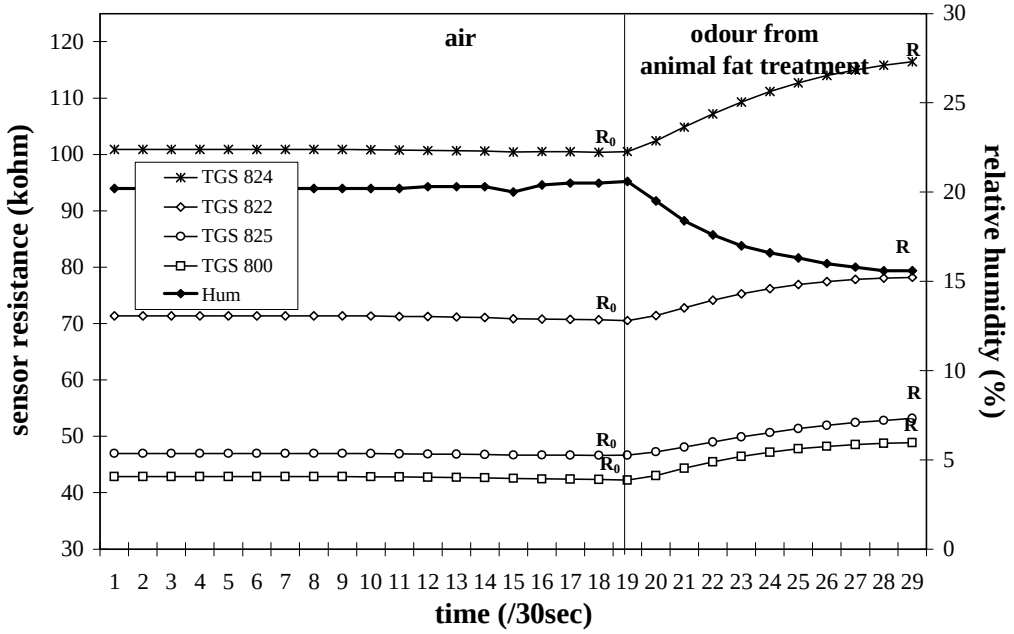

air
odour from
animal fat treatment
TGS 824
TGS 822
TGS 825
TGS 800
Hum
R
R0
sensor resistance (kohm)
relative humidity (%)
time (/30sec)
120
110
100
90
80
70
60
50
40
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29

Fig. 2. *Effect of moisture.*
Responses of 4 sensors to animal fat treatment odour (left scale). Relative humidity variation from 20% to 15% (right scale). An unexpected increase of the signals is observed due to the humidity value.

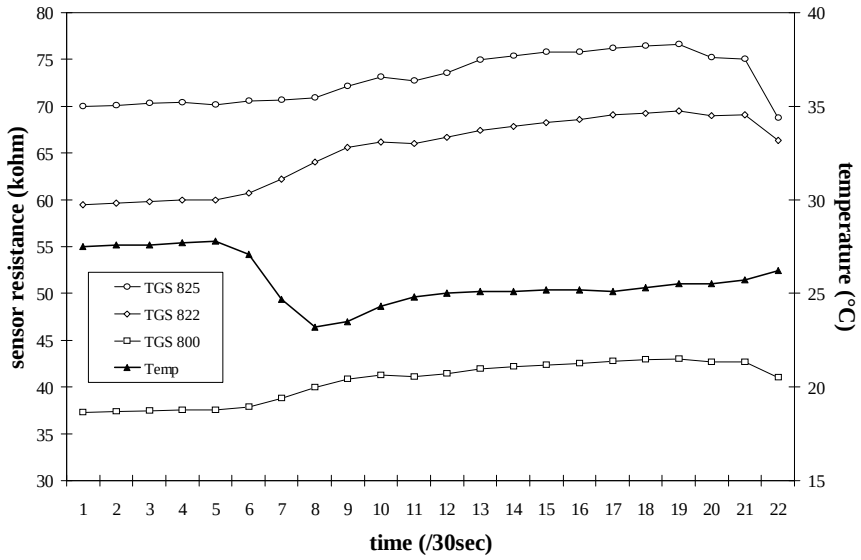
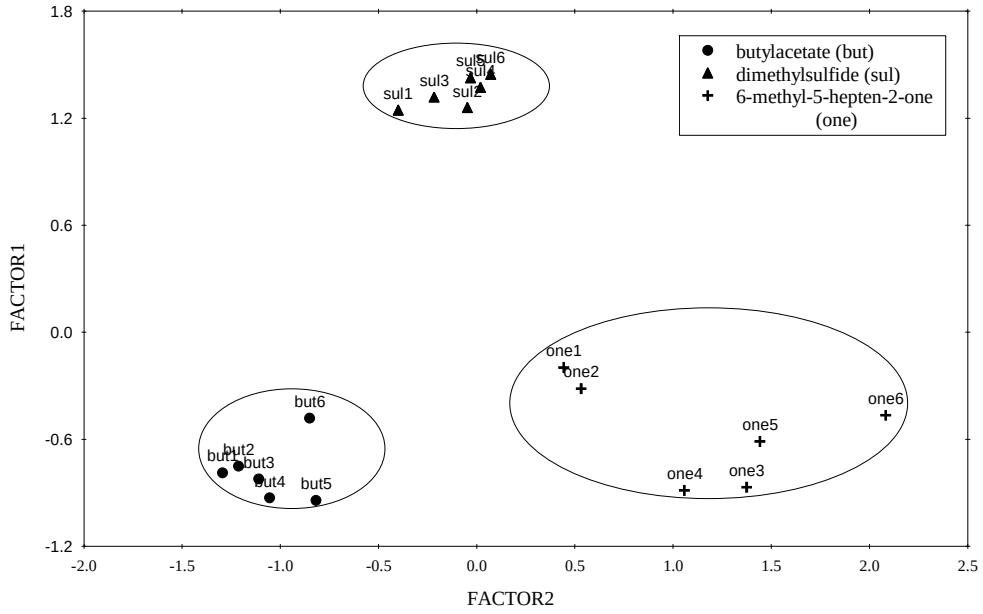

sensor resistance (kohm)
temperature (°C)
time (/30sec)
TGS 825
TGS 822
TGS 800
Temp
80
75
70
65
60
55
50
45
40
35
30
40
35
30
25
20
15
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22

Fig. 3. *Fluctuation of the base resistance of 3 sensors (left scale)due to the array chamber temperature variations (right scale).*


butylacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
sul1
sul2
sul3
sul4
sul5
sul6
but1
but2
but3
but4
but5
but6
one1
one2
one3
one4
one5
one6
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5

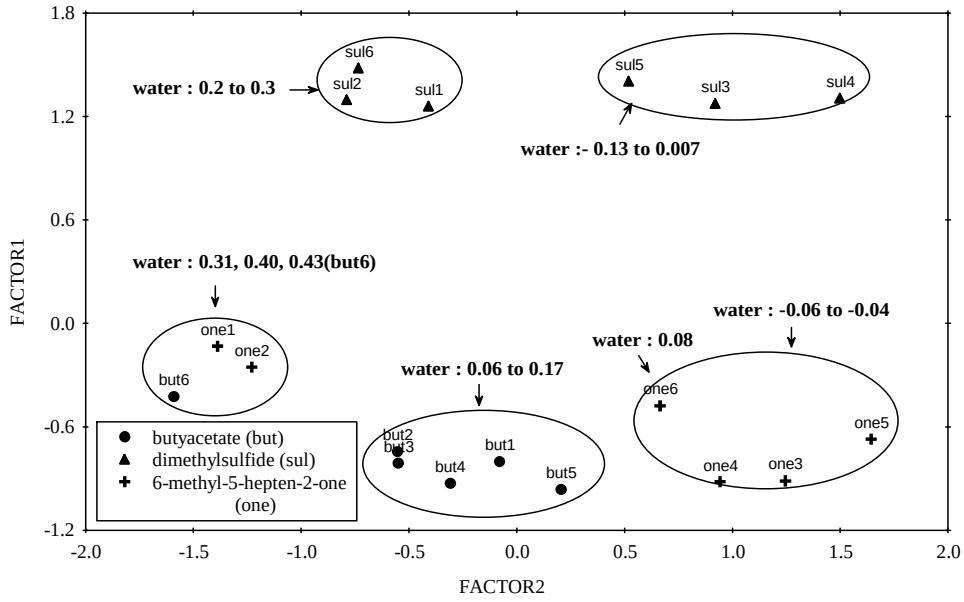

water : 0.2 to 0.3
sul6
sul2
sul1
sul5
sul3
sul4
water :- 0.13 to 0.007
water : 0.31, 0.40, 0.43(but6)
one1
one2
but6
water : 0.06 to 0.17
but2
but3
but1
but4
but5
water : 0.08
water : -0.06 to -0.04
one6
one5
one4
one3
butyacetate (but)
dimethylsulfide (sul)
6-methyl-5-hepten-2-one (one)
FACTOR1
FACTOR2
1.8
1.2
0.6
0.0
-0.6
-1.2
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Fig. 4. *Results of principal components analysis of 10 sensors responses (a) and 12 sensors responses (b) (10 previous sensors + 2 sensors sensitive to water vapour) to 3 compounds.*
(water=[(AH-AH_0)/AH_0], AH:absolute humidity)

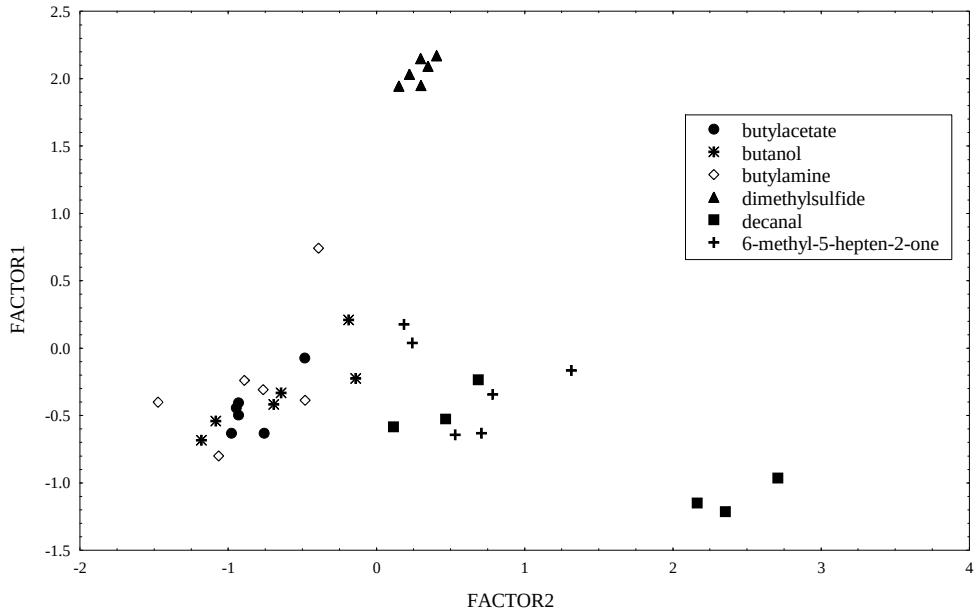

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
FACTOR1
-2
-1
0
1
2
3
4
FACTOR2
butylacetate
butanol
butylamine
dimethylsulfide
decanal
6-methyl-5-hepten-2-one

Fig. 5. *Results of principal components analysis of 10 sensors responses (without the 2 sensors sensitive to water vapour) to 6 compounds under various humidity levels.*

Table 1. Target outputs for the network trainingf

	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hepten-2-one
output 1	1.000	0.000	0.000	0.000	0.000	0.000
output 2	0.000	1.000	0.000	0.000	0.000	0.000
output 3	0.000	0.000	1.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	1.000	0.000	0.000
output 5	0.000	0.000	0.000	0.000	1.000	0.000
output 6	0.000	0.000	0.000	0.000	0.000	1.000

Table 2a. Results of the training with various humidity levels for all compounds

Network outputs																															
	compounds																														
outputs	butyl acetate					n-butanol					n-butylamine					methyl sulfide					decanal					6-methyl-5-hepten-2-one				
output 1	0.994	0.997	0.996	0.999	0.997	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.003	0.001	0.000	0.000	0.000	0.000	0.000
output 2	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.996	0.994	0.992	0.005	0.000	0.008	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.006
output 3	0.004	0.002	0.003	0.002	0.001	0.000	0.001	0.002	0.000	0.001	0.999	0.994	0.998	0.996	0.997	0.003	0.001	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.005	0.998	0.997	0.998	0.998	0.998	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output 5	0.001	0.003	0.001	0.006	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.998	0.998	0.998	0.999	0.991	0.000	0.006	0.002	0.000	0.001
output 6	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.002	0.000	0.001	0.000	0.005	0.001	0.000	0.001	0.000	0.001	0.001	0.003	0.000	0.000	0.007	0.999	0.993	0.999	1.000	0.995

Table 2b. Validation results with the "test" compounds

Network outputs						
	compounds					
outputs	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.
output 1	0.994	0.000	0.063	0.000	0.003	0.000
output 2	0.000	0.991	0.000	0.000	0.000	0.000
output 3	0.003	0.004	0.890	0.002	0.000	0.000
output 4	0.000	0.000	0.000	0.998	0.000	0.000
output 5	0.001	0.000	0.000	0.000	0.996	0.010
output 6	0.000	0.001	0.000	0.000	0.010	0.995
classification results	butyl acetate	n-butanol	n-butylamine	methyl sulfide	decanal	6-methyl-5-hep.

Table 3a. Results of the training for compounds with absolute humidity level < 3(g water/kg air)

Network outputs																	
	compounds																
outputs	butyl acetate			n-butanol		butylamine	methylsulfide			decanal				6-methyl-5-hepten-2-one			
output1	0.991	0.995	0.996	0.000	0.000	0.010	0.000	0.000	0.000	0.003	0.001	0.006	0.000	0.000	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.992	0.993	0.007	0.004	0.003	0.004	0.000	0.000	0.000	0.000	0.004	0.001	0.000	0.000
output3	0.004	0.003	0.004	0.007	0.007	0.989	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
output4	0.000	0.000	0.000	0.003	0.004	0.000	0.997	0.998	0.997	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
output5	0.004	0.005	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.998	0.993	0.997	0.000	0.000	0.001	0.006
output6	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.002	0.999	0.999	0.996	0.999

Table 3b. Validation results for "test" compounds with absolute humidity level >3 (g water/kg air)

Networks outputs																			
	compounds																		
outputs	butyl acetate			n-butanol				n-butylamine					methyl sulfide			decanal		6-methyl-5-hepten-2-one	
output1	0.990	0.983	0.992	0.002	0.000	0.000	0.001	0.014	0.603	0.006	0.605	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
output2	0.000	0.000	0.000	0.844	0.996	0.903	0.298	0.102	0.000	0.125	0.000	0.996	0.005	0.005	0.004	0.000	0.000	0.783	0.100
output3	0.041	0.166	0.003	0.521	0.942	0.381	0.783	0.999	0.997	0.988	0.787	0.986	0.000	0.000	0.000	0.000	0.000	0.120	0.040
output4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.993	0.994	0.994	0.000	0.000	0.000	0.000
output5	0.001	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.978	0.015	0.000	0.000
output6	0.000	0.000	0.000	0.000	0.011	0.002	0.001	0.000	0.000	0.000	0.000	0.023	0.000	0.000	0.000	0.006	0.987	0.425	0.958
classification results	butylac.	butylac.	butylac.	false	false	false	false	butylam.	false	butylam.	false	false	met.	met.	met.	decanal	false	false	6-methyl.