

Qualifying food flavours with near infrared spectroscopy and chemosensor-arrays (electronic nose)

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Introduction

The origin and useage of food flavours and aromas prior to written civilisation remain a mystery. However, the existence of flavour production on an industrial scale is thought to date from the beginning of the 19th century. Flavours are connected to the food industry mainly through confectionery products, liquors and other distilled products and is interwoven with the production of perfumes. As the knowledge of chemistry expanded, natural products were synthesised, others were altered and new products were created. In modern times, product quality can be defined, to some extent, in terms of composition. Numerous regulations exist which restrict the use of synthetic materials. Yet, to understand food quality, researchers keep coming back to sensory tests, tests that depend on fallible human opinion. Training humans to make subjective judgements of quality is very expensive. Consequently, researchers are constantly searching for objective instrumental techniques for determining quality.

The term “Electronic Nose” (or, e-nose) is a generic name for an analytical instrument that profiles headspace volatiles over or around a sample. The technology is based on an array of chemical sensors whose outputs are integrated by advanced signal processing to rapidly identify complex aromatic mixtures.

Near infrared (NIR) spectroscopy and e-nose technology were used in this study to classify food flavours. E-nose data was related to NIR data with the help of chemometric methods that involved “sequence optimisation” and the polar qualification system (PQS).¹⁻⁵

Materials and methods

The aims of this work were to discriminate and identify eight artificial flavours used in the food industry and to discriminate the same aromas originating from different production circles. (The previous sentence is not understandable in english) The investigated food flavours were as follows: cacao, mint, hazelnut, melon, egg liqueur, toffee, vanilla and green apple.

A Spectralyzer, Model 1025, spectrometer was used to record all NIR spectra over the range 1000–2500 nm at 2 nm intervals. A SamSelect chemosensor array (Daimler Chrysler Aerospace RST Rostock, Germany) was used to record the e-nose data. The e-nose instrument incorporated six individual quartz crystal sensors coated with different gas-sensitive materials. The adsorption of volatile molecules on the sensor surfaces caused mass changes resulting in frequency changes of the oscillators. The frequency changes of the six crystals gave six data (one point in the multidimensional space) per measurement from the che3mosensor array. During our experiments we repeated the measurements 15 times per sample (15 points per sample). After normalising the data, (by dividing each sensor

signal with the average of the signal coming from the six sensors of the array) principal component analysis (PCA) was used, in conjunction with PQS optimisation techniques, to create classification models from the sensor array data.

PQS was developed to work with NIR spectra. The basic principles of the method are described in the relevant literatures.¹⁻⁵ PQS requires the determination of "quality points" defined as the centre of the spectra represented in polar co-ordinates. While the sequence of the data are naturally determined using NIR spectroscopy, there are several multivariate tasks where the order of the data can be changed. The goal is to determine the optimal data sequence with respect to a given classification (giving the best distinction between two samples using their respective quality points). Sequence optimisation was developed to do just that.

Figure 1 shows normalised data from the sensor array for the eight food aromas studied. The data is shown in (a) rectangular and (b) polar coordinates.

The effectiveness of classification was expressed numerically by calculating the normalised distance and sensitivity.⁵ The normalised distance is the absolute distance (distance between the centre of the clusters) divided by the sum of the absolute distance and the sum of the standard deviations of the quality point coordinates of the investigated samples. By optimising the normalised distance, the calculated data sequence provides the smallest standard deviations of the quality points of the investigated sample groups relative to their distance.

In the first step of our statistical evaluation (carried out on the e-nose data), PCA was used for classification. The eight food aromas were measured six times. Figure 2(a) shows the location of the quality points of the samples in the projection plane determined by the first two principal components. As

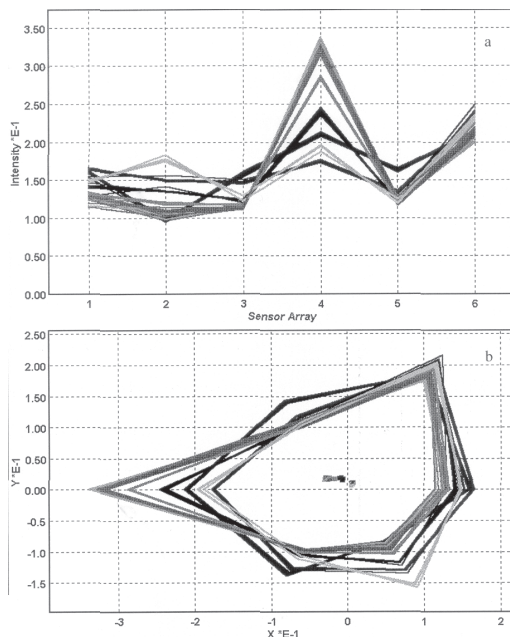


Figure 1. The normalised data of the sensor signals of the investigated eight food flavours measured by electronic nose represented as a spectra in the rectangular (a) and in the polar (b) co-ordinate system.

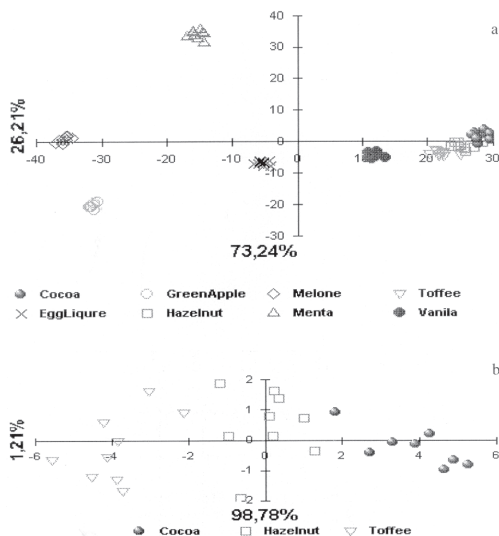


Figure 2. Multi-step discrimination using PCA. (a) The location of the quality points of the eight flavour samples in the first projection plane determined by the first two principal components. (b) The overlapping quality points of cacao, toffee and hazelnut samples can be well separated in an other projection plane.

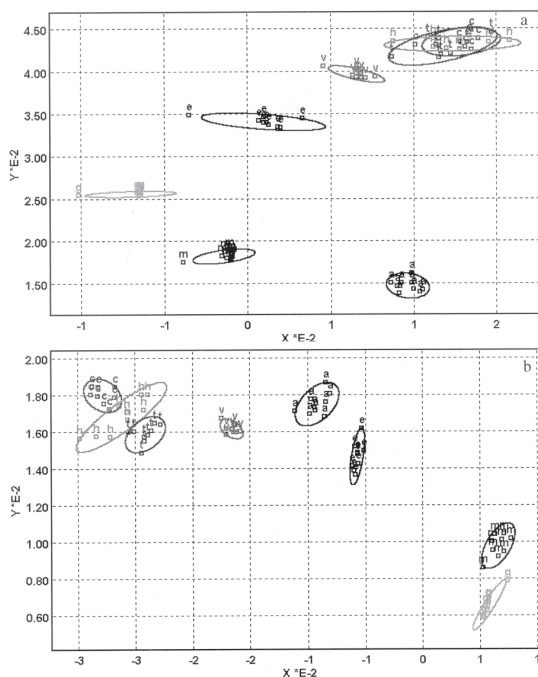


Figure 3. The location of the quality points of the investigated eight food flavour samples in (a) original order and (b) after sequence optimisation. The optimal data sequence is (S1 S5 S3 S4 S2 S6).

can be seen, the quality points of cacao, hazelnut and toffee samples are overlapping and the total identification of all samples can not be performed using only one projection plane. In such cases, multi-step classification can be used to perform the identification. The overlapping samples can be well separated in another projection plane calculated by omitting the already classified samples [Figure 2(b)].

During the second stage of our evaluation work, by defining the term of “sequence optimisation”, the PQS technique—used to work with NIR spectra—was further developed and generalised as an evaluation method for almost any multivariate problems. By representing the data sets in the polar co-ordinate system, some data can be situated opposite each other balancing their shifting effect to the location of the quality points. As was mentioned, the aim of “sequence optimisation” is the determination of the optimal data sequence providing the best separation (highest normalised distance and sensitivity).

Figure 3(a) shows the location of the quality points (centre of their normalised data sets drawn as polar spectra) of the measured food flavours, in original data sequence, coming directly from the instrument. As can be seen, the normalised distances and the sensitivities are high. The distances are considerably higher among the groups compared with their standard deviations, but the separation of all samples can not be observed in the quality plane using the original data sequence, as the quality points of cacao, toffee and hazelnut samples are also overlapping here. After sequence optimisation to

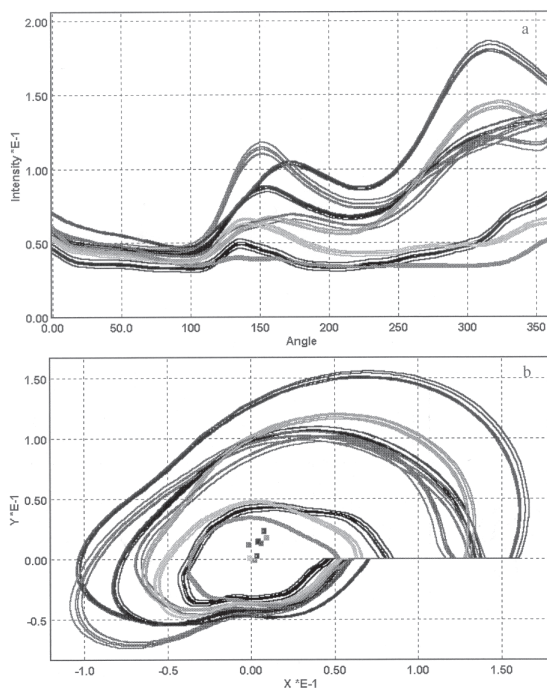


Figure 4. The NIR spectra of the investigated eight food flavour samples in the rectangular (a) and in the polar (b) co-ordinate system using the 1772–2128 nm wavelength range of the spectra. The non-selected points are omitted.

normalised distance, all the investigated flavour samples can be identified in one plane [Figure 3(b)]. The calculated optimal signal sequence is S1 S5 S3 S4 S2 S6.

Passing over to the NIR measurements, the optimal range of the NIR spectra of the investigated flavour samples providing the best separation is 1772–2128 nm. Figure 4 shows the optimal range of the NIR spectra of the food flavour samples in the (a) rectangular and (b) polar co-ordinate system. As was already published in our previous works, the goal of the used wavelength range optimisation is to determine that wavelength range (that part) of the spectrum which gives the best distinction of two sam-

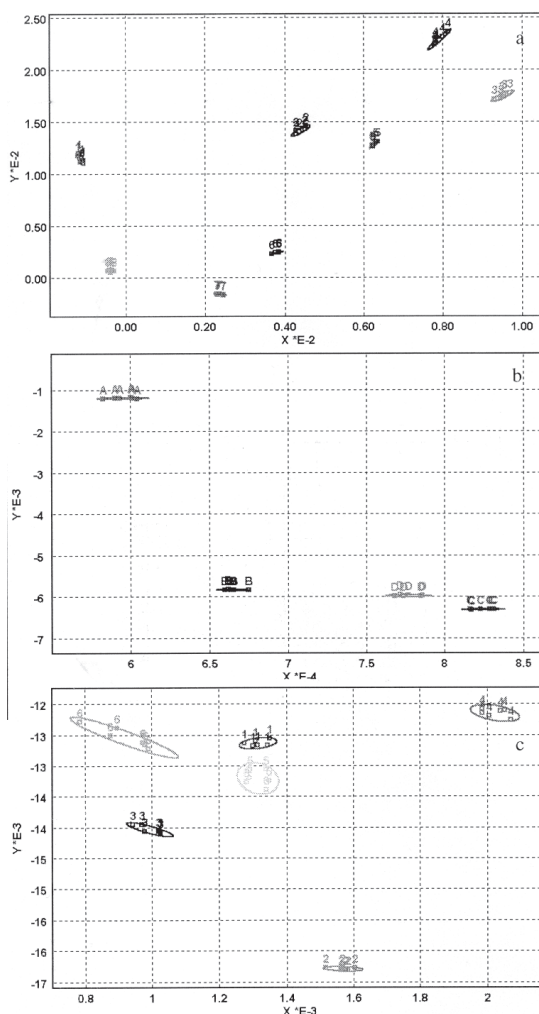


Figure 5. The location of the quality points of (a) the investigated eight food flavour samples using the 1772–2128 nm range, (b) the four lemon flavour samples using the 1628–1662 nm range and (c) the six vanilla flavour using the 1608–1984 nm range of their NIR spectra. The non-selected points are omitted.

ples according to one selected chemical or physical property using their quality points. The criterion of the "best distinction" must, of course, be defined. The maximum of the "normalised distance" or the "sensitivity" are the possible criteria of the optimum, with the help of which the best distinction could be determined. The results of the tasks formulated in our objectives are summarised in Figure 5. Figure 5(a) shows the location of the quality points of the eight flavour samples also investigated by electronic nose and classified in Figures 2 and 3. As can be seen in Figure 5 [four lemon groups (b), six vanilla groups (c)] even the products with the different production circles could be separated well. The used wavelength ranges providing the best separation are based on the normalised distance and the sensitivity.

Conclusion

The sensor signal response of the electronic nose, combined with principal component analysis or polar qualification system as well as NIR spectroscopy, are suitable technologies for discriminating and identifying the eight food aromas. The sequence optimisation opens new perspectives in the application of PQS, offering a rapid, accurate, cheap and simple method for qualifying or identifying products, using their different data sets.

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