Monitoring the Stability of Perfume and Body Odors with an "Electronic Nose"

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Among the various methods used to detect volatile compounds emitted by a sample, the one which is most widely used is the human nose within sensory panels. Although the human nose can be used in this way for product design, it cannot be used routinely for 100% product control in applications such as the monitoring of perfumes in soaps and cosmetic bases, the monitoring of body odors in deodorant development, and the monitoring of aromas in the food industry. For this reason, a few laboratories have developed "electronic noses" based on an array of gas sensors and suitable artificial intelligence. This article discusses one such electronic nose—the FOX 2000—as a new fast analytical technique.

The Human Nose

The outstanding capabilities of the human nose can be used either at the outlet of a gas chromatography column or directly on a product sample. To detect the volatile substances, the olfactory system uses an array of nonspecific biological sensors, the selectivity of the nose coming largely from the signal processing. Some studies have shown that the odor detection process leads at the olfactory bulb level to a spectral signature characteristic of the type of odorants. This signature, which is a kind of Fourier transform[1] of the olfactory signals, involves the entire transduction mechanism. The patterns detected in the olfactory bulb strongly resemble the olfactory images[2] described in some previous articles.

The odor classification is done with some oral descriptors or some subjective associations. The language used stays somewhat imprecise and is closely linked to the personal experience of each member of the sensory panel. Certain activities try, however, to use a restricted number of descriptors precise enough to describe the olfactory space associated with the studied products. Tables like those of Arctander and Moncrieff[3] give numerous descriptors limited only by the verbal language.

In order to illustrate the complexity of certain perfumes or natural aroma, we are going to consider the case of a chyphre perfume with a floral note. The chyphre perfume is an harmonious equilibrium of ten different notes. Within the same note, a large variety of essential oils or synthetic products can be used. Each essential oil or synthetic odorant product contributing to a note is itself constituted of hundreds of simple molecules. For example, a woody note is made with patchouli oil, vetivert oil and sandalwood oil, while a spicy note is due to pimento oil and isoeugenol. Table I shows the list of constituents and their relative proportions.[4]

Coffee, tea or cocoa are natural products with thousands of molecular compounds making up their headspace, each of them partially contributing to the aroma. The human nose does not analyze such a complex composition but processes it, like a simple geraniol or camphor, into a pattern (Figure 1).[5]

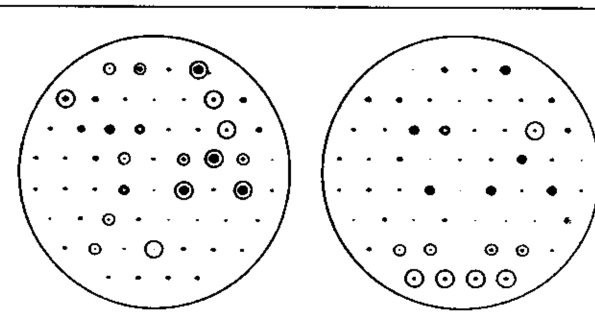

Figure 1. Representation of the unitary activity of the olfactory nerve of a frog in the presence of geraniol or camphor.

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The Electronic Nose

The pattern recognition process which takes place in the brain allows us to immediately classify any odor with known odor descriptors (e.g., woody, grassy, ethereal). Therefore the concept of the electronic nose is the arrangement of an array of non-selective sensors—instead of biological sensors—feeding data to a pretrained neural network. The FOX 2000 uses an array of 6, 12 or 18 sensors to capture up to 60 data points for each sample stored in the odor library. The network is trained using a set of known samples with their appropriate odor classes or labels.

The signals recorded by the sensors give a spectral signature or characteristic pattern that can be associated with a given odor. For example, in the case of a Brazilian coffee and a Colombian coffee sampled by an electronic nose with twelve sensors, the signatures of the two coffees are very different (Figure 2).

These signatures are the relative normalized sensor responses after recording the headspace for two minutes. When they are stored as a reference, all 60 points of their odor files can be used to train the neural network. Then, when the network is queried, the FOX 2000 propagates the 60 data points through the data base to determine the quality (Good/Bad) or identity (Brazilian/Colombian/Not Recognized) of the sample. For example, the comparison of the signature of an unknown coffee with a library of Brazilian/Colombian coffees allows the FOX 2000 user to display the response COLOMBIAN by simply pushing a key (Figure 3).

Electronic Sensors

Most research and quality control in olfaction is done with gas chromatography (GC) and mass spectrometry (MS). Classical analytical techniques are limited because the trapping and thermodesorption on GC columns lead to a relatively long analysis time and complex spectra. The chromatograms are difficult to use and they do not correlate well with the human olfactory response for the following reasons:

- The nose is not a separative technique but detects the headspace as a whole.
- Except for some rare cases, the intensity of the odors is not directly related to the concentration of each simple molecular compound. For example, it is not necessarily true that when a chromatographic peak is twice as large as in a previous analysis that the intensity of the smell is higher. Moreover, some minor peaks can contribute strongly to the overall smell. On the other hand, sensors are more reactive to an equivalent amount of charged and unsaturated odorant molecules.

In order to develop an electronic nose, one must look for sensors able to detect volatile compounds at a very low concentration and to give strong responses for odorant molecules which have generally a strong electronic charge (i.e., a high sensitivity to sulfur derivatives, amines, oxygenated compounds and unsaturated molecules).

Two gas sensor technologies can satisfy those requirements as well as the general requirements (high sensitivity, good reproducibility, etc.) of any analytical instrument. These technologies are the semiconducting metal oxides and the conducting polymeric materials.

Metal Oxide Semiconducting Gas Sensors: Metal oxide is a semiconductor material and is gas-sensitive. Oxygen in the air reacts with lattice oxygen vacancies of the bulk material and removes electrons from the conducting band.

$$e^- + {}^1\!/_2 O_2 \rightarrow O^-_{(s)}$$

The oxidation state is temperature dependent but O^- occurs at around 400°C. In the presence of a gas or an odorant molecule R, the chemisorbed oxygen species react irreversibly and products (such as CO_2 and water) are usually evolved.

$$R + O^-_{(s)} \rightarrow RO + e^-$$

The resistance of the sensor thus decreases in the presence of an odor, and the size of the decrease depends on the nature of the detected molecules and the type of metal oxide used. The response time also depends on the reaction kinetics, the dead space and volume of odor headspace as well as the flow rate of the carrier gas.

Table I. A formula for a classical floral chyphre perfume

Synthetic odorants	
Lilial (Givaudan)	3
Aurantiol	2
Terpineol extra	3
Isoeugenol	5
Isoamyl salicylate	3
Ethyl acetoacetate	0.4
Isobutyl phenylacetate	4
Phenyl acetate	4
Phenylethyl alcohol	3
Anisaldehyde	1
Trimethylundecylenic aldehyde	0.5
Civetone	2
Heliotropin	2
Vanillin	3
Galaxolide (IFF)	1
Androl (CPL)	1
Pyrolide	0.1
Natural oils	
Pimento	1
Coriander (Russian)	2
Nutmeg (East Indian)	1
Petitgrain (Paraguay)	1
Ylang-Ylang premier	2
Lavender (English)	4
Bergamot (Sicily)	8
Patchouli (Indonesia)	3
Vetiver (Haiti)	1
Sandalwood (Mysore)	1
Oakmoss resinoid	4
Rose abs. (Grasse)	16
Jasmin abs. (Grasse)	16
Immortelle abs.	0.5
Tuberose abs.	1
Hyacinth	0.5
Total	**100**

Conducting Polymer Gas Sensors: Conducting polymers can also provide a gas-sensitive material for use in a gas sensor. Conductometric elements are formed by the electropolymerization of a thin film (sensitive layer) between two electrodes. The large variety of monomers and hence different sensors are attractive and could be used to establish an odor library. Poly(pyrrole) films are materials sensitive to organic vapors; electronic noses of this type are being studied by English brewers.[7] The reactivity of the

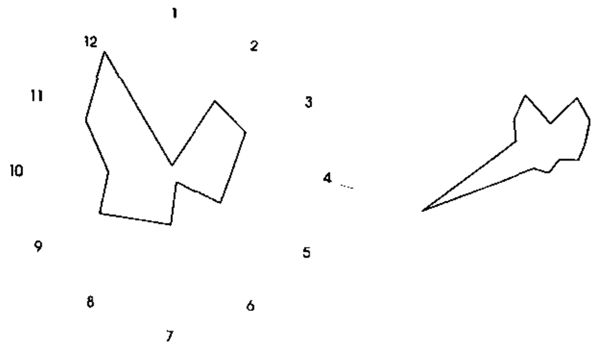


Figure 2. Signatures of two coffees (Brazilian on the left, Colombian on the right) using an array of twelve sensors.

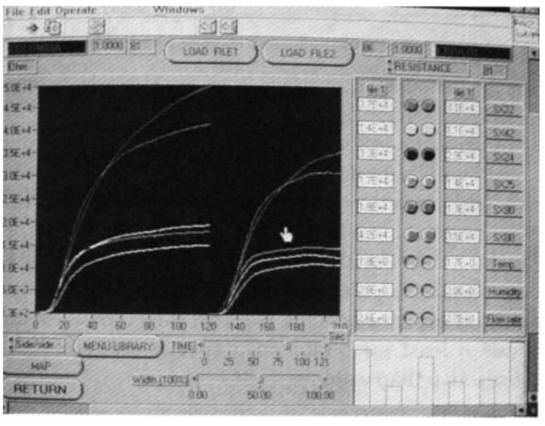
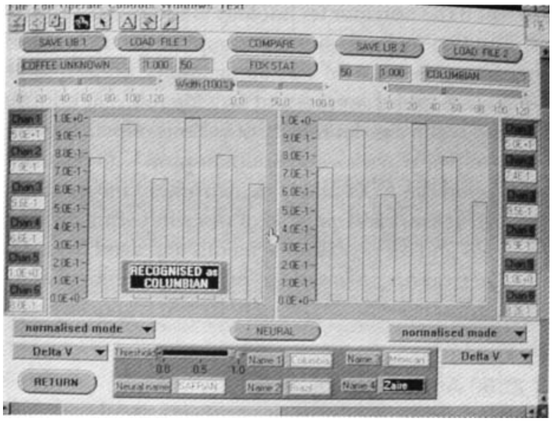


Figure 3. Response of FOX 2000 (below left) to an unknown coffee by comparing the unknown's 60 data points from six sensors with reference coffees (Colombian above left, Brazilian above right) previously sampled and stored in the database for reference (below right).



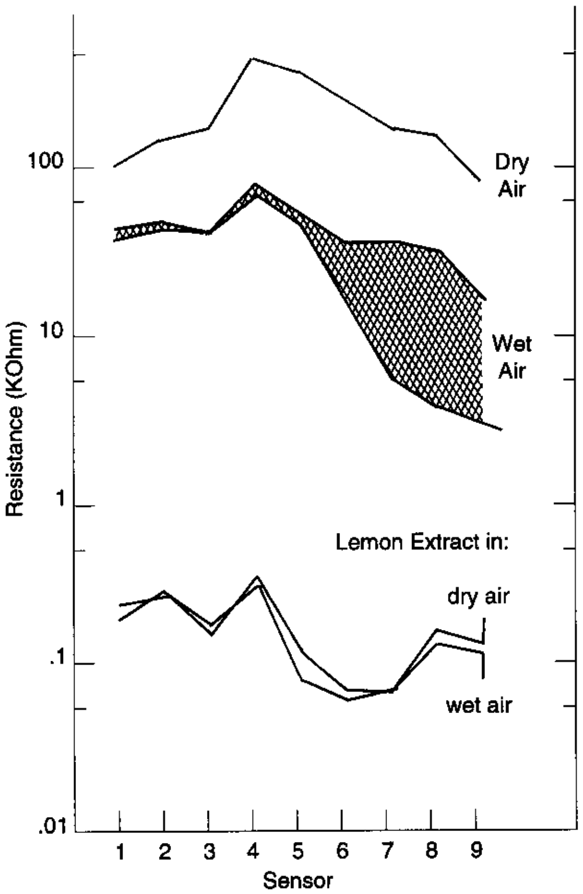


Figure 4. Effect of humidity on sensor response.

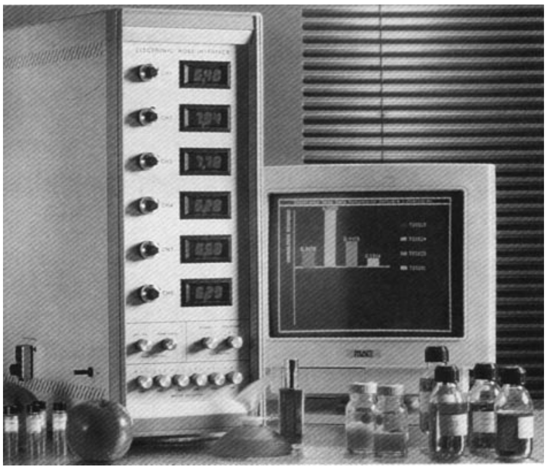


Figure 5. FOX 2000 Instrumentation.

coordination bond R - O at the sensor surface plays an important role in the signal amplitude and correlates strongly with the oxidation levels of the molecules (rancid odors appearing with aging). Alcohols, ketones, fatty acids (such as hexenoic and isovaleric acids) and esters are well detected, however fully oxidized species like CO_2, NO_2 and H_2O lead to lower responses.

Effect of humidity: In some applications, the ambient humidity does not greatly influence the response of the metal oxide sensors, while in others it is possible to compensate for its effect. Sensor response to essential oils with different humidity contents has been described in the work of the North American researchers B.S. Hoffeins and R.S. Lauf at Oak Ridge Laboratories, where an array of 9 metal oxide sensors has been used to study the aroma of different essential oils and foodstuffs instead of the 6, 12, or 18 sensors in the FOX 2000 electronic nose. The level of humidity plays an important part in the food industry. An experiment has been performed on an essential oil with and without water vapor. Such an array did not differentiate between a lemon essential oil in dry air and in an atmosphere saturated with humidity. This is illustrated in Figure 4, in which the Y axis is the resistance of the sensors, and the X axis is the sensor number 1 to 9. The upper curve represents the shape of the sensors' response in dry air with a clean atmosphere. In the presence of an atmosphere saturated with humidity, the resistance of the sensors decreases and lies in the shaded area. The measurement of an odorant product like a lemon oil in dry air or humid air leads to similar values by decreasing the resistance of all the sensors (lower responses). The absence of a sensitivity to humidity is explained by the fact that the odorant mixture includes at least some molecular species (i.e. citronellol) more reactive than water.

Comparison: The comparison of the different technologies of sensors that we have studied in our research laboratory leads us to the following conclusions. The metal oxide sensors are very sensitive (0.3 µl of pure acetone saturates certain sensors) and have very fast response time (around 5 to 30 seconds). Conducting polymer sensors are not quite as fast and require a higher concentration in odorant compounds to reach the same level of response. However the selectivity and the discrimination level increase when the polymer technology is added to the instrument. The two technologies are complementary and both are necessary in most of the applications; consequently, both types are useful sensors and provide relevant information on the quality and intensity of various odors. Together with the help of Warwick and Southampton Universities,[6,7] we developed the FOX 2000, an instrument incorporating 6, 12, or 18 sensors and capable of discriminating different odors (colas and diet colas, unaged oils and aged oils). This type of electronic nose based on "hybrid technology" allows us to optimize its sensitivity, selectivity and response time to complex odors.

FOX 2000 Applications

The FOX 2000 electronic nose (Figure 5) which will be described here has an array of six or twelve metal oxide or

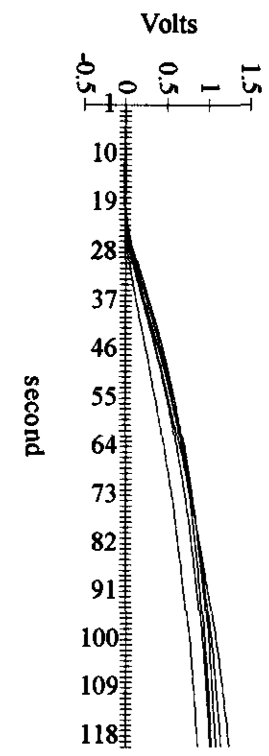


Figure 6. Axillary odor from a right underarm.

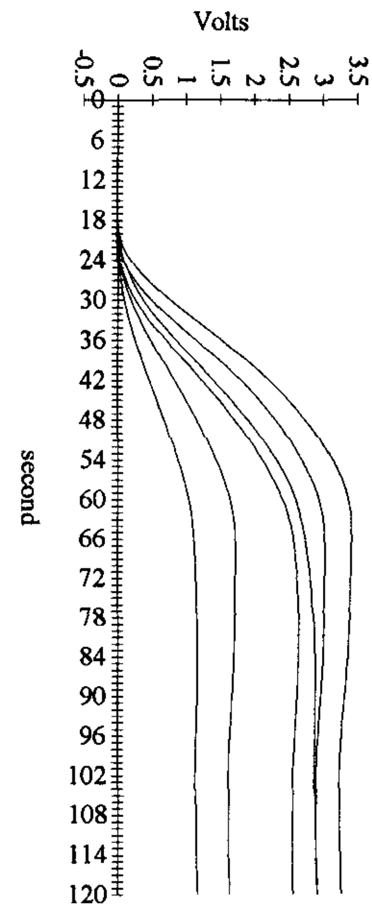


Figure 7. Axillary odor from a right underarm soon after application of a deodorant.

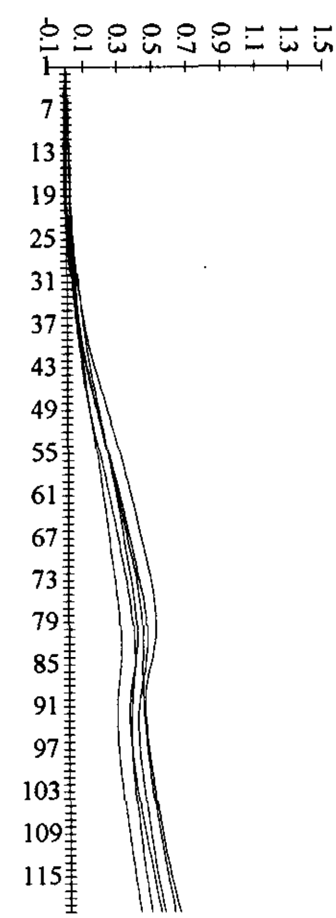


Figure 8. Axillary odor from a right underarm two hours after application of a deodorant.

conducting polymer sensors and can be used to detect the headspace of 0.5 µl of a lemon oil. The flow rate can be regulated between 5 and 500 ml/min and in this case was fixed at 20 ml/min. The response time of the sensors (first olfactory sensation perceived) is around 30 seconds.

In order to sniff odors, the inlet part of the electronic nose can be placed near the odorant sources (such as hairs or underarms), or connected to plastic bags containing odors, or connected to the measurement chamber of the FOX 2000 unit.

Axillary odor: In an experiment measuring axillary odor, the inlet part of the FOX 2000 was placed directly within the right underarm of a man at the end of his working day. The headspace was monitored by six odor sensors during a two-minute period (Figure 6). Similar measurements were taken soon after application of a deodorant (Figure 7). One can see (in Figure 7) that the response of the sensors is different and higher due to the detection of the perfume contained in the deodorant itself. Desorption of the sensors in this case (Figure 7) is not as fast as for the no-deodorant situation (Figure 6) due to the high responses obtained in the presence of perfume. When measurements were taken again two hours after application of the deodorant (Figure 8), the perfume was still detected but at low concentration, and the absolute sensor responses showed the axillary odor had been halved.

Figure 9 shows the ability of the FOX 2000 to store and display data. The immediate post-deodorant-application measurements are displayed on the left of the screen. On the right, the scale (1.5 volt) from the initial axillary odor readings is being used to study the long-term effect of the deodorant (0.6 volt after 2 hours). Again, the recorded values for axillary odor two hours after deodorant application are much lower than the values before deodorant application. This example shows the utility of such an instrument for a quick evaluation of the deodorant efficiency or to assess evolution of an odor.

Perfumed towels: When odorant compounds are present at very low concentration levels, it may be necessary to concentrate the volatile compounds before the measurement. In Figure 10 the headspace of perfumed towels has been analyzed by coupling a dynamic headspace instrument with the FOX 2000. The objective of such measurement was to study long-term stability of the perfume on washed towels.

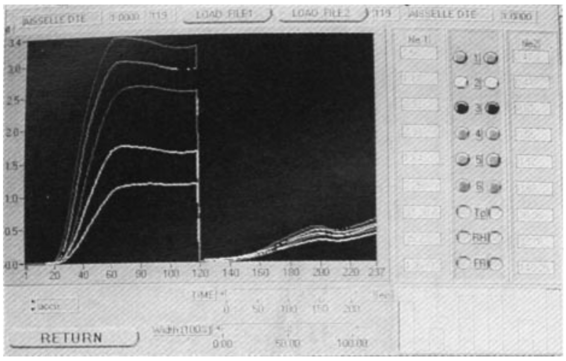


Figure 9. Axillary odor from a right underarm soon after application of a deodorant (left) and two hours after application of a deodorant (right) showing the long-term effect of the deodorant (low detection of the perfume at times less than 90 seconds, and reduced detection of axillary odor at times greater than 90 seconds).

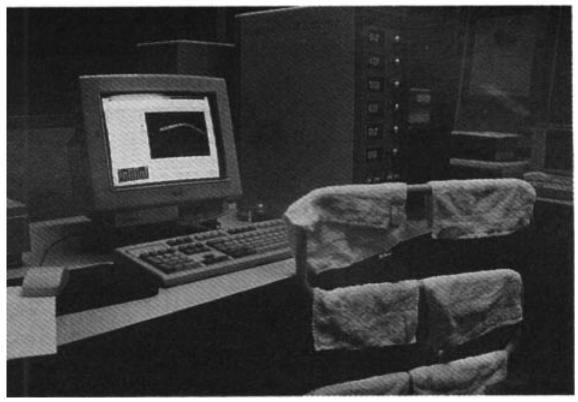


Figure 10. FOX 2000 setup for measuring stability of perfumes on towels after washing.

Summary

An electronic nose able to distinguish complex mixtures needs two things: the equivalent of a nose to smell and the equivalent of a brain to learn and recognize the odors. Besides the choice of the sensors, the quality of the pattern recognition system is essential. This is why it is necessary to get the help of an Artificial Intelligence technique like an artificial neural network. It is possible to develop a specific pattern recognition system by designing a neural network topology for each application. Such neural networks can be easily integrated on chips in the microprocessor of an electronic nose such as the FOX 2000.

In conclusion, the performance of an electronic olfactory system requires a good set of sensors and advanced interactive pattern recognition algorithms. At last it seems that electronic noses are soon going to be powerful quality control and development tools complementary to existing techniques such as organoleptic panels and gas chromatography.

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