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An electronic nose for the identification of Forane R134a in an air conditioned atmosphere

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Abstract

An electronic nose based on a TGS type sensor array for the main detection of Forane R134a has been characterised under closely controlled gas temperature and humidity conditions. This paper presents the dependence of the TGS sensor array to the gas temperature and the relative humidity rate values. A model is proposed for the sensor array behaviour for each of these parameters. Afterwards, the importance of these two atmospheric parameters is underlined and the need to control or to include them into a database is proven. We present the ability to identify the target gas with the discriminant factorial analysis method even if the relative humidity or the gas temperature differs from the nose database learning process. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tin oxide gas sensors; TGS sensor array; Electronic nose applications; Humidity and temperature effects

1. Introduction

With a technology based on an array of chemical sensors associated with signal processing techniques followed by data analysing systems, electronic noses have raised a great interest during the last years. Nowadays, current electronic noses produce a classification or fingerprints for odours composing complex mixtures [1,2]. In a lot of commercial electronic nose applications, tin oxide sensors like Tagushi type devices are used because of their low cost and their high sensitivity. However, one of the major problems of these sensors is their lack of selectivity but also their dependence to different atmospheric operating conditions like gas humidity and temperature [3–5].

We are conceiving an electronic nose for the main detection of a refrigerant gas Forane R134a leakage and carbon dioxide excess in an air conditioned atmosphere. For this application, we use an array of Tagushi type sensors coupled with a processing system based on pattern recognition methods. To have a good knowledge of our sensor array behaviour, we have characterised the array in several humidity and temperature controlled atmospheres.

In this paper, we present the effect of gas humidity and temperature on the sensor array in dry synthetic air and a mixture of Forane R134a in dry air. First, the sensor steady-state responses are studied and empirical exponential models are proposed. Afterwards, we show the ability to identify unknown cases with pattern recognition methods like discriminant factorial analysis (DFA) whatever the gas temperature and the relative humidity (RH) may be.

2. Experimental

For all the following experiments, we have designed a performed system able to create closely controlled conditions of humidity and temperature. For this electronic nose, a dynamic type gas sampling system is used. Three main parts compose this system (Fig. 1): controlled gas lines, a humidification set-up and a test chamber.

The gas lines. The studied gases (Forane R134a and carbon dioxide) and the carrier gas (synthetic air) are provided by Air product bottles. Their flows are measured and controlled by mass flow controllers (M.F.C., 5850TR, Brooks Instruments) with an electronic control unit (5878, Brooks Instruments).

A humid air generator. It's a divided flow generator based on the saturation principle. It consists of bubbling a dry air flow into water to create air saturated with water

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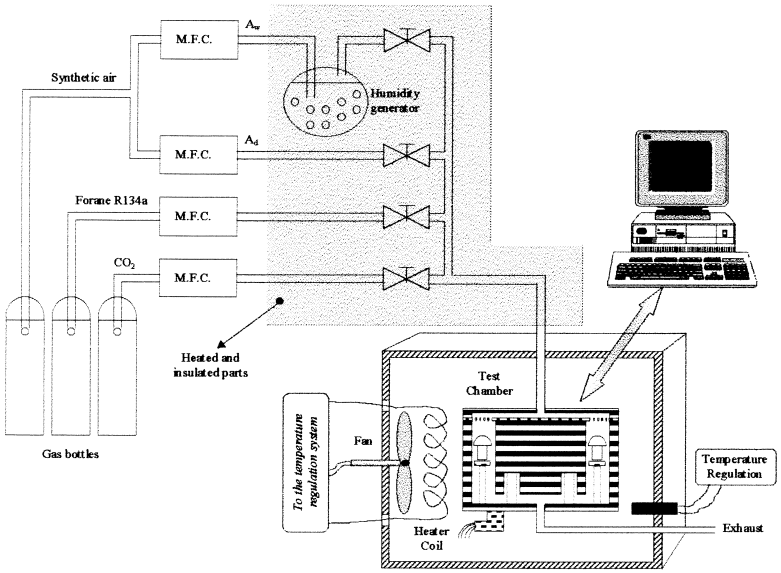

Fig. 1. Structure of the experimental system.

vapour at a fixed temperature (30°C). At a defined environmental temperature (33°C), this saturated flow is mixed with another dry air flow, creating constant RH rate. So, by varying these two different flows, we are able to produce humid air in the 5–85% RH range [6].

A test chamber. It was circularly designed in stainless steel and encloses six regularly placed Tagushi gas sensor (TGS) type devices provided by Figaro Engineering. This chamber is equipped with a filled central piece of metal to reduce volume and provide short exchange time. Moreover, it is equipped with a grid plate placed just under its cover to provide similar laminar flow conditions to each sensor. As shown in Fig. 1, this test chamber is put in an environmental temperature controlled atmosphere to apply the same controlled gas temperature conditions to each sensor and also avoid any condensation problems. With this system, we are able to create atmospheres in the 30–50°C temperature range.

For our application, our sensor array is composed of six TGS: two TGS 832, two TGS 813 and two TGS 832, application gas types of which are summarised in Table 1. These sensors are placed in a half bridge circuit, as shown in Fig. 2, to pick up the sensor conductance variation. They are supplied with a 10 V circuit voltage and a 5 V heating voltage providing an operating temperature of about 420°C according to Figaro Engineering operating data sheets. Two other types of sensors have been added to this array to check the gas humidity rate and temperature via an appended chamber placed at the test chamber exhaust: two RH sensors (NH3, Figaro Engineering; and MHS1101, Humirel) and a temperature device (LM35CZ, National Semiconductor). To be treated, the gas sensor output signals are measured via a half bridge circuit and collected by a data acquisition board (LabPC +, National Instruments). Afterwards, the collected data are analysed and then treated by pattern recognition methods by way of a powerful statistical and data analysing software (SPSS 8.0, Spss).

Table 1
TGS sensor array and their application gases

Model	Main applications, target gas
TGS 832	Halocarbon gas detection (Forane R134a)
TGS 813	Combustible gas detection (general hydrocarbons)
TGS 800	Air quality control (general air contaminants)

3. Results

3.1. Temperature influence

First, the sensor array has been studied in dry synthetic air and in a mixture of 600 ppm Forane R134a in dry air. During 1 h, a dry air flow is brought inside the chamber with an environmentally controlled temperature (or gas temperature) fixed at a desired value. Afterwards, the Forane R134a gas concentration is brought and the TGS

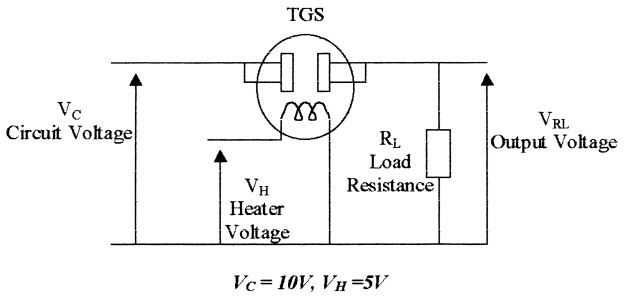

Fig. 2. TGS sensor operating circuit.

sensor steady-state conductance values are collected. These measurements are done several times in the 30–50°C temperature range. For all the studied sensors, similar results are found. We present in Figs. 3 and 4 the steady-state conductance behaviour in function of the temperature.

We note that the sensor responses in dry air or in a mixture of Forane R134a–dry air increase with the environmental temperature. In the studied temperature range, this evolution can be well fitted by an exponential model as follows:

$$G(T) = G_0 + A_1 e^{(T/T_0)}, \quad (1)$$

where G is the sensor steady-state conductance, T is the environmental temperature (°C) value, G_0 is a constant conductance, T_0 is a constant temperature (°C) and A_1 is a constant value. A_1, T_0, G_0, are sensor-dependent constants.

As the chemisorption reactions and the redox reactions on the sensor sensitive layer depend on the sensor operating temperature T itself [7], the sensor conductance can be obtained by the following equation (Eq. (2)) depending on the barrier energy E_s:

$$G = A\exp^{(E_s/kT)} \quad (2)$$

So, a modification of the environmental temperature value can induce a variation of the sensor operating temperature, modifying the sensor sensitivity and then the steady-state conductance value.

As the conductance differs when the gas temperature varies, it could create false gas concentration detection. As shown in Fig. 5, to eliminate this temperature drift, we have studied the relative conductance ($G_{gas} - G_{air}$). Unfortunately, the relative conductance also increases in function of the temperature. This result proves that the temperature steady-state conductance variation is quite important and has to be taken into account in electronic nose applications.

3.2. Humidity influence

We have studied the humidity dependence of the sensor array in synthetic air and in Forane R134a gas concentrations. For these measurements, the environmental temperature is kept constant at 33°C. The measurement procedure consists of the following cycle: first, a constant wet air flow is brought for 1 h, afterwards, the known concentration gas mixture is added to the wet air and the sensor responses are collected during 1 h. For a same RH rate, the measurements are done for several Forane R134a concentrations in synthetic air in the 200–1000 ppm range. For all the studied RH rates (18%, 35%, 52% and 68%) similar results as shown in Fig. 6 were found for the three types of sensors. Moreover, we have noted that for an upper RH rate (85%), the lowest gas concentrations (200 ppm and 400 ppm) are masked.

As shown in previous papers [8,9], the sensor response is similar to a reducing gas response: the sensor conductance increases in the presence of humid air and its steady-state value increases along with the RH rate. For a mixture of Forane R134a in humid air, the response is the result of two reducing effects: the first one is due to the humid air, and the second one is due to the Forane R134a, which is a reducing gas. Moreover, each of these two

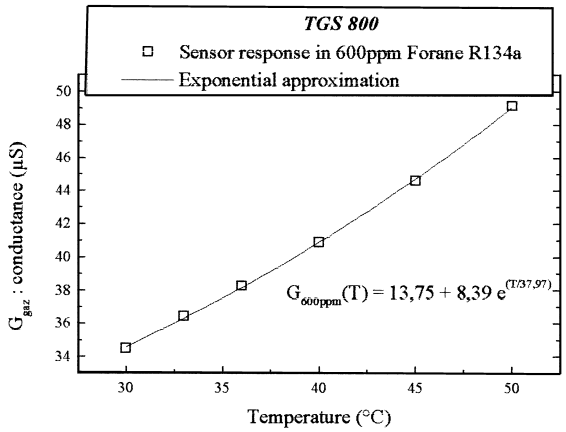

Fig. 4. TGS 800 conductance temperature dependence in 600 ppm Forane R134a–dry air.

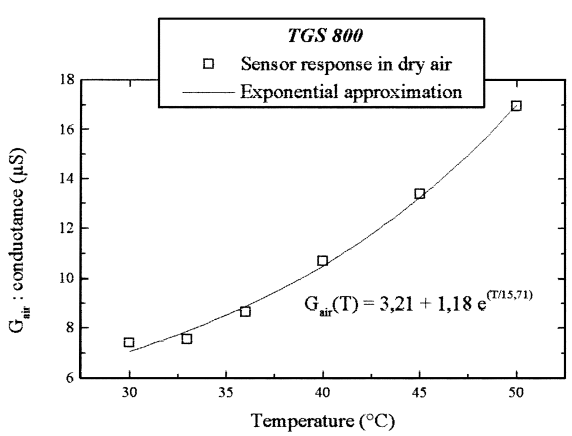

Fig. 3. TGS 800 conductance temperature dependence in dry air.

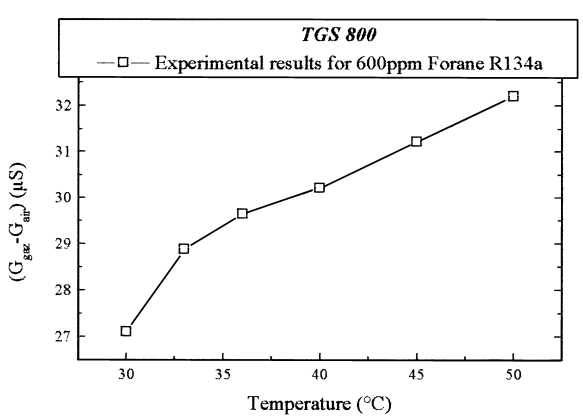

Fig. 5. TGS 800 relative conductance in function of the temperature.

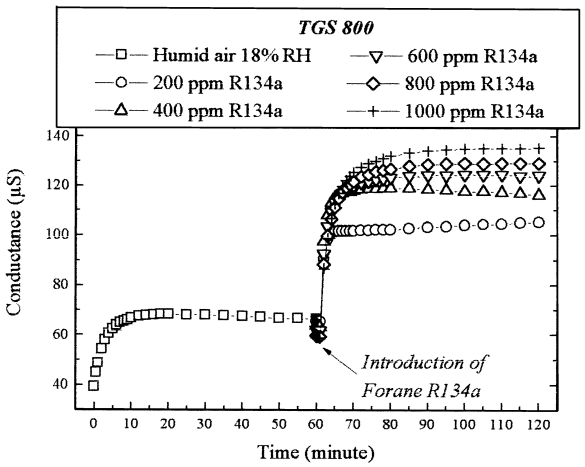

Fig. 6. TGS 800 response to humid air (18% RH) and Forane R134a gas concentrations.

responses can be well fitted by a double exponential function written as follows:

$$G(t) = G_0 + A_1(1 - e^{(-t/\tau_1)}) + A_2(1 - e^{(-t/\tau_2)}) \qquad (3)$$

where G is the conductance, t the time, G_0 a conductance constant, A_1 and A_2 two constants, τ_1 and τ_2 two time constants. All the constants are sensor dependent constants.

For the different RH rate and gas concentrations, we have studied the sensor behaviours in term of relative fractional conductance (Fig. 7). We can note that the relative fractional conductance values increase with the gas concentration but decrease with the RH rate. These responses are well distinct and show us that humidity has a great influence on the gas concentration identification. Thus, in commercial applications, the humidity rate has to be controlled or taken into account with pattern recognition systems to avoid false gas detection, and improve the gas identification.

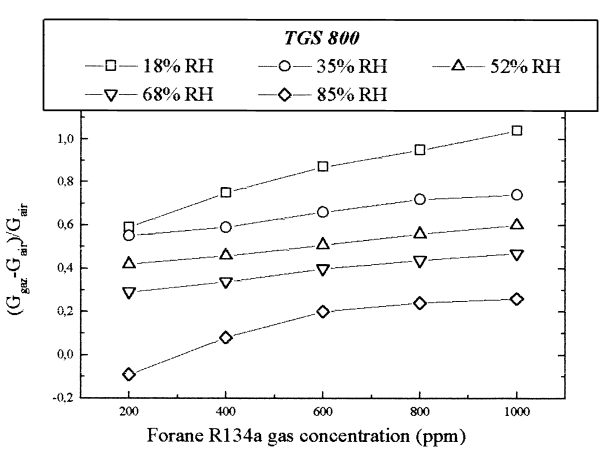

Fig. 7. TGS 800 relative fractional conductance for different relative humidity rates.

3.3. Data analysis

To obtain a performed electronic nose, we have characterised the sensor array in closely controlled conditions of humidity and temperature. Thus, we have created a database with the measurement responses in humid air and in mixtures of Forane R134a in dry and wet air for the humidity range 18–85% at 33°C. In other papers [10], we have shown that two variables best characterise the sensor responses: the steady-state conductance value measured after 60 min of gas exposition and the conductance dynamic slope taken in the first 5 min of the time-dependent response. We have grouped the responses corresponding to these two types of variables into one database and we have studied it with the DFA method.

For this method, all the subjects in the database are arranged in a priori groups. These groups correspond, respectively, to the measurement types: Humid air, Forane R134a–dry air and Forane R134a–wet air. Afterwards, by way of a discriminant procedure, the differences inside the groups will be minimised and the differences between the groups will be maximised. In fact, with such a method, several coefficients are estimated and they constitute a discriminant function corresponding to the obtained linear combination of the variables. Thus, this function can be used to classify new or unknown cases.

We present in Fig. 8 the DFA results for our database. Only one reclassified data over 150 subjects has been found. In fact, it is a 200 ppm dry Forane R134a concentration, which corresponds to the sensor detection limit value, reclassified in the humid air group. Thus, 99.4% of the measurement in the database have been classified in their a priori group, as also well checked by the cross validation method.

In order to verify the efficiency of this electronic nose, we have added four unknown cases in the database to be

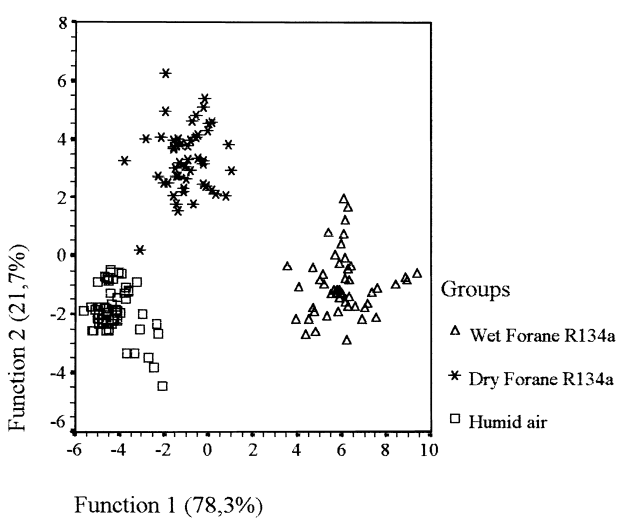

Fig. 8. DFA results for the steady-state conductance and the conductance dynamic slope values as representative variables of the sensor array responses.

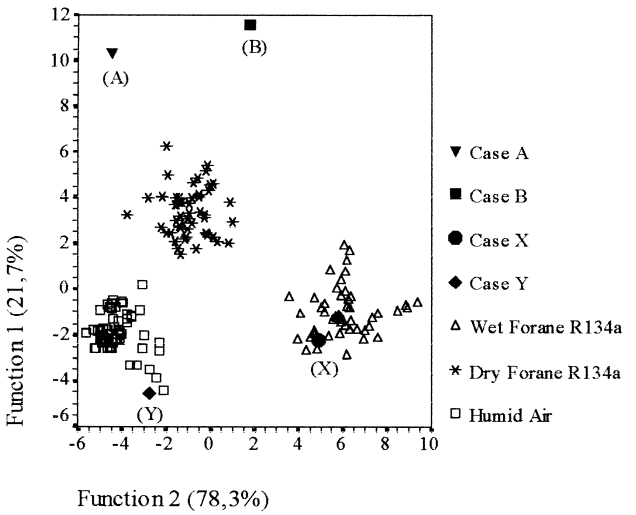

Fig. 9. Discrimination of unknown cases with the DFA method.

classified. The two first ones, cases A and B, correspond to 600 ppm dry Forane R134a at 40°C and 50°C, respectively. The other two, cases X and Y, are a 600 ppm wet Forane R134a at 35% RH and a 35% RH humid air, respectively. For the last two cases, the temperature was 33°C. As shown in Fig. 9, we present the classification results for the unknown cases. The DFA calculation results indicate that the four unknown cases are well classified in their corresponding groups. This proves that the discriminant function is correct and can be used for identifying the target gas whatever the RH rate and the environmental temperature variation. However, as all the characterisation values in the database groups are given for a 33°C gas temperature, we could improve this identification by completing the database with measurement under other different gas temperatures as for the RH rates. Moreover, the use of other pattern recognition methods like the artificial neural networks could help to better identify the target chemical species.

4. Conclusion

We have characterised an electronic nose under closely controlled conditions of humidity and temperature, and we have shown that the gas temperature and humidity rates are important parameters that widely affect tin oxide type sensor responses. These two parameters can cause important drifts when they are uncontrolled and then induce false or unrecognised alarms in gas leaks control systems. Thus, for electronic nose applications, the environmental temperature or gas temperature as well as the gas RH rate must be controlled. For these two parameters, we have successfully modelled their influence and this model could be included with the characterisation results to obtain a better pattern recognition. Now, we have successfully applied this method with the RH by using the DFA method. The same method should be applied with the two parameters (humidity and temperature) to improve gas identification.

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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 at the same university. And 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, humidity and temperature dependence of gas sensors 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 electronics circuits development.

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