APPLICATIONS OF ELECTRONIC NOSES IN FOOD ANALYSIS

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Abstract

This review examines the applications of electronic noses in food analysis. A description of the definition of the electronic noses, how they function and the electronic working principles is made. As pattern recognition techniques, electronic noses are widely used to analyse the data obtained from these multisensor array. A discussion of principal components analysis and artificial neural networks is essential. An introduction to the integration of electronic noses is also incorporated and the strengths and weaknesses of both are described. The described applications include identification and classification of flavour and aroma and other measurements of quality using the electronic nose. At least there are presented some perspectives in the application of electronic noses in the food industry.

Keywords: electronic nose, biosensor, food analysis, pattern recognition, sensor arrays

1. INTRODUCTION

Analysis of odor and flavor in food has traditionally been performed either by a trained sensory panel or by head-space gas chromatography or mass spectrometry. These methods are time consuming and costly and there is a need in the food industry for objective automated non-destructive techniques that can characterize odor and flavor in food.
New methods should allow a high number of samples to be analyzed within a short period of time with a sufficient reproducibility and accuracy. During recent years there has been a rapid development of a concept named electronic nose (artificial nose) based on chemical gas-sensor array technology which seems to fulfill these requirements.
Over the last decade, "electronic sensing" or "e-sensing" technologies have undergone important developments from a technical and commercial point of view. The expression "electronic sensing" refers to the capability of reproducing human senses using sensor arrays and pattern recognition systems.
Since 1982 [9], research has been conducted to develop technologies, commonly referred to as electronic noses, that could detect and recognize odors and flavors. The stages of the recognition process are similar to human olfaction and are performant for identification, comparison, quantification and other applications. However, hedonic evaluation is a specificity of the human nose given that it is related to subjective opinions. These devices have undergone much development and are now used to fulfill industrial needs.
In this study is made a description of the definition of the electronic noses, how they function and the electronic working principles. A discussion of the principal components analysis and artificial neural networks is made. At least there are presented some perspectives in the application of electronic noses in the food industry.

2. WHAT IS AN ELECRONIC NOSE

With the term Electronic Nose is understood an array of chemical gas sensors with a broad and partly overlapping selectivity for measurement of volatile compounds within the headspace over a sample combined with computerized multivariate statistical data processing tools [6]. The sensor array of an electronic nose has a very large information potential and will give a unique overall pattern of the volatile components.
So, an electronic nose (e-nose) is a device that

identifies the specific components of an odor and analyzes its chemical makeup to identify it.

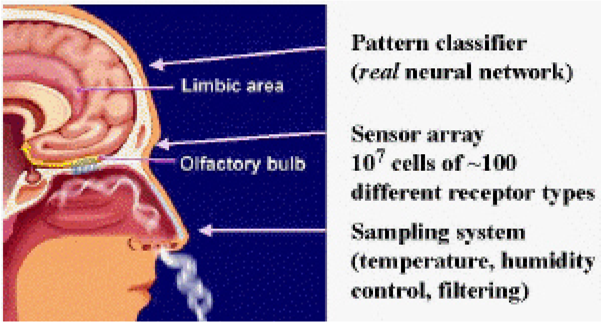

Figure 1. The "Biological Nose"

An electronic nose consists of a mechanism for chemical detection, such as an array of electronic sensors, and a mechanism for pattern recognition, such as a neural network .

Electronic noses have been around for several years but have typically been large and expensive. Current research is focused on making the devices smaller, less expensive, and more sensitive. The smallest version, a nose-on-a-chip is a single computer chip containing both the sensors and the processing components.

3. HOW ELECTRONIC NOSES FUNCTION

One cannot discuss the "electrochemical nose"

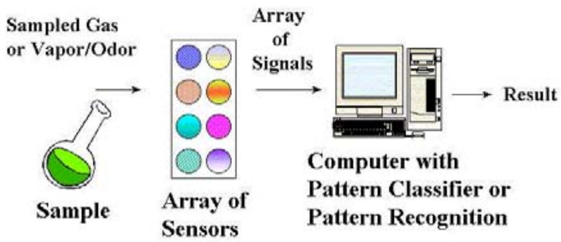

Figure 2. The basic design of the "Electronic Nose".

without first discussing the human or biological nose and the factors that led to the development of artificial olfaction technology.

An odor is composed of molecules, each of which has a specific size and shape. Each of these molecules has a correspondingly sized and shaped receptor in the human nose. When a specific receptor receives a molecule, it sends a signal to the brain and the brain identifies the smell associated with that particular molecule (Figure 1).

Of all the five senses, olfaction uses the largest part of the brain and is an essential part of our daily lives. Indeed, the appeal of most flavors is more related to the odor arising from volatiles than to the reaction of the taste buds to dissolved substances. Our olfactory system has evolved not only to enhance taste but also to warn us of dangerous situations. We can easily detect just a few parts per billion of the toxic gas hydrogen sulfide in sewer gas, an ability that can save our life. Olfaction is closely related to the limbic or primitive brain, and odors can elicit basic emotions like love, sadness, or fear. In fact life-saving nauseous revulsion is at least as ancient and universal in the mammalian world as the animal that takes most exquisite advantage of its existence, "Mephitis mephitis", the striped skunk!

Electronic noses, based on the biological model, work in a similar manner, albeit substituting sensors for the receptors, and transmitting the signal to a program for processing, rather than to the brain (Figure 2).

Electronic noses are one example of a growing research area called biomimetics, or biomimicry, which involves human-made applications patterned on natural phenomena.

Several commercial gas sensor array instruments are now available on the market covering a variety of chemical sensor principles, system design and data analysis techniques.

The entire genus of electronic noses includes those with conductive polymer, polymer composite, quartz microbalance, surface acoustic wave, calorimetric, and other classes of sensors. All of them can be simply refered to as "E-nose" to indicate artificial olfaction, since many modern E-noses are constructed with more than one class of sensor in them. These latter instruments are said to employ "heterogeneous" sensor arrays. Many sources of multi-parameter chemical data including infrared spectrometers, gas chromatographs, and mass spectrometers have been used to identify odors and therefore called E-noses.

A series of different detection principles can be used in chemical gas sensors: heat generation, conductivity, electrical polarization, electrochemical activity, optical properties, dielectric properties and magnetic properties [2].

By chemical interaction between odor compounds and the gas sensors the state of the sensors is altered giving rise to electrical signals which are registered by the instrument analogue with the secondary neurons. In this way the signals from the individual sensors represent a pattern which is unique for the gas mixture measured and is interpreted by multivariate pattern recognition techniques like artificial neural network, the brain of the instrument (Figure 2) [3, 7, 12].

Samples with similar odorous generally give rise to similar sensor response patterns and samples with different odorous show differences in their patterns. When the sensor patterns for a series samples are compared, differences can be correlated with the perceived sample odor. The sensors of an electronic nose can respond to both odorous and odorless volatiole compounds.

In principle, the electronic nose can be applied to any product that gives off volatiles with or without smell provided that this occurs within the sensitivity range of the sensors [1,3].

The data processing of the multivariate output data generated by the gas sensor array signals represent another essential part of the electronic nose concept.

The statistical techniques used are based on commercial or specially designed software using feature extraction and pattern recognition routines like principal component analysis (PCA), partial least squares (PLS), functional discriminant analysis (FDA), cluster analysis, fuzzy logic or artificial neural network (ANN).

Other newer techniques that seem to have an interesting potential are multiway decomposition and independent component analysis (ICA).

In Figure 3 there are presented some modern electronic noses. These instruments are available to perform comparisons of unknown gas, vapor, and odor samples with a calibration library that can be provided by the manufacturer and sometimes created by the user.

Figure 3. Modern electronic noses.

4. ELECTRONIC NOSE WORKING PRINCIPLE

The electronic nose was developed in order to mimic human olfaction that functions as a non-separative mechanism: i.e. an odor / flavor is perceived as a global fingerprint.

Electronic Noses include three major parts: a sample delivery system, a detection system, a computing system [4,7].

The **sample delivery system** enables the generation of the headspace (volatile compounds) of a sample, which is the fraction analyzed. The system then injects this headspace into the detection system of the electronic nose. The sample delivery system is essential to guarantee constant operating conditions.

The **detection system**, which consists of a sensor set, is the "reactive" part of the instrument. When in contact with volatile compounds, the sensors react, which means they experience a change of electrical properties. Each sensor is sensititive to all volatile molecules but each in their specific way. Most electronic noses use sensor-arrays that react to volatile compounds on contact: the adsorption of volatile compounds on the sensor surface causes a physical change of the sensor. A specific response is recorded by the electronic interface transforming the signal into

a digital value. Recorded data are then computed based on statistical models [10,11].
The more commonly used sensors include metal oxide semiconductors (MOS), conducting polymers (CP), quartz crystal microbalance, surface acoustic wave (SAW), and field effect transistors (MOSFET).
In recent years, other types of electronic noses have been developed that utilize mass spectrometry or ultra fast gas chromatography as a detection system [10,11].
The **computing system** works to combine the responses of all of the sensors, which represents the input for the data treatment. This part of the instrument performs global fingerprint analysis and provides results and representations that can be easily interpreted. Moreover, the electronic nose results can be correlated to those obtained from other techniques (sensory panel, GC, GC/MS).
As a first step, an electronic nose need to be trained with qualified samples so as to build a database of reference. Then the instrument can recognize new samples by comparing volatile compounds fingerprint to those contained in its database. Thus they can perform qualitative or quantitative analysis [10, 11].

5. APLICATION OF ELECTRONIC NOSES

Electronic noses were originally used for quality control applications in the food, beverage and cosmetics industries.
Current applications include detection of odors specific to diseases for medical diagnosis, and detection of pollutants and gas leaks for environmental protection.
In principle, the results obtained from a gas-sensor array represent qualitative and quantitative information of the composition of the headspace gas mixture of a sample. The technique should therefore have a great potential in a number of applications related to food. Numerous electronic nose studies related to food already have been published. Many of them represent preliminary feasibility studies, but a limited number of them represent basic studies including long term validation of the technique on a specific application.

Electronic noses have great potential in the following areas:

· odour analysis
· lipid oxidation
· freshness and spoilage
· taints and off-flavour
· food safety
· process control
· packaging

6. ANALYTICAL SIGNIFICANCE

The E-nose has the interesting ability to address analytical problems that have been refractory to traditional analytical approaches [4, 7].
The volatiles from coffee, for example, contain at least 640 different compounds. These interact in such a way that no single compound or group of compounds is associated with the subjective assessment of flavor or odor. The flavor/odor of "good" coffee cannot be traced to a specific molecular origin or simple list of chemicals by traditional analytical techniques like gas chromatography or mass spectroscopy. One analyzes "good" coffee and "bad" coffee as described by coffee experts and finds differences in concentrations of hundreds of the compounds in the samples.
Today, it is still not possible to add or subtract these known compounds according to a rational system, and make the "bad" coffee "good" or vice versa. We do not have a sufficient compositional understanding at the molecular level of the gustatory terms "good" and "bad" coffee. Yet the E-nose can learn the fingerprints of coffees and easily tell these different coffees apart. A statistical relationship between the array patterns for "good" and "bad" can be easily found. Somewhere within the complex response of the sensors in the array is encoded the difference between "good" and "bad" in the chemical fingerprint, just as it is in the complex response of the millions of receptors in our nose. We still do not know exactly the molecular basis for this difference but we can definitely say that array response vectors are different and statistically related to the quality "good" or "bad" coffee. Frequently no such chemical marker(s) or specific

molecular cause can be found for the quality of many perfumes or the off-odor of a group of recycled plastic parts. In such cases, the determination of flavor or odor is performed by an olfactory panel, that is, a panel of skilled and trained human noses (attached to highly paid human beings). The response of a chemical gas sensor array or electronic nose can be statistically related to such properties as odor, flavor, explosive, or even bacterial content. Thus, the E-nose offers an opportunity to develop an instrumental approach for the human analytical endpoints like odor, flavor, hazardous, contaminated, spoiled, and the like.

7. PERSPECTIVES IN THE APLICATION OF ELECTRONIC NOSES IN THE FOOD INDUSTRY

In industry, aroma assessment is usually performed by human sensory analysis, chemosensors or by gas chromatography (GC, GC/MS). The latter technique gives information about volatile organic compounds but the correlation between analytical results and actual odor perception is not direct due to potential interactions between several odorous components [5].

The electronic nose technology applied on food must be regarded as being in its early stage. So far, the applications in the scientific literature seem promising for future use in the food industry. There is a rapidly advancing research and development going on both sensors and instrument hardware and software in order to enhance selectivity, sensitivity and reproducibility of the gas sensors. Much effort is also put into solving the drift problem of the sensors by increasing the stability and life-time of the sensors [8].

There is also carried out research in order to develop improved mathematical algorithms for drift counteraction, automatic calibration and standardization and transferability between gas sensor array instruments.

At the same time development of different applications by the industry and research centers in different fields is proceeding.

On-line sensors play a key role in the automation of food control and processing. In near future when the basic issues of the gas-sensors have been solved, we will see more on-line gas-sensors implemented in the industry.

For each application, however, technical problems have to be solved for implementation on-line. One interesting vision for the future would be to have a fully automated platform of different kind of sensors to monitor the essential information required for the characterizing of quality of the raw material, process or product. Gas-sensors would make up a vital part of such a multi-sensor system. This may be realized in the food industry in the near future.

Presently, the research in the field of electronic electronic nose is performed in the following areas:

- Monitoring and analysis of different fermentation processes;
- Determination of fish quality (development of a ”fish-nose”);
- Data transfer between instruments and data standardization;
- Drift compensation;
- Application and testing of various statistical methods for improved explotation of raw data.

8. CONCLUSIONS

- Electronic noses are being developed as systems for the automated detection and classification of odors, vapors, and gases.
- An electronic nose is generally composed of a
- chemical sensing system (e.g., sensor array or spectrometer) and a pattern recognition system
- (e.g., artificial neural network).
- There were developed electronic noses for the automated identification of volatile chemicals for various applications (e.g. medicine, environment, food industry, a.s.o.).
- The major differences between electronic noses and standard analytical chemistry equipment are that electronic noses:

(1) produce a qualitative output,
(2) can often be easier to automate
(3) can be used in real-time analysis

9. REFERENCES

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