Electronic Nose Based Discrimination of a Perfumery Compound in a Fragrance

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Electronic nose based discrimination of a perfumery compound in a fragrance

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Abstract

An electronic nose (e-nose) device developed at the University of Buenos Aires was applied to detect the presence of a given perfumery compound (also so-called the perfumery note, refereed as mangone) in a fragrance, at very low weight percentages. The results were compared with sensorial analysis performed by trained panelists and gas chromatography mass spectroscopy (GCMS) measurements.

The triangle test for detection of the perfumery note in the fragrance was performed by a set of 20 trained panelists. Less than 40% of the panelist could identify the presence of the strange note for concentration 10^{-2}% (w/w), and similar percentages were obtained for lower concentrations. Detection by CGMS was difficult at those concentrations, because of the low percentages of the perfumery note and the similar retention times obtained for the note and other compounds included in the fragrance.

The developed electronic nose provided fingerprints for different odors, associated to different samples that were used to build up an odor database. Then, two different multivariate data analysis were performed, the non-supervised principal component analysis (PCA) and an artificial neural network (ANN), in order to discriminate the samples with or without mangone. Measurements of several dilutions of mangone up to 10^{-4}% (w/w) were performed to obtain the database. Both methods, PCA and ANN, were successful in the discrimination process of samples with from those without mangone. In particular a 100% success was obtained by using a radial basis function (RBF) artificial neural network, even when considering the more diluted samples.
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1. Introduction

Since the last decade, electronic noses (e-noses) have become powerful tools for discrimination of odors. According to the usually accepted definition [1] an electronic nose is a device composed of an array of gas sensors, with non-specific responses, having pattern recognition ability from the multivariate data analysis of the whole set of responses. The device should be able to provide a fingerprint for each odor without any information of the chemical composition. The whole group of fingerprints is then globally analyzed with multivariate data analysis methods, like artificial neural networks (ANN) or principal component analysis (PCA) [2].

In the case of perfumes and essential oils, the electronic noses have been used to identify very different perfumes [3] and essential oils [4] of well-separated olfaction families. The stability of perfumes has also been studied with electronic noses [5].

In a previous work the ability of a portable electronic nose, developed at the University of Buenos Aires, to identify the number of storage days of commercial fish was demonstrated [6]. The device has some innovative characteristics, such as the possibility to analyze solid and liquid samples without pretreatment, easy manipulation of the samples without requiring gas syringe injections, portability and easy choice and exchange of sensors. The aim of the present work was to investigate the ability of the developed electronic nose to detect the presence of a given perfumery note in a fragrance. The performance of the e-nose was compared to that of trained panelists and GCMS.

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2. Materials and methods

2.1. Chemicals

The fragrance, referred as F, is a trade mark product of International Flavors and Fragrances (IFF). It contains, among others, two greens, pine cone like notes, terpenile acetate and γ-terpinene, in a well-defined confidential proportion. The additional (strange) perfumery note, p-mentha-8-thiol-3-one, $C_{10}H_{18}OS$, refereed as mangone (CAS number 38462-22-5), was provided by IFF and used as purchased. Mangone is an unsaturated cyclic mercaptane that belongs to the citrus olfaction family (grapefruit subfamily) and that was selected for its low threshold value of sensorial detection.

2.2. Electronic nose

The developed e-nose has been described elsewhere [6]. Briefly, it comprises an array of 11 tin-dioxide based gas sensors incorporated into a sample chamber, whose electrical conductance increase in the presence of reducing gases. Hundred microlitres of the liquid samples are placed into the chamber in a small flat recipient at time zero. The sensor signals are recorded as function of time up to steady-state is reached and then a previously recorded baseline is subtracted from the signals.

For the e-nose determinations, a broader range of mangone dilutions was considered, compared to the panelists and CGMS determinations, ranging from 1 to 10^{-4}% (w/w) of mangone in the fragrance.

2.3. Data acquisition and multivariate data analysis

The signals are digitized and stored in a laptop as function of time. For a fixed time a vector is considered, composed by the signals at that time. The results presented here correspond to the time at which all signals reach a plateau (steady-state situation), which is about 30 min since time zero, but similar results and the same conclusions were obtained when considering the signals recorded at 15 min.

The e-nose methodology is based on multivariate data analysis. There are several well-known methods of multivariate data analysis, but perhaps the most popular are principal component analysis and the artificial neural networks [7–9].

A vector of N components, $\{S_1, \ldots, S_N\}$, where N is the number of sensors and S_i the signal of the ith sensor ($N = 11$ in our case), was obtained for each experiment. Then, each data vector was normalized by the squares-root of the squared sum, which removes fluctuations due to concentration changes [1]. Principal component analysis, a linear unsupervised method that is useful for a graphic visualization of the differences of the data, was performed with these vectors. Thus, the so-called principal compo-

nents, $\{PC_1, PC_2, \ldots, PC_N\}$, where calculated for each experiment.

The two principal components, PC_1 and PC_2 associated to samples of pure F and dilutions of mangone in F, which contain more than 90% of the relevant information to discriminate the odors, were used as vector inputs for an artificial neural network. The same methodology was successfully applied in a previous work for a different application case [10]. We used a radial basis function (RBF) neural network, composed by a first hidden radial basis layer of 20 neurons and a second output linear layer of 1 neuron. Twenty of the 31 measurements were used as training set (calibration data set), with two possible targets (0 and 1) as output: 1 for samples of the pure fragrance (without mangone), and 0 for samples containing mangone (at different concentrations) in the fragrance. The other vectors (11 vectors) were used as validation data set to test the network. Other design parameters were a 0 goal and a spread value of 1.

2.4. Panelists

A total number of 20 trained panelists performed the so-called triangle test. The test consists of presenting three samples, two samples of the pure fragrance F (without mangone) and one with a certain amount of mangone, to each panelist. The panelists know that two samples are identical and one is different, and must indicate which sample is different. This process was repeated for different percentages from 1 to 10^{-4}% (w/w) of mangone in F. The considered samples were those with 1, 10^{-1}, 10^{-2}, 10^{-3} and 10^{-4}% (w/w) of mangone, presented to the panelist in an increasing mangone concentration order. The total time required for the analysis of the samples was about 30 min. A positive individual identification is considered when the panelist can identify correctly the different sample, among the three that smells. For the case of 20 panelists, a global positive identification of the whole panel is considered when the number of panelists that give a correct identification is equal or higher than 14, the 70% of the group. The panelists are familiarized with the fragrance of mangone and qualified to recognize mangone.

2.5. Gas chromatography

A gas chromatography equipment with mass detection (GCMS, Hewlett-Packard Model HP G1800A GCD) in the range 10–450 mass/charge range was used. The initial injection temperature was 75 °C, with a temperature slope of 2 °C/min, up to a final temperature of 225 °C. Helium was used as gas carrier. These conditions are standard for the analysis of fragrances and perfumery notes. The identification of mangone was performed with an IFF software library.

Table 1
Comparison between the CGMS, the trained panelists and the e-nose performance for discriminating samples with mangone

Sample[a] (%)	GCMS[b]	Panelists[b,c]	E-nose[d]
1	Yes	Yes (100%)	Yes
10^{-1}	Yes	Yes (89%)	Yes
10^{-2}	No	No (37%)	Yes
10^{-3}	No	No (45%)	Yes
10^{-4}	No	No (30%)	Yes

[a] The values indicate the percentages (w/w) of mangone in F.

[b] "Yes" and "no" refer to the ability to discriminate or not the presence of mangone in F, respectively.

[c] The percentages are related to the number of successful identifications among the panelists.

[d] "Yes" means that the e-nose can correctly classify the samples with and without mangone (see the text for details).

3. Results and discussion

3.1. Panelists

The results of the panel analysis are shown in Table 1, where it can be seen that the panel was unsuccessful to identify, with significant results, the presence of mangone for samples with equal or less than 10^{-2}% (w/w) of Mangone. In fact, only the 37% of the panelist could identify the presence of Mangone for samples with 10^{-2}% of mangone. Neither the panel could globally identify with significant results the presence of mangone in the samples with 10^{-3} and 10^{-4}% (w/w) of mangone (a successful result is considered when 70% of correct identifications are obtained, as it was mentioned in the previous section).

3.2. GCMS results

The presence of mangone was detected by the library's software for the samples with 1 and 10^{-1}% (w/w). In the case of the samples with lower concentration of mangone, the library identifies the peak as associated to chemical compounds that compose the original fragrance formulation without mangone. The pattern formed by the whole group of chromatographic peaks with low concentrations of mangone in F has not differences from the one obtained with pure F. That is, according to the GCMS analysis the samples with 10^{-2}, 10^{-3} and 10^{-4}% of mangone concentration could be incorrectly classified as samples without mangone, as in fact it was by the library software.

3.3. E-nose results

The set of sensor's signals (after subtracting the respective base lines) represent the information obtained from each experiment. Graphical displays of the array response vectors for some representative samples are exemplified in Fig. 1a as bar plots. The e-nose provides very well differentiated fingerprints for the pure fragrance (F), pure mangone (G)

and dilutions of G in F. The fingerprints of ethanol and phenyl-ethyl alcohol are also shown for comparison in Fig. 1a. The fingerprints associated to F and a particular dilution of G in F are also shown as radar plots in Fig. 1b, which are very common to show multivariate data in a simple manner [6].

The graphic visualization of fingerprints is very useful to discriminate between very different odors, like the pure fragrance, F, and pure mangone. However, it does not help when the odors are very similar, like in the case of F and very diluted solutions of mangone in F (see for example Fig. 1b). In this case it is necessary to perform multivariate data analysis for the pattern recognition.

Previous to analyze the dilutions of mangone in F, PCA was performed with the measurements of samples of the pure fragrance, F, pure mangone, G, dilutions of G in F, ethanol and phenyl-ethyl alcohol. This was done in order to verify if the array and the PCA were able to identify these odors. The total numbers of measurements for each sample are indicated in Table 2. In this case only the two first principal components were considered, because the whole set of $\{PC_1, PC_2\}$ data contains the 97% of the total variance. In Fig. 2, a two-dimensional representation of PC_1 versus PC_2 is shown where each PC_1–PC_2 point corresponds to one measurement. The samples of G, Ph-EtOH, and the dilutions of G in F (which include pure F) appear in well-separated groups, indicating that the array is able to discriminate between these samples. This is in agreement with the very different fingerprints shown in Fig. 1a. The points associated to EtOH are also shown for comparison. The normalized responses of the sensor signals were used for PCA in all cases, as indicated in Section 2.

The next step was to analyze by PCA the samples of pure F and the dilutions of mangone in F, referred as 1–5, and F in Table 2. Again the two first principal components set contains the 97% of the data variance. The plot of PC_1 versus PC_2 is shown in Fig. 3, where is seen that data points associated to F are separated of those associated to dilutions of mangone in F. The $\{PC_1, PC_2\}$ points constitute a database

Table 2
Samples analyzed with the e-nose

Symbol	Sample[a]	Number of determinations[b]
G	Mangone 100%	3
1	Mangone 1%	2
2	Mangone 10^{-1}%	6
3	Mangone 10^{-2}%	4
4	Mangone 10^{-3}%	6
5	Mangone 10^{-4}%	7
F	Fragrance 0%	6
C	Cereal alcohol	5
M	Sugar alcohol	6
Ph	Phenyl-ethyl alcohol	1

[a] The percentages refer to the concentration (w/w) of mangone (G) in the fragrance (F).

[b] Corresponds to the number of measurements with the e-nose.
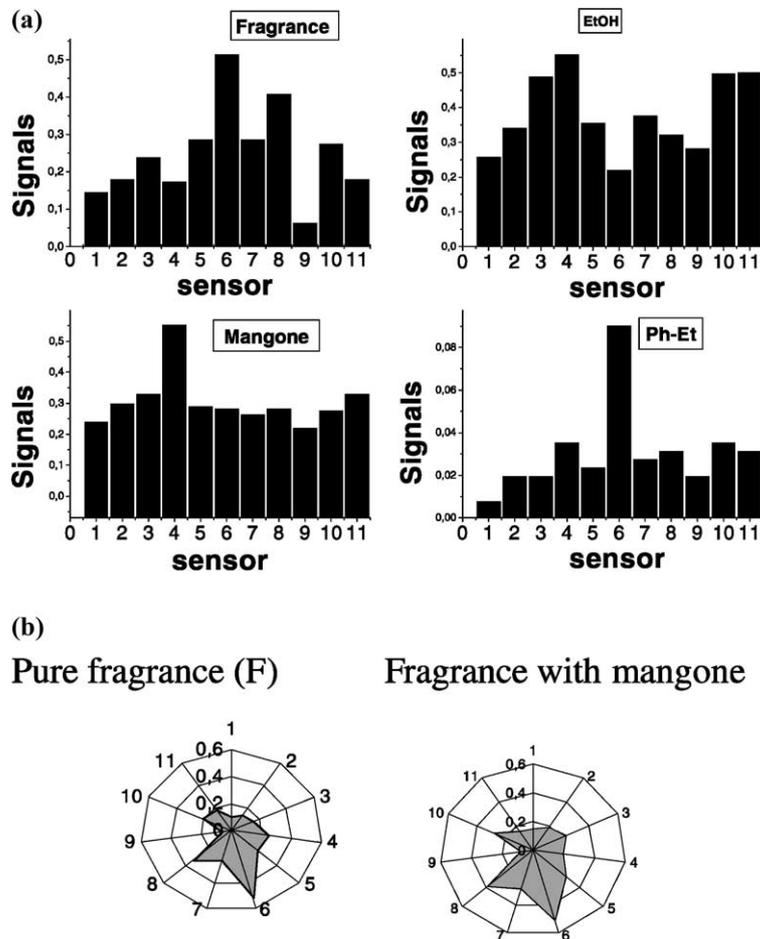
Fig. 1. Graphical displays of some representative fingerprints: (a) bar-plots the pure fragrance, pure mangone, ethanol (EtOH) and phenyl-ethyl alcohol (Ph-EtOH); (b) radar-plots of the pure fragrance (F) and a dilution of G in F.
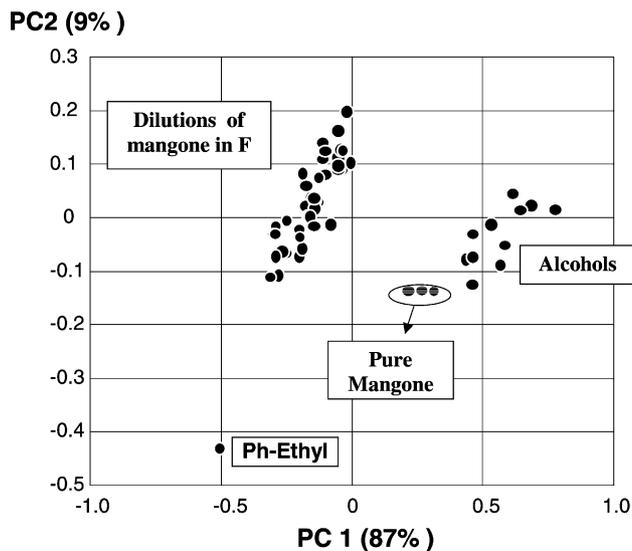
Fig. 2. PCA plot of the total group of measured samples (indicated in Table 2).

which suggests that is possible a better discrimination of samples with and without mangone (the last referred as F in Fig. 3). This was validated by alternatively extracting one of the measurement vectors associated to F and using each of them as a validation data vector into the database. In every case, a point in the expected region of the $\{PC_1, PC_2\}$ plot $(PC_2 > 0.5)$ was obtained. The fact that the points associated with pure F are slightly but systematic separated of the others is promising about the potentiality of the e-nose to recognize pattern differences of samples with and without mangone.

PCA is a parametric non-supervised method that provides a simple manner for visualizing the different samples, as can be seen in Figs. 2 and 3. Its main drawback is the assumption of linearity of the sensor responses with the concentration of the odor chemical components in the particular working range, whose verification is not straightforward. Additionally, the separation of the points associated to pure F in Fig. 3 is not well enough defined to establish a quantitative decision boundary line with a minimum influence of statistical fluctuations.

Therefore, the data were analyzed by the artificial neural network method that as a difference with PCA is non-
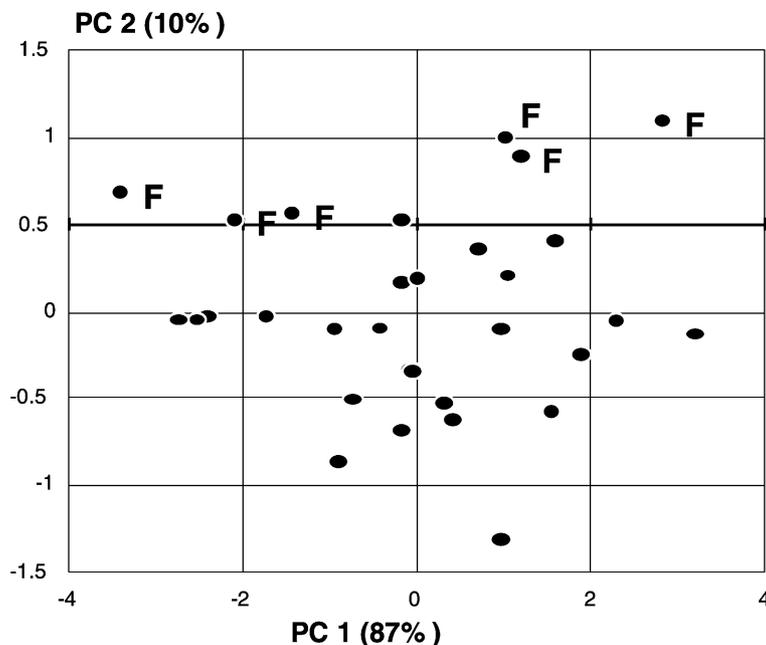
Fig. 3. PCA plot, considering only the samples of the fragrance (F) and dilutions of mangone in F.

parametric and does not require linearity. It is necessary to define several logical operations and parameters, so there are many different types of artificial neural networks [2]. It is also necessary to define the input information and the classification outputs. The two principal components, PC_1 and PC_2, obtained for each experiment, were used as inputs for the ANN. The radial basis function, which is a self-supervised method that allows the basis function to be modified itself during the learning process, was used for classification the samples into two categories: with or without mangone. Thus, a subset of data points were used for training the RBF based neural networks. After the learning process, the capability of the system for discriminating between a sample with or without mangone, which are our classification outputs, was tested.

The results of the network are illustrated in Table 3, which shows the network performance on the selected test set. The used RBF neural network was able to classify the 100% of the test samples correctly. As mentioned above, two categories were defined: samples with mangone and samples without mangone. The network was trained in order to produce an output equal to 1 for the samples with mangone and 0 for samples without mangone, that is, the targets outputs were 1 and 0, respectively. The average output value obtained with the test set for the samples with mangone was (1.0 ± 0.1). This is a remarkable result, which supports the suggestion of Gardner and Bartlett [1] about the use of RBF neural networks for electronic nose data analysis.

The work represents a typical real situation, where an international company has to solve a specific problem: is it possible with the e-nose methodology to detect the presence of mangone in these samples? The number of samples to be analyzed is limited and the conditions for panelists and

Table 3
Discrimination of F and dilutions of mangone samples using a RBF neural network

Sample	Expected output	RBF's results
F	0	0.1
F	0	0.2
5	1	0.8
5	1	0.99
5	1	1.0
4	1	0.99
4	1	0.99
3	1	1.1
2	1	0.95
2	1	1.0
1	1	1.0

Results of the validation data set. The expected output of the network is 1 for the samples with mangone and 0 for samples without mangone, that is, the target outputs are 1 and 0, respectively. Sample numbers refer to Table 2.

CGMS are given by standard protocols. The electronic nose data resulted to be very sensitive to the presence of a compound (mangone) that belongs to a different olfaction family (citrus, grape fruits) with respect to the compounds of olfaction relevance of the fragrance (which are green, pinecone), even at very diluted concentrations of mangone. Thus, the positive results of the electronic nose are of high relevance in the area of cosmetic chemistry, encouraging for searching new applications in this field, particularly as an alternative to conventional methods for routine analysis. A fundamental aspect of the methodology is the possibility to build up a relatively large database, incorporating the results of several measurements with different samples of different concentrations. This specific application database is used in

conjunction with powerful multivariate data analysis methods to discriminate or classify the samples. Our results point out a similar conclusion to that obtained by Romain et al. [11], about the importance of using pattern recognition methods and previous data pre-processing specifically adapted to the particular application case.

4. Conclusions

It is not the aim to present the three detection methods (e-nose, panelists and CGMS) as competitive, but to illustrate the ability of a gas sensors array to detect decreasing concentrations of mangone in a fragrance (background). It is worth noting that under standard conditions (triangle test for trained panelist familiarized with mangone and standard protocols for CGMS detection of fragrances and oils), neither the panelists nor the GCMS analysis could detect, with significant statistical results, the presence of mangone for samples more diluted than $10^{-1}\%$ (w/w) of mangone. An excellent classification and discrimination was obtained with the electronic nose device. That is, the developed electronic nose device could discriminate the presence or absence of the added perfumery note at the lowest concentrations.

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