

# An electronic nose using time reduced modelling parameters for a reliable discrimination of Forane 134a

Claude Delpha<sup>\*</sup>, Maryam Siadat, Martine Lumbreras

*Laboratoire Interface Composants et Microélectronique, LICM-CLOES-SUPELEC, Université de Metz, 2 rue E. Belin, 57070 Metz, France*

## Abstract

For lots of applications, new systems based on gas sensor array and called electronic noses are in investigations. To be used for the toxic gas detection, these systems need to be accurate and must provide a rapid evaluation of the target gas.

In this application, we use metal oxide sensor array to detect, in presence of several humidity rates (18–85%), a refrigerant gas (Forane 134a) which can cause health troubles and greenhouse effects. In this aim, several families of representative variables as the transient or modelling parameters are extracted from the time sensor responses. These variables are then grouped in learning databases and tested with recognition methods to select the best association between database and method. Next, unknown gas samples were taken to validate this choice. The results show the possibility of a good discrimination and also identification of the target gas in presence of different humidity rate. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Tin oxide gas sensors; TGS sensor array; Humidity effects; Modelling parameters; Data processing; Principal component analysis; Discriminant factorial analysis

## 1. Introduction

Our environment is more and more affected by the release of several chemical pollutants in the atmosphere. These pollutants (CO<sub>2</sub>, CH<sub>4</sub>, NO<sub>2</sub>, fluorocarbon, halocarbon, etc.) can induce greenhouse effects or activate the ozone layer depletion. So, intense efforts are made to detect the responsible gases [1], and new systems based on smart and portable multisensors, called electronic noses [2], are widely investigated. As for all the gas detection systems, these electronic noses require a rapid and efficient detection of the target gases.

Electronic noses are principally composed of an array of gas sensors coupled with one or several pattern recognition methods [3,4], like principal component analysis (PCA), discriminant factorial analysis (DFA) or artificial neural networks (ANN).

In this work, we are mainly interested in the detection of a fluorocarbon gas (Forane 134a or R134a) leakage, in an air conditioned atmosphere. We study an array of six cross-sensitive tin oxide gas sensors (2 TGS-832, 2 TGS-813, 2 TGS-800) coupled with two pattern recognition methods: PCA and DFA. These types of sensors are very sensitive but

their response can be widely influenced by the gas humidity rate and temperature [5–8]. So, we have characterised the sensor array under closely controlled variable humidity, temperature and gas concentration conditions.

To obtain a rapid and reliable gas identification, we have selected from the experimental characterisation of all the sensors two families of representative variables: the conductance dynamic slope taken during the first 5 min of the sensor response, and the modelling parameters deduced from the double exponential model [9,10] fitting the first 12 min of the sensor response. Three different learning databases were created using these two families of representative variables, separately and together, and then treated by PCA and DFA methods. The obtained discriminations were compared to select the best method and the best database. To conclude, the discrimination capacity of our chosen system is tested with unknown data taken for different relative humidity rates and gas concentrations.

## 2. Experimental set-up

The test equipment, designed to characterise our sensor array under closely controlled experimental conditions, is chosen as a dynamic flow system [11]. It is mainly composed of three parts: the gas lines, a humidification system and a test chamber (Fig. 1).

<sup>\*</sup> Corresponding author. Tel.: +33-3-87-75-96-15;

fax: +33-3-87-75-96-01.

*E-mail addresses:* delpha@ese-metz.fr (C. Delpha), siadat@ese-metz.fr (M. Siadat).

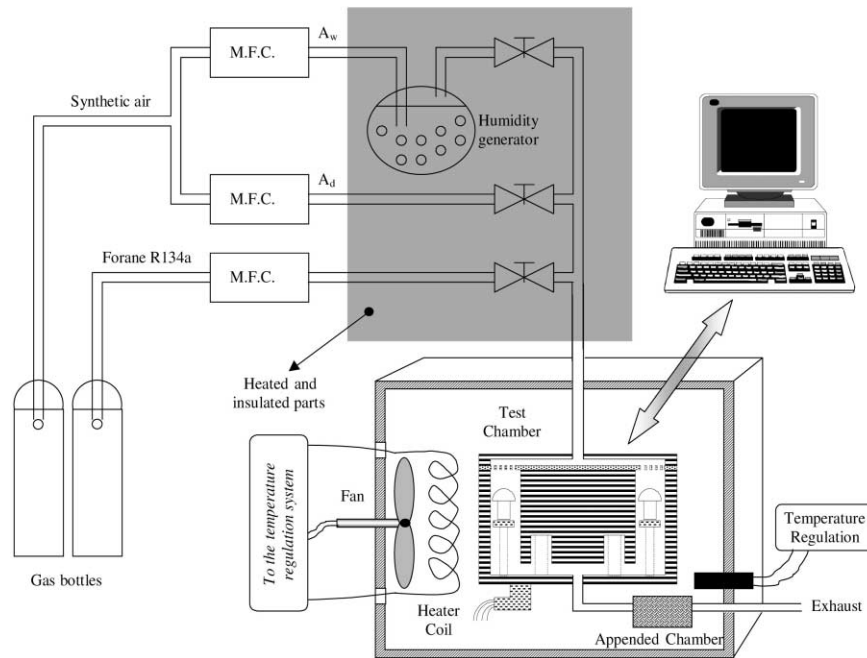


Fig. 1. Structure of the complete experimental set-up.

- The gas lines. They are connected to bottles containing the studied gas (Forane 134a) and its carrier gas (synthetic air) provided by air products. These lines are controlled by mass flow controllers via an electronic control unit (Brooks Instruments).
- The humidification system. It is a divided flow system including a humidity generator. This generator, based on the saturation method, allows us to create a saturated air flow. By mixing this flow to a dry one, we are able to generate humid air in the relative humidity rate range 5–85% at 33°C.
- The test chamber. Specially designed circular, it encloses the sensor array in a regular arrangement to allow short exchange time, laminar flow and similar gas concentration conditions. It is placed in a temperature controlled environment to avoid condensation problems and to provide stable gas temperature conditions.

For our application, the sensor array is composed of six Tagushi type sensors: 2 TGS-832, 2 TGS-813, 2 TGS-800 provided by Figaro Engineering Inc. These devices are placed in half bridge circuits for collecting their conductance variation. The sensors are supplied with a 10 V circuit voltage and a 5 V heating voltage providing an operating temperature at about 420°C according to Figaro Engineering Inc. sensor operating data sheet. Moreover, in order to check the created environmental conditions, two other types of sensors were placed in an appended chamber to control the atmospheric conditions: a humidity sensor (Humirel Inc.) and a temperature device (National Semiconductor).

The sensor array output signals are then collected via a data acquisition board (National Instruments) and treated with pattern recognition methods by using a statistical and data analysing software (SPSS 10.0, Spss Inc.).

### 3. Results

#### 3.1. Sensor response

Our sensor array have been characterised under three controlled atmospheres: humid air, Forane 134a in dry air noted “dry R134a” and Forane 134a in humid air, noted “wet R134a”. For these measurements, we have used five relative humidity rates: 18, 35, 52, 68 and 85% at 33°C. The range of Forane 134a concentration in synthetic air was 200–1000 ppm with a 200 ppm step. For these three types of measurements the sensor array was exposed to the studied atmosphere for 1 h, and their time-dependent response was collected. Between each measurement, a synthetic air flow (dry or humid along with the experiment) is introduced into the test chamber for 1 h, to purge the whole system and also to stabilise the sensor sensitive layer in order to reach the initial conductance value.

For the three studied atmospheres, all the gas sensors offer a reducing gas behaviour: all the TGS sensor responses are similar and increase when introducing any studied atmosphere in the test chamber (Fig. 2). From the time sensor responses, we have deduced the conductance dynamic slope values measured between the first to the fifth minute of the gas exposure.

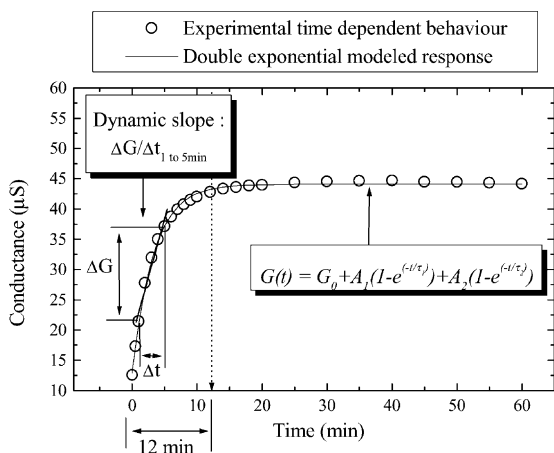


Fig. 2. Sensor typical response to reducing gas.

In a humid air atmosphere, the conductance dynamic slope values increase in function of the relative humidity rate (Fig. 3) which is similar to a reducing gas behaviour [9]. In presence of the reducing gas R134a, the conductance dynamic slopes increase when increasing the gas concentration (Figs. 4 and 5). Nevertheless in presence of humidity, this behaviour differs along with the R134a concentration (Fig. 5): the conductance dynamic slope values increase rapidly for the two first gas concentrations (200–400 ppm) and afterwards are slightly constant, and for a same R134a concentration value, the conductance dynamic slopes vary randomly when increasing the humidity rate. We have also noticed that the sensor responses are masked for the two lowest gas concentrations (200–400 ppm) at the highest relative humidity rate (85%).

For the three studied atmospheres, the conductance dynamic slopes corresponding to all the sensors are grouped in a database noted Base 1.

In previous works, we have shown that the entire sensor time-dependent behaviour (60 min) for each of the three studied atmospheres, can be modelled (Fig. 2) in a double exponential function [9,10] as the following Eq. (1).

$$G(t) = G_0 + A_1 \left(1 - e^{-t/\tau_1}\right) + A_2 \left(1 - e^{-t/\tau_2}\right) \quad (1)$$

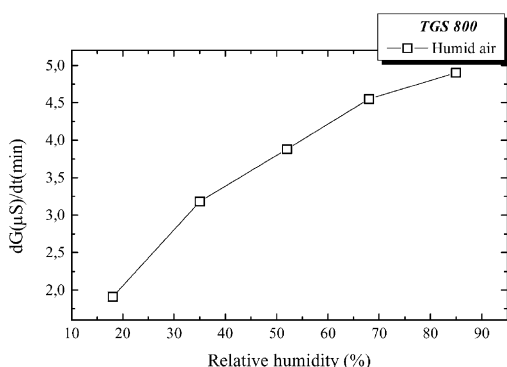


Fig. 3. Dynamic slope response in a humid air atmosphere.

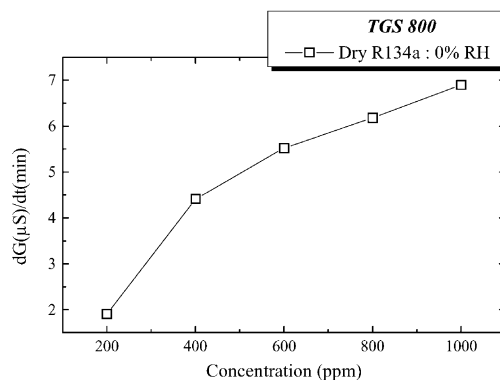


Fig. 4. Dynamic slope response in a dry R134a atmosphere.

where  $G_0$  is the initial conductance value,  $t$  the time,  $\tau_1$  and  $\tau_2$  denote two time constants,  $A_1$  and  $A_2$  are two constants depending on the sensor and gas types.

With such a model, we propose to reduce the sensor response time. For this purpose, we have fitted the sensor time-dependent response in several time intervals ( $0, t_1$ ) with  $t_1 < 60$  min. Afterwards, we have extracted the corresponding modelling parameters and used them to estimate the steady-state sensor response by using Eq. (1). An acceptable relative error (less than 3%) on the estimated steady-state conductance value was found for  $t_1 = 12$  min (Fig. 6).

So, we have fitted the time-dependent response of all the sensors in only the first 12 min with the previous double exponential model (Eq. (1)). The values corresponding to the obtained modelling parameters ( $G_0, A_1, A_2, \tau_1, \tau_2$ ) were collected, for each TGS sensor of the array and all the measurement results. They were grouped in a second database noted Base 2.

For this study, we have treated separately the two databases (Base 1 and Base 2) with two factorial pattern recognition methods PCA and DFA and compared the obtained results. Then, we proposed to improve the discriminant capacity of our system by coupling the two bases in a single database (Base 3). In this work, 148 measurements were made for the three databases.

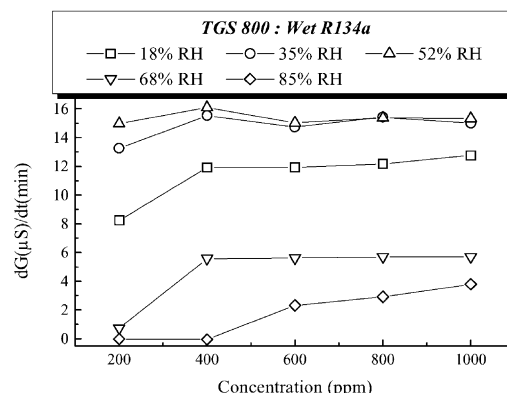


Fig. 5. Dynamic slope response in a wet R134a atmosphere.

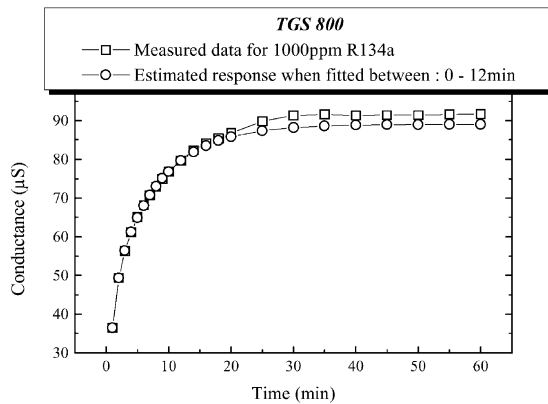


Fig. 6. TGS 800 estimated response in a time interval.

### 3.2. Principal component analysis (PCA)

This data analysis method is an unsupervised technique usually used with metal oxide gas sensor array applications. It is applied to a database created with the representative variables selected from the sensor responses. This database is considered as a matrix  $X$  where the  $x_{ij}$  element is the  $j$ th measurement value for the  $i$ th considered variable. The main objective of PCA [12–14] consists of expressing the information contained in the database by a lower number of variables called principal components and then show the liaison between the measurements. These principal components are linear combinations of the original response vectors  $\vec{x}_j$  for the responses of the  $n$  variables of all the studied gas sensors. So the  $k$ th principal component is noted.

$$PC_k = \sum_{i=1}^n \alpha_{ik} x_{ij} \quad (2)$$

where  $\alpha_{ik}$  is the eigenvector for the  $i$ th variable, and corresponds to the contribution of the original response vectors for the considered principal components. This contribution expresses the data variance percentage contained in each principal component. Generally, these components are chosen to contain the maximum data variance and then to give the best representation of the considered measurement in an orthogonal space. In fact, the aim of this technique consists of removing any redundancy and reducing the dimensionality of the studied problem and permit a representation of the database measurements [14].

In this work, we have first treated the Base 1 with the PCA method. When using this base we are able to represent 95.5% of the information present in the database with the two first principal components (Table 1). In fact, with such a representation, we can observe a slight separation between the three types of measurements (Fig. 7); the values measured for the dry R134a atmosphere seem to be well separated with the wet R134a ones, however, there are not real boundaries with the humid air measurements. We

Table 1  
Eigenvalues for the PCA with the conductance dynamic slope

Principal component	Eigenvalue	Variance (%)	Variance cumulated (%)
1	4.97	82.87	82.87
2	0.76	12.66	95.53
3	0.12	1.94	97.47
4	9.08E–2	1.51	98.98
5	4.14E–2	0.69	99.67
6	1.94E–2	0.33	100

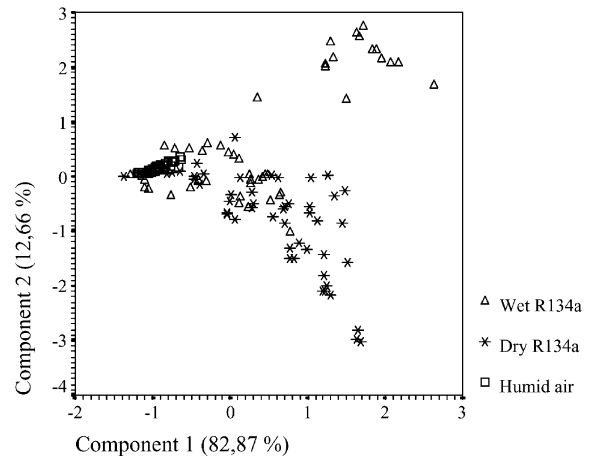


Fig. 7. PCA results using the conductance dynamic slope.

have also noted important dispersions in the wet R134a measurements due to the presence of variable humidity.

When studying Base 2 we found for the two first components a representation containing only 34.1% of the information in the database (Table 2). With this base, we are not able to well separate the three types of measurement (Fig. 8). In fact only the wet R134a measurements are distinctly separated with the others.

Such representations with PCA are not really sufficient to well distinguish the three types of measurements. Thus, this method is not good enough to conclude the capacity of the array to discriminate correctly the three types of atmospheres. So we propose to apply the DFA method to these two databases.

Table 2  
Eigenvalues for the PCA with the reduced modelling parameters

Principal component	Eigenvalue	Variance (%)	Variance cumulated (%)
1	5.82	19.4	19.4
2	4.41	14.71	34.11
3	3.53	11.78	45.89
4	2.43	8.11	54.00
5	2.30	7.67	61.67
vdots	⋮	vdots	vdots
30	9.8E–4	3.27E–3	100

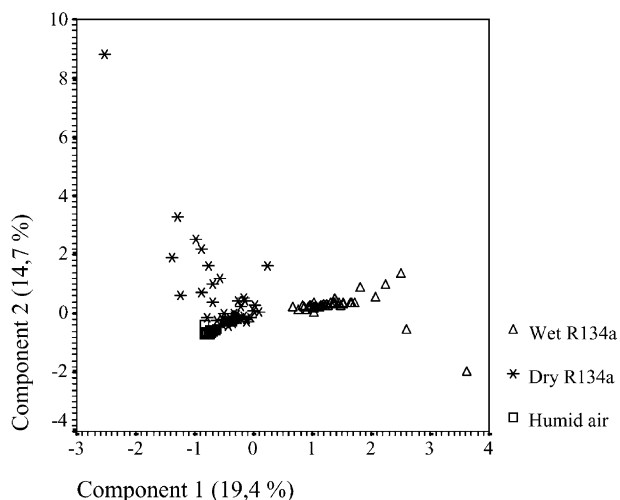


Fig. 8. PCA results using the reduced modelling parameters.

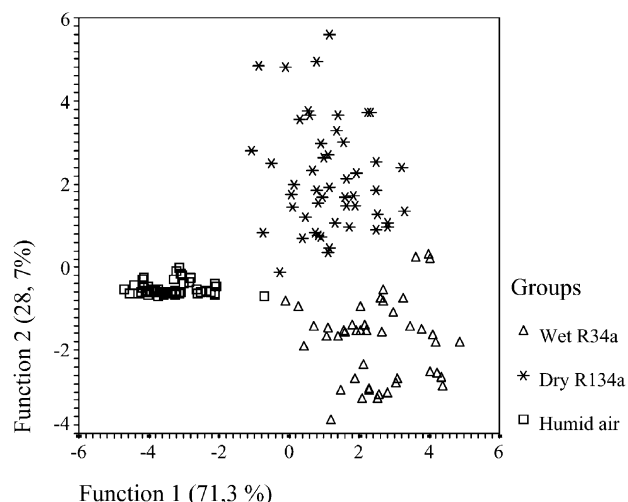


Fig. 9. DFA results using the conductance dynamic slope.

### 3.3. Discriminant factorial analysis (DFA)

The discriminant factorial analysis (DFA) also belongs to the class of multivariate supervised statistical methods. As for the PCA method, the database consists of a matrix  $X$  where the  $x_{ij}$  element is the  $j$ th measurement value for the  $i$ th considered variable. But for the DFA method, all the database elements are affected in an  $k$  a priori groups. In this case, we have to show if the variables are sufficient or not to allow a well a posteriori classification of the data in their a priori groups. For this aim, the discriminant procedure consists of maximising the differences between all the groups and minimising these differences inside each group. Afterwards, linear combinations of the variables in each group are used to create  $k - 1$  new factorial axis (or discriminant axis) with different data variance percentages. As for PCA, these variance percentages are given by the corresponding eigenvalues. A decisive law is then generated. This law corresponds to a multiple regression equation using linear combinations of variables as coefficients. With such a law, we are able to identify and classify new cases [14].

For the first database (Base 1), we have applied the DFA method by using as a priori groups the three measurement types. In this case, we are able to well represent 100% of the information in the database by using two factorial axes as in PCA (Fig. 9). Three groups are well identified, but a large

intra-group dispersion still exists. For this base, we are able to well classify a posteriori 98.6% of the whole database observations in their a priori group: two errors were found (Table 3). The first one is due to a low dry R134a gas concentration (200 ppm) classified as a humid air measurement. The second error corresponds to a wet R134a measurement (18% relative humidity — 400 ppm R134a) classified in the dry R134a group.

With Base 2, DFA allows us to well represent (Fig. 10) 100% of the total information with two axis. We obtain here a better separation than for the previous base presented in Fig. 9 and the classification result is 99.3%. Only one error was found: a dry R134a measurement (200 ppm) classified in the humid air group (Table 4).

In the case of Base 2, the classification rate and the separation between the three groups are better, so we have used its resultant decisive law to identify a test data set composed of 25 new test measurements supposed to be unknown. In this test data set, several measurements with different humidity rate and gas concentration conditions were taken (Table 5) and we are able to well identify 15 test cases over the 25 (Fig. 11). All the wet R134a measurements were well identified (9/9). However, only 5/8 dry R134a measurements and only 1/8 humid air unknown cases were well identified (Table 5). Many cases appeared to be misidentified with this base.

Table 3  
DFA classification results with the conductance dynamic slope

	Groups	A posteriori affectation			Total (%)
		Humid air	Dry R134a	Wet R134a	
A priori groups affectation	Humid air	100	0	0	100
	Dry R134a	2	98	0	100
	Wet R134a	0	2.2	97.80	100

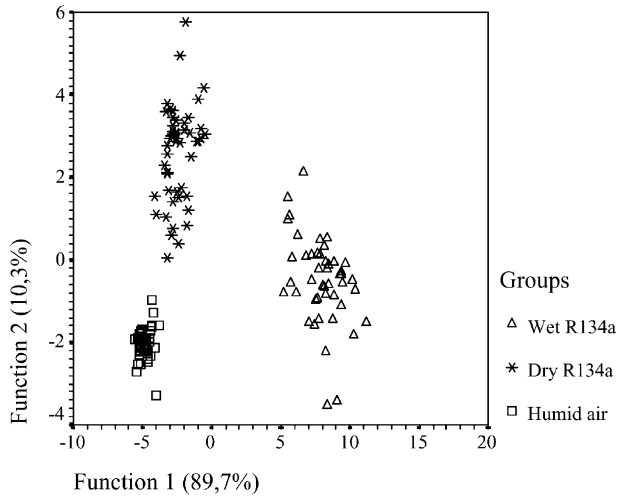


Fig. 10. DFA results using the reduced modelling parameters.

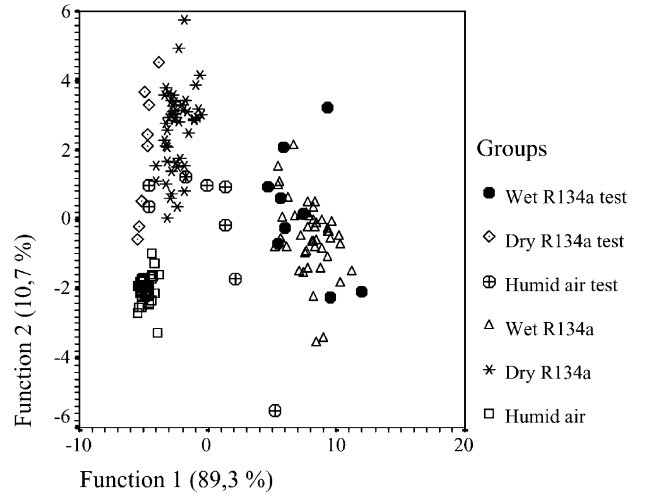


Fig. 11. Identification of unknown cases using the reduced modelling parameters with DFA.

Table 4  
DFA classification results with the reduced modelling parameters

	Groups	A posteriori affectation			Total (%)
		Humid air	Dry R134a	Wet R134a	
A priori groups affectation	Humid air	100	0	0	100
	Dry R134a	2	98	0	100
	Wet R134a	0	0	100	100

Table 5  
Unknown cases and their identification results

Unknown cases	Corresponding measurement	Predicted group with Base 2	Predicted group with Base 3
Humid air test	Air — 18% RH	Wet R134a	Humid air
	Air — 18% RH	Dry R134a	Humid air
	Air — 35% RH	Wet R134a	Humid air
	Air — 35% RH	Dry R134a	Humid air
	Air — 52% RH	Humid air	Humid air
	Air — 52% RH	Dry R134a	Humid air
	Air — 68% RH	Dry R134a	Humid air
	Air — 68% RH	Dry R134a	Humid air
Dry R134a test	R134a — 200 ppm	Dry R134a	Dry R134a
	R134a — 200 ppm	Humid air	Dry R134a
	R134a — 400 ppm	Humid air	Dry R134a
	R134a — 400 ppm	Dry R134a	Dry R134a
	R134a — 600 ppm	Humid air	Dry R134a
	R134a — 600 ppm	Dry R134a	Dry R134a
	R134a — 800 ppm	Dry R134a	Dry R134a
	R134a — 800 ppm	Dry R134a	Dry R134a
Wet R134a test	R134a — 200 ppm — 18% RH	Wet R134a	Wet R134a
	R134a — 200 ppm — 35% RH	Wet R134a	Wet R134a
	R134a — 200 ppm — 52% RH	Wet R134a	Wet R134a
	R134a — 600 ppm — 18% RH	Wet R134a	Wet R134a
	R134a — 600 ppm — 35% RH	Wet R134a	Wet R134a
	R134a — 600 ppm — 52% RH	Wet R134a	Wet R134a
	R134a — 1000 ppm — 18% RH	Wet R134a	Wet R134a
	R134a — 1000 ppm — 35% RH	Wet R134a	Wet R134a
	R134a — 1000 ppm — 52% RH	Wet R134a	Wet R134a

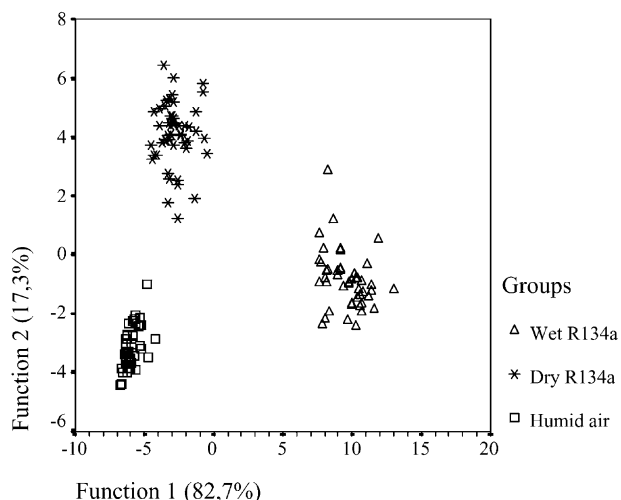


Fig. 12. DFA results using the reduced modelling parameters coupled with the conductance dynamic slope.

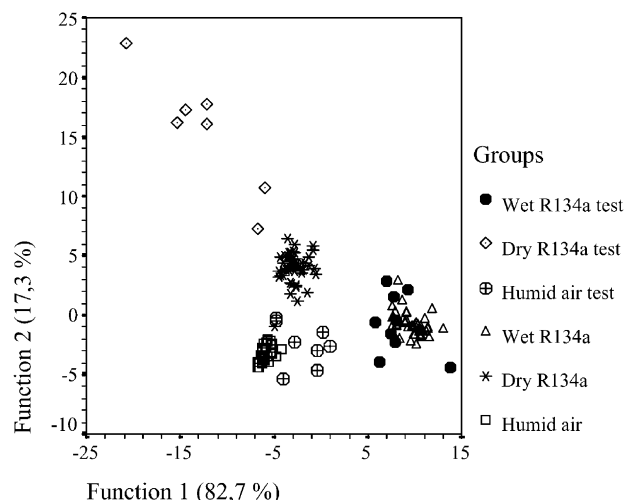


Fig. 13. Identification of unknown cases using the reduced modelling parameters and the conductance dynamic slope with DFA.

Table 6

DFA classification results with the conductance dynamic slope and the reduced modelling parameters

	Groups	A posteriori affectation			Total (%)
		Humid air	Dry R134a	Wet R134a	
A priori groups affectation	Humid air	100	0	0	100
	Dry R134a	2	98	0	100
	Wet R134a	0	0	100	100

To improve the identification, we propose to couple the conductance dynamic slope database (Base 1) with the time modelling parameters database (Base 2) to form a new base (Base 3). With this base, we obtain a best discrimination as we can observe in Fig. 12, where the intra-group dispersion is very well reduced compared to the two other previous cases. The a posteriori classification rate obtained here is as good as for Base 2: 99.3%; the same error is found (Table 6). We use the same unknown data set to be tested with the new decisive law created (Fig. 13). In this case all the 25 test measurements were well identified in their corresponding groups: 9/9 for the wet R134a group, 8/8 for the dry R134a group and 8/8 in the humid air group (Table 5). So, we are able with this Base 3 to perfectly identify R134a whatever the gas concentration or the relative humidity rate of the atmosphere. This result can be explained by the fact that the information contained in Base 1 and Base 2 are complementary and not redundant.

#### 4. Conclusion

In this paper, we have proposed two families of representative variables for the discrimination of Forane 134a in a humidity controlled atmosphere with a TGS sensor array: the conductance dynamic slope in the first 5 min of the time-dependent response and the time modelling parameters in

the first 12 min of gas exposure. The values corresponding to these variables were grouped in two separate databases for different atmospheres. We have then studied the discrimination ability of these two families of variables by using PCA and also DFA methods.

With the first method, we show that it is difficult to obtain a sufficient separation between the three types of measurements: humid air, dry R134a and wet R134a. So, we have used the DFA method to improve this separation. With such a method, we show that the use of these two families of variables in separate databases allows us to well discriminate the R134a gas even if the humidity rates or the gas concentrations vary but the identification of unknown data is not completely satisfactory. To obtain a more performed identification of unknown cases we propose to associate these bases in a single database. With this base, we show the ability of our system to well identify R134a in a reduced time (12 min) whatever its humidity rate or gas concentration in the studied atmospheres.

So for an electronic nose application we are able to prevent R134a leakage in an air conditioned atmosphere.

#### References

- [1] N. Yamazoe, N. Miura, Environmental gas sensing, *Sens. Actuators B* 20 (1994) 95–102.

- [2] W. Göpel, Chemical imaging: concepts and visions for electronic and bio-electronic noses, *Sens. Actuators B* 52 (1998) 125–142.
- [3] J.W. Gardner, P.N. Bartlett, Performance definition and standardization of electronic noses, *Sens. Actuators B* 33 (1996) 60–67.
- [4] H.T. Nagle, R. Gutierrez-Osuna, S.S. Schiffman, The how and why of electronic noses, *IEEE Spectrum* 35 (9) (1998) 22–34.
- [5] P. Van Geloven, M. Honore, J. Roggen, The influence of relative humidity on the response of tin oxide gas sensors to carbon monoxide, *Sens. Actuators B* 4 (1991) 185–188.
- [6] D.S. Vlachos, P.D. Skafidas, J.N. Avaritsiotis, The effect of humidity on tin oxide thick films in the presence of reducing and combustible gases, *Sens. Actuators B* 24/25 (1995) 491–494.
- [7] C. Delpha, M. Siadat, M. Lumbreras, Environmental temperature and humidity variation effect on the response of a TGS sensor array, in: *Proceedings of ISOEN 99*, Tübingen, Germany, 20–22 September 1999, pp. 156–159.
- [8] C. Delpha, M. Siadat, M. Lumbreras, Relative humidity: an interfering parameter for the characterisation of a TGS sensor array, *SPIE Proceedings Series*, Boston, USA, 19–22 September 1999, pp. 223–230.
- [9] C. Delpha, M. Siadat, M. Lumbreras, Humidity dependence of a TGS gas sensor array in an air conditioned atmosphere, *Sens. Actuators B* 59 (2/3) (1999) 255–259.
- [10] C. Delpha, M. Siadat, M. Lumbreras, Discrimination of a refrigerant gas in a humidity controlled gas atmosphere by using modelling parameters, *Sens. Actuators B* 63 (3) (2000) 234–240.
- [11] C. Delpha, M. Siadat, M. Lumbreras, Humidity effect on a commercially available refrigerant gas sensor TGS 832, Vol. 3539, *SPIE Proceedings Series*, Boston, USA, 2–6 November 1998, pp. 172–179.
- [12] E. Llobet, J. Brezmes, X. Vilanova, J.E. Sueiras, X. Correig, Qualitative and quantitative analysis of volatile organic compounds using transient and steady-state responses of a thick film tin oxide gas sensor array, *Sens. Actuators B* 41 (1997) 13–21.
- [13] J.W. Gardner, Detection of vapours and odours from a multisensor array using pattern recognition. Part1. Principal component and cluster analysis, *Sens. Actuators B* 4 (1991) 109–115.
- [14] D.F. Morrisson, *Multivariate Statistical Methods*, McGraw-Hill, Singapore, 1988, p. 415.

## Biographies

*Claude Delpha* graduated in biomedical electronics engineering from the University of Nancy in 1995. He obtained an Instrumentation and Microelectronics post graduate degree in the field of gas sensing and signal processing techniques in 1996 from the same university. Since 1997, he has been a PhD student in the Laboratory of Interfaces, Components and Microelectronics in the University of Metz. His main areas of interest are in semiconductor chemical sensors, chemical vapour discrimination using sensor arrays, gas sensors humidity and temperature dependence, electronic nose, and pattern recognition methods.

*Maryam Siadat* received her engineer diploma in electronics in 1983 and her PhD in biomedical electronics engineering in 1989 from the Polytechnic Institute of Lorraine (ENSEM/INPL) at Nancy, France. She is an associate professor at the University of Metz since 1991 and her research interests are in gas detection, signal and data processing, sensor characterisation and numerical electronic circuit development.

*Martine Lumbreras* graduated in electrical engineering with specialisation in solids electronics from the University of Montpellier in 1969. She was awarded a PhD degree in 1979 from the same university. She joined the University of Metz in 1979, and she was awarded a doctorate of Sciences degree in 1987 from this University. She has been Professor at the University of Metz since 1991, and she created a sensor research group in 1994, part of the Laboratory of Interfaces, Components and Microelectronics.