Discrimination and identification of a refrigerant gas in a humidity controlled atmosphere containing or not carbon dioxide: application to the electronic nose

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Abstract

Atmospheric pollution and green house effects are now one of the major preoccupations to improve the general quality of life. With an electronic nose application we propose a system dedicated to the main detection of refrigerant Forane 134a (R134a) gas leakage in air conditioned systems and atmospheres. For our application based on a metal oxide type gas sensor array (six TGS elements) mainly coupled with discriminant factorial analysis (DFA) for the pattern recognition, we propose to study the effect of the relative humidity and an antagonist gas carbon dioxide as interfering gases on the R134a gas and concentration discrimination. We show that the relative humidity in a wide range (18–85%) has a more important influence on the target gas and concentrations discrimination than carbon dioxide. We present the discrimination results for the gases and afterwards for the R134a concentrations. Then we show the ability of our system to identify correctly a test data set composed of unknown gas samples. For the gases concentrations identification we also show that a correct identification rate can be obtained specially when the relative humidity rate range is reduced.

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1. Introduction

Nowadays, lots of efforts are done all over the world to protect the atmosphere from the greenhouse effects. In the field of smart sensors new applications named electronic noses are under development [1–3], to be used for environmental air quality control. These applications are generally based on a multisensor array coupled with pattern recognition methods. In our case we are developing such an application for the main detection of a new refrigerant gas which highly takes part in the greenhouses effects: Forane 134a noted R134a (halocarbon gas CH 2 F–CF 3 ) in an air conditioned atmosphere. For this application two main considered interfering gases, highly present in the green house effects, are taken into account: a carbonic gas (CO 2 ) and the air relative humidity (H 2 O). For this aim, we are developing a system based on a Tagushi type sensor array (TGS metal oxide sensors) in association with multidimensional recognition methods: principal component analysis (PCA) and discriminant factorial analysis (DFA). The studied type of sensor are sensitive, but unfortunately, they present lack of selectivity effects and are influenced by the variation of the gas temperature [4–6], and the presence of humidity [7–9].

For our study, we have characterised this sensor array under closely controlled conditions of humidity, temperature and gas concentrations in wide ranges to provide the largest learning process to our system. Then the characterisation results were grouped in data bases and they were represented via three selected variables: the conductance dynamic slope (dG/dt) and the steady-state conductance (G s ), which allow us to take into account the sensors short and long time drift effects [13,14]. With such variables, we obtain the best discrimination results.

We propose, in this paper, to study with these variables the ability of our system to well discriminate R134a and specially its concentrations in the presence or not of carbon dioxide and/or humid air. Thus, we note the real effect of the
relative humidity and carbon dioxide on this gas discrimination specially with the DFA method.

For all the discrimination results, we show that it is possible to successfully identify unknown test gas samples by the way of the created decisive laws obtained during our system learning process with the DFA method.

2. Experimental

For our study, we have characterised our sensor array by using a specially designed dynamic flow system (100 ml/min) able to create closely controlled conditions of humidity, temperature and gas concentrations [15]. In this system, the carrier gas (synthetic air) is brought into a humidity generator based on the bubbler principle and then mixed with the target gas (R134a) and the main interfering gas (CO₂) via gas lines controlled by mass flow controllers. Afterwards, the mixture is introduced in the specially designed and optimised test chamber which is placed in a 33 °C controlled temperature atmosphere. In the test chamber, the studied TGS sensor array is enclosed: 2 TGS-832, 2 TGS-800 and 2 TGS-813. A humidity sensor and a temperature device are placed in an appended chamber to check the created humidity and temperature conditions.

All the measurements were done in a dry atmosphere (0%RH) or in presence of humidity (18, 35, 52, 68 and 85%) and for the 200–1000 ppm (with 200 ppm step) gases (R134a and CO₂) concentration range. Two way of introduction of the gas were mainly used:

- In the first case, the target gas (R134a) is brought to the sensors placed in a stabilised atmosphere containing the interfering gases (CO₂ and/or humid air).
- In the second case, the R134a and the interfering gases (CO₂ and/or humid air) are introduced simultaneously in the measurement test system.

For the two cases, all the gas sensor output responses are collected via a data acquisition board, treated and then analysed by a pattern recognition method (DFA) with a statistical and data analysing software (SPSS).

3. Results and discussion

In previous papers, the characterisation results obtained in the different atmospheres were already presented and discussed [5,9,12,13,16]. We have shown that the humidity has a wide influence on the sensor array responses but doesn’t mask the target gas except for the highest humidity rate for the lowest R134a concentration. We have also noted that as for R134a the observed behaviour for humid air is a reducing type one in the opposite of the CO₂ response which has an oxidising type (antagonist effect). Moreover, the presence of humidity tend to decrease the sensitivity to R134a concentrations and increase the sensitivity to CO₂ concentrations [13].

All these measurements were grouped in data bases according to the three selected representative variables G₀, dG₀/dt and G₁. Then they were treated by the DFA method, and we show here the influence of humidity on the gas discrimination.

The discriminant factorial analysis is related to both multivariate analysis of variance and multiple regressions. For this method, all the subjects in the data base are arranged in a priori groups. The discriminant procedure identifies a linear combination of quantitative predictor variables which best characterise the differences among the groups. In fact, with this procedure, the differences inside the groups, called intra-class variance, are minimised and the differences between the groups, or inter-class variance are maximised. With such a method, several coefficients are estimated and given as a discriminant function corresponding to the linear combination of the variables. Afterwards, this function can be used to classify new or unknown cases. With such a method, the discrimination with three chosen groups allows to obtain a representation with two discriminant axis containing the maximum of variance (100%) in the considered data base [17,18].

3.1. Discrimination of R134a, CO₂ and their mixture

In a first discrimination step, we have studied the influence of the relative humidity as the major pollutant as well for Forane 134a than for carbon dioxide. So, we have tried to separate the specified gases from the dry than the humid atmospheres.

In the case of R134a, the data base (base 1, 176 measurements) was composed with three types of measurements affected in a priori groups and noted: dry R134a (R134 in dry air), wet R134a (R134a in wet air) and wet air. For these three groups we obtain DFA result presented in Fig. 1. We are able to correctly separate the chosen groups: 99.4% of the 176 used measurements were correctly classified. Only one measurement (200 ppm R134a) initially belonging to the dry R134a group was classified back in the humid air group. This very good result was checked and confirmed by the cross validation method: 99.4% of the measurement was correctly classified. The same misclassification error for the same 200 ppm R134a measurement was found. This is probably due to the slight limitation of the sensors for this R134a concentration value.

For carbon dioxide, the same investigation was done (base 2, 162 measurements). In this case, the chosen groups were noted: dry CO₂ (CO₂ measurements in dry air), wet CO₂ (CO₂ measurements in wet air) and humid air (measurements only with humid air). For this data base we present in Fig. 2 the discrimination result obtained with DFA. A perfect classification result is obtained: 100% of the original data was classified in the corresponding group. The same rate is obtained by checking with the cross validation method: the
separation is perfect proving that the relative humidity has a wide influence on the measurements and induces large differences between the measurements types. The created decisive law can be used to identify new unknown tests samples.

In a third base (base 3, 183 measurements), we have studied the discrimination of these two gases R134a and CO2 mixed together in presence or not of humidity in a wide range. For this base composed of dry mixture, wet mixture and humid air measurements, the three chosen groups also corresponds to the measurements types. By the way of DFA, we obtain in this case a very perfect discrimination of the mixtures R134a + CO2 (Fig. 3): no misclassification errors were found, 100% of classification success of the original data. With the cross validation method, the same success rate was found confirming the perfect separation of the measurements and the wide influence of humidity. With such a success rate, the created decisive law is successfully used to identify correctly unknown test samples.

All these measurements (air, R134a, CO2 and mixture) were grouped in a data base noted base 4 (439 measurements in the dry and wet atmospheres). For this base, the chosen groups correspond to the measurement types. For these four, a priori chosen groups, three discriminant axis are obtained. With the two first axis, we are able to correctly represent the discrimination analysis results: we are able to well represent 85.4% of the data variance contained the data base (Fig. 4). The discrimination obtained is correct: the gases separation is good and few classification errors were found (96.1% of classification success, 422/439). Most of the errors (12/17) correspond to mixture measurements with low R134a and CO2 concentrations classified a posteriori in the...
CO₂ group (Table 1). The others are also low R134a concentrations measurements (200 ppm) which were classified in the CO₂ group. With the cross validation method, this result was checked and three more similar errors were obtained: 95.4% of success. This highlights slight difficulties for our system to perfectly discriminate the lowest concentrations certainly due to the gas detection limit for the chosen sensors to 200 ppm R134a.

Afterwards, we have tested the created decisive law by using 44 new measurements not included in the data base as unknown tests samples (Fig. 5). Those samples correspond to other measurements with different experimental conditions (gas, concentrations and relative humidity rates). We have used the created decisive law and we are able to identify correctly 41/44 test samples (66% for humid air, 12/12 for R134a, 12/12 for CO₂ and 11/14 for mixture). The three errors found (Table 2) correspond to mixture measurements with low R134a concentrations identified in the CO₂ group. This confirms the limitation to obtain a perfect identification for the lowest concentrations of R134a.

Nevertheless, the identification is still correct and the decisive law is enough efficient to identify correctly the studied gases.

As the gases discrimination and identification are correct and enough accurate, we propose to study the discrimination of R134a concentrations in dry or wet air containing or not carbon dioxide. For this kind of quantification, CO₂ and humid air are the interfering gases for the R134a.

Table 2

<table>
<thead>
<tr>
<th>Unknown data set</th>
<th>DFA identification results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Corresponding measurement</td>
</tr>
<tr>
<td>6</td>
<td>Humid air</td>
</tr>
<tr>
<td>12</td>
<td>R134a</td>
</tr>
<tr>
<td>12</td>
<td>CO₂</td>
</tr>
<tr>
<td>14</td>
<td>Mixture</td>
</tr>
</tbody>
</table>

3.2. Discrimination of R134a concentrations

For this part of the study, the considered measurements are affected a priori in concentrations groups 200, 400, 600, 800 and 1000 ppm corresponding to the R134a concentration value whatever the considered interfering gases (H₂O and/or the pollutants concentrations of CO₂). With these five groups, four factorial axis will be found with the DFA method and the best representation will generally be obtained by using the two first axis containing the maximum of data variance.

In a first time we have considered the R134a measurements in a dry atmosphere (base F₁, 44 measurements) affected in groups. For the chosen groups we are able to well represent with the two first factorial axis obtained 98.8% of variance in the data base (Fig. 6a). With this base 100% of the original data are correctly classified but with the cross validation method 93.2% of the measurements were correctly checked (only three errors found): we are able to classify the R134a measurements in dry atmospheres according their concentration with a very large success percent.

In a wet atmosphere (base F₂, 88 wet R134a measurements) the discrimination is more difficult specially when considering a large concentration range (Fig. 6b). With the chosen axis, we obtain a representation containing 98.8% of data variance. Nevertheless, the original discrimination result percentage obtained is only 80.7% (17 classification errors) and with the cross validation only 51.1% of the measurements are correctly classified. All these classification errors are mainly due to the presence of humidity in the considered measurements and specially because we have taken into account each R134a concentrations in a wide range of humidity: it is not possible to accurately discriminate the R134a concentrations whatever the relative humidity rate. But when the relative humidity rate is known and then when the data base is specially done for
For the end of the present work, we have studied the discrimination of R134a concentrations in the dry or wet mixture. In the dry mixture (base M1, 45 measurements), the discrimination under five concentration groups can be represented with the two first factorial axis reproducing 99.5% of the data variance in the data base. We obtain a good separation of the R134a concentrations (Fig. 8a). We are able to discriminate accurately with 100% of classification success the R134a concentrations whatever the presence of CO2 gas with several different concentrations. With the cross validation method a 97.8% classification success rate was found: only one error corresponding to a 200 ppm R134a concentration mixture measurement. This is due to the detection limit value observed for the sensor array underneath 200 ppm for R134a. Compared to the discrimination of the pure R134a concentrations in dry air (Fig. 6a), we can note that the discrimination obtained for R134a concentrations in the mixture is very close: the classification success rate is similar. So the presence of the carbon dioxide gas with its antagonist effect in a wide concentration range in the mixture hasn’t got a wide influence on the R134a discrimination in a dry atmosphere. The sensitivity of the chosen sensors to the oxidising CO2 already shown in other papers has not a too important influence during the discrimination process for the R134a quantification in such mixtures.

In the wet mixture (base M2, 94 measurements), we have also studied the R134a concentration discrimination. For this study, we are able to represent with the two first factorial axis 99.8% of data variance (Fig. 8b). We obtain a correct separation and a good classification success rate: 97.9% of the R134a concentrations given a priori were found a posteriori whatever the CO2 concentrations and
the relative humidity rate. The only two errors found correspond to two high R134a concentrations which were misclassified. With the cross validation a 92.6% success rate is obtained: 5 more similar errors are obtained. Compared to the R134a concentrations discrimination in the dry mixture (Fig. 8a), the discrimination is more difficult. This is due to the presence of humidity in a wide range in the data base measurements. As shown for the pure wet R134a (Fig. 7), an improvement can be obtained if the relative humidity is known and it range is reduced and focused in the data base.

Compared to the wet R134a concentration discrimination whatever the relative humidity, we obtain for the wet mixture a best discrimination rate and the separation in the discrimination space is improved. This is due to the oxidising effect of CO2 which reduce the measurement variation range but increase the variability in the data base in function of the R134a concentrations measurements. So with the created decisive law we are able to identify with a correct success rate the target gas R134a gas concentrations.

We have used new mixture measurements (five in a dry mixture and six in a wet mixture) not belonging to the original data base and noted test samples (tests M1 and M2, Table 3). By the way of the decisive law created with base M1, we are able to correctly identify the R134a concentration of all the test samples in the dry atmosphere whatever the CO2 concentrations (Fig. 9a). With the decisive law created with base M2 we can easily identify the R134a concentrations of all the chosen test samples whatever their CO2 concentrations and their relative humidity rate (Fig. 9b). In the cases of the middle range concentrations (600 and 800 ppm) a very good identification is more difficult because the discrimination was not perfectly efficient for these conditions. A discrimination and identification with a reduced range of relative humidity rate will be more helpful to obtain more accurate identification for the middle range R134a concentration. Nevertheless, it could be possible to identify the R134a in more general level concentrations (low, high and middle).

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Table 3
Test data set corresponding measurements and identification results for the R134a concentrations

<table>
<thead>
<tr>
<th>Test samples: dry mixture samples</th>
<th>Corresponding measurement</th>
<th>DFA identification results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test M1</td>
<td>R134a 1000 ppm + CO2 200 ppm</td>
<td>R134a 1000 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 800 ppm + CO2 400 ppm</td>
<td>R134a 800 ppm</td>
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<tr>
<td></td>
<td>R134a 600 ppm + CO2 600 ppm</td>
<td>R134a 600 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 400 ppm + CO2 800 ppm</td>
<td>R134a 400 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 200 ppm + CO2 1000 ppm</td>
<td>R134a 200 ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test M2: wet mixture samples</th>
<th>Corresponding measurement</th>
<th>DFA identification results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R134a 1000 ppm + CO2 400 ppm + 18%RH</td>
<td>R134a 1000 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 400 ppm + CO2 1000 ppm + 18%RH</td>
<td>R134a 400 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 1000 ppm + CO2 400 ppm + 35%RH</td>
<td>R134a 1000 ppm</td>
</tr>
<tr>
<td></td>
<td>R134a 400 ppm + CO2 1000 ppm + 35%RH</td>
<td>R134a 400 ppm</td>
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<tr>
<td></td>
<td>R134a 1000 ppm + CO2 400 ppm + 52%RH</td>
<td>R134a 1000 ppm</td>
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<tr>
<td></td>
<td>R134a 400 ppm + CO2 1000 ppm + 52%RH</td>
<td>R134a 400 ppm</td>
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</tbody>
</table>
Concerning the discrimination of the R134a concentrations we have shown that the humidity rate in a wide range has an important influence. In a large humidity range the discrimination of the R134a concentrations is quite difficult. So we have proposed to discriminate the concentrations for this gas in a reduced relative humidity range, thus it is possible improve the results and then to perfectly discriminate this gas. For this improvement we suggest to do the gas discrimination process for separate humidity level (high or low rates). We have also noted a slight improvement in the gas discrimination process for separate humidity level (high or low rates). We have also noted a slight improvement in the gas discrimination process for separate humidity level (high or low rates). We have also noted a slight improvement in the gas discrimination process for separate humidity level (high or low rates). We have also noted a slight improvement in the gas discrimination process for separate humidity level (high or low rates).

So we are able to develop an electronic nose with a good identification success rate for the identification of R134a and its concentration in presence or not of carbon dioxide and relative humidity which are widely present in green house effects. So this study is pursued by investigations with other pollutants and also the development of a portable system for onsite measurements.

4. Conclusion

In this paper, we have shown the effect of the relative humidity rates and the carbon dioxide concentrations on the gases discrimination and the Forane 134a gas concentrations. We have first studied the gases discrimination and we have noted that the relative humidity has a wide influence on the responses because we are able to widely separate the sensors responses for the two studied gases in dry or wet atmospheres. Nevertheless, this influence can alter the full gases discrimination but didn’t mask the target gas to be discriminated. Moreover, we have shown that it is possible to correctly identify the unknown samples of the studied gases whatever the considered atmosphere and the relative humidity rate by the way of the created discriminant law.

Fig. 9. Identification of Forane 134a concentrations in tests samples for: (a) a dry mixture containing carbon dioxide and (b) a wet mixture containing carbon dioxide.

**Fig. 9. Identification of Forane 134a concentrations in tests samples for: (a) a dry mixture containing carbon dioxide and (b) a wet mixture containing carbon dioxide.**

### References


**Biographies**

Claude Delpha is a doctor in electronics. 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. In 2000, he obtained his PhD in the same field in the Laboratory of Interfaces, Components and Microelectronics at the University of Metz. He is now an associate professor in the Laboratory of Signals and Systems of the University of Paris XI. His main areas of interest are in semiconductor sensors, discrimination and identification, electronic noses and telecommunication applications, Pattern recognition methods and signal processing techniques.

Martine Lumbreras is a professor in electronics. She is graduated in electronics with specialisation in solids electronics at the University of Montpellier in 1969. She awarded a PhD degree in 1979 at the same university. She joined the University of Metz in 1979, and she awarded a doctor of Sciences degree in 1987 in this University. She has been profesor 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.

Maryam Siadat is a doctor in automatics. She 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.