Electronic noses: Sniffing fast, safe and objective

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For these last ten years, technologies linked to "electronic sensing", aimed at reproducing human sensory mechanisms, have known an important development, both at a technical and a commercial point of view.

Among them, the smell has generated a great interest as a matter of research and the term "electronic nose" appeared in 1987, with the first systems marketed in 1993.

Such analyzers were designed to detect and analyze odors, and more generally volatile organic compounds. Their specificity lies in the fact that the steps of the detection and analysis process are strongly similar to human sense of smell that allow to identify, quantify or compare odors. However, hedonic evaluation remains a specificity of the human nose given that it is related to preference.

Electronic noses have undergone many improvements and are now used to fulfill industrial needs in Research & Development departments, Quality Control for Flavor & Fragrance, Cosmetic & Perfumes, Pharmaceutical, Chemical companies, Food & Beverage, Packaging.

HUMAN SMELL AND ELECTRONIC NOSES

The electronic nose, which mimics human olfaction, works as a non-separative mechanism (Figure 1). An odor / flavor is perceived as a global fingerprint that can be related with organoleptic assessment, whereas separative techniques analyze chemical compounds.

A detection system (gas sensors, fingerprint mass spectrometry or flash chromatography) reacts to volatile compounds in the same way as odor receptors are sensitive to odorous stimuli in humans. A computing system records a specific response for each sample (change of electrical resistance of all sensors, mass spectrometry peaks or gas chromatography peaks), then data are computed and interpreted with statistical models. Typically, results consist of graphs or tables: two-dimension graphs for products' comparison or group identification, multi-bands control card to monitor the various grades of quality, quantification models to predict a score, a concentration.

THE ADVANTAGES OF USING AN ELECTRONIC NOSE

To set-up an analysis with an E-Nose, the first step consists of training the analyzer with qualified samples so as to build a

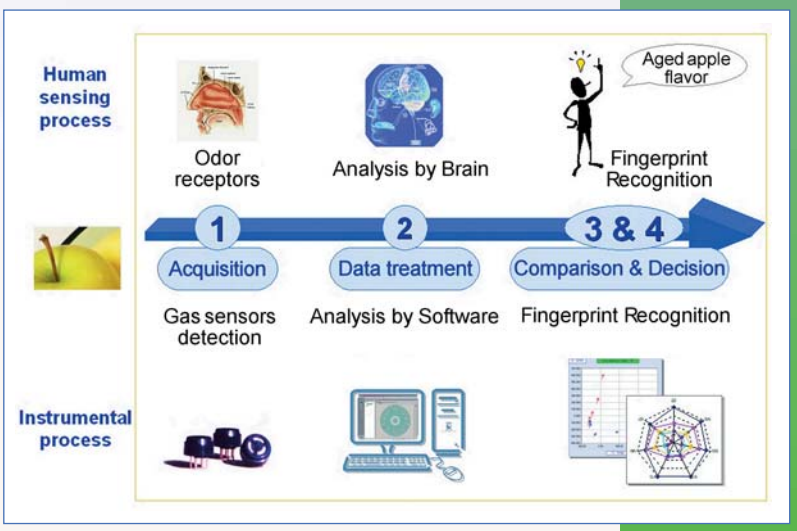

Figure 1 – Comparison of human smell and E-Nose working principles

database of reference. Then, the instrument can recognize new products by comparing data to those stored in its memory.

These analyzers require no or very little sample preparation. They provide consistent and reproducible measurements. In comparison with alternative methods, results are delivered much more rapidly (in minutes instead of hours in some cases). Moreover, instruments are permanently available.

Finally, fingerprint results, which can be compared and correlated to human assessment, are easy and convenient to interpret so that a decision can be taken rapidly.

E-NOSE IN THE COSMETICS & PERFUME INDUSTRIES

Electronic noses are used by major companies of the cosmetic and fragrance areas, in various departments:

– In Research & Development, the E-Nose, which can compare rapidly several products, allows to speed-up the development of new products by testing larger numbers of formulations and to benchmark target references. The analyzer can also follow-up the ageing of products, the stability of aromatic compounds over time, the interaction between a perfume and the packaging, and thus select properly raw materials and packaging based on the results delivered.

Figure 2 – FOX Electronic Nose

– In Quality Control laboratories, the Electronic Nose is used to check the conformity of raw materials or end products, to select suppliers, to guarantee reproducibility of products and assure batch to batch consistency, to detect possible contamination, to follow-up the influence of storage conditions.

– At Production stage, the Electronic Nose is used to evaluate, monitor or select manufacturing processes in order to guarantee the invariability of products, to reach the desired quality, to assess the efficiency of a cleaning process, to maintain quality during scale-up process, to check the concentration of a compound.

– For Marketing services, the Electronic Nose is a useful tool to develop products that will fulfill market expectations in terms of sensory features.

Given that the E-Nose measurement is instrumental and objective, the analyzer cannot provide information related to preference and opinion.

Table I – Comparison of GC/MS, sensory panel and electronic nose for the detection of mangone in a fragrance

Mangone concentration *	GC/MS **	Sensory panel ** (% of successful identification in the panel)	Electronic Nose **
1	Yes	Yes (100%)	Yes
10^{-1}	Yes	Yes (89%)	Yes
10^{-2}	No	No (37%)	Yes
10^{-3}	No	No (45%)	Yes
10^{-4}	No	No (30%)	Yes

* percentage (weight / weight) of mangone in the fragrance

** Yes = the GC/MS is able to distinguish the presence of mangone in the fragrance

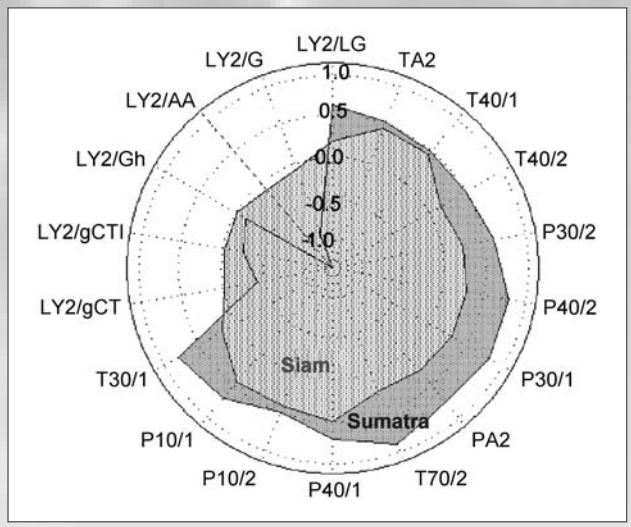

Figure 3 – Radar plot of two gums from different origins

STUDY CASE: COMPARISON OF THREE ANALYZING TECHNIQUES FOR THE DETECTION OF A PERFUMERY COMPOUND

The identification of the notes composing a fragrance is a common issue in the perfume industry. Usually, this evaluation is done by humans. More recently, the detection of a compound (the mangone) in a fragrance was conducted by three methods in order to compare their performance: an electronic nose including an array of 11 tin-oxide based sensors, a GC/MS system and a sensory panel of 20 trained panelists.

The mangone was

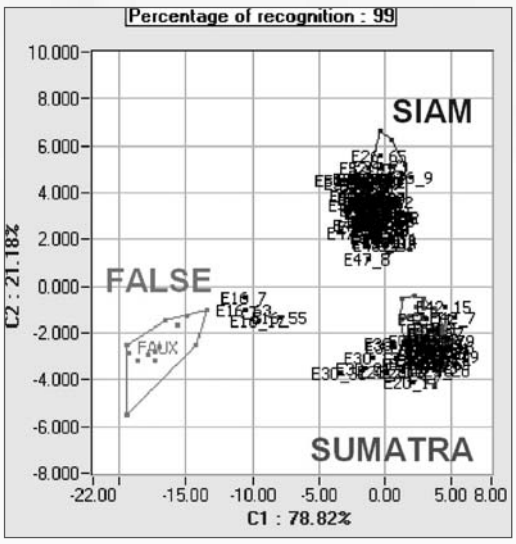

Figure 4 – Discriminant Factorial Analysis of benzoin gums based on origin

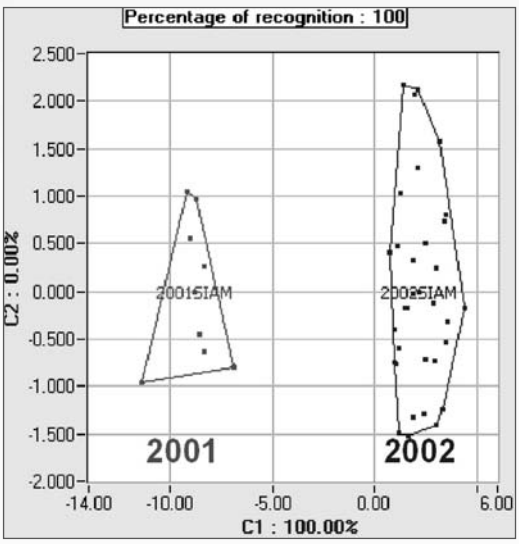

Figure 5 – Principal Component Analysis of gums based on the harvesting year

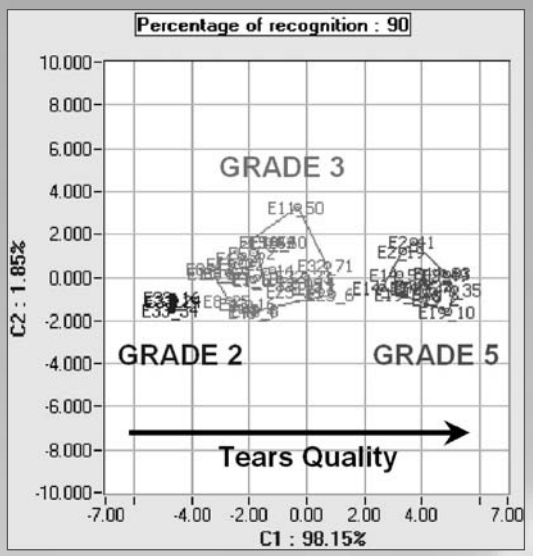

Figure 6 – Discriminant Factorial Analysis of benzoin gums based on quality grade

selected for its low threshold value of sensory detection and because it belongs to a different olfaction family (citrus, grape fruit) with respect to the compounds of the fragrance (green and pinecone notes).
Successive dilutions of the mangone in the fragrance were tested. The range of dilution assessed was comprised between 10^{-1} and 10^{-4}%.

The sensory panel evaluation consisted of a triangle test: each panelist had to smell three samples, two samples of pure fragrance and one sample containing mangone. The panelist had to indicate which of the three samples is different. An individual identification was considered as positive when the panelist had successfully recognized the different sample. For the global panel of 20 panelists, identification was deemed positive when 70% of panelists had passed the test.

Between a concentration of 1 and 10^{-1}, the three techniques allowed to detect the presence of mangone in the fragrance (Table I). Starting from lower concentrations (10^{-2}%), the electronic nose was the only method that could pick-up the mangone presence.

For the mangone compound diluted in a fragrance, the electronic nose showed a lower threshold of detection than GC/MS and trained sensory panel.

COSMETIC NATURAL RAW MATERIALS: CHARACTERIZATION OF VOLATILE CONSTITUENTS OF BENZOIN GUM

Benzoin gums are commonly used in the formulation of luxury flavors and fragrances.

The quality and consistency of raw materials are difficult to check given that they can be produced by craft methods, graded locally by each producer and traded by brokers. Moreover their prices are defined according to the claimed quality.

So it is crucial both for users and brokers to objectively assess the quality of raw materials.

Several types of gums were analyzed with an Electronic Nose using 18 metal oxide sensors (FOX 4000, Alpha M.O.S., France) to determine the quality and the olfactive features of benzoin gums. The selected factors were the harvest year, the country of origin, the grade of fragrance, the method can also be used to detect counterfeited benzoin gums.

A clear discrimination between the two origins was observed: Siam (red) and Sumatra (blue) gums (radar plot, Figure 3). In the same way, Siam, Sumatra and false gums were clearly separated (Discriminant Factorial Analysis, Figure 4). Blind samples were successfully identified with a high percentage of recognition (99%).

A clear differentiation based on harvesting year was achieved (PCA, Figure 5).
The three qualities of gums were clearly separated as shown for the Siam benzoin gum in DFA (Figure 6).

The FOX Electronic Nose successfully and rapidly discriminated benzoin gums based on various relevant criteria. It offered an alternative rapid technology to conventional techniques such as chromatographic methods and sensorial analysis for raw material quality control and prediction.

The electronic nose proved to be a fast and objective tool for the flavor & fragrance industry to check raw material quality.

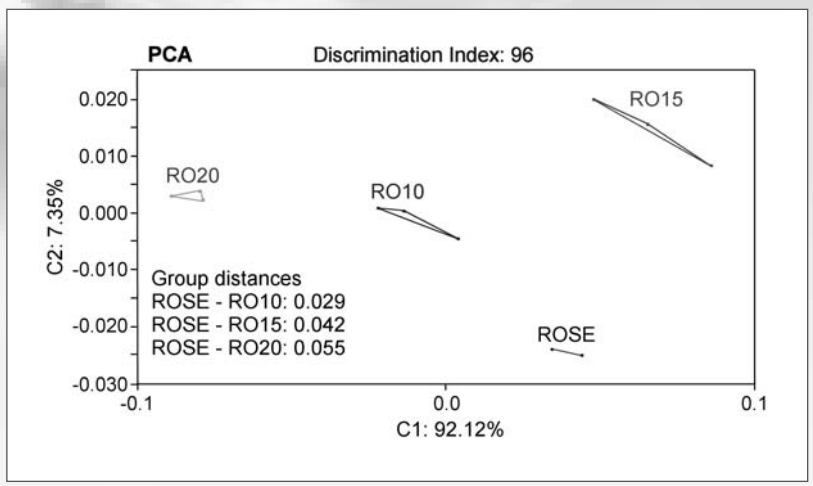

Figure 7 – Principal Component Analysis of rose perfumes from three different suppliers and reference perfume

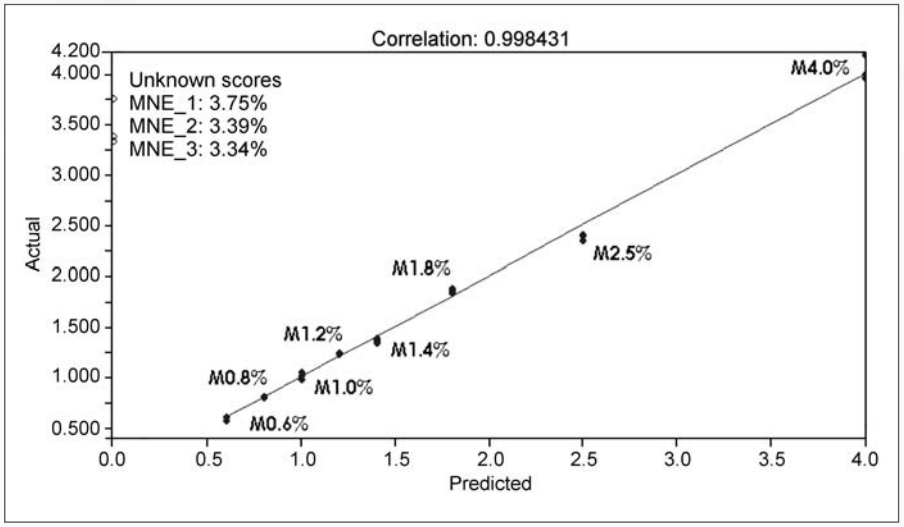

Figure 8 – Partial Least Square model for the quantification of rose perfume

PERFUMED PRODUCTS: BENCHMARKING AND QUANTIFICATION USING AN ELECTRONIC NOSE

A MOS-based E-Nose was used for qualitative and quantitative analysis of perfumed cleaner products with an aim to identify the closest product for a target reference and to determine the level of perfume added in the final

formulation.

In order to determine which perfume in a set of three (elaborated by various suppliers, noted RO10, RO15 and RO20) could be used to copy an existing ROSE perfume, an E-Nose allowed to compare product smell-prints and to find which one was the most similar to the reference. ROSE perfume was considered as the reference.

All samples were separated (PCA, Figure 7) and the group distance enabled the measurement of the proximity between samples. Consequently, the supplier of ROSE10 was selected as the one being the closest to the target.

In order to measure the level of perfume in a blind sample perfume MNE, a set of eight prepared formulations containing different concentrations (0.6-4%) was used to set-up the quantification model (Partial Least Square or PLS, Figure 8). The PLS showed a high correlation coefficient (99.8%), and allowed to determine the concentration of rose perfume in the coming batches. The MNE sample was found to contain a perfume concentration of 3.49%.

For perfume benchmarking, the results obtained were consistent with sensory evaluation.
For quantification, after building a calibration model, the system could accurately predict the level of perfume introduced into solutions.

Electronic noses cannot replace human beings for the creation steps, but in unpleasant routine analyses, for example, they can represent a substitute allowing to reduce human workload while avoiding safety concerns.

As a conclusion, the E-Nose offers a very efficient solution for R&D and marketing departments working on product development and positioning. It can also be used successfully for routine monitoring of process variations at a production stage or for Quality Control of raw materials or end products.