Published in European Food Research and Technology 214, issue 2, 160-162, 2002
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Data transferability between two MS-based electronic noses using processed cheeses and evaporated milk as reference materials

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Abstract Electronic noses produce data which are difficult to transfer between identical instruments because of differences in the characteristics of "identical" instruments and because of sensor drift. The transportability of data is, however, essential for the setting up of databanks. Results of the present investigation, using processed cheeses and evaporated milk as reference materials, show that data transfer between two electronic noses based on mass spectrometry is possible and simple.

Keywords Processed cheese · Evaporated milk · Electronic nose · Mass spectrometry

Introduction

Electronic noses (ENs) have been developed to mimic the human sense of smell using an array of chemical sensors able to detect volatile compounds, and have been used in many sectors of the food industry [1]. There are four types of commercially available chemical sensors: the quartz microbalance (QMB), the conducting polymer, the metal oxide sensor (MOS) and the field effect transistor MOS. Apart from those traditional ENs, a further technology based on mass spectrometry (MS) is emerging. In this type of instrument, the mass selective detector acts as sensor array, each mass-to-charge ratio representing a sensor type. MS-based ENs are commercially available from a few manufacturers (chronologically SMartnose, Epagnier-Marin, Switzerland; AlphaMos, Toulouse, France; Agilent, USA).

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To be effective, ENs need databases containing a set of measurements describing a reference product and other sets related to geographic origins, off-odour, adulteration, etc. By comparing the fingerprint of an unknown sample with fingerprints of the database, it is then possible to classify it into a defined group. To gain widespread acceptance, such databases must have international validity. As pointed out by Balaban et al. [2], this requires two conditions: (1) a database obtained from one instrument must be usable with other similar instruments, and (2) data collected from different laboratories with similar instruments must be identical so that a unique database can be built up.

Furthermore, ENs based on chemical sensors often suffer from sensor drift, so that calibration is made very difficult [3, 4] and the database becomes useless. This problem is hardly mentioned in the literature: Bazzo et al. [5] confirmed the possibility of transfer between ENs working with MOS sensors; without, however, mentioning the method used. Three different mathematical functions and two neural network configurations have been tested for transformation of data from one QMB to another [2]. When using the calibration data from QMB 1 and the transformed unknown milk samples from QMB 2, a correct classification rate of only 7/12 with the matrix based mathematical function as well as with the neural networks was found. Such a transferability rate is absolutely useless for any industrial application.

The present investigation aims to test the ability of MS-based ENs to overcome this problem. To compare two ENs, at least one reference material is needed. Instead of using standard solutions, it would be of great interest to have available a reference material with matrices similar to the test samples, e.g. cheese in our case. A study on four processed cheeses and one evaporated milk which could be used as reference materials for a preconcentration step followed by gas chromatography or EN is in progress. These materials have been tested within the current study on two MS-based ENs to check their suitability as reference materials and to investigate the transferability of data between two instruments.

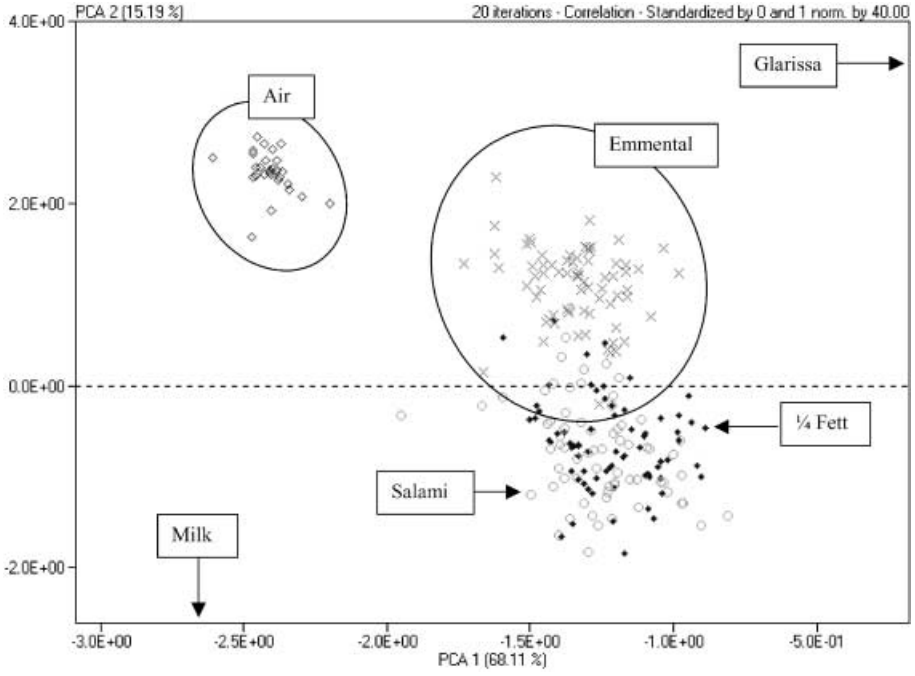

Fig. 1 Discrimination with a SMartnose between four different processed cheeses (1/4 Fett, Emmental, Glarissa, Salami), one evaporated milk and ambient air using a principal component analysis (*PCA*)

Materials and methods

Reference materials. Four commercial processed cheese varieties were supplied by Tiger Käse (CH-3550 Langnau): "1/4 fett", "Emmental", "Glarissa"(with herbs) and "Salami" (with small salami pieces and spices). They were all conditioned in gas-tight polymer coated aluminium cans (approximately 25 g). All cans of the same variety originated from the same production batch ensuring the required homogeneity and reproducibility for the samples.

Full cream unsweetened evaporated milk was supplied by Hochwald, Nahrungsmittelwerke, Thalfang, Germany. The milk all originated from the same production batch and was conditioned in tin cans.

All samples were stored at –20 °C and brought to room temperature prior to sample preparation.

Sample preparation. Processed cheese samples were cut into eight uniform pieces of approximately 3 g and filled into 10-ml vials adapted for the Combi Pal autosampler. Samples of evaporated milk (3 g) were placed in 10-ml vials with a Pasteur pipette. All vials were closed with a butyl/PTFE septum and a cap.

Analytical instruments and conditions. Two SMartnose (LDZ, CH-2074 Marin), referred to for simplicity as SN1 and SN2, were equipped with a Combi PAL autosampler (CTC Analytics, CH-4222 Zwingen). The main operating conditions were as follow: incubation temp, 60 °C; incubation time, 20 min; injection volume, 2.5 ml; syringe temp, 110 °C; injector temp, 130 °C; purge gas, nitrogen; purge flow, 200 ml/min; syringe purge time, 5 min; mass spectrometer scan speed, 0.5 s/mass; mass range, 10–140 amu; SEM voltage, 1030–1080 V (set to obtain a constant value for m/z=40 when air is injected). The total acquisition time was set to 170 s so that three cycles were measured for each injection, the first one being used to equilibate the measuring system.

SN1 and SN2 were located in two different laboratories, SN2 being an older version of SN1. Under these conditions, the robustness of the transferability test described below was ensured.

Samples analysis. The four cheeses and the evaporated milk were analysed seven times (called series 1) using SN1 over a period of 2 months, and twice (called series 2) using SN2 over 1 week. For each series, eight true replications of each sample were carried out. For air analyses, only five replications were performed. All samples were analysed in a randomised order. At the beginning of a series, eight test cheese samples were analysed (but not considered) to allow the system to equilibrate.

Data treatment. All the following data set transformations were carried out using the software supplied with the SMartnose. First, the mean value of the second and third cycle was calculated. Then the processed data set was normalised using the atomic ion of argon (m/z=40) from air. This mass-to-charge ratio is subject to practically no contamination from other compounds and the concentration of this gas in the headspace can be considered as constant. Such a normalisation makes it possible to correct the drift both within a single series of measurements and between different series. Then a principal component analysis (PCA) and a discriminant function analysis (DFA) were calculated. The data obtained with SN1 on seven different dates were thereafter used as the training set. The data obtained for air and for evaporated milk were then used as references for standardising the other values. This means that the axes of the PCA and DFA from each series of measurements were set in such a way that evaporated milk and air samples from each series overlapped. The data obtained using SN2 on two different dates were then imported as unknowns into the training set of SN1, undergoing the same standardisation procedure.

Results and discussions

Prior to performing a PCA, it was necessary to select the most discriminating variables (m/z). As evaporated milk, air and Glarissa processed cheese are highly differentiated, only 1/4 Fett, Emmental and Salami processed cheeses were considered for calculating the discriminating power of the mass-to-charge ratios. Therefore the following m/z values were selected from the training set: 58, 56, 54, 60, 41, 44, 64, and 47 (in order of decreasing discriminating power).

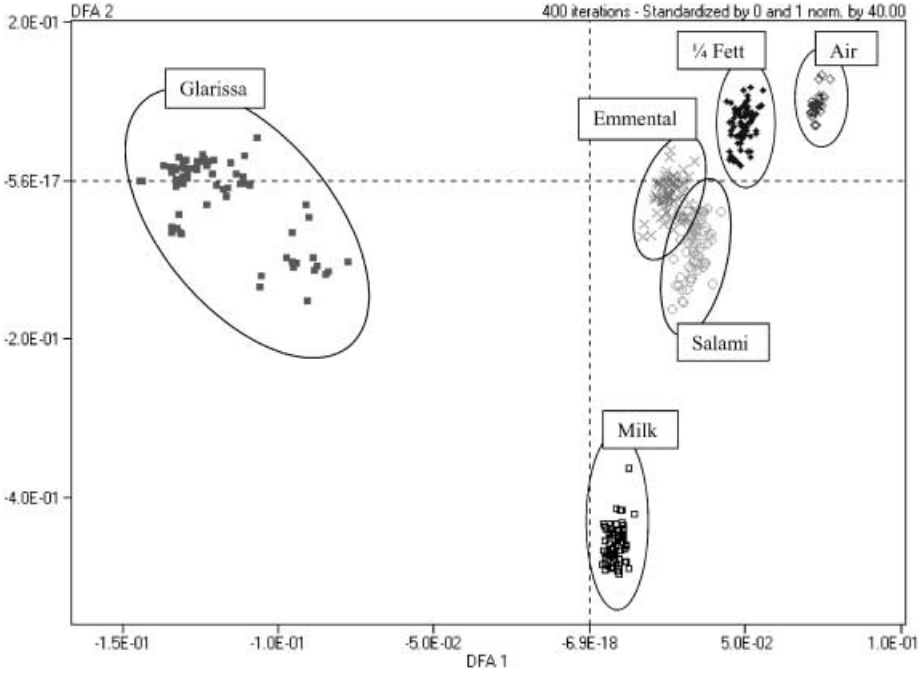

Fig. 2 Discrimination with a SMartnose between four different processed cheeses (1/4 Fett, Emmental, Glarissa, Salami), one evaporated milk and ambient air using a discriminant function analysis (DFA)

Figure 1 shows the results of a PCA on the seven series of SN1, with the two series of SN2 being added as unknowns. In the training set, 97.3% of the samples are correctly recognised whereas 96.9% of the unknowns are located in the correct group. The fact that failures occur within the training set proves that the discrimination is not trivial and increases the robustness of this test.

The results of a DFA for the same parameters are shown in Fig. 2. In the training set, 99.1% of correct placement is achieved, whereas 100% of the unknowns are located correctly (Fig. 1, Fig. 2).

In conclusion, the transfer of data between two SMartnoses does not require any complicated operations and is very user friendly. We showed that data imported from another instrument could easily be transferred to the training set of the original instrument and fit into the discrimination profile. In this study, we used evaporated milk and air as references for standardisation. Except for Glarissa, which shows a poorer repeatability in the PCA, all other cheeses (1/4 Fett, Emmental, Salami) and evaporated milk can be used as reference materials for standardisation.

Acknowledgements The authors thank Mrs G. Urbach for her careful reviewing of the paper and M.T. Zesiger for his technical and scientific support. This work was supported by a grant from the Swiss Federal Commission for Technology and Innovation (CTI, project 4614.1).

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