Sensors & Transducers

www.sensorsportal.com

Electronic Noses and Applications

Martine LUMBRERAS and Maryam SIADAT

LCOMS, University of Lorraine, Metz, France
Tel.: +33 387547613
E-mail: martine.lumbreras@univ-lorraine.fr

Abstract: Electronic noses are customized devices employed to detect and to identify gaseous mixtures, even to give the concentration of the atmosphere components. Nowadays, the research in this domain is more and more growing, in Europe and other countries in the world, for many applications, such as environmental protection, food industries, perfumery, public safety, medicine, and pharmacy. Electronic noses allow to detect many organic volatile compounds, for which there is no specific detector. They constitute an alternative to complex, long, and too expensive existing methods, unable to ensure continuous monitoring. Their conception deals with many related areas (metrology, chemistry, physics, electronics, informatics, statistics, modelisation) as well as areas related to the molecules to be detected. The system training is a primary step: during a measurement under a gaseous atmosphere, we must record the sensor time-responses in a treatment system, while specifying the name of the concerned odor. This process must be repeated many times for each studied atmosphere, and for all the chosen atmospheres. So a learning data base can be created, made from representative parameters of all the realized measures. After this training stage, clustering software will classify the data analysis in "concentration" or "nature" groups. Using the group separation rules given by this supervised classification, the system will be able to find itself the name of an odor or a concentration. *Copyright © 2014 IFSA Publishing, S. L.*

1. Introduction

1.1. Historical Background

This concept seems to be first mentioned in 1923 by Jean-Michel Fabre in his book «Souvenirs entomologiques» (Entomological memory book) hoping for the advent of an «odor radiograph» [1]. In 1961, Moncrieff developed a mechanical nose [2], then Wilkens and Hartman realized the first electronic nose in 1964 [5]. It's more than 10 years after that an olfaction research group of the Warwick University revived this concept by the development of gas multisensory device technology, coupled with data treatment techniques [3]. In 1993, the first prototypes appeared, to see in 1994 the first commercial devices. Since then, new researchers are coming into this field, as well in sensor development (sensitivity and performance enhancements) than the intelligent devices themselves (process, signal treatment, detection rate) or even the diversification of the applications [4-6].

1.2. The Electronic Nose

In humans, olfactory epithelium of the nasal mucous membrane contains almost ten of millions of receivers on only several cm^2 area. Human nose selectivity able to distinguish a few millions of odors

is not provided by ultra-specialized sensors, but it is obtained by cross-checking data and convergences of many information realized in the brain. It is able to detect some particles at a very small concentration (10^{-12}) while experimental and commercial gas sensors react to particles over only millions (10^{-6}).

Like for the human olfactory system (Fig. 1), the electronic nose consists in four functional parts comprising a gas sampling system of the gaseous substances to be studied (nostrils, lashes), an array of non specific gas sensors (receptors cells) able to detect ppm concentrations, which can be realized by different technologies, a signal treatment system related to the selected sensors (axons), and lastly an analysis and identification system based on pattern recognition algorithm (brain). The used classification methods are Principal Components Analysis (PCA) and Discriminant Factorial Analysis (DFA) (used in our work) and also Neural Networks (NN),

Multi-linear Logistic Regression (MLR), Support Vector Machines (SVM).

Our first used method (PCA) is an unsupervised method which combines measures into "classes" of similar data, without an a priori assignment and offers in 2 or 3 dimensions a visualization of the determined groups. When introducing additional data, we can follow on the graph the evolution of the previous determined classes along the time. The second method (DFA) is a supervised one. Measures are a priori assigned into "classes" (concentration, humidity rate, gas number). Using the classes determined first by PCA is a good beginning. DFA determines class unbundling rules, to allow us to identify unknown samples. It provides also a graphical class representation. These two methods will be described in more details in the following sections.
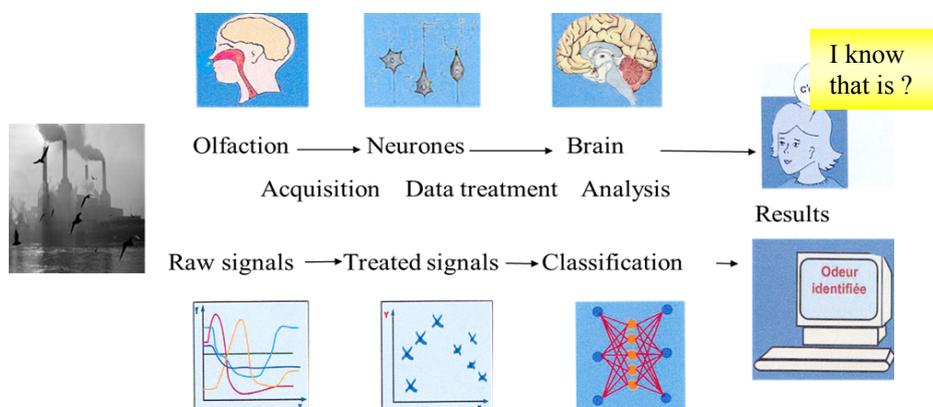

Fig. 1. Analogy between human and electronic noses.

2. Conception and Realization of an Electronic Nose

2.1. Prototype Description

In our group, we have developed and realized a portable electronic nose (Fig. 2) presented in this paper as an example.
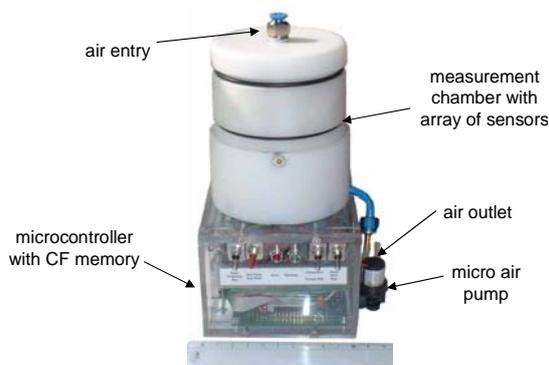

Fig. 2. Portable electronic nose of our laboratory.

It is composed of two parts. Firstly, the measure unit: an optimized cell system containing 6 to 12 sensors, 1 humidity sensor, 1 temperature sensor, a micropump placed downstream to avoid gas swirls [7]. The second part is based on a microcontroller and an additional flash memory for data storage. This unit ensures gas intake, signal acquisition, extraction of the representative parameters, and finally the recognition of the composition of the gaseous sample, using decision-making rules implemented in the microcontroller based on a prior learning phase.

2.2. Sensor Selection

The gas sensors used nowadays are not perfectly selective to a particular chemical. So, in order to best identify the components of a gaseous atmosphere, the sensors must be chosen with cross-sensitivities: for one atmosphere, the sensor responses must be different as possible, and, for different atmospheres, each sensor must responds with distinct differences. In addition, the fact that one sensor of the array has

no sensitivity for only one gas or humidity ensures a good reference for the future gas identification. All these properties will allow us to create distinct behavior patterns (summary of all the responses of the sensor array for each studied atmosphere), essential for the sensor response processing by recognition method.

The more used sensors are the chemical semiconducting metal oxide sensors, principally based on SnO_2, ZnO_2, TiO_2, doped with different metals (Pd, Pt, Ge ….). They are cheap, and commercially available. Due to these advantages, they are present in many electronic noses. Their principle is based on a chemical modification, by prior oxygen adsorption, involving a sensor resistance change. The olfactory compounds dissemination on the sensor sensible layer induces a reaction with oxygen atoms, releasing conduction electrons, and leading a sensor resistance change. Each oxide/dopant combination offers a different reactivity: certain ones are more sensible to aldehydes, other ones to amine, or sulphur compounds. These sensors remain rather stable along with the time, but they are sensible to humidity. Generally, these sensors detect ppm gas concentrations, but the operating temperature must stay constant (200 - 450 °C range) during all the sensor array life to avoid notable drift.

Based on the same principle but with a room operating temperature, semiconducting polymer sensors offer a wide variety range. But they have less sensitivity than the metal oxide based sensors, and they are heavily influenced by humidity. Surface Acoustic Wave (SAW) sensors can be also used, with a resonance frequency change. Biosensors are very promising devices, involving enzymatic reactions. They are very selective, but only for very specific applications.

There is no rule for the choice and the number of the sensors. But a too great number needs an important treatment, and calculation time. The knowledge of the properties of the molecules to detect is the first important point. Hence, in a first phase, a strong collaboration with the concerned specialists is required to properly identify the problem, and also to compare eventually the electronic nose identification with classical method results. The second phase concerns the choice of the more adequate sensors for the studied application, respecting specified cross-sensitivity and a notable sensitivity of all the sensors.

2.3. Measure Cell

The sensors array has a circular disposition, in order to have the same experimental conditions under all the gaseous atmospheres. Each gas exposition (for example 10 min) is followed by a corresponding air regeneration corresponding phase (20 min). Because the sensor resistance is determined via the sensor electric potential, each sensor coil is connected to a pin of the conversion acquisition board of the microcontroller to digitalize the signals with selected conditions (sampling time, bit number).

2.4. Intelligent Unit

We have implanted an acquisition and conditioning program in this microcontroller to obtain first digitalized sensor time responses, followed if necessary by filtering to reduce electric signal noise. So the reactions with the volatile compounds are transformed in an exploitable electric signal. These pre-treatments will allow us to extract reliable representative parameters of the sensor time-responses.

3. Learning Phase

This phase is essential in an elaboration of a dedicated electronic nose. It must be constituted with a sufficient number of measurements (several hundred), to apply statistical analysis. Each real measure condition must be taken into account: concentration, humidity, and gas temperature. For a reducing gas the resistance of the sensitive layer decreases, so, the measured voltage (taken at the sensor load resistor) increases. Humidity reacts like a reducing gas. For an oxidizing gas, we obtain an opposite effect, very often with smaller response amplitude than for a reducing gas. When using mixtures of reducing and oxidizing gas, the sensor response behavior differs according to the sensor sensitive layer composition, and the concentration of each component of the gaseous mixture. Fig. 3 shows us this phenomena by using the TGS 2106 sensor (dedicated to H_2S) and the TGS 2610 (dedicated to NO_2) in the case of gas mixtures composed of 4 ppm H_2S with NO_2 at 1, 3, 5 ppm.

We can see on Fig. 3(a) that response behaviors of the sensor for H_2S, reducing gas, correspond to a reducing type whatever the NO_2 concentration. In Fig. 3(b), for the NO_2 sensor the situation is more ambiguous: the sensor response is first increasing and then decreases when NO_2 concentration is weak (1 ppm), while it is totally decreasing for the two other NO_2 concentrations (3 and 5 ppm).

In the study of three pollutant gases (H_2S, NO_2, SO_2) at different concentrations these behavior diversities bring us to characterize the three gases in this following manner: alone, their binary mixtures, and their ternary mixture, in dry or humid (different humidity rates) atmospheres [7, 8].

For each sensor, time-responses corresponding to mixtures are not the algebraic sum of the responses corresponding to the pure gases, because the chemical reactions on the sensor sensitive layer are different. We have realized a sufficient number of measurements (10 to 20) in each case, to obtain reliable information and to verify the "Gaussian" character of the representative parameters extracted from the sensor time-responses.
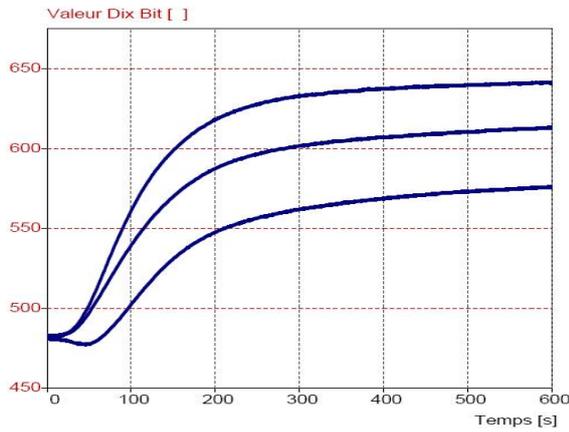
(a)
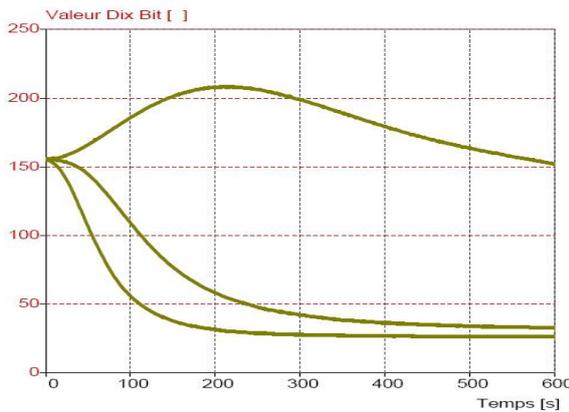
(b)

Fig. 3. Time-responses of two sensors to NO_2 (1, 3, 5 ppm) and H_2S (4 ppm) mixtures; (a) TGS 2106, (b) TGS 2610.

From this step, we can design several distinct behavior patterns (radar plot representation), characterizing all the sensor time-responses to give us a rapid qualitative estimation. On Fig. 4, we have drawn the Vs/V0 ratio (Vs is the final value, and V0 the initial value of the measurement potential) of the six gas sensors for given atmospheres: in case (a) NO_2 5ppm, NO_2 5ppm+ SO_2 20ppm, SO_2 20ppm. We note that the yellow pattern gets longer for the sensor number 5 (TGS 2610) which is dedicated to NO_2. Similar behavior is found when SO_2 is added (brown pattern). Finally all the values increase approaching the blue area because of the NO_2 lack: all the sensors react more strongly to SO_2 (reducing gas) than to NO_2 (oxidizing gas). In the case (b), the SO_2 concentration remains constant while the NO_2 concentration differs (1, 3, 5 ppm). The global scheme of (b) is different from the precedent case and we can observe that all the sensors react with more or less sensitivity. All the patterns of the case (b) are similar and increase when the NO_2 concentration decreases. These signatures give a rapid indication of one atmosphere evolution.
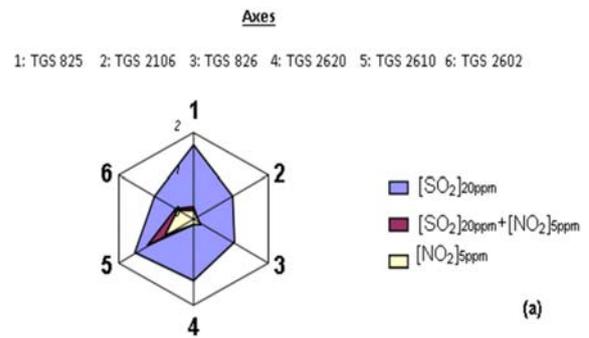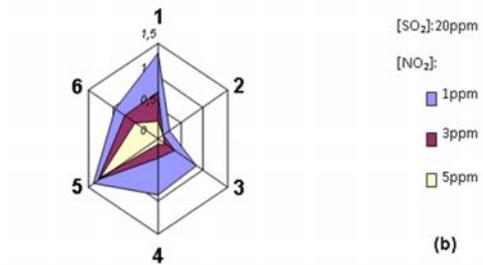

Fig. 4. Radar plot representation for the 6 used sensors in the terms of Vs/V0: (a) NO_2 (5 ppm), SO_2 (20 ppm) and their mixture; (b) mixtures of SO_2 (20 ppm) and different NO_2 concentrations in the pure air.

3.1. Data Construction

A data basis containing the entire sensor time-responses recorded at 1 point per second has a too important size to be analyzed. For this reason, we have selected representative parameters, which must characterize even dynamic part or the steady-state part of the sensor time-response (Fig. 5). So, we have first extracted from the sensor time-response (a) initial values V0, final values Vs, the slope of the dynamic part "Pente"= "Slope", the surface under the response curve St, and also combinations of the these parameters.

Since a few years, we work also on the derivative curve of the sensor time–responses, to explore the transient phase of the sensor signal. This treatment permits to obtain more rapidly detection indication [9]. As we can see on the Fig. 5, the derivative curve presents a characteristic maximum, and we have extracted two parameters: the peak height (Peak) and the surface under the derivative curve (Sp).

Table 1 resumes the performance inquiries of several parameter combinations in term of conductance (inverse of resistance) by using AFD analysis. The classification success rates vary from 90.4 % to 98.2 %.
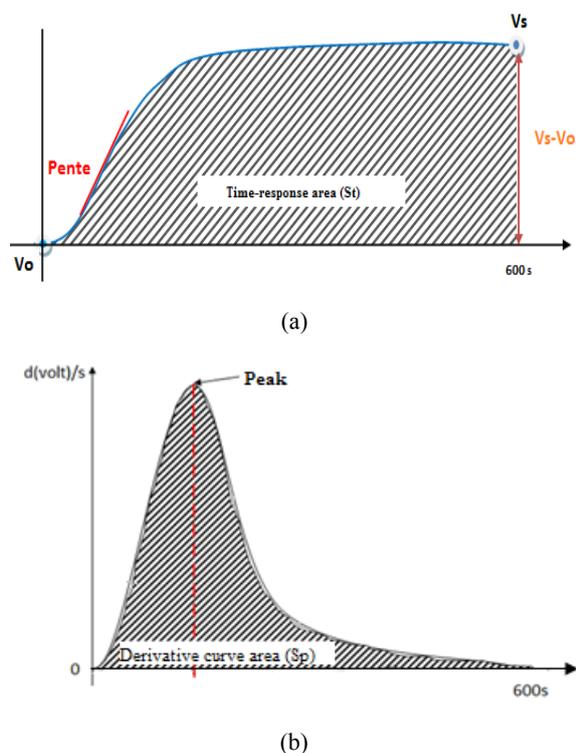
(a)

(b)

Fig. 5. Representation of parameters extracted from (a) the time-response of each sensor and (b) its derivative curve.

Table 1. AFD classification results using combinations of representative parameters.

Explicative parameters of each sensor	Success rates	
	Original data (%)	Cross validation, (%)
G_0+dG/dt	93.6	90.4
G_0+G_{10}	93.6	92.9
G_0+G_s	94.3	92.4
$dG/dt+G_{10}$	90.3	87.2
$dG/dt+G_s$	88.5	82.2
$G_0+dG/dt+G_{10}$	96.2	91.6
$G_0+dG/dt+G_s$	97.4	91.6
$G_0+dG/dt+(G_s-G_0)/G_s$	99.3	98.2
$G_0+dG/dt+(G_{10}-G_0)/G_{10}$	97.8	96.4
$G_s+dG/dt+(G_{10}-G_0)/G_{10}$	97.8	96.4
$G_0+dG/dt+(G_s/G_0)$	96.8	91.1
$G_{10}+dG/dt+(G_{10}-G_0)$	96.4	91.3

Another way to select the best parameters or the best sensors can be done by using the projection of the explicative variables on the plane made from the two first principal components determined by PCA. Fig. 6 shows this projection in the case of perfume recognition (internal bachelor thesis report): two explicative parameters labeled with each gas sensor (A, B, C, D) are presented. We can confirm the selection of all the sensors because their coordinates are near to 1. Moreover, representative parameters are situated in each side of the component axes, which confirm that selected sensors have no high correlation and then give crossed information.
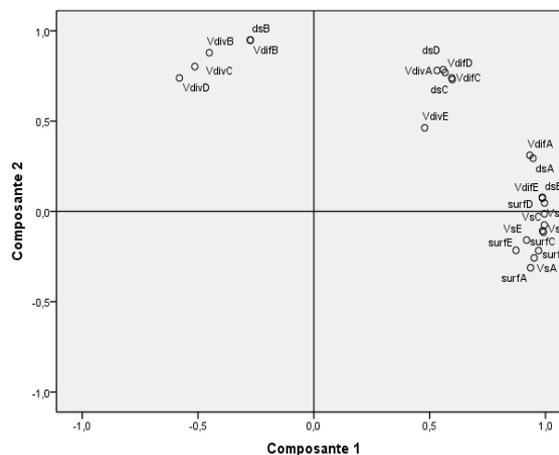

Fig. 6. Component diagram obtained by PCA: explicative parameters projected on the two first components.

3.2. Data Treatment

We have grouped the *p* extracted representative parameters from the *n* sensors in a data basis to be explored with pattern recognition methods cited above: PCA and DFA. Each column is constituted with one representative parameter of each sensor. We have then *p*x*n* columns. Each row corresponds to one measurement. PCA and DFA techniques give both graphical representations of the observations in the best reduced space. The aim of the PCA, unsupervised technique, is to describe a set of data by reducing their characteristic variables: new variables are defined by a linear combination of the original ones, called "Principal Components". Then ACP can give a visual representation in the form of clusters by projecting all the data on the two first principal components axes. So, we obtain classification information about all the data.

DFA is a linear supervised technique, offering like PCA a visual representation of the whole data. In the case of *m* classes, DFA method calculates *m-1* new discriminant axes by recomputing the variables in order to increase the distances between the barycentres of the data classes, and to decrease the distance between all the data points in one data group. Discriminant rules permit, in the first step, to a posteriori validate the affectation of the learning data, and give the overall success classification rates by using cross validation method.
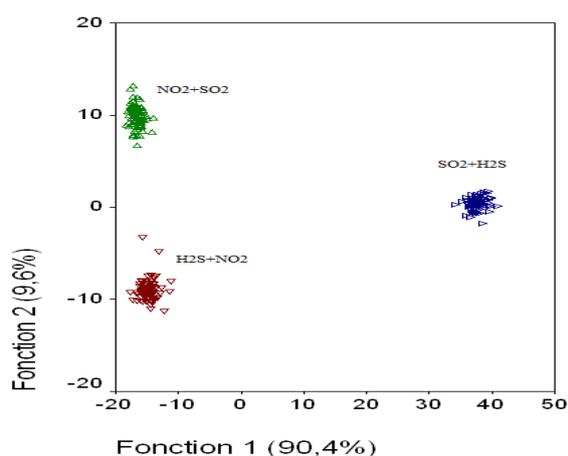
4. Data Identification

In a second step, the discrimination rules will permit to classify new unknown atmospheres. For example, canonical rule technique calculates the coordinates of the projection of an unknown data sample on the *m-1* discriminant axes, and then determines the distance of this point to the barycentre of each group. This distance calculation allows to affect the unknown data to the nearest
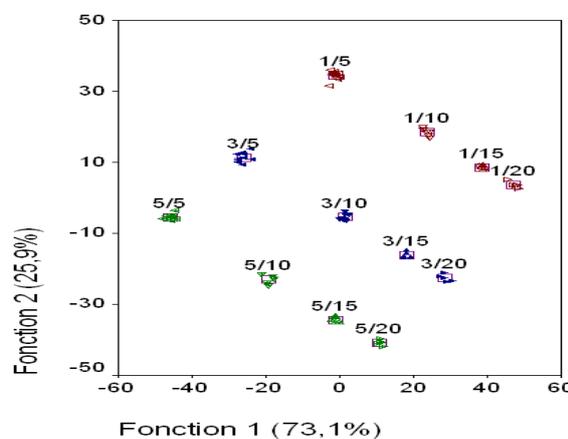
barycentre group. Consequently, DFA permits to make a decision on the nature (or the concentration) of the sample.

For our applications, we had sometimes to make the identification using hierarchical manner: dry or humid atmosphere, then, according to the mixture types (2 or 3 components), the identification of the preponderant gas on the sensor time-response and then the other gases (gas nature followed by its concentration).

Fig. 7 (a) presents the identification [7] of binary mixtures after a first separation in three groups: gases alone, binary mixtures, ternary mixture. The unknown data are "well classified".

In an other application, concerning the odor nuisance [10] of a duck farm, we have established daily odor scales which showed a good correlation with the animal activities. On the Fig. 8 we present the real time-dependent signal of the ammoniac gas sensor recorded during one day. We observe three levels of concentration, reflecting duck activities. All the measurements obtained during this study for all the used sensors were analyzed by PCA: we can regain the three levels of concentration. The electronic nose trained for a dedicated application can prevent odorant pollution, and so the complaints from the neighbors.
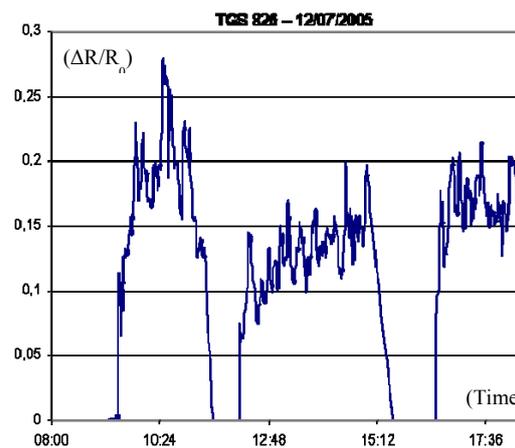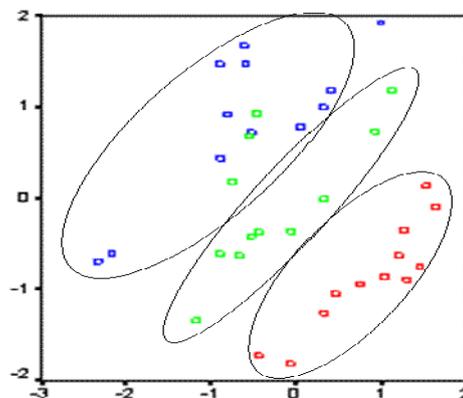

(a)

(a)

(b)

Fig. 7. Pollution characterization: (a) identification of the mixture type; (b) concentration identification in the following detected group (SO_2+NO_2).

(b)

Fig. 8. Measurement in a duck farm with the portable electronic nose: (a) a TGS sensor response during one day with regeneration interval; (b) data projection on the two first principal components (PCA).

Fig. 7 (b) illustrates a detailed identification of the different compositions of the binary mixtures NO_2/SO_2. Axes are formed from the two first discriminant functions with their contribution percentage. The sum of the two percentages must be superior to 80 % to be representative (in our representation, the sum is between 99 % and 100 %).

A study by PCA analysis of commercial perfume in three different concentrations (decreasing concentrations: "elixir", "eau de toilette", "eau de cologne") permitted to recognize each product, and to connect dilutions of elixir made with water or alcohol to the lowest concentrated products. This application can be used to prevent commercial frauds.

During the learning phase, data acquisition, data treatment and analysis were made using a computer more powerful than a microcontroller. After that, the calculated decision rules, implemented in the microcontroller, allowed to identify practically in real time gaseous atmospheres. This identification is provided [7] by our portable electronic nose in different manners (Fig. 9): display on the electronic nose box, on a computer screen if it is connected, and on a cellular phone via an antenna. We can also store the measurement data in a compact-flash memory of the microcontroller. An independent power supply has been added for outside measurements (pollution cartographies).
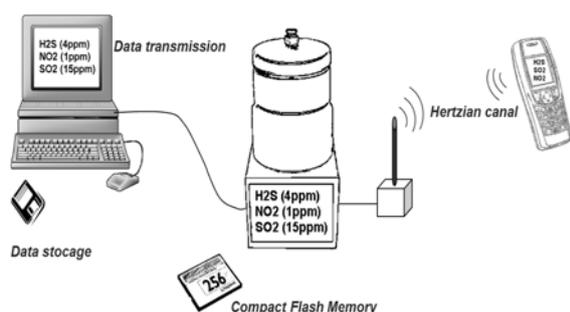

Fig. 9. Functionalities of the portable electronic nose.

5. Conclusion

Electronic noses are conceived for the gas recognition for those they are trained. So they must necessary work in adapted environment to avoid any risk of error.

In identification aspect, electronic noses constitute a reliable, objective and cheap alternative to "human panels" requested till now: these devices are more rapid and present the advantage to also permit the detection of odorless but harmful gaseous constituents (carbon oxides, nitrates). Moreover, they don't get used to smells and tastes, in contrary to humans, whose their olfactory or gustatory capacities reduce rapidly as soon as the first contact.

Electronic noses allow to determine in a few minutes, and sometimes a few seconds, an alimentary product composition (wines, oils), its freshness (fishes, fruits) or to detect frauds (for example, composition or dilution of perfumes, oils, wines). So, they give gaseous composition and concentration. They also ensure a control atmospheric pollution by using trained pattern of the quality level of indoor or outdoor atmosphere of the living house. In this case, only the global level of pollution is followed.

In the world, only some companies commercialize electronic noses, which are very expensive, because these devices must always be adapted to the situation. Montreal city has installed an equipment of electronic noses to control its atmospheric pollution.

One of the major challenges is their miniaturization, which could make possible to equip people working in delicate area. Some hope is the detection of explosives, but current gas sensors can't work at this very weak concentration (ppb, parts per billion).

References

[1]. http://michael.ozanon.free.fr
[2]. Moncrieff R., An instrument for measuring and classifying odours, *J. Appl. Physics*, 16, 1661.
[3]. Gardner J. W. and Bartlett P. N., A brief history of electronic noses, *Sensors and Actuators B*, 1994, pp. 18-19.
[4]. Cointre N., Pressions exercées sur l'environnement, Atlas atlantique permanent, *Espace Atlantique Français*, Dec. 1998.
[5]. Wilkens W. and Hatman A., An electron analog for the olfactory process, *ANN NY Acad. Sci.*, 11, 1964, p. 608.
[6]. D. C. Levy, D. A. Barnett and G. A. Bell, Electronic noses: prospects and application in Australian industry, *in Proceedings of the 2nd Int. Conf. on Knowledge-based Intelligent Electronic Systems,* Adelaide, Australia, April 1998.
[7]. Strobel P., Thèse d'Université, *Université de Metz,* France, 30 juin 2006.
[8]. Lfakir A., Thèse d'Université, *Université de Metz,* France, 31 mars 2006.
[9]. Sambemana H., Thèse d'Université, *Université de Metz,* France, 20 juin 2012.
[10]. Fuchs S., Thèse d'Université, *Université de Metz,* France, 31 mars 2008.