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The electronic nose applied to dairy products: a review

S. Ampuero, J.O. Bosset*

Swiss Federal Dairy Research Station, FAM, Schwarzenburgstrasse 161, Liebefeld, CH-3003 Bern, Switzerland

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Abstract

The state-of-the-art and current trends in the development of "aroma" analysis with electronic noses are reviewed with special reference to applications to dairy-products. Some of the reported problems with electronic noses have recently been reduced, e.g. the correction/reduction of signal drift, the influence of humidity and temperature. New promising and reproducible sensor manufacturing techniques are being implemented, e.g. electro-spray for QMB sensor production. The development of more selective and sensitive sensors, especially of QMB and conducting polymer (CP) type, should improve their applicability. Interesting novel sampling techniques, such as SPME or SBSE, offer more possibilities for the analysis of semi-volatile compounds which are generally more odoriferous. However, standard calibration procedures and reference materials are not yet available. Although they are normally less powerful than human noses, electronic noses offer some significant advantages in the analysis of volatiles, for example, in instrumental classifications based on hedonic or sensory analyses and in potentially automated on-line monitoring of volatiles. Several groups have explored the application of different electronic noses in the investigation of various aspects of dairy products. The present review includes as examples the evaluation of Swiss and Cheddar cheese aroma, the assessment of the ripening of Pecorino Toscano cheese (ewe's), the detection of mould in Parmesan cheese, the classification of milk by trademark, by fat level and by preservation process, the classification and the quantification of off-flavours in milk, the evaluation of Maillard reactions during heating processes in block-milk, as well as the identification of single strains of disinfectant–resistant bacteria in mixed cultures in milk.

Keywords: Gas sensor; Electronic nose; Artificial nose; Dairy product; Group classification; Volatile compound analysis

1. Introduction

Since the first applications of solid state gas sensors in arrays, some twenty years ago, "electronic noses" have undergone a great deal of development. Around a thousand articles on this subject have been published over the last 4 years, mainly in relation to the food and beverage industry [1], but also concerning environmental, agricultural, and medical topics, in the automotive industry, etc. However, the number of studies dedicated to dairy products is still very limited, probably due to the complexity of their matrices. The aim of the present paper is to review recent exploratory studies of electronic noses applied to dairy products, in order to perceive the prospects and trends in this field.

Traditionally in the food industry, monitoring of products in terms of quality and control of production processes (e.g. mixing, heating, drying, cooking, baking, extruding, fermenting, etc.) are performed via physicochemical measurements, i.e. pH-value, colour, concentration of given chemicals or biomolecules generally determined by spectroscopy (e.g. FTIR, NIR, UV-Vis, etc.) [2] and this despite the extreme importance of aroma as an indicator of quality and product conformity. This was mainly due to the lack of reliable odour assessing instruments and the practical impossibility of employing sensory panels to the continuous monitoring of aroma. Electronic noses have the potential to fulfil this task. Compared to sensory panels the main advantage of electronic noses is that once calibrated they can perform odour assessment on a continuous basis with a minimal cost. Furthermore, once established this technique does not require trained personnel like a sensory panel does, is not subject to individual breakdown or variation of sensitivity [3], is not overloaded under normal operation and takes comparatively very little time.

Before the advent of electronic noses the only possible instrumental analysis of "aroma" (the mixture of volatiles present in the headspace of a product) was the identification/quantification of individual chemical compounds, after a separation step (e.g. GC–MS, GC–FID, etc.). However, the relationship between this sequential analysis and the perception of the global aroma of a product is not easily

* Corresponding author. Tel.: +41-31-3238167.
E-mail address: jacques-olivier.bosset@fam.admin.ch (J.O. Bosset).

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established since the rules governing the combination of individual chemical compounds in the generation of odours are not yet fully understood [4–6].

It should be kept in mind that instrumental analyses, whether classical such as GC–MS, etc. or by electronic nose are performed not only on odorous volatiles but also on non-odorous compounds occurring in the headspace. This can be interesting when analysing hazardous non-odorous compounds (e.g. carcinogens, toxins, solvents) but also implies that instrumentally performed classifications/analyses might not be based on aroma relevant molecules. Furthermore, hedonic assessment can not be performed by any instrument. Classification models have to be defined based on the results of sensory panels prior to performing analyses with odour significance.

2. The electronic nose concept

The name "electronic nose" comes from a certain parallel of the measurement concept of the instrument and that of the mammalian olfactory system. In the latter, upon being sniffed through the nose, or through the retro-nasal pathway when a product is tasted, volatile compounds reach the olfactory epithelium which is an area of approximately 5 cm^2 located in the upper nasal cavity. There, the interactions of odorants with the appropriate chemosensory receptors, olfactory neurons ($\sim 10^7$ belonging to $\sim 10^3$ different classes [6]) produce electrical stimuli which are transmitted to the brain [3,6–9]. A pattern recognition process assisted by the memory then takes place using all the data in order to identify, classify, or perform an hedonic analysis [9]. Evidence exists showing that a single olfactory neuron responds to several odorants and that each odorant is sensed by multiple olfactory neurons [10]. In the same way, electronic noses base the analysis on the cross-reactivity of an array of semi-selective sensors. Hence, products with similar aroma generally result in similar sensor response patterns (similar "fingerprints") whereas products with different aroma show differences in their patterns (different "fingerprints"). The sampling step is carried out either by taking an aliquot of the sample headspace, with a syringe, and injecting it into the detector, or by carrying the headspace with a gas stream into the detector. Sometimes the carrier gas is bubbled through the sample to strip out compounds. The interaction of volatiles with the array of sensors provokes a series of signals which are then processed by the computer via a pattern recognition program.

Table 1
Detection threshold levels of human olfactory systems and electronic noses

Volatile compound	Reported human threshold (ppm)	Electronic nose threshold (ppm)	Type of electronic nose	Reference
Ethyl acetate[a]	7–17[b]	5–25	Fox 3000 (12 MOS)	[27]
Butyric acid[a]	0.4–10[b]	<1	Fox 3000 (12 MOS)	[27]
Diacetyl[a]	$(4–15) \times 10^{-3}$ [b]	$(50–100) \times 10^{-3}$	Fox 3000 (12 MOS)	[27]
n-Hexanal[a]	$(10–50) \times 10^{-3}$	$(10–50) \times 10^{-3}$	Fox 3000 (12 MOS)	[27]
Methional[a]	$(2–50) \times 10^{-3}$	$(10–50) \times 10^{-3}$	Fox 3000 (12 MOS)	[27]
Furanol[a]	$(20–40) \times 10^{-6}$ [b]	$(50–100) \times 10^{-6}$	Fox 3000 (12 MOS)	[27]
n-Nonane[c]	0.2–7	<0.2	20 CP composite	[13]
n-Octane[c]	3–9	0.6	20 CP composite	[13]
n-Heptane[c]	7–13	<2	20 CP composite	[13]
n-Hexane[c]	13–30	<10	20 CP composite	[13]
n-Pentane[c]	20–50	40	20 CP composite	[13]
1-Pentanol[c]	0.13–1.3	<0.06	20 CP composite	[13]
1-Butanol[c]	0.2–1.3	0.3	20 CP composite	[13]
1-Butanol[d]	0.7	–	Aromascan (32 CP)	[1]
1-Butanol[d]		–	Fox 3000 (12 MOS)	[1]
1-Butanol[d]		+	6 Taguchi (SnO_2)	[1]
1-Propanol[c]	0.9–1.9	1.3	20 CP composite	[13]
Ethanol[c]	5–500	2	20 CP composite	[13]
Methanol[c]	13–600	3	20 CP composite	[13]
Acetone[d]	141	–	Aromascan (32 CP)	[1]
Acetone[d]		+	Fox 3000 (12 MOS)	[1]
Acetone[d]		+	6 Taguchi (SnO_2)	[1]
Ethanethiol[d]	0.1×10^{-3}	–	Aromascan (32 CP)	[1]
Ethanethiol[d]		–	Fox 3000 (12 MOS)	[1]
Ethanethiol[d]		–	6 Taguchi (SnO_2)	[1]

+: Detected at the same concentration as submitted to human noses; –: not detected (when response <3× back ground noise) at the same concentration as submitted to human noses.

[a] Concentration in water.

[b] Orthonasal analysis.

[c] Concentration in air.

[d] Concentration in vapour in equilibrium with a liquid phase at 22.5–25 °C.

A special type of system is slowly appearing in the market, the so called portable [4,11,12]. These are small instruments where the sensors array is confined to a chip. The analysis proceeds by placing the instrument near the sample. Portables can be useful in simple and well determined cases, and when interference from the surroundings are minor or constant.

Just like the human olfactory system, electronic noses do not need to be specially designed to detect a particular volatile. In fact, they can learn new patterns and associate them with new odours via training and data storage functions as humans do. However, training of electronic noses based on sensory panel classifications is required in order to obtain odour-meaningful classifications. Often the sensitivity of electronic noses is similar to that of human noses but humans are specially gifted in sensing specific compounds (e.g. thiols, biogenic compounds, pyrazines, thiazoles, some aldehydes [13]). The biological sensitivity can go down to ppt levels with a response time in the order of milliseconds whereas instruments barely go under ppb levels with a response time in the order of seconds (Table 1) [2,14].

3. Overview of gas sensors: technology and characteristics

The non-selectivity of solid state sensors (metal oxide sensors, MOS) was considered a severe drawback of this technology intended as analytical tool. Back in the early 1980s the idea of assembling arrays of such sensors with different sensitivities and selectivities was put into practice. Thus, although both the qualitative and quantitative information obtained from each sensor was highly ambiguous, their combination resulted in some sort of "fingerprint" of the sample. And with the help of statistical programs the classification of samples into groups could be achieved.

Once the concept of assembling arrays of non-selective sensors had been developed, various detection principles were tested, some of them almost accidentally as in the case of MOSFET [15]. A few of them have given consistent results and can be found on the market. Links to producers, as well as to university groups performing R&D in this field, can be found among others at the web address: http://www.nose-network.org/review/. Other types of devices have also been tried-out such as electrochemical sensors, optical fibres coated with dye-impregnated polymers, biosensors, etc. Several good papers [3,8,10,14,16–21] provide interested readers with a more extensive insight into different gas sensor technologies. A brief description of some of the commercially available sensors follows.

3.1. MOS

Metal oxide sensors consist of a metal-oxide semiconducting film (e.g. SnO_2, TiO_2, ZnO, ZrO_2) coated onto a ceramic substrate (e.g. alumina). Most often the device also contains a heating element. Oxygen from the air is dissolved in the semiconductors' lattice, setting its electrical resistance to a background level (stable when at equilibrium). During the measurement, the volatile molecules (mainly non-polar) are adsorbed at the surface of the semiconductor where they react (oxidation/reduction) with the dissolved oxygen species causing a further modification of the resistance (or conductivity) of the device. This last change is taken as the response of the system to that particular sample (Fig. 1) [10].

The sensitivity and selectivity of MOS sensors are determined by the choice of the semiconductor material. Modifications are induced by doping the semiconductor with noble metal catalysts (e.g. Pt, Pd, Al, Au), by modulating the operational temperature (e.g. 200–500 °C) or by introducing thermal gradients/cycles. Changing the particle size and the thickness of the semiconductor film has also been tried with the same aim, as well as sensor coating with a gas permeable membrane with varying thickness for enhancement of the selectivity [17]. Doped sensors show greater sensitivity to oxygenated volatile organic compounds (e.g. alcohols, ketones, etc) than to aliphatic, aromatic or chlorinated compounds [10]. Doping with Pt and Pd increases the sensitivity of SnO_2 sensors to gases such as benzene and toluene
[10].

Due to the logarithmic dependence of the sensor response on the concentration of volatiles, loss of sensitivity arises (towards low-volatile aroma compounds) in the presence of highly concentrated detectable species such as ethanol [17]. Schaller and co-workers [22–24] have reported large background drift of CP and MOS sensors and MOS sensor poisoning when attempting to analyse cheese samples of Emmental type. The poisoning of sensors was probably due to the volatile fatty acids from the cheese. The recent models in the market seem to be able to correct for drift and they usually include a temperature and humidity monitoring/control device. Higher operating temperatures apparently make it possible to cope with poisoning as they allow for a better sensor regeneration after each analysis.

3.2. CP

Conducting organic polymer sensors (also called intrinsically conducting polymer (ICP)) are made of semiconducting materials, aromatic or heteroaromatic (e.g. polypyrrole, polyaniline, polythiophene), deposited onto a substrate and between two gold-plated electrodes [25]. Upon interaction with volatile molecules a reversible change of the devices' electrical conductivity is observed.

Although mainly sensitive to polar volatile compounds, their selectivity and sensitivity can be modified by the use of different functional groups, polymer structure and doping ions [26]. Thus, composites of polymer with thermoplastic binders or glass fibres (e.g. polypyrrole with polyimide, polypyrrole with SnO_2, or with copper and palladium

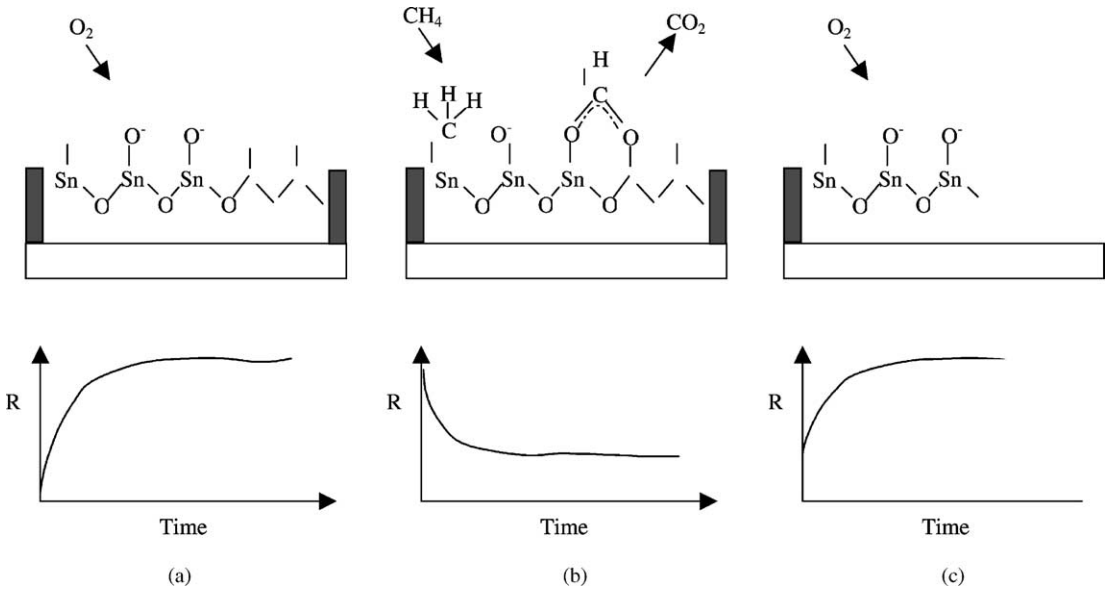

Fig. 1. Working principle of a MOS sensor. *R* on the *y*-axis represents the sensor electrical resistance or conductivity. (a) The MOS sensor in presence of air and at a given temperature. Oxygen dissolves in the sensor lattice setting its electrical resistance/conductivity to a background level. (c) Volatile compounds, in this case methane, get in contact with the sensor. Upon adsorption/absorption of volatiles on the sensor oxidation/reduction reactions take place changing the electrical resistance/conductivity of the sensor. The difference between steps (a) and (b) is usually taken as the response of the sensor to the sample. (c) The sensor is regenerated to the background level under a flux of air and is ready to analyse the next sample.

inclusions) show large responses to non-polar volatiles [17]. In addition, biomaterials such as enzymes, antibodies, and cells may readily be incorporated into polymer structures [10].

A variant of this type of sensors is based on electrically insulating polymers loaded with carbon black as an electrically conducting filler. When exposed to volatile compounds the volume of the insulating polymer increases, enlarging the distance between the conducting carbon black particles. This results in an increase in the electrical resistance [18].

Generally polymers readily absorb water vapour and, as a result, the concentration of available binding sites for other volatiles decreases drastically. This is the reason for the reduced sensitivity of CP gas sensors at high humidity levels. Some authors have suggested the implementation of "filters" to retain undesirable compounds such as ethanol or water prior to analysis [14,27], or during analysis in the case of QMB sensors [28]. The other big drawback of this technology is the poor reproducibility in manufacturing polymer sensors which is a continuing problem. However, CP-based sensors show linear responses and higher selectivities compared to MOS sensors. In contrast with MOS sensors, no poisoning effect with sulphur-containing compounds or weak acids has been observed. They show faster responses and base-line recoveries, and do not need high operating temperatures. A comparative study of sensors done by Harper [29] showed that an Alpha MOS instrument was the least sensitive to water vapour compared to two CP-based sensors, one from AromaScan and the second one from Neotronics. Whereas the system of AromaScan was difficult to operate due to the complex control of the relative humidity of samples and carrier gas, the system of Neotronics, although easier to operate, showed a reduced sensitivity.

3.3. TSM

Thickness-shear mode (or QCM quartz crystal microbalance), BAW bulk acoustic wave, and SAW surface acoustic wave sensors, consist of a piezoelectric quartz crystal, with gold electrodes, coated with a membrane which, depending on its affinity, selectively adsorbs the volatile molecules present. Adsorption of volatile compounds onto the sensing membrane increases the mass of the device resulting in a change in its resonance frequency. Selectivity and sensitivity of this type of sensor depend on the composition of the coating membrane (e.g. most frequently polymers but also biomolecules or metals) and on the operating frequency. The difference between SAW and QMB is the mode of oscillations, at the surface and in the bulk respectively, determining the available range of oscillations: SAW operate at 50–1000 MHz while QMB at 5–30 MHz. SAW devices are more sensitive but also more unstable and require a high-tech control set-up.

Different functional groups can be used as a coating membrane, offering the possibility of tailoring the sensor for the detection of specific volatiles. This represents a very interesting issue for TSM as well as for CP sensors. Indeed, combined approaches of computer (molecular) modelling and combinatorial synthesis are undertaken to obtain affinity selective sensors [30]. Another approach is the production of molecularly imprinted polymers as very selective traps for specific volatiles [31], much in the way of a key and lock

system that would work even in a noisy background. As an example, classification of enantiomers has been reported by the use of polymers with chiral functions both with CP and QCM sensors [9,17].

The reproducibility in sensor manufacture is a recurrent problem given the fact that the life-time of sensors is relatively short (e.g. 6–12 months for MOS and CP). An example of the development of new techniques of coating deposition is electrospray, instead of spin coating, for the deposition of uniform films with controlled thickness on QMB sensors [32]. Besides reproducible sensors, there is also a need for good calibration techniques so as to be able to correlate data obtained with different sensors [29,33,35].

Finally, in an attempt to broaden the applicability of gas sensors, some companies offer hybrid sensor arrays combining MOS and CP, MOS and MOSFET, MOS and MS, etc.

3.4. MS

Mass detection-based electronic noses. Although not precisely being gas sensors they can be used together with chemometric programs to obtain a fingerprint of the "aroma" of a product and to proceed to classifications. Electronic noses based on mass detection typically use a quadrupole mass spectrometer as a sensor array. Upon injection an MS pattern of the unresolved volatiles mixture is created. In other words, each mass to charge ratio (m/z) acts as a sensor that detects any molecule or fragment with that particular m/z. In this way, an MS-based electronic nose has potentially hundreds of sensors. Particular fragment ions (m/z) can be excluded from the data analysis to remove the influence of certain components such as water, ethanol, etc. In the same way, fragment ions (m/z) aroma-relevant to the case under study can be selectively chosen to be included in the data processing; provided that the aroma-relevant compounds are known. In this context, the creation of a data base of electronic nose MS spectra as suggested by some authors can be very useful, these spectra being different from those obtained for individual compounds.

A big advantage of this system over all the others is that it uses a very well-known technology [35]. The reproducibility, stability and sensitivity of mass spectrometers have long been well established. An additional advantage is that discrimination between groups provides with "relevant masses" [37]. This information may be correlated to corresponding chemical structures and further studied in combination with other techniques such as GC–MS. All these features make this system particularly interesting in the field of R&D. On the other hand, because of the bench-top type of MS electronic noses they are not foreseen as portables for in-field applications in contrast to other types of sensors [17,36].

Among related sensor techniques are electronic tongues which have recently appeared in the market. They are mentioned here because they also work by classifications based on "fingerprints". They measure organic and inorganic compounds in liquids (e.g. beverages, foods, etc.) and in some cases could be complementary to electronic noses. Typically, electronic tongues measure attributes such as saltiness, sweetness, bitterness, sourness and metallic taste [37]. So far, some interest has arisen for such sensors, for instance in the pharmaceutical field testing the capacity of masking bitterness in medications which is not readily done with a sensory panel for obvious reasons.

4. Data treatment

An essential step in the analysis with an electronic nose of any kind is pattern recognition. In fact, together with the progress in electronics, which made possible the development of sensors, it is the high performance attained by statistical programs which made possible the introduction of electronic noses. Although the best performing programs are sophisticated and, therefore, require the operation of skilled personnel, most companies have implemented user-friendly software for data treatment in commercially available electronic noses.

There exists linear multivariate analysis such as principal component analysis (PCA), discriminant factor analysis or discriminant function analysis (DFA), non-linear methods such as artificial neural networks (ANN) [38,39]. A classification can be supervised (e.g. DFA) or non-supervised (e.g. PCA), in other words based on predetermined groups or not. A parametric classification is very seldom possible. Usually the inclusion into a given group is determined by the Euclidian or the Mahalanobis distance. The latter takes into account the actual shape of the group whereas the former assumes that the data points belonging to the group are evenly distributed in a sphere around the centre of the group (Fig. 2). Only a short description of some of the most frequently used pattern recognition methods is given here. Readers are referred to specialised literature for more information.

PCA is a linear combinatorial method which reduces the complexity of the data-set, from the initial n-dimensional space (n sensors) to a few dimensions. The inherent structure of the data-set is preserved while its resulting variance

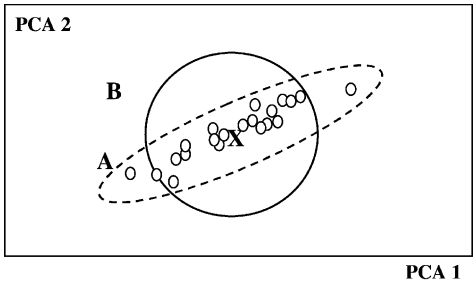

Fig. 2. Representation of Euclidian (solid line) and Mahalanobis (dotted line) distances. There are two outlayers according to Euclidian distance and none according to Mahalanobis distance. A and B are equally far from the group according to Euclidean distance, whereas A is closer to the group than B according to Mahalanobis distance.

is maximised. In other words, data points will be scaled along new dimensions, linear combinations of the initial dimensions. The magnitudes of the coefficients, in the resulting linear combinations, give an indication of the relative importance of the initial dimensions in the data structure. PCA is performed with no information on the classification of samples. It is based solely on the variance of the data-set.

On the other hand, DFA is based on a priori data classification. The linear combinations maximise the contribution of those dimensions that generate the largest difference between predetermined groups. With this method, different classifications on the same data-set are possible, following different properties (e.g. freshness, fruitiness, etc.). Particular care should be taken however to avoid over-fitting of errors, i.e. classifications based on noise rather than on real differences. The resulting DFA classification is highly dependant on the data-set used for training, i.e. it is important to verify the size of the training data-set in terms of the complexity of the groups.

ANN methods are very powerful and are inspired by the way the mammalian brain processes information. Supervised classifications are common with ANN. The non-linear character of this method makes it interesting specially for non-linear technologies such as MOS [1]. Future developments will probably include adaptive neural networking, hybrid intelligent models based on Fuzzy-NN or Genetic algorithms-NN, specially aiming at automated industrial applications [40].

In all cases, to avoid classification errors, the ratio of data points (analyses) to variables (sensors), employed in the pattern recognition, should be at least three, but preferably six [36]. Thus, replication of samples five to eight times is usual in order to obtain a large number of data points as well as to ascertain the repeatability of the measurement. Since individual analyses are performed within a few minutes, or even seconds with any of the systems currently available, and also because automatic sampling devices are generally implemented, the total analysis time remains competitive compared to other analytical techniques such as GC–MS. Model validation with data points not used for the generation of the model is also recommended [36], as well as randomisation of sample analyses to avoid systematic errors. Some authors have tried data pre-treatment to reduce noise, and data correction to target a given classification by the use of reference standards chosen among the key compounds under study [41,42]. Although so far absolute calibration is still lacking, calibration with reference compounds allows for correction of drift as well as for instrument to instrument matching [29,34,38].

5. Additional factors affecting the analysis

Very often the importance of the sampling step is ignored. Nevertheless the quality of the analysis can be greatly improved by adopting an appropriate sampling technique.

Aroma compounds are typically small hydrophobic organic molecules, with a relatively low molecular mass, from 30 to 300 amu, and often with a single polar group. Volatility is reduced with higher molecular mass or higher molecular polarity. Although little is known about the process underlying odour sensing, there is some evidence that the size and the shape of molecules are more relevant with regard to odour recognition than the chemical function or the position of the chemical function in the molecule [24].

The concentration of a given compound, i, in the headspace of a sample is given by the partition coefficient K_i:

$$K_i = \frac{C_{i(\text{gas})}}{C_{i(\text{matrix})}}$$

where $C_{i(\text{gas})}$ and $C_{i(\text{matrix})}$ are the concentrations of compound i in the gas phase and in the sample, respectively. By displacing the equilibrium, i.e. by trapping the gaseous compound i with a polymer for instance, more of this compound must volatilise to restore the equilibrium. This extraction (dynamic headspace sampling) performed prior to analysis will potentially help the detection of compounds with a low volatility. In any case, the concentration of most of the volatiles will be increased depending on the affinity of the trap for the different volatiles and on the different equilibria taking place [5,43–45]. Among commercially available devices for this purpose are: solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), etc. The SPME is a fibre of fused silica coated with 1–3 polymers. The fibre is carried into a needle and is exposed only for physical–chemical sorption/desorption of volatiles during sampling and during measurement. The twister (SBSE) is a magnetic bar coated with polymers, which can be held in the headspace for sampling. Its loading capacity is much higher than that of SPME. The coatings can be chosen depending on the polar groups or the size of the targeted compounds. Among available polymers used for coatings are: polydimethylsiloxane (PDMS), polyacrylate (PA), carboxen (CAR), etc. Other devices use porous traps such as Tenax. More information is available in the specialised literature and is not given here as this is beyond the scope of this article.

The effect of the matrix on the release of aroma is well known. Steinhart and co-workers [5,46] showed that there is a decrease in the concentration in the headspace of volatile 2,3-ethyl-5-methalpyrazine (roast smell) with an increase in the fat level in a coffee matrix. In general, most organic flavour compounds are readily adsorbed and solubilised in lipids, depending on their lipophylic character. Proteins present in the matrix may influence the volatility of flavour compounds via weak Van der Waals interactions or by the formation of amides, esters and salts. Polysaccharides can hinder the volatility of certain compounds whereas other carbohydrates such as mono and disaccharides may cause a salting-out effect [5,46].

Other parameters that influence the volatility of compounds are: temperature (most samples release volatiles better at higher temperatures), equilibration time and to a lesser extent pressure, pH-value (molecules can pass from a polar state to a non-polar state and vice versa by changing the pH [47]), ionic concentration (sometimes the addition of a salt provokes a "salting-out effect", increasing the volatility of certain compounds), surface area (grinding of a solid, mixing of a liquid). When analysing with electronic noses, the aim is very often the classification of samples into different groups. In such a case it is important to maximise differences even if samples are slightly denatured during the analysis (by temperature, changes in pH, etc.) as long as the same treatment is used for all samples.

Finally, changes in atmospheric temperature and humidity may influence not only the sensors response but also the concentration of volatiles in the gas phase.

6. Applications to the dairy industry

A list of recently reported applications of electronic noses to dairy products is given below.

6.1. Ageing of milk and shelf-life prediction

The headspace of milk typically presents a complex mixture of organic volatiles (e.g. acetone at overwhelming concentration, hexanal, 2-butanone, toluene, limonene, heptanal, styrene, chloroform, etc.) at varying concentrations and with a high percentage of relative humidity. Furthermore, the matrix is highly heterogeneous containing different levels of lipids, proteins and carbohydrates.

Correct classification of groups of different ages was obtained for UHT [48,49] and pasteurised milk [48]. Groups of UHT milk aged 1–8 days, and 1–3 days of pasteurised milk were classified by PCA performed on normalised data. A home-made MOS sensors array was used (five SnO_2 thin film sensors, of which four were doped with Ni, Os, Pt and Pd). 10 ml of milk were placed in 20 ml vials, four to five measurements per sample. Samples were incubated 15 min at 30 °C during analysis, the headspace was carried into the injector with a flow of N_2 (where the total gas flow was 100 sccm N_2/100 sccm dry air), sensor temperature was set at 250 °C. Sensors showed a response and recovery time of 2–3 min.

Shelf-life prediction of 2%-fat pasteurised milk and whole-fat chocolate milk was obtained with a home-assembled SPME–MS–MVA system (solid phase microextraction, mass spectrometry, multivariate analysis) [50,51]. 3 ml of milk sample and 5 μl internal standard (10 μg/ml chlorobenzene) were placed in 6 ml vials. A 75 μm Carboxen/PDMS SPME fibre was used. Samples were incubated 20 min at 50 °C during fibre exposure, otherwise they were stored at 7.2 °C. The injector temperature was set at 275 °C and the transfer line followed a temperature program between 150 and 180 °C. The measurement of milk volatiles lasted not more than 7 min. Eighty-four samples of milk and 73 samples of chocolate milk were used, taken directly from production lines over a 7-month-period. Twenty samples of each set were used for model validation solely. Mass intensities were normalised by the intensity of chlorobenzene (*m*/*z* 112). Partial least-squares modelling predicted sample shelf-life with respect to sensory results with an accuracy of ±0.62 and ±0.88 days and a correlation coefficient of 0.9801 and 0.9832 for milk and chocolate milk, respectively. A significant increase in concentration with ageing was detected by GC–MS for certain volatiles such as: dimethyl sulphide, 2-heptanone, ethyl acetate, pentanal, pyrrolidine, hexanoic acid, 2-methyl-butanal, furfuraldehyde, etc. [51].

6.2. Classification of off-flavours in milk

Oxidation off-flavours in milk originate mostly from bacterial metabolism, enzymatic activity, photo-oxidation, heat, and oxidation catalysed by chemicals such as sanitizers for production lines or pro-oxidant metals (copper, iron and nickel) [51]. Exposing milk to light induces two major effects: The first 2–3 days a burnt oxidised flavour develops probably due to the degradation of sulphur-containing amino acids from the whey into methional (relatively unstable), mercaptans, sulphides and disulphides (e.g. dimethyl disulphide from methionine) [52]. After the second day a persistent metallic, cardboard-like off-flavour occurs, attributed to the autoxidation of unsaturated fatty acids (β-oxidation) by the formation of free radicals induced by light. On the other hand, heat provokes a typical boiled off-flavour probably resulting from the formation of sulphur compounds. Great efforts have been devoted to the optimisation of UHT milk processing in order to avoid this effect. In general, low molecular weight aldehydes, ketones and fatty acids are responsible for most off-flavours observed in foods and beverages of which hexanal is the major by-product of the degradation of linoleic acid (major polyunsaturated fatty acid in milk) upon exposure to light.

Marsili has published several papers on the discrimination of off-flavours in milk [42,45,50–52]. The system used was a prototype SPME–MS–MVA system above described. PCA correctly classified the set of samples by the origin of off-flavours: sanitizer-contaminated, copper-contaminated, spoiled by bacteria and fresh 2%-fat milk samples. Prior to analysis, samples were conditioned at 19 °C for 16 h except for fresh milk control samples, and then heated at 45–50 °C during the 12–15 min of fibre exposure (75 μm Carboxen/PDMS SPME fibre). Masses corresponding to volatiles normally present in non-defective milk were disregarded (e.g. acetone, 2-butanone) and intensity of masses from target compounds were amplified (e.g. *m*/*z* 127, 142 and 94, this last one corresponding to dimethyl disulphide). The intensities of all masses were normalised by the intensity of the internal standard (4-methyl-2-pentanone, *m*/*z*

100). A fairly steady increase in pentanal and hexanal was observed with increasing exposure time to 200 ft^3 of fluorescent light (typical light exposure of milk in supermarket dairy cases) [52]. Typically, hexanal and dimethyl disulphide were found to be good indicators of light damaged milk, whereas pentanal, isopentanal, hexanal, heptanal, octanal, nonanal, and 1-octen-3-one usually indicated copper induced oxidation in milk [45].

The application of an electronic nose to the study of boiled off-flavour in UHT milk was performed with an NST 3220 which typically uses MOSFET, MOS, and QMB sensors (CSP, UK) [53]. Different dilutions of boiled milk in pasteurised 0.5%-fat milk were prepared. 40 ml of each mixture were placed in 100 ml bottles and incubated for 30 min at 20 °C. During incubation a 60 ml/min flow of ambient air (filtered by active charcoal) carried the headspace into the injector. Each dilution was prepared four times. PLS analysis (partial least square) was able to discriminate down to 10% of boiled milk into reference milk, compared to 30% for a sensory panel.

Di Natale [54] reports a correct discrimination between UHT and pasteurised milk with a home made electronic tongue based on metaloporphyrin whereas a QMB sensors array, based also on metaloporphyrin, failed.

An eNose 4048 with 12 CP sensors (Neotronics, UK), was used to distinguish between different intermediate products during process of block-milk (milk and sugar mixture evaporated to powder, used in the preparation of milk-chocolate) [55]. Eight samples were taken at the different drying and concentrating stages, from the initial raw material (milk and sugar mixtures with 20 wt.% dry matter) to the final block-milk product (97.8 wt.% dry matter). 60.0 g of sample were mixed with an equal amount of MilliQ water just before analysis. No control of the relative humidity in the electronic nose was undertaken. The response values were taken after 3 min of signal recording. The results correlate well with GC–MS and sensory analysis. PCA analysis showed some association to descriptors such as caramel, nutty, burnt and chocolate, typical of volatiles generated by Maillard reactions during heating.

An unusual type of off-flavour was detected in milk from cows bearing a genetic defect. The loss of FMO3 enzyme activity apparently hinders the oxidation of trimethylamine (TMA) into a non-odoriferous compound. Thus, TMA concentrates in milk to significant levels resulting in a disagreeable fishy off-flavour. Parametric classification of trimethyl amine concentration in pasteurised milk was obtained with an MS-based electronic nose, SMart Nose^{TM} (LDZ,CH) [47]. 7.5 g of milk and 150 μl of 5 mol/l NaOH were placed in 10 ml vials. After conditioning at 60 °C for 16 min 2.5 ml of headspace were sampled with a syringe and transferred into the injector. Three to five vials were prepared from each sample. Normalised data were processed with a PCA based on *m/z* 58 and 59. Modelling with calibration samples (several concentrations of synthetic TMA in fresh non-defective UHT milk) enabled the execution of a parametric classification (Fig. 3). The intensity of the ionic mass of TMA, *m/z* 59, was also used for quantification, the results corresponded

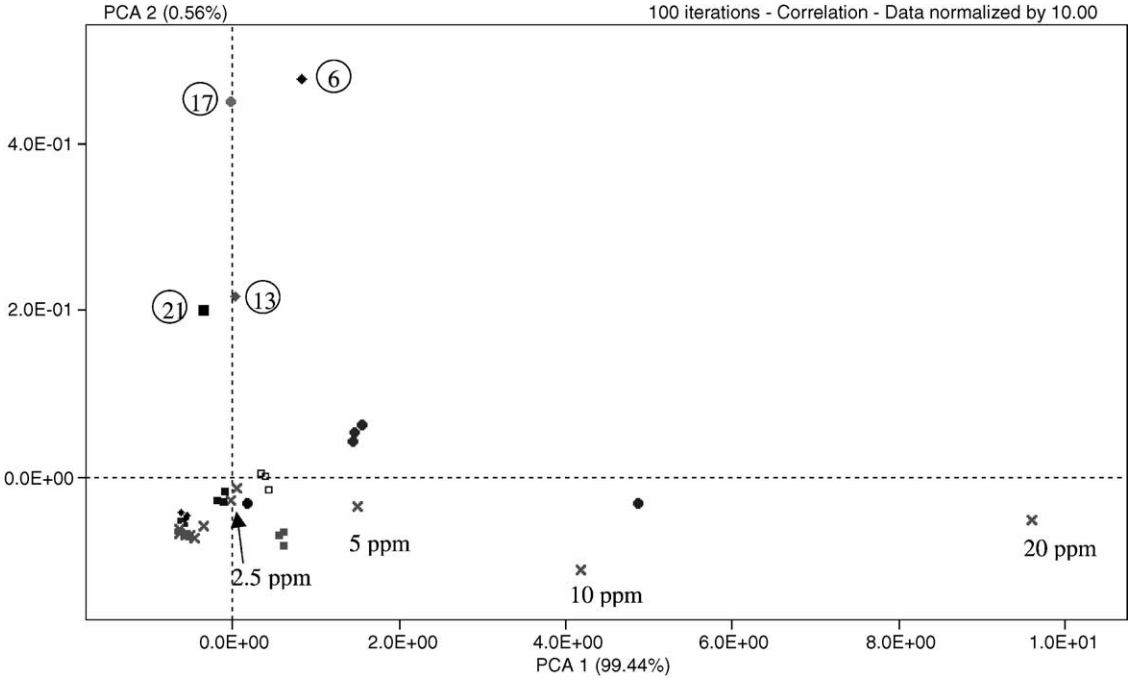

Fig. 3. Parametric analysis of trimethylamine concentration in milk (fishy off-flavour) performed with an electronic nose based on mass spectrometry. The PCA is based on the ionic masses 58 and 59 amu. Symbol × represent calibration solutions in milk with increasing concentration from left to right (low concentrations are better visible in an expanded figure, not shown). Symbols other than × represent milk samples. Samples numbered 6, 13, 17 and 21 show an additional off-flavour. Reference [4] shows a similar figure obtained with a smaller number of iterations.

well to the parametric ones. These results were also validated by a sensory panel and GC–MS analyses. Actually, the MS-electronic nose showed a better sensitivity (sub-ppm) than the other two methods (ppm). Additionally, the system detected further off-flavours in a few samples, also detected by the sensory panel but not by the GC–MS method. By the addition of NaOH the pH-value of the sample was strongly increased resulting in an increased volatility of the TMA, which otherwise is in an ionic state at the normally slightly acidic pH of milk.

6.3. Classification of bacteria cultures in milk

Microbial milk spoilage causes not only undesirable off-odours but can even develop some toxicity. It has been shown that some bacterial species such as *Bacillus cereus*, *Pseudomonas fragi*, *Pseudomonas perolens* and *Bacillus pumilus* produce volatile compounds such as 3-methyl-1-butanol, ethyl butyrate, ethyl 3-methylbutanoate, ethyl hexanoate, acetyldehyde, acetic acid, ethanol and other alcohols, etc. [40].

Magan et al. [40] used an electronic nose composed of 14 CP sensors, BH-114 (Bloodhound Sensors Ltd., UK), to investigate the early detection of spoilage bacteria and yeast in milk-based media. Inoculums of 10^3–10^4 cells/ml were mixed with 15 ml of 10% skimmed milk in 50 ml bottles, with three vials per sample. All samples were allowed to equilibrate for 30 min at ambient temperature, in some cases a further incubation was performed at 30 °C prior analysis. The headspace was carried by a flow of 200 ml/min of carbon filtered air into the injector. Response values were taken as the difference between the signal measured 15 s after beginning sample injection and 22 s after beginning sensor regeneration. Sensors showed <10% background drift. DFA correctly discriminates between unspoiled milk, control-milk (with butanol addition) and two different cell concentrations (2 and 5 h incubation) of *Staphylococcus aureus* or *Kluyveromyces lactis*. Different concentrations of *Pseudomonas aureofaciens* were also correctly classified with a DFA analysis: 0, 10^6, 3.5×10^8, 8×10^8 cells/ml and butanol control-milk. A correct classification of individual strains after 5 h incubation was performed by DFA on *C. pseudotropicalis*, *S. aureus*, *K. lactis*, *B. cereus*, *Pseudomonas* spp., unspoiled skim milk and butanol control-milk. A model was built with a three-layer back-propagation NN which was successfully cross-validated.

Haugen [14] used an NST 3220 instrument consisting of 10 MOSFET, 5 MOS and 1 IR-based CO_2 sensor (Nordic Sensor Technologies, S) for the discrimination of three different disinfection–resistant bacteria (*Pseudomonas*, *Cedecea* and *Serratia*) as well as a mixture of all three strains cultured in milk. Only the *Pseudomonas* culture showed clear differences from the others. The identification of growth phases of lactic acid bacteria could be performed with this system [14].

Marsili [42] also reported the use of an in-house-assembled system, SPME–MS–MVA, described above, for the classification of cultures of *Pseudomonas fluorescens*, *P. aureofaciens* and *P. putrefaciens* in milk. They all had a Cheddar cheese-like odour.

6.4. Classification by the cheese variety

A Fox 2000 with six MOS sensors (Alpha MOS, F) was used for the discrimination of four different Swiss cheese samples (0%-fat, 33%-fat, sharp and bland) together with a Jarlsburg cheese [29,56]. 5 g of grated cheese were placed in glass vials, with four replications per sample. Samples were incubated at 40 °C for 30 min. The carrier gas was compressed air flowing at 250 ml/min. Data were recorded for 1 min. Sensor recovery time was 7 min. Discriminatory analysis produced a correct classification in agreement with sensory and SPME-GC–FID analyses. The latter was based on the intensity of acetic, propionic, butyric, isovaleric and hexanoic acids, known as key compounds in Swiss type cheese flavour. The use of two additional compounds (acetoin and octanoic acid) resulted in a similar classification whereas the increase in the number of volatiles used in the discrimination to 30 resulted in failure.

6.5. Detection of “rind-taste” in Swiss Emmental cheese

Schaller et al. [57] unsuccessfully tried to detect defective (rind taste) Swiss Emmental cheese samples with an NST 3320 instrument (Nordic Sensor Technologies AB, Linköping, S). This electronic nose was equipped with 10 MOSFET and 12 MOS sensors. However, a GC–MS analysis did not show any compound that would be responsible for off-flavours. Also, a sensory panel was unable to detect any off-flavour. The rind taste in defective cheese samples was evident only by tasting probably due to a negligible volatility of the compounds responsible for the taint.

6.6. Classification by the geographical origin of a dairy product

The objective is to classify samples of a given product by their place of production. In this case differences in the composition of volatiles are expected to originate from “minor” variations in the production technology, raw materials or produce conditioning.

Five samples of caseinate from three different suppliers were classified with a FOX 4000 based on MOS sensors (Alpha MOS, F) [58]. 0.2 g of sample were placed in 10 ml vials. Samples were incubated at 70 °C for 15 min. Thereafter, 2 ml of headspace were injected with a 150 ml/min flow of dry air. The acquisition time was 120 s. PCA and DFA analyses correctly classified samples from the different suppliers. Results were validated with unknown samples. A sensory analysis found differences in quality between the different suppliers.

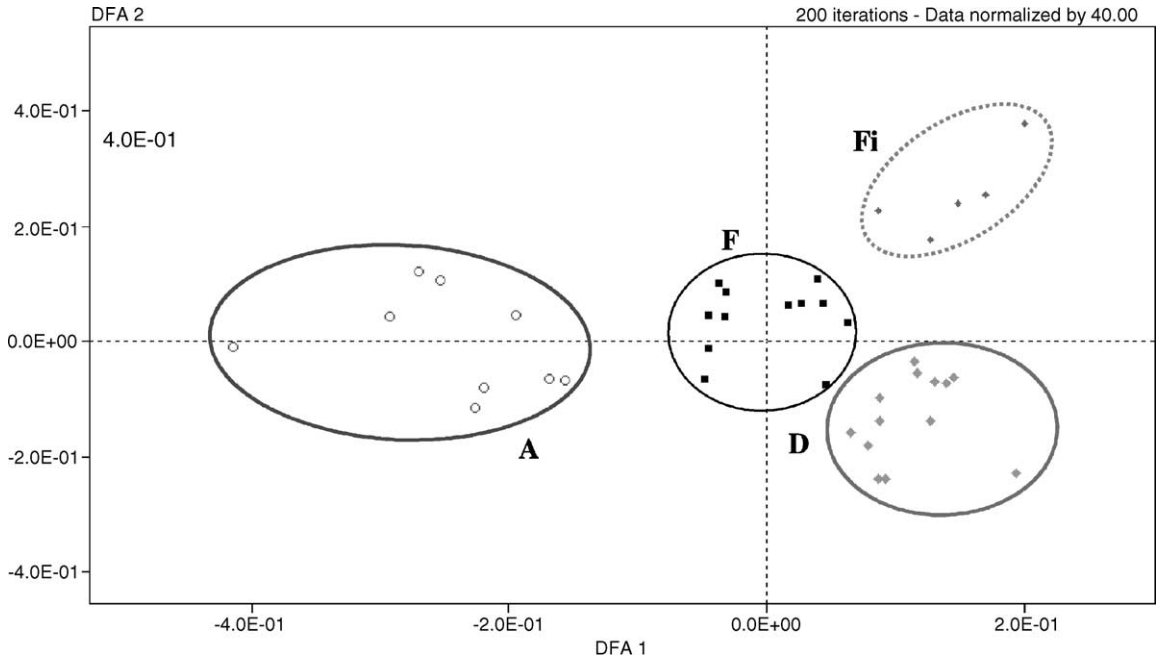

Fig. 4. Classification of Emmental cheese by the geographic origin performed with an electronic nose based on mass spectrometry. The graph shows DFA 1 vs. DFA 2 with 100% group classification based on five variables. No validation set was considered due to the limited number of samples. A: Austria, D: Germany, F: France, Fi: Finland.

A good classification was also performed by another Fox system on two different brands of whole UHT, skimmed UHT and half-creamed UHT milk [59]. In addition, a whole and a half-cream pasteurised milk were identified as a separate group from the set of UHT samples.

The classification of Emmental cheese based on geographical origin was explored with an MS-based electronic nose, SMart Nose™ (LDZ, CH) [60]. Twenty samples (2.5–4 months old) from different European countries were analysed: Austria, France, Finland, Germany and Switzerland). 4 g of grated cheese were placed in 10 ml vials, with 3–5 replicates per sample. Samples were incubated at 90 °C for 30 min but the rate of analysis was only 3.5 min thanks to automated sampling and a multiple-vial incubating device. PCA and DFA analyses gave 90–100% classification rates for different sets of groups (Fig. 4) whereas a sensory panel analysis failed in the classification probably due to too short a ripening time for full aroma development.

6.7. Classification of cheese by the ripening stage

An AromaScan electronic nose (Electra House, UK) with 32 PC sensors was used to discriminate two different Pecorino Toscano cheeses (ewe's cheese), which differed mainly in their maturation time [61]. 10 g of the ewe's cheese were placed in 500 ml Duran bottles (12 and 15 samples, 20 days and 4 months old, respectively), with three replicates per sample. Samples were allowed to equilibrate at room temperature for 30 min prior to analysis. The headspace was directed to the sensors by a constant air flow kept at 50% humidity. Sammong mapping gives a fairly good discrimination between 20 days and 4 months old samples. These results are comparable to those obtained with a purge & trap GC–MS–PCA whereas Curie-point pyrolysis mass spectrometry failed. The GC–MS–PCA analysis was based on hexanal, acetic acid, 2-butanone and tetrahydrofuran peaks.

Several instruments were tested for the classification of Swiss Emmental cheese by ripening stage [23]. A QMB6 with six QMB sensors (HKR Sensorsysteme, D) and the 12 CP sensors of an eNose 5000 (Neotronics, UK) gave unsatisfactory results, probably due to a low sensitivity and a large drift of CP sensors. A SMart Nose™ based on mass spectrometry (LDZ, CH) showed only partial classification, whereas the eight MOS sensors of the eNose 5000 and the 10 MOSFET + 5 MOS sensors of a NST 3220 (Nordic Sensor Technologies, S) showed correct classifications of samples ripened for 1, 21 and 98 days.

Capone et al. [62] explored the response of a thin film MOS sensor (SnO_2) to Parmesan cheese. They found a significant response difference when analysing fresh and 30 days old (with mould) cheese samples.

7. Concluding remarks

Although still under development, electronic noses can potentially be applied to process control and monitoring, acceptance or rejection of raw material, intermediate and final products, assistance in the development of new products, as well as to the assessment of synergistic effects of individual odorants.

Most of the reported applicability studies of electronic noses to different aspects of quality assessment in dairy products show satisfactory results. Published literature reports the classification of dairy products by sample type with MOS sensors; by ageing with MOS, CP and MS-based instruments; by geographic origin with an MS-electronic nose; by processing stage with CP sensors. A successful model for milk shelf-life prediction was implemented with a MOS system. The identification and classification of different types of quality-deterioration have also been published: different off-odours in milk with an MS-based tool, lower quality of casein samples with MOS sensors, identification of microbial contamination in milk with CP, MS, etc. Nevertheless, in most cases the results will have to be confirmed on a larger scale to make sure that the classifications obtained are still valid with a larger intra-group variability, which is generally found in the case of natural products.

It is interesting to note that classifications performed by gas sensors are not directly based on chemical features, in practice only MS-based electronic noses can provide some chemical information related to the differentiation of groups of samples. Adequate sampling techniques can improve the signal to noise ratio by improving the volatility or by increasing the concentration of discriminating compounds with odour relevance, e.g. use of SPME, a given pH, etc. The development of standard calibration techniques should improve the universal applicability of this type of instruments.

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Biography

Silvia Ampuero obtained a chemical engineer degree from the Swiss Federal Institute of Technology (EPFL), Lausanne, in 1989. She acquired a PhD degree from the Materials Department of the same institution in 1995. Since 2001 she has been working in the field of aroma analysis, specialising on instrumental analysis of volatile compounds, particularly of dairy products, at the Swiss Federal Dairy Research Station.