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Practical Experience with 'Electronic Nose' Systems for Monitoring the Quality of Dairy Products

Emmanuelle Schaller^{a)*}, Jacques O. Bosset^{a)} and Felix Escher^{b)}

Abstract. The present paper reports some practical experience acquired by testing five sensor technologies and four instruments over approximately one year with Swiss Emmental cheese samples of different stage of ripening. Up to now, the metal-oxide semiconductor (MOS) technology has given the best discrimination between the measured samples. However, sensors of this type seem to be damaged by short-chain fatty acids released from Swiss Emmental cheese. Organic conducting polymer sensors showed a poor sensitivity to volatile components of cheese, the main problem being a rapid drift of the sensors. The response of quartz microbalance sensors was too weak to detect differences between cheese samples. Discrimination using a newly designed mass-spectrometry system was difficult due to the low sensitivity of this instrument for the volatile compounds of cheese. Metal-oxide semiconductor field effect transistor sensors did not give good discrimination between the samples. However, their combination with MOS sensors seems to produce a favourable system for application in cheese evaluation. Further studies with other types of cheese and other dairy products are still necessary to define reliable and practical applications of this analytical tool in the dairy industry.

1. Introduction

Quality evaluation of intermediate and final dairy products is mandatory for the introduction of new technologies for raw-material treatment, process optimisation of lactic acid fermentation and new methods of cheese ripening. Quality monitoring has to correspond to the sensory evaluation of food products. Non-sensory methods, which describe sensory properties in a reliable way and, at the same time, may be used for rapid on-line and on-site quality control, are of particular interest.

Traditionally, the evaluation of volatile flavours by non-sensory, *i.e.*, instrumental means, has been carried out by GC analysis. Here, one or more GC peaks in the chromatogram are related to the senso-

ry score by various statistical methods. By this procedure, key values for the odour properties of any food products are obtained, and different products could be compared with each other and the differences elucidated.

In the eighties, a novel method for odour evaluation was developed at the University of Warwick (UK) [1]. The combination of non-selective gas sensors and pattern-recognition techniques (often called 'electronic' or 'artificial nose') has provided analysts with the means to 'measure' odour objectively based on human perception. Improvements in gas sensors based on several physical principles and intelligent network systems have led to the introduction of a series of commercially available electronic nose instruments. At present, the main sensors are based on the following principles: metal-oxide semiconductors (MOS), metal-oxide semiconductor field effect transistors (MOSFET), organic conducting polymers (CP), bulk acoustic wave (BAW), also called quartz microbalances (QMB), and mass spectrometers (MS) (for detailed working principles, see [2]).

Electronic nose systems are described to be useful for the quality assurance for a variety of products in the food industry.

The suitability of electronic noses to discriminate odour has been tested for several types of food products, among them roasted coffee, beer, grains, fruits and meat preparations [2a][3]. Preliminary results on the use of an artificial nose for the evaluation of cheese and dairy products have been published [2f][4]. However, these data sets are still very limited, and many more products have to be measured and compared with sensory analysis by experts or panels before the system can be introduced as a routine tool for quality-control purposes in the dairy industry. In particular, a well-defined methodology for the early screening of potential off-flavours is lacking.

The present report deals with a sub-project (5002-44551) of the module 'Food-Related Biotechnology' within the 'Swiss Priority Programme Biotechnology' of the *Swiss National Science Foundation*. The aim of this project is, firstly, to test the above-mentioned sensor technologies in order to select the most appropriate one(s) for dairy applications. In a second step, the discrimination potential and reliability of the system(s) will have to be investigated in order to evaluate the flavour quality of raw, intermediate and final dairy products with specific applications as proposed by

*Correspondence: E. Schaller

^{a)} Federal Dairy Research Station of Liebefeld
Department of Chemistry
Schwarzenburgstrasse 161
CH-3003 Bern
Tel.: +41 31 323 08 03
Fax: +41 31 323 82 27

E-Mail: Emmanuelle.Schaller@fam.admin.ch

^{b)} Swiss Federal Institute of Technology (ETH)
Institute of Food Science
CH-8092 Zürich

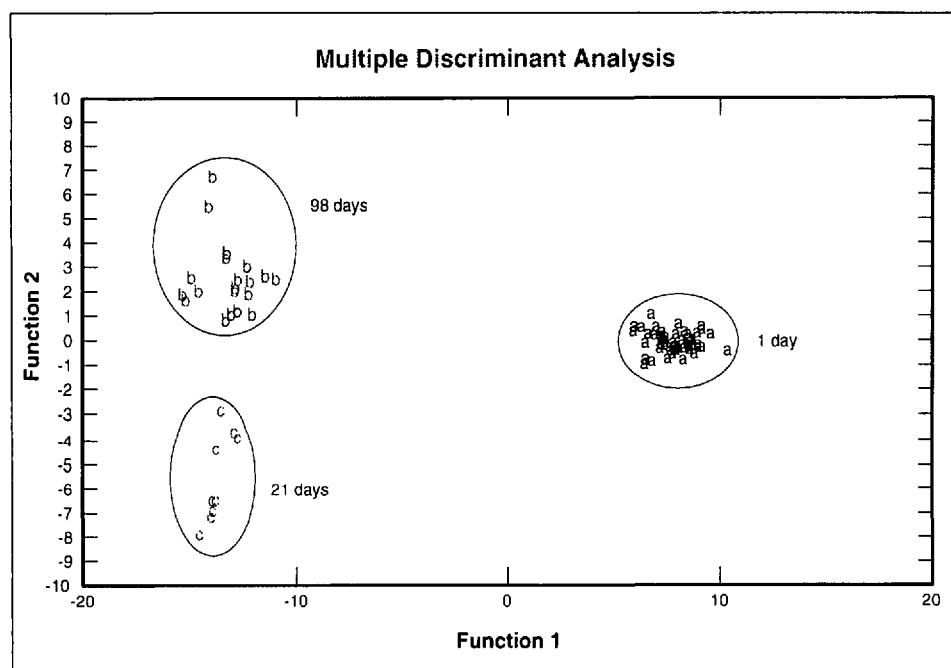


Fig. 1. MOS-sensor-based discrimination between Swiss Emmental cheeses after 1, 21 and 98 days of ripening. The cheese producers are pooled.

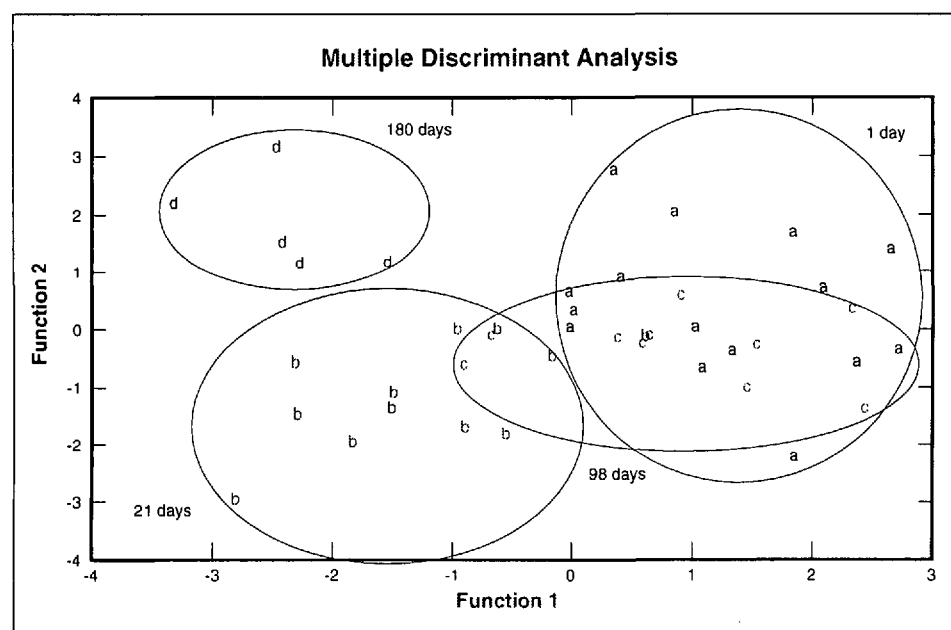


Fig. 2. Tentative CP-sensor-based discrimination between Swiss Emmental cheeses after 1, 21, 98 and 180 days of ripening. The cheese producers are pooled.

the Swiss dairy industry. Emphasis is laid on early detection of off-flavours or precursors thereof during cheese processing and ripening.

2. Evaluation of Different Sensor Technologies and Electronic Nose Systems

After a careful evaluation of the main instruments available on the market in 1997, the following four instruments were selected and tested: 1) *eNose 5000* from *EEV* (formerly *Neotronics*, UK) with 12 CP and 8 MOS sensors, 2) *QMB6* from *HKR Sensorsysteme* (D) with 6 QMB (or BAW) sensors, 3) *NST 3220* from *Nordic Sensor Technologies* (S) with 10 MOS-

FET and 5 MOS sensors, and 4) *SMart Nose™* from *LDZ* (CH) based on a mass spectrometer (MS).

Five sensor technologies on four different instruments were tested with the same Swiss Emmental cheese samples. The aim of these tests was to differentiate cheese samples at four different ripening stages, *i.e.*, after 1, 21, 98 and 180 days, respectively. Because of the specific characteristics of each instrument, new parameters were defined each time in order to obtain optimal sensor responses. Among the parameters which could be modified, the most potent factors on the sensor responses were found to be the incubation time and temperature of the samples. Other parameters, such as the gas flow rate or gas pressure, had less impact on the sensor

responses. The humidity factor could not be monitored on the tested instruments. All sensor technologies showed a very fast response within a few seconds. The sensor regeneration time was usually the most time-consuming step of the measurement process, from a few seconds for QMB sensors, to 15–20 min for CP and MOS sensors. The tests gave the following main results:

- The MOS sensors were very efficient in discriminating samples (*Fig. 1*) but seemed to suffer from unexplained poisoning effects.
- The CP sensors showed poor sensitivity to the volatile components of cheese. Therefore, the discrimination between the four ripening stages was not satisfactory (*Fig. 2*). Discrimination be-

tween the four ripening stages was only possible when a single production site was considered. When different production sites were pooled together, the differences between the factories were nearly as large as the difference between the different cheese ages. A rapid drift of the sensors presented the main problem with this technology. Differences in the baseline as well as in the response values could be observed from one hour to the next. This drift

was all the more obvious because the sensor responses were quite low, which implies a low response-to-drift ratio.

- The QMB sensors were not even able to discriminate between cheeses ripened for 1 day and 180 days (Fig. 3). The reproducibility was good but the sensitivity of the sensors was too low to detect differences between the measured cheese samples.
- Discrimination using the MS system was difficult due to the low sensitivity

of this instrument for the volatile compounds from the cheese, even at a high incubation temperature (90°) (Fig. 4).

- The MOSFET sensors alone did not give good discrimination. However, in combination with MOS sensors, as is done on the *NST 3220* system, they seem to provide a good system for cheese applications (Fig. 5).

This test series leads to the principal conclusion that the MOS sensors are the most efficient tools for discriminating between the four stages of ripening. The other tested sensor technologies gave responses which were too low to provide good discriminations.

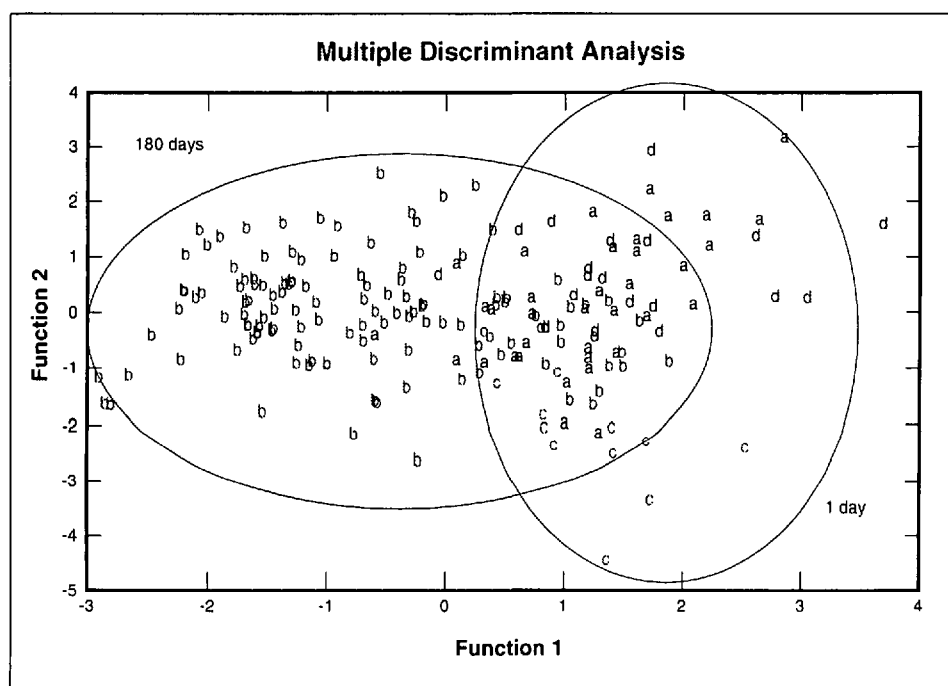


Fig. 3. Tentative QMB-sensor-based discrimination between Swiss Emmentaler cheeses after 1 and 180 days of ripening. The cheese producers are pooled.

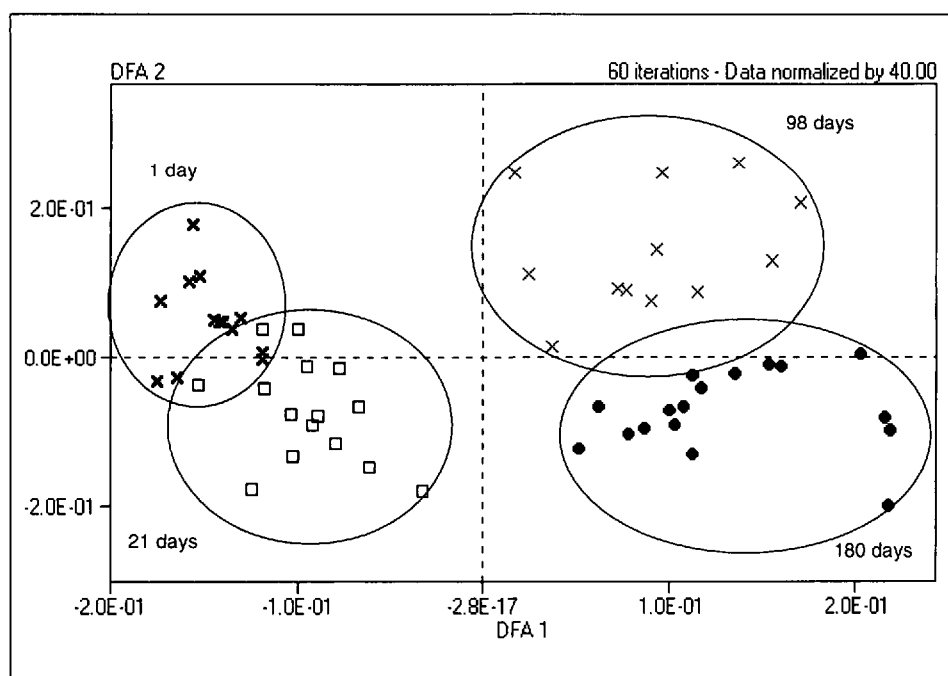


Fig. 4. MS-based discrimination between Swiss Emmentaler cheeses after 1, 21, 98 and 180 days of ripening. The cheese producers are pooled.

3. Encountered Problems and Trouble Shooting

Each tested system comprises two parts: *i*) the hardware with the sensor chamber(s) and the corresponding electronics, and an autosampler which is implemented in most instruments in order to receive more reproducible results; and *ii*) a software to monitor the hardware and to analyse the data. Both parts still need improvement and may cause irritation to the user due to improper working processes. An exception is the *DANI* autosampler from the *QMB6* system, which was already developed some years ago as a GC autosampler. Our tests showed that the currently available commercial electronic nose instruments are still prototypes. Consequently, a lot of technical problems still occur with these systems, and the user should not expect to obtain an instrument which can be used like a GC, IR or any other well-established analytical instrument. A lot of time and effort is necessary to identify and solve the emerging problems.

In addition to the numerous software crashes, the user should also expect to face hardware failures, including the autosampler. The most common autosampler failure is probably the positioning problem, in which the instrument is not able to find the vial or the injection port of the electronic nose. We also encountered difficulties due to the fact that the manufacturer himself was not fully aware of possible malfunctions of his system. For example, the syringe of the autosampler is supposed to be purged with the carrier gas through a small hole at the top of the syringe after each injection. However, the positioning of this hole is not always correct, and therefore, depending on the particular syringe used, the purgation may or may not be performed. The syringe manufacturer has now corrected this defect on the new syringes.

We had another negative experience in trying to find suitable septa for the vials. For volatile-compound analyses, septa should be completely tight and chemically inert. For these reasons, we had chosen septa made of a *Teflon* disc for neutral odour, and inserted in a butyl coating for tightness. Measurements performed with this type of septum often ended by the needle being bent. After having damaged three needles in a row, we found that the *Teflon* disc was too hard. The motor moving the syringe did not have enough strength to completely pull the needle out of the septum, which bent it during the next move.

Concerning the sensors themselves, we noticed that all types of technologies suffer from a drift of the baseline values with time, noticeable from one hour to the next in the case of CP. We also encountered a poisoning of MOS sensors, probably due to weak acids, *i.e.*, volatile, free fatty acids (C-1 to C-6), present in the headspace of the Swiss Emmental cheese samples. The manufacturers seem to be unaware of this problem. This last example highlights the general fact that the manufacturers of electronic noses still need to learn a lot about their own systems, and as a user one may encounter problems that the manufacturers have never even heard of. Another example of the lack of knowledge by the manufacturers is the stopping of one particular system every midnight. During the trouble shooting, every possible measurement was carried out on the power supply to detect some possible voltage peaks at this hour, such as $233\frac{1}{3}$ Hz signals on the net used to monitor automatic remote controls. But the EC requirements were obviously fulfilled and nothing strange was found. The manufacturer was not able to solve this problem. These few examples illustrate the possible disappointments that a user should expect. Of course, we do not claim to have come across all types of possible problems and we would be very interested to know what other users have experienced.

4. Measurements of Swiss Emmental Cheese with MOS Sensors

Despite the above-mentioned problems, we also experienced some successes in distinguishing between Swiss Emmental cheeses at different stages of ripening, as well as different production sites within the same stage of ripening. The results presented in Figs. 1 and 6 were obtained with the *eNose 5000* equipped with eight

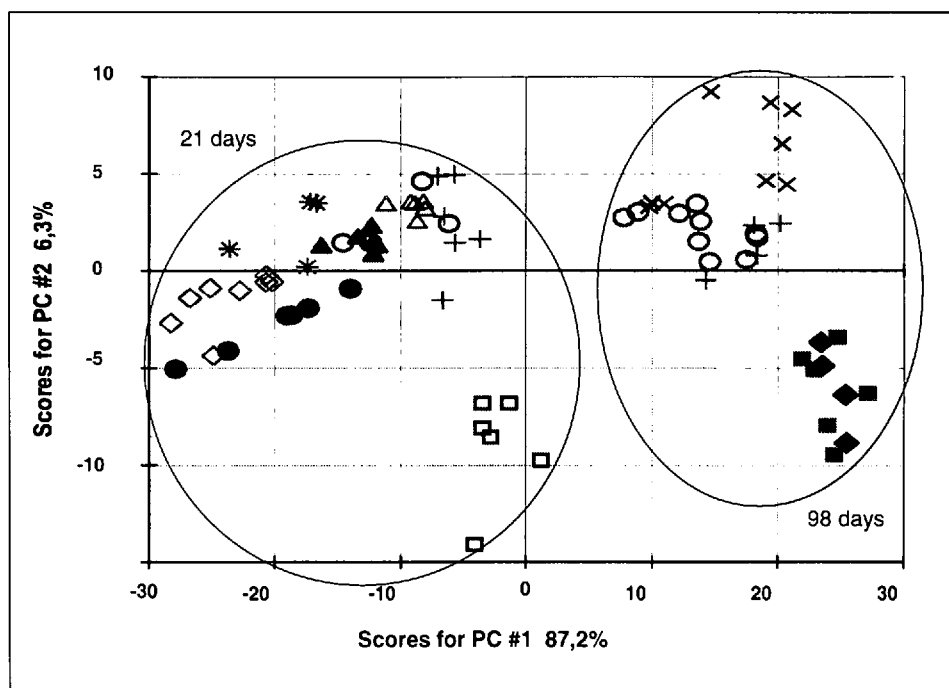


Fig. 5. MOSFET- and MOS-sensor-based discrimination between Swiss Emmental cheeses after 21 and 98 days of ripening. The cheese producers are pooled.

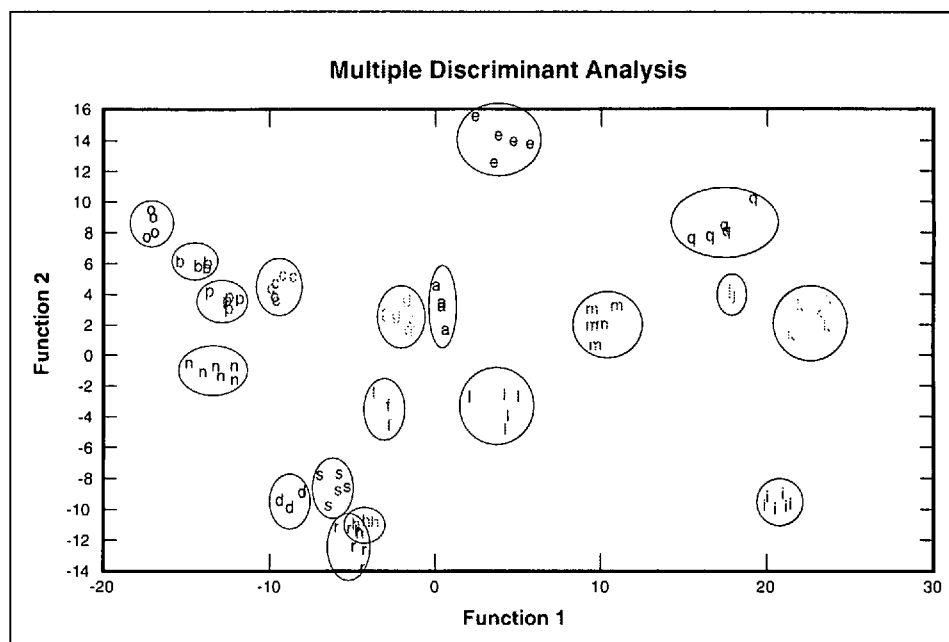


Fig. 6. MOS-sensor-based discrimination between Swiss Emmental cheeses from 19 producers after 21 days of ripening. Each circle represents one producer.

MOS sensors, as this technology has given the best responses. Two types of measurements were carried out with this system, using a 'trapped' and a continuous-flow mode, respectively. The first measurement mode refers to a stopping of the headspace compounds in the sensor chamber for a certain amount of time, in our case 1 min, allowing a good interaction with the sensor coatings. In the second mode, the volatile compounds just pass over the sensor without stopping in the sensor chamber. The switch from 'trapped' to continuous-flow mode was done to pre-

vent an accelerated aging of the MOS sensors observed with the 'trapped' mode. As one would expect, the sensor responses in the continuous-flow mode were lower than in the 'trapped'-flow mode. Therefore, the sample incubation temperature was raised from 40 to 50° when using the continuous-flow mode. For both temperatures, the incubation time was set to 10 min. As expected, the gas flow rate plays a more important role in the continuous mode. On one hand, if the gas flow rate is too high, the volatile compounds pass over the sensors too quickly. The result-

ing, short contact time does not allow a sufficient interaction between the volatiles and the sensors. On the other hand, if the gas flow rate is too low, the volatile compounds break up in the tubing, and therefore arrive gradually in the sensor chamber over a longer period of time. In both cases, the sensor responses are too low. In both measurement modes, the gas flow rate was set to 100 ml/min, with a lowering to 80 ml/min during measurement in continuous-flow mode. *Fig. 1* shows the differences between three ripening stages, *i.e.*, 1, 21 and 98 days, of Swiss Emmental cheese from different producers. These measurements were performed in the 'trapped'-flow mode. *Fig. 6* shows the discrimination between Emmental cheeses from 19 producers after 21 days of ripening, each circle representing one producer. These measurements were performed in the continuous-flow mode. As expected from a consumer point of view, some cheeses show similarities, and others exhibit big differences.

We considered these results as promising for further studies with Swiss Emmental cheese. However, within less than one year, four MOS-sensor chambers had to be replaced. The damaging of the sensors is probably due to free fatty acids present in a relatively high concentration in this type of cheese. These weak acids may react irreversibly with the sensor coatings and, therefore, cause an artificial, accelerated aging of the sensors [2b].

5. Perspectives and Conclusion

The present project was started with the objective of using as many sensor technologies for as many dairy applications as possible. So far, only the MOS technology and the MOSFET, as a complementary technology, could be used. Our main experiments were focused on cheeses, and especially on Swiss Emmental cheese. We now suspect that this type of cheese is harmful for MOS sensors, especially with regard to long-term experiments, and can therefore no longer be considered the main target of application in the present project. Currently, other types of cheese, such as Swiss Gruyère and Raclette-type cheese, both of which release less free fatty acids than Swiss Emmental cheese, are tested with MOS and MOSFET sensors. Other types of dairy products, such as cream and yoghurt, will also be investigated. Some tests will be carried out using a modified version of the *SMart Nose*TM system. CP sensors will only be considered again if some substan-

tial improvements, particularly in terms of humidity and temperature control or calibration, are achieved.

When the first electronic-nose instruments appeared on the market, approximately five years ago, they were presented as ideal and highly efficient systems capable of detecting any kind of odour in any kind of product. Since then, one or more new systems came out each year, leading to much competition between manufacturers. Consequently, most instruments look much more attractive in description than they really are. Furthermore, most publications on investigations with 'electronic noses' show only 'positive' and successful results. The disadvantages and failures are consciously or unconsciously ignored. Therefore, a person not familiar with this topic would automatically think that these systems stand up to their overrated reputation. We learnt from our preliminary investigation with Swiss Emmental cheese that most instruments are currently only prototypes, which will need to be tamed and trained.

The electronic nose technology should be seen as a futuristic technology. The systems currently available are already much more sophisticated than systems of the first generation. However, a lot of know-how and improvements are still needed until these instruments could be considered equivalent to any other analytical instruments. Problems can only be solved when they are recognised, and at the present state of development, most problems still seem to be unknown. The current work of the equipment manufacturers should be to collect information about failures of their systems, and to propose a solution if there is one. For more complex problems, such as the drift of sensors or the lack of reproductibility of measurements, improvements may be expected within the next few years.

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