

Qualification of volatile oils using near infrared spectroscopy and electronic nose

Gabriella Kiskó^a and Zsolt Seregély^b

^a*Szent István University, Faculty of Food Science, H-1118 Budapest, Ménesi út 45, Hungary*

^b*Metrika R&D Co., H-1119 Budapest, Petzvál J. u. 25, Hungary*

Introduction

People have used natural aromatic plants from the beginning of history. Yet, chemical information related to these same products only began to appear a century ago. The use of natural plants in curing, pharmaceutical and other industries has become increasingly important in recent years. Increased use of bioproducts and the use of natural additives (aromas, colourants etc.) are but two of the more noticeable trends within the food industry. More than 1400 species of aromatic plants produce volatile oils on an industrial scale. The potential use of these ingredients for natural anti-microbial agents has been exploited to a lesser extent. Consumers tend to use and consume bio-products, essential oils as aromas, preservatives, colorants, etc. more than ever before. Attempts have been made to use active ingredients from medicinal and aromatic plants for bio-preservatives rather than resorting to synthetic derivatives.

Quality parameters of volatile oils are usually determined for aroma, taste and other organoleptic criteria. Detailed quality specifications from sensory data are lacking due to fallible human opinions. People panels demand extensive training, are slow to respond and the results are noticeably variable.

Materials and methods

This project is part of an international effort. Its objective was to discriminate and identify seven natural volatile oils obtained from dried plant materials. The oils were prepared by a hydrodistillation process used for the inhibition of food spoilage microorganisms and foodborne pathogens. The investigated plant materials were as follows:

- Thyme (*Thymus vulgaris* L.) marked with “t” in the figures
- Peppermint (*Mentha piperita* L.) marked with “p”
- Dill (*Anethum graveolens* L.) seed marked with “s”
- Dill (*Anethum graveolens* L.) weed marked with “w”
- Cassia (*Cinnamomum cassia* Presl) marked with “c”
- Oregano (*Oreganum vulgare* L. spp. *vulgare*) marked with “v”
- Oregano (*Oreganum vulgare* L. spp. *hirtum*) marked with “h”

Spectra of the samples were recorded with a Spectralyzer (PMC Model 10-25, Switzerland) scanning NIR spectrometer. Log (1/R) spectra were recorded over the range 1000–2500 nm in 2 nm steps. Qualitative indices were calculated according to Kaffka and Gyarmati^{1,2} using the polar qualification system (PQS) program. The indices were determined in a “quality plane”. The index was defined as the centre of the spectrum (of the spectral points) represented in polar co-ordinate system.

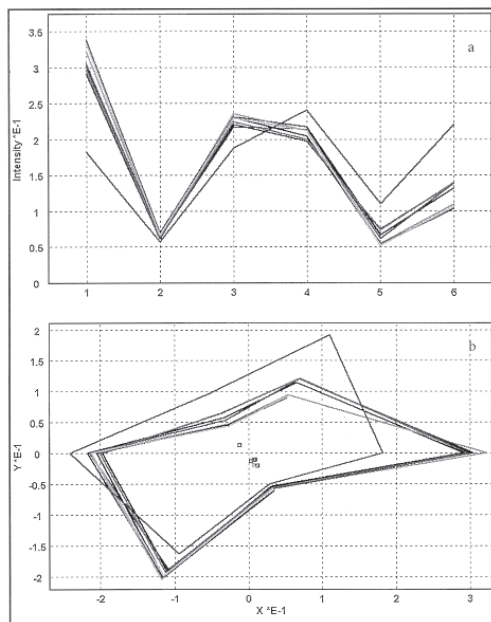


Figure 1. The normalised e-nose data for the seven volatile oils studied in the rectangular (a) and polar (b) coordinates.

“Electronic nose” (or e-nose) is a generic name for an analytical instrument that contains an array of chemical sensors whose outputs are integrated by an advanced signal processing system in order to rapidly identify complex odour mixtures. Current e-nose systems use comparative techniques and produce “fingerprints” of a volatile in a headspace over or around a sample.

SamSelect electronic nose (Daimler Chrysler Aerospace,) was used to take odour measurements. All samples were measured in the standard headspace vials. Headspace auto-sampling were used as a standard and reproducible sampling technique. After normalising the spectral data, principal component analysis (PCA) and a newly developed method, the polar qualification procedure was applied to create classification models from the sensor array data.

The polar qualification system was developed to work with near infrared spectra. The basic principles of the method are described in the relevant literatures.^{1–5} A “sequence optimisation” technique was developed to allow PQS to work with non-spectral data. Figure 1(a) shows the normalised sensor data for the seven measured volatile oils represented in Descartes co-ordinate system as a spectrum. Figure 1(b) shows the same data set in polar co-ordinates.

Results and discussion

Principal component analysis (PCA) was used in the classification procedures. E-nose data for the seven volatile oils was measured nine times. Figure 2(a) shows the location of the quality points of the volatile oil samples in the projection plane determined by the first two principal components. As it can be seen, the quality points of thyme and dill weed samples overlap and the identification of all samples cannot be performed using only one projection plane. In such cases, cascade classification must be used. This means that identification is performed in multi-steps. The overlapping samples become

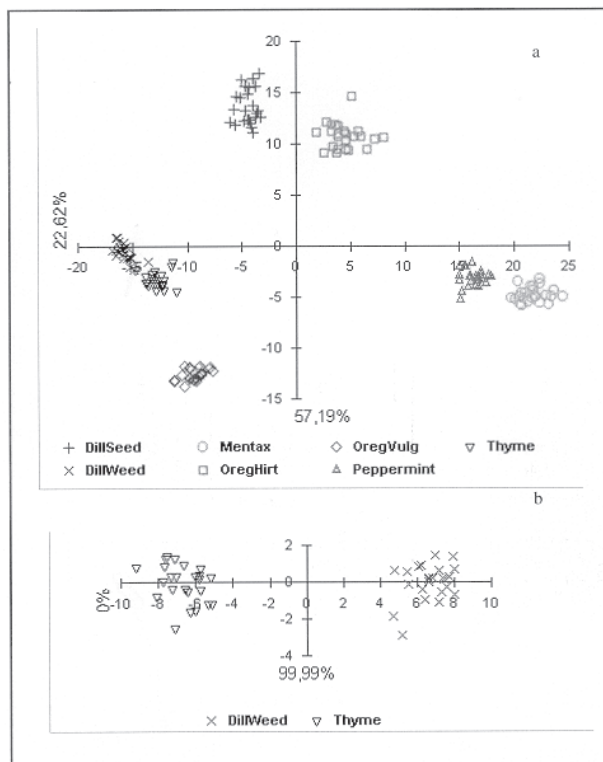


Figure 2. Multi-step discrimination using PCA: (a) location of the quality points for the oil samples in the first projection plane determined by the first two principal components and (b) overlapping quality points of thyme and dill weed samples can be separated in another projection plane.

separated in another projection plane calculated by omitting the already classified samples [Figure 2(b)].

In the second step (sequence optimisation), the PQS technique, designed to work with NIR spectra, was enhanced to be applied to almost any multivariate problems. Figure 3(a) shows the location of the quality points (centre of their normalised data sets drawn as polar spectra) of the measured volatile oils in original data coming directly from the instrument. It can be seen the normalised distances and the sensitivities are high. In addition, the distances are considerably higher among the groups compared to their standard deviations. Separation of all samples was not possible for the quality plane using the original data sequence for the quality points of peppermint. Also, *oreganeum hirtum* samples overlap a bit. After applying sequence optimisation to normalised distances, all the investigated oil samples can be identified in one plane [see Figure 3(b)]. The calculated optimal signal sequence was S1 S5 S3 S4 S2 S6.

The cascade identification was also a possible tool in the PQS evaluation. By classifying an unknown sample into separated clusters having overlapping subclasses using a given data sequence, the clusters can be further evaluated using some other data sequence (very difficult to follow) providing full classification.

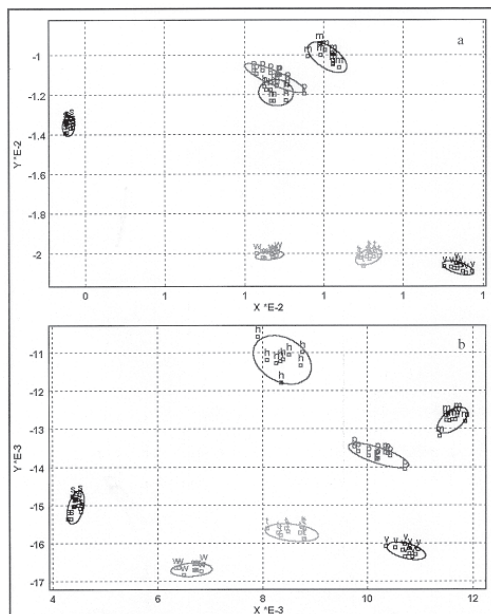


Figure 3. Location of the quality points of the volatile oil samples in (a) original order and (b) after sequence optimisation. The optimal data sequence is (S1 S5 S3 S4 S2 S6).

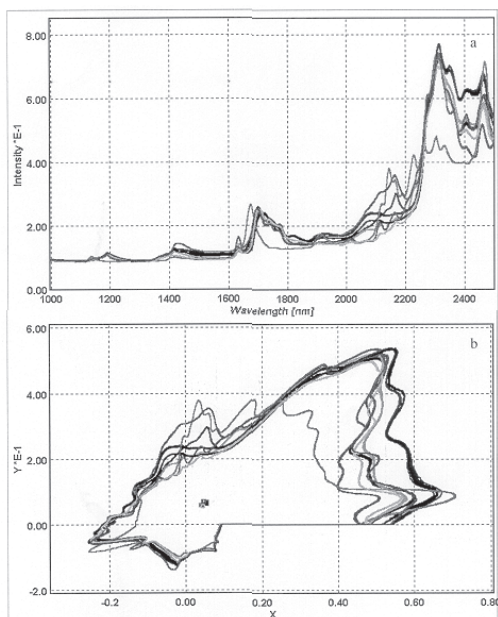


Figure 4. NIR spectra of the volatile oil samples in (a) the rectangular and (b) in the polarco-ordinates using the 1000–2500 nm range.

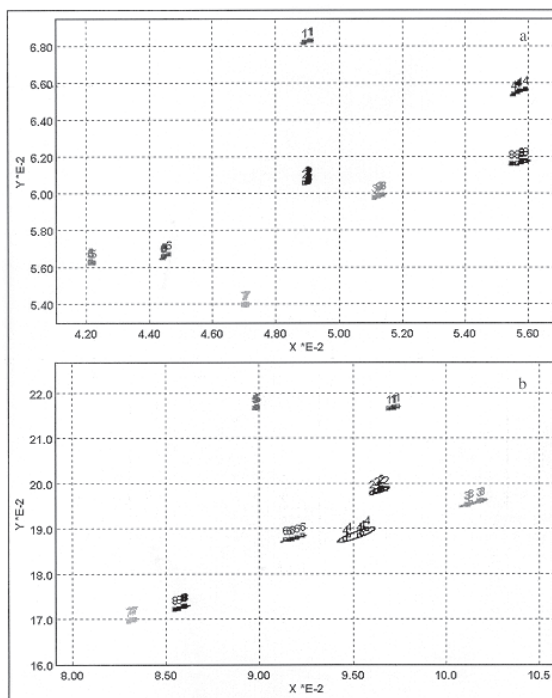


Figure 5. Location of the quality points for the volatile oils using the 1000–2500 nm range (point method) (a) and using the 1408–1436 nm, 1696–1720 nm and 2132–2280 nm ranges (b) The regions among the selected ranges are zero (surface method).

An NIR polar qualification system using wavelength range optimisation was used to create classification models. In Figure 4, the $\log(1/R)$ spectra of the samples can be seen in (a) rectangular and (b) polar co-ordinates. It was found that well-defined clusters could not be achieved using $\log(1/R)$ spectra [see Figure 5(a)]. However, after using wavelength range optimisation, clusters could be separated.

The wavelength range optimisation program was repeated several times in order to define the highest optimum range. By determining the best second and third wavelength ranges and by using the whole near infrared region the optimal ranges can be situated opposite to each other resulting in a worse classification. By omitting the ranges among the selected ones the optimal ranges can be collected together, the direction of their shifting effect to the location of the quality point can be turned to the same direction, summarising their effects. The spectrum ranges providing the best separation were as follows: 1408–1436 nm; 1696–1720 nm; 2132–2280 nm, which are associated with oil peaks [see Figure 5(b)].

Conclusion

Both e-nose and NIR data are suitable for identifying the seven volatile oils studied. Sequence optimisation opens new perspectives in the application of PQS. The method offers a rapid, accurate, cheap and simple method for identifying products using different data sets.

Acknowledgement

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