Comparison of efficiency and stability of two preconcentration techniques (SPME and INDEx) coupled to an MS-based "Electronic Nose"

Laurent Pillonel[1], Dario Altieri[1], Raphael Tabacchi[2] and Jacques Olivier Bosset[1]

[1]Swiss, Federal Dairy Research Station, Bern-Liebefeld, Switzerland
[2]University of Neuchâtel, Neuchâtel, Switzerland

Introduction

Electronic noses (ENs) may be very useful instruments for rapid analyses of volatile organic compounds (VOCs). They use an array of sensors which react differently to given volatile compounds, delivering a fingerprint which can be analysed by multivariate statistical analysis. MS-based ENs consider each m/z signal as one "sensor" instead of the chemical sensors encountered in the traditional ENs. The advantages of the former are the high number of "sensors" available, their robustness, selectivity and reproducibility (1). Furthermore, it is possible to explain some of the differences found in the MS fingerprint in terms of chemical compounds in particular when the corresponding GC-MS data are available (2).

However, to gain widespread acceptance, ENs need databases with international validity (3). It means that repeatability and reproducibility of the measurements must be ensured. Both factors were investigated by *Pillonel et al.* (4) using various processed cheese samples as standard materials. These guarantee excellent long term stability when stored deep frozen in small canned portions from a single production batch. A database was actually produced using one instrument and measurements carried out using a second instrument were successfully imported and classified in this database. An indirect correction for signal drifts was carried out by standardising the signals with two control standards (4). The analyses were however carried out in the static headspace mode and, though the three processed cheese types analysed had quite different volatile profiles, the separation into three groups was

only just achieved. This weakness, which strongly limits the use of MS-based ENs for compounds with a lower volatility, can be drastically improved by preconcentrating the headspace prior to the analysis.

A comparison between SPME, Purge & Trap and static headspace techniques for classifying Swiss Emmentaler at four different ripening times has already been carried out by *Schaller et al.* (5). They established that for small molecular masses (i.e. up to m/z=45) the signal intensity was comparable between the three techniques, whereas for the medium and higher molecular masses, the static headspace exhibited very low responses in comparison to the other two techniques. But while static headspace and SPME showed a good repeatability, the variation was significantly higher using Purge & Trap. Further drawbacks of the latter system are the size of the instrument and the numerous manual operations required even with a new system for automated Purge&Trap-(GC)-MS analysis as was recently described (2).

Two commercial systems which can easily be coupled to an EN are available: solid phase micro-extraction (SPME) and inside needle dynamic extraction (INDEx), a special type of solid phase dynamic extraction (SPDE). Both techniques can be automated using an auto-sampler. SPME has already found many applications in analysis of food volatiles whereas INDEx/SPDE is a newly developed device. So far few investigations have been carried out using the latter. *Lachenmeier et al.* (6) used SPDE coupled with gas chromatography/tandem mass spectrometry (SPDE/GC-MS/MS) to determine drugs of abuse in hair samples. *Musshoff et al.* (7) used SPDE-GC-MS for the determination of amphetamines and synthetic designer drugs in identical samples. *Lipinski* (8) applied the same technique to analyse pesticides in water. *Ampuero at al.* (9) compared the use of INDEx, SPME and static headspace for the classification of monofloral honeys.

Compared to SPME, INDEx/SPDE often shows a more effective and faster extraction of VOCs due to the advantage of a mechanically robust metallic steel needle instead of a fragile polymer fibre. The INDEx/SPDE device consists of a hollow needle internally coated (SPDE) or packed (INDEx) with an absorption material. The headspace may be aspirated several times consecutively through the syringe needle by moving the plunger up and down.

The objective of this paper was to compare the performances of SPME and INDEx applied to a MS-based EN and to check their stability by carrying out analyses with different syringes of the same type using canned processed cheese stored deep frozen which has already been shown to be a stable and well defined control material (10). Furthermore, the correlation between the highly discriminating masses selected from the EN and differences in compound concentrations analysed using GC-MS were investigated for SPME.

Materials and methods

Sample selection

The processed cheeses (¼-Fett, Emmental and Salami) and the unsweetened evaporated milk were conditioned in gas tight metallic cans and stored at approx. –18 °C. A detailed description can be found in (10).

Mass Spectrometry-based Electronic Nose

The instrument used was a SMart Nose (LDZ, CH-2074 Marin) equipped with a Combi Pal autosampler (CTC Analytics, CH-4222 Zwingen) controlled by the software CTC Cycle Composer.

SPME and INDEx

Of each sample 3 g were filled into 10 ml vials closed with a silicon septum and a cap. They were then incubated with agitation for 10 min at 60 °C for headspace equilibration.

The SPME preconcentration was carried out using a 1 cm Divinylbenzene/Carboxene/Polydimethylsiloxane (DVB/CAR/PDMS) fibre (Supelco, Bellefonte, PA) left in the headspace of the vials for 30 min at 60 °C. The overall analysis time (i.e., equilibration, absorption, desorption, data acquisition) was 44 min per sample.

The INDEx extraction was carried out using a modified 2.5 ml Hamilton syringe (LDZ, CH-2047 Marin), whose needle was packed with Divinylbenzene, active charcoal and polydimethylsiloxane (diameter <0.3 mm) with a mass ratio 1:1:1. The manufacture is still under development, possibly leading to poor reproducibility from batch to batch. For this extraction, ten push and pull movements of the plunger (2 ml each) were carried out. The syringe temperature was set at 130 °C. To eliminate the possibility of water condensing on the wall of the needle and the packing material, the syringe was purged with dry nitrogen for 30 s prior to injection. Again ten push and pull movements of the plunger were executed in the injector port to help desorption. The overall analysis time was 21 min per sample.

Data acquisition and treatment using the SMart Nose

Injector temperature (200 °C) and acquisition parameters were identical for both SPME and SPDE modus. The quadrupole mass spectrometer was used in the EI ionisation mode (70 eV). The mass range was 10–130 amu and the mass spectrometer scan speed at 0.5 s/mass. The fibre, or the needle, was conditioned in the injector flushed with 200 ml/min nitrogen.

The total ion current (TIC) profile gave a global MS fingerprint of each sample headspace. All the data sets recorded were processed by the software supplied with the SMart Nose. The mass intensities were normalized with m/z 100 (a fragment of the background to correct the drift both in a single series of measurements and between series). The data obtained for air and evaporated milk were used as refer-

ences for standardising the other values (4). 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 in an optimal way. Using the SMart Nose, the three cheese types and the evaporated milk were analysed in three series using a new SPME fibre for each series and in a further series using a fibre used previously for 80 injections. For INDEx, only two series were analysed because only two INDEx syringes were available (still in the stage of development).

A principal component analysis (PCA) treatment was performed on the selected most discriminating masses. In both analyses (SPME and INDEx), the first series of data was used as training set and the remaining series as validation set. Eight true replications were carried out for each series. For air analysis (as second reference), only four replications were performed. All samples were analysed in randomised order.

Gas chromatography

To study the correlations between EN data and the chemical compounds present in different concentrations, a normal GC-MSD analysis was also carried out using SPME as preconcentration system. The three cheese types and the evaporated milk were analysed without replicate.

Extraction conditions and SPME fibre were the same as those used for the SMart Nose. Analyses were carried out on a Hewlett-Packard (HP) 5890, Series II gas chromatography system equipped with a narrow bore liner and a mass-sensitive detector (MSD) HP 5971. The temperature for the splitless injection was 260°C. The volatiles were separated on a SPB-1 (Supelco) capillary column (60 m×0.32 mm i.d., film thickness, 4 µm). Helium was used as carrier gas with a constant inlet pressure of 50 kPa. The temperature program was the following: initial temperature 35°C for 3 min, heating rate, 5°C/min to 260°C and then 12 min at 260°C.

MS detection was performed on a quadrupole mass spectrometer (model HP 5972) operating in full scan EI ionisation mode (70 EV). The scan range was 19–250 amu and the scan speed was 2.9 scans/s.

Data acquisition and processing were performed with the Hewlett Packard HP-Chem Station data software. The volatiles were identified using NIST MS library and further confirmed by comparison of retention indices of authentic reference compounds (10).

Statistical interpretation

Descriptive statistics and pairwise comparisons of mean values with Fisher's LSD test (P≤0.001) were performed with Systat for Windows version 9.0 (SPSS Inc., Chicago, IL).

Results and discussion

Discrimination using SPME

Three series of analyses were carried out using three new fibres of the same type (DVB/CAR/PDMS) to test their reproducibility and, a further series was repeated with one of the three fibres which had been used for 80 injections to test its robustness.

Data from the first series were used as training set to select the most discriminant variables (m/z). The three processed cheeses were considered for the elaboration of the PCA model (air and unsweetened evaporated milk were only used for the standardization). The following masses were chosen (in order of decreasing discriminant power): 74, 54, 58, 93, 94, 119. The data obtained by the remaining series were imported as unknowns into the PCA (validation set).

Figure 1 shows the plot of the PCA scores with the four series. All samples were correctly grouped. SPME therefore seemed to be a repeatable and reproducible preconcentration technique for this application. The samples analysed with the 80-times used fibre (empty marks) were also classified correctly, though the groups clearly laid closer together. This decrease in efficiency after a certain number of injections is a known weakness of SPME (ageing of the fibre).
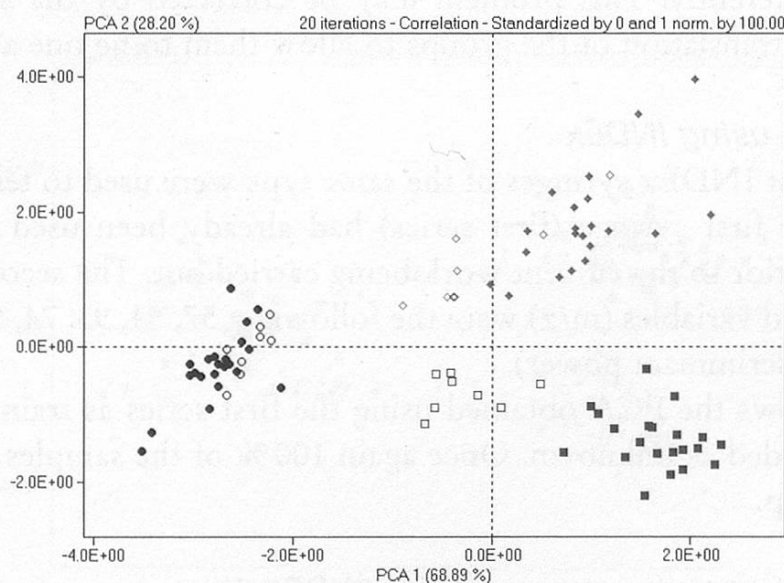

Figure 1 **Discrimination between three different processed cheeses (Emmental, ¼-Fett, Salami) using a new SPME fibre coupled to a MS-based electronic nose**
Score plots of the principal component analysis carried out using the masses m/z 74, 54, 58, 93, 94, 119.
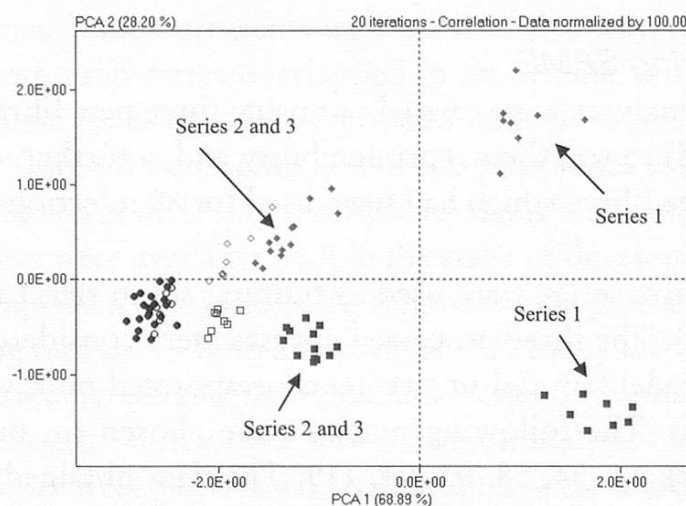(■) Emmental, (●) ¼-Fett, (♦) Salami, empty marks indicate the results obtained by an aged fibre.

Figure 2 **Same PCA as in figure 1 but without applying the standardisation against air and unsweetened evaporated milk**
(■) Emmental, (●) ¼-Fett, (♦) Salami

To illustrate the magnitude and the efficiency of the standardisation, a PCA of the results was carried out omitting this correction (figure 2). The points of the first series were far away from the other series, probably due to the mass spectrometer being tuned differently. This problem may be corrected by the standardisation, which is only a translation of the groups to allow them to lie one above the other.

Discrimination using INDEx

Two different INDEx syringes of the same type were used to test their "reproducibility". The first syringe (first series) had already been used for more than 500 injections prior to the current work being carried out. The second syringe was new. The selected variables (m/z) were the following: 57, 94, 93, 74, 91, 48 (in order of decreasing discriminant power).

Figure 3 shows the PCA obtained using the first series as training set and the second series added as unknown. Once again 100% of the samples were placed in the correct group.

Comparison of static headspace/SPME/INDEx

The PCA results obtained using both preconcentration techniques mentioned above (figures 1 and 3) as well as the results obtained using a static headspace (SHS) extraction (figure 4) were compared with one another.

For the latter technique, the data previously obtained by *Pillonel et al.* (4) were used to calculate the PCA omitting the Glarissa cheese data. The selected variables (m/z) were the following: 45, 64, 55, 58 (in order of decreasing discriminant power). In all three PCA, samples were placed 100% correctly.
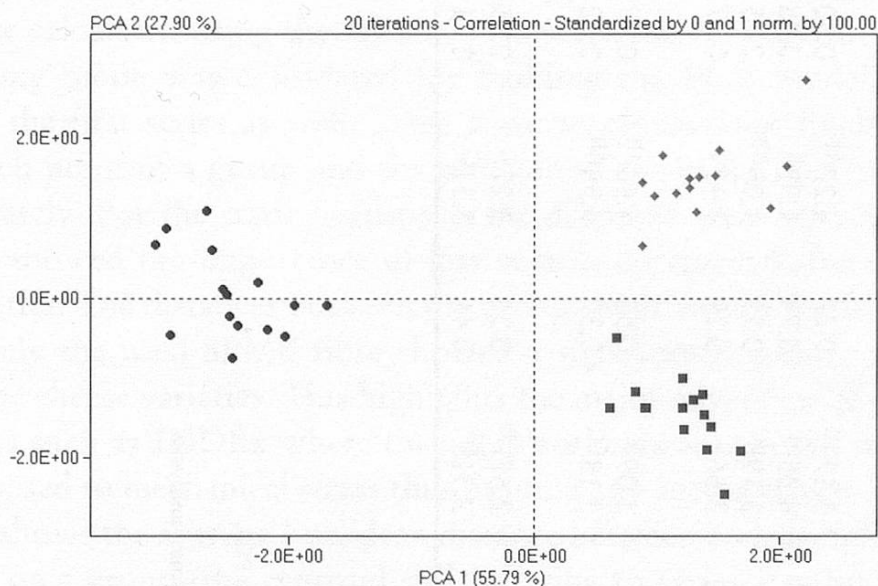
Figure 3 Discrimination between three different processed cheeses (Emmental, ¼-Fett, Salami) using INDEx coupled to a MS-based electronic nose
Score plots of the principal component analysis carried out using the masses m/z 57, 94, 93, 74, 91, 48.
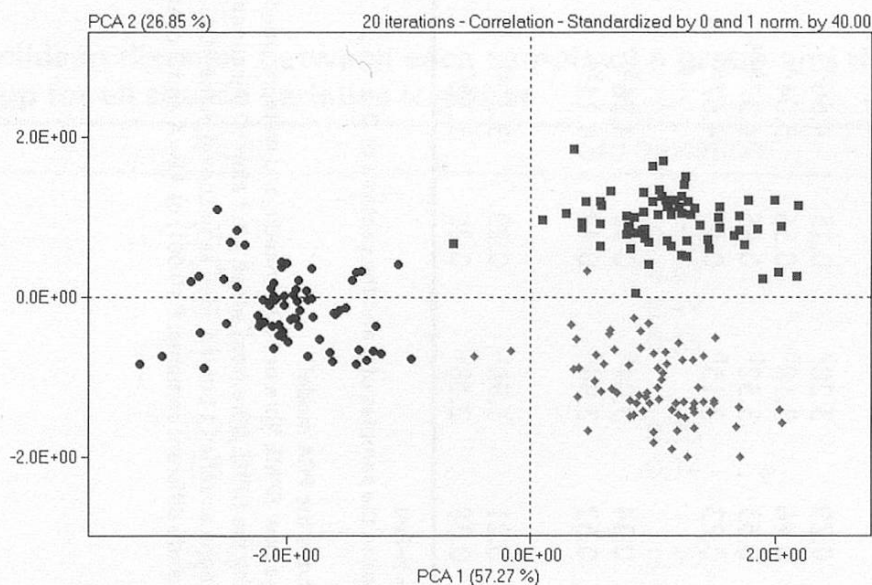(■) Emmental, (●) ¼-Fett, (♦) Salami

Figure 4 Discrimination between three different processed cheeses (Emmental, ¼-Fett, Salami) using static headspace extraction coupled to a MS-based electronic nose
Score plots of the principal component analysis carried out on the masses m/z 45, 64, 55, 58.
(■) Emmental, (●) ¼-Fett, (♦) Salami

Table 1

Average Euclidean distance between the points of a group and the centroid of another group for each series

	E-Q		E-S		Q-E		Q-S		S-E		S-Q	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
SPME												
Series 1[1]	4.68^{AB}	0.29	3.20^B	0.15	4.66^{AB}	0.09	4.26^A	0.11	3.17^{BC}	0.27	4.27^{AB}	0.30
Series 2[2]	4.63^{AB}	0.46	3.18^B	0.56	5.04^A	0.21	4.73^A	0.69	4.35^A	0.74	4.97^A	0.98
Series 3[2]	4.52^{AB}	0.53	3.32^B	0.45	4.37^{ABC}	0.38	4.29^A	0.39	3.19^{BC}	0.29	4.05^{ABC}	0.75
Series 4[3]	3.06^C	0.23	3.15^B	0.45	4.67^{AB}	0.10	4.15^A	0.32	3.66^B	0.29	3.42^C	0.77
INDEx												
Series 1[1]	4.22^B	0.34	3.04^B	0.32	4.26^{BC}	0.40	4.46^A	0.30	3.09^{BC}	0.53	4.46^{AB}	0.47
Series 2[2]	4.84^A	0.52	3.94^A	0.42	4.11^{BC}	0.30	4.61^A	0.38	3.18^{BC}	0.37	4.35^{AB}	0.22
SHS												
Series 1[1]	2.86^C	0.21	1.96^C	0.29	3.30^D	0.33	3.23^B	0.34	2.57^{CD}	0.26	3.27^C	0.25
Series 2[4]	3.37^C	0.38	2.18^C	0.20	3.32^D	0.51	3.38^B	0.54	2.31^D	0.46	3.31^C	0.71

E = Emmental, S = Salami, Q = ¼-Fett

E-Q means the distance between the samples of E and the centroid of Q

Std = standard deviation

[1] These series were used to build the PCA model.

[2] These series correspond to a new SPME fibre or INDEx needle and were included as unknowns in the PCA.

[3] This series was obtained with the SPME fibre from series 1 but after 80 injections and was included as unknown in the PCA.

[4] Analysis under same conditions as series 1 but included as unknown in the PCA.

Series: A>B>C>D (=significantly different contents; P≤0.001) or AB=A and B overlap when using a univariate discriminant analysis

To compare the performances of the sampling modes, the distances between the groups were calculated using the SMart Nose software. As only the first series of each sampling mode was considered for building the PCA model, the centroid referred to the first series as well. Table 1 shows the average Euclidean distance between each point of a group and the centroid of the other two groups for each series separately. For the static headspace, the distances were virtually always the smallest. It showed the importance of less volatile compounds for differentiating cheese varieties. The distances between the groups were similar for both SPME and INDEx. Only the used SPME fibre showed a significantly poorer ability to discriminate the cheese varieties. This highlights the major advantage of preconcentration systems such as INDEx where the ad(ab)sorbents are packed into the needle and not exposed to mechanical stress thus limiting any ageing effects.

Table 2 shows the average Euclidean distance between each sample and the centroid of its own group (the centroid still referring to series 1 only) for all cheese types together. The eight replicates measured in series 1 shows the repeatability of the sampling whereas the replicates from the other series are more likely to be representative of the reproducibility due to changing the fibre or the syringe. For the first series, the lowest scattering was achieved using SPME. However the mean distance to the centroid in the case of SPME was not significantly different from the distance in the cases of SHS or INDEx. This means that all three sampling modes are equally repeatable.

Table 2

Average Euclidean distance between each sample of a group and the centroid of its own group for all cheese varieties together

	Mean	Std deviation
SPME		
Series 1[1]	0.44[D]	0.26
Series 2[2]	1.33[B]	0.63
Series 3[2]	1.10[BC]	0.49
Series 4[3]	2.15[A]	0.65
INDEx		
Series 1[1]	0.75[CD]	0.35
Series 2[2]	1.83[A]	0.34
SHS		
Series 1[1]	0.58[CD]	0.30
Series 2[4]	1.29[BC]	0.56

[1-4] see Table 1
Series: A>B>C>D (=significantly different contents; $P \leq 0.001$) or
AB=A and B overlap when using a univariate discriminant analysis

The scores obtained with the two other SPME fibres (series 2 and 3) were further away from the centroid. However they were still in the same range as that obtained using SHS (series 2), indicating a good reproducibility of the fibres. A large change

occurred with the aged fibre (series 4). The distance from its own centroid increased markedly. This was also translated into a closer grouping of the three cheese varieties.

The scores obtained using the second INDEx syringe were also significantly different from the ones from the first syringe. They were in the same range as that obtained using the aged SPME. However with the new INDEx, the distances between the groups were mostly increased (table 1). This may indicate some ageing effect of the older syringe. The liquid polymer particles filling the needle fuse together with time, decreasing the exchange surface with the headspace. The performances of the older INDEx after more than 500 injections were however still significantly better than those of the SPME fibre after 80 injections.

Interpretation of the discrimination using SPME-GC-MS

One major advantage of MS-based EN over the conventional EN is the possibility of interpreting the results by correlating them with compounds present in the sample.

Using SPME as preconcentration system for the SMart Nose analyses, the following ion mass values (m/z) were selected for their high discriminant power: 74, 54, 58, 93, 94, 119 (in decreasing order of discriminant power). Figure 1 shows the score plot of the PCA and figure 5 the corresponding loading plot. Ion masses 54, 58 and 74 were clearly characteristic of Emmental, 119 and 93 of Salami and 94 of ¼-Fett processed cheese.

To trace the chemical compounds responsible for the separation in the PCA, the selected ion masses were extracted from the chromatogram obtained using SPME-GC-MS. Peaks whose area was less than 4% of the total peak area were not taken
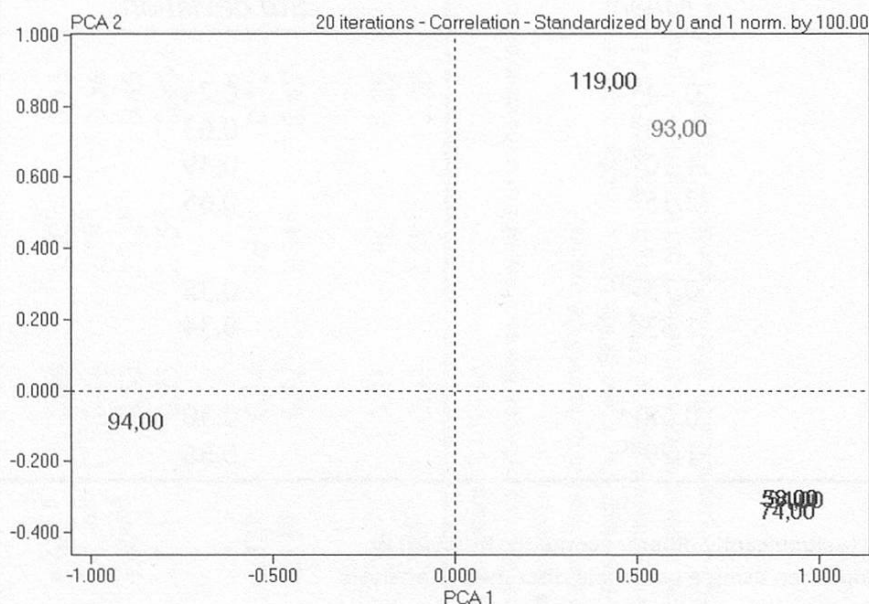

Figure 5 **Loading plots of the same PCA as in figure 1**
The masses 74, 58 and 54 are overlaid.

Table 3
Masses selected using the SPME-SMart Nose and their corresponding compounds from a SPME-GC-MS analysis
For each ion mass, the highest total ion mass of the three cheese varieties was taken as 100%.

Sample Ion mass (m/z)	E	Q 54	S	E	Q 58	S	E	Q 74	S	E	Q 93	S	E	Q 94	S	E	Q 119	S
Compounds																		
Acetic acid							11.0	7.0	6.6									
Propanoic acid	18.5																	
Butanoic acid							24.4	15.2	11.6									
Hexanoic acid	22.3		15.7				50.9	13.3	33.3									
Octanoic acid	18.0	6.4					13.7	4.2	12.6									
Decanoic acid	12.4		17.0															
2-Heptanone				33.1	11.0	20.8												
2-Nonanone	12.4		6.6	58.5	5.9	36.3												
2-Undecanone				8.4		6.3												
8-Nonen-2-one	7.8		24.4															
Nonanal		6.7	12.4															
Pirazine tetramethyl[†]	8.6		24.4															
Terpenes[*]												100.0						100.0
Phenol														88.2				
Disulfide dimethyl														11.8				
Total	100.0	13.1	76.1	100.0	16.9	63.4	100.0	39.7	64.2	0.0	0.0	100.0	0.0	100.0	0.0	0.0	0.0	100.0

[*] Terpenes: α-Thujene, α-Pinene, Sabinene, β-pinene, α-Phellandrene, γ-3-Carene, Limonene, β-Phellandrene, Caryophyllene
[†] Tentatively identified with MassLib

into consideration. The selected masses and their corresponding compounds are listed in table 3. For each ion mass, the highest total ion mass of the three cheese types was taken as 100%.

The results obtained from the SMart Nose were all confirmed by the GC-MS technique. The masses 54, 58 and 74 achieved the maximal values with processed Emmental cheese. The major compounds responsible were identified as carboxylic acids (m/z=54, 78) and ketones (m/z=58). The intensities of ion masses 93 and 119 were much higher in Salami due to the presence of a series of terpenes, probably originating from spices added in this processed cheese type. ¼-Fett processed cheese contained much more phenol which caused the significantly higher signal for m/z 94.

Further masses possessed high discriminant power but the information they contained were often redundant with information already obtained. For instance, the mass 48 was very specific for sulphur compounds contained only in ¼-Fett (methanethiol and disulfide dimethyl). The discrimination was however not improved by integrating it into the PCA.

Conclusion

The performances and stability of two different sampling modes, i.e. SPME and INDEx, for use with a MS-based electronic nose of type SMart Nose were compared. The discrimination between three processed cheeses analysed (Emmental, Salami and ¼-Fett) was clearly enhanced compared to the static headspace sampling mode. The most discriminating and therefore selected ion masses (m/z) for the PCA were as follows (in order of decreasing discriminant power): 45, 64, 55, 58 for SHS, 74, 54, 58, 93, 94, 119 for SPME and 57, 94, 93, 74, 91, 48 for INDEx. The improved discrimination after preconcentration was explained by the higher concentration of medium and low volatile compounds in the injection port.

The repeatability of the measurements was comparable for all sampling modes. The reproducibility between different SPME syringes was good except for the aged one (>80 injections) which showed a reduced retention power. The signal was therefore much lower than for the new SPME syringes. In the case of INDEx, the reproducibility was in the same range as for the aged SPME. The old INDEx was however used for more than 500 injections and still could compete with new SPME fibres for the discrimination. INDEx offers therefore an interesting alternative to the fragile and expensive SPME fibres, also with regard to the time of analysis per sample which was 21 min for INDEx compared to 44 min for SPME for similar performances.

Finally it could be shown that the discrimination obtained using an MS-based EN can be explained by differences in the concentrations of various compounds.

Acknowledgments

Summary

Preconcentration of medium boiling organic compounds is generally useful to improve the efficiency of mass spectrometry-based electronic noses. Two different techniques, i.e. solid phase micro-extraction (SPME) and inside needle dynamic extraction (INDEx), a particular type of solid phase dynamic extraction (SPDE), were compared discriminating three processed cheeses used as standard materials. The reliability of these techniques was also investigated by repeating analyses using different SPME fibres and INDEx syringes of the same type. Both preconcentration techniques improved the efficiency of the MS-based electronic nose. The discrimination between the processed cheeses was complete, even when the syringe was exchanged. A significant loss of efficiency was observed for SPME which had previously been used for 80 injections (ageing of the fibre). The volatile organic compounds making possible the discrimination between the processed cheeses considered were identified by a parallel SPME-GC-MS analysis, tracing the characteristic fragments corresponding to the ion masses selected for the electronic nose.

Zusammenfassung

Vorkonzentration von mittelsiedenden organischen Verbindungen ist nützlich, um die Effizienz von auf Massenspektrometern basierenden elektronischen Nasen zu verbessern. Zwei verschiedene Techniken, Festphasenmikroextraktion (SPME) und die sogenannte «inside needle dynamic extraction» (INDEx), eine spezielle Art der dynamischen Festphasenextraktion (SPDE), wurden zur Diskriminierung zwischen drei Schmelzkäseproben als Standardmaterialen verglichen. Um ihre Zuverlässigkeit zu prüfen, wurden verschiedene SPME Fasern und INDEx Spritzen vom gleichen Typ ausprobiert. Beide Vorkonzentrationsmethoden verbesserten die Leistungsfähigkeit der elektronischen Nase. Die Diskriminierung der Schmelzkäseproben gelang vollständig, auch wenn die Spritze ausgetauscht wurde. Eine signifikante Abnahme der Leistungsfähigkeit der vorher 80-mal verwendeten SPME Faser wurde beobachtet. Die flüchtigen organischen Verbindungen, die die Diskriminierung zwischen den untersuchten Schmelzkäseproben ermöglichten, wurden mit Hilfe einer SPME-GC-MS Analyse identifiziert. Dabei wurden nur die charakteristischen Massenfragmente herangezogen, welche den ausgewählten Massen der elektronischen Nase entsprachen.

Résumé

La préconcentration des composés organiques volatils à moyen point d'ébullition est souvent utile pour améliorer les performances des nez électroniques basés sur la spectrométrie de masse. Deux différentes techniques, à savoir la micro-extraction sur phase solide (SPME) et celle dite «inside needle dynamic extraction» (INDEx), une forme d'extraction dynamique sur phase solide (SPDE), ont été comparées pour la discrimination de trois sortes de fromages fondus utilisés comme matériels standards. La fiabilité de ces techniques a été testée à l'aide d'analyses

répétées utilisant des seringues différentes mais de même type. Les deux techniques ont permis d'améliorer les performances du nez électronique. La discrimination des fromages fondus était complète, même après avoir changé de seringue. Cependant la seringue SPME déjà utilisée pour 80 injections antérieures a montré d'importants signes de vieillissement. Les composés organiques volatils qui permettent la discrimination des fromages fondus considérés ont été identifiés à l'aide d'une analyse SPME-GC-MS parallèle en traçant les fragments caractéristiques correspondants aux masses sélectionnée pour le nez électronique.

Key words

Electronic nose, processed cheese, mass spectrometry, SPME, SPDE, INDEx, preconcentration, volatile organic compounds (VOC)

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Address of correspondent: Dr. Jacques Olivier Bosset, 8 ch. des Prés, CH-1530 Payerne