Portable Electronic Nose Applied to Determination of Contaminants in Milk

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1. Abstract
This work shows the potential application of a portable electronic nose on the discrimination of contaminants in milk. The developed device is an embedded system composed of an array of non-selective chemical sensors associated with an artificial neural network to pattern recognition. Samples were collected from five trademarks of UHT (Ultra High Temperature) milk and subjected to the addition of different concentrations of contaminants - urea, sodium hydroxide and formaldehyde -. In total, 40 samples were analyzed and from them more 160 samples were created by bootstrap resampling. A neural network MLP (Multilayer Perceptron) type was developed for the recognition and classification of each contaminant, in the adjustment of network parameters was used the sequential simplex optimization method, so it went possible to correctly classify all test set of contaminants, 97.1% of the samples used for training and 95.7% of validation samples. Among the advantages of the device compared to other physicochemical analysis methods is their low cost, real-time response, portability and simple interface.

2. Keywords: Electronic nose, discrimination of milk, artificial neural networks, MOS sensors.

3. Introduction
Milk is one of the most consumed foods in the world and the most likely to suffer adulterations either by the addition of water or even chemicals representing a serious risk to consumer health, before that the development of more effective tools for the analysis of milk has been the subject of constant studies. Among the characteristics of milk, the aroma is one of the most important and can say much about the quality of the product. A relatively new tool to monitor the quality of food based on the perception of smell is the electronic nose or e-nose that takes in consideration the global feature of the smell as occurs in the human olfactory system [13]. An electronic nose is generally composed by a chemical system of sensors and an electronic system associated with artificial intelligence techniques for pattern recognition [17].

The term “electronic nose” makes analogy to biological olfactory system for presenting the same principle of operation. The aroma consists of a grouping of molecules, each having specific shape and size. The human nose contains more than 100 million of specialized receptors or sensors, which act together in complex operations for identification of these molecules [7]. A layer of mucus dissolves the molecules soon as they arrive to these receptors. The brain is able to interpret these patterns in order to distinguish the various types of odors [7]. In contrast, an electronic nose consists of a much smaller set of sensors connected to a computer or an artificial neural network able to recognize patterns of molecules [16]. An artificial neural network, in turn, is a set of computational processes that operate similarly to a human brain. Evidence exists showing that a single olfactory neuron responds to several odorants and that each odorant is sensed by multiple olfactory neurons [10]. In the same way, electronic noses base the analysis on the cross-reactivity of an array of semi-selective sensors. Just like the human olfactory system, electronic noses do not need to be specially designed to detect a particular volatile. In fact, they can learn new patterns and associate them with new odors via training and data storage functions as humans do [18]. The sensors used in the development of sensory array must exhibit selectivity wide, so that a single sensor is able of responding to a large number of compounds. Although each sensor of the set is able to respond to a particular substance, such responses are usually different [19]. Furthermore, the sensors must present fast response, stability and high sensitivity to organic vapors. Using a set of different sensors that respond to various compounds can be identified vapors, gases and gas mixtures. Among the types of sensors to be employed in electronic noses, the sensors of the type MOS (Metal Oxide Semiconductor) demonstrate good sensitivity to organic vapors (ppm or ppb) for a wide range of chemical compounds [13]. The interaction of volatiles with the array of sensors provokes a series of signals which are then processed by the computer via a pattern recognition program [18]. Artificial neural networks have been widely used in electronic noses for pattern recognition. Analyzing many standard samples and storing the results in the computer memory, the application of RNA allows the Electronic Nose 'understand' the meaning of the outputs of the various sensors and better use this information for future analysis [13].

The neural network of the perceptron type of multiple layers has been widely used in pattern classification together with the electronic nose [6]. Your training is performed in a supervised manner through consecrated backpropagation algorithm, which is based on the learning rule for error correction [8].

Electronic noses have been widely applied in the dairy industry for classification and recognition of the validity of milk [3], of UHT and pasteurized milk [4], off-flavors in milk [14], geographical origin of dairy products [5], culture of bacteria in milk [11], screening aroma producers lactic acid bacteria [12], evaluating the quality [15], and recognition of different types of milk [2]. However, there aren’t still reports of application of electronic nose to recognize chemical adulterants in milk.

Development of a portable electronic nose system, therefore, has become a demanding requirement because of its advantages such as small size, low cost, and easy manipulation in comparison with the ordinary electronic nose system [9].
The present work had as objective the developing of a portable electronic nose able to recognize different substances adulterants in milk being the main ones: urea, sodium hydroxide and formaldehyde. The device is composed of an array of MOS sensors, a microcontrolled system for signal processing and neural network Multilayer Perceptron type for recognition of aromatic profiles of each contaminant.

4. Materials and Methods

4.1 Sensory array
Three sensors MOS type were used in the construction of the sensory array. The following table shows the specificity of the sensors used.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Especificity</th>
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<tbody>
<tr>
<td>MQ3</td>
<td>Alcohol, ethanol and smoke</td>
</tr>
<tr>
<td>MQ138</td>
<td>Formaldehyde, benzene, toluene, ethanol, acetone, propane and hydrogen gas</td>
</tr>
<tr>
<td>MQ137</td>
<td>Ammonia</td>
</tr>
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</table>

The interaction of volatiles with the array of sensors provokes a series of signals which are then processed by the control algorithm, to embark such an algorithm was used Arduino UNO development board based on microcontroller ATMEGA 328P of AVR architecture. The development of the neural network was performed in software Matlab that has a toolbox exclusively dedicated to the implementation of RNAs with the most diverse graphic and statistical tools for better analysis of the results. Serial communication allows Matlab to acquire all data provided by Arduino UNO and its subsequent manipulation. For coupling the sensory array was designed a sampling chamber (Fig. 1) allowing the entry, storage and removal of VOCs (Volatile Organics Compounds) in milk. At the base of the chamber has been installed a heating plate whose temperature control is made by the microprocessor system TCM58 with technology based on microcontroller RISC of high performance. The ideal temperature for liberation of VOCs and acquisition of electrical measurements in the shortest possible time was 200 °C.

4.2 Preparation of samples
Five trademarks of UHT milk were analyzed and all samples collected from different lots in order to ensure a broad and diverse sample space for subsequent classification. Formaldehyde, urea and sodium hydroxide were chosen as adulterants substances to be identified as the main substances used to adulterate milk. To ensure accuracy in measurements a micropipette high-precision DIGIPET and a chemical balance of Bel Engineering were used. Each sample containing 10 ml of UHT milk with a specific amount of a particular contaminant was conditioned around 10 minutes at room temperature and then taken to the sample chamber where it stayed for 2 minutes and a half at a temperature of 200 °C. For the same lot, four measures (pure milk - milk with urea - formaldehyde milk - milk with sodium hydroxide) were performed per day.

4.3 Normalization and bootstrap resampling
When submitted to the VOCs present in the milk the MOS sensors have changed their conductivity resulting in a characteristic curve, the area under each curve is then integrated numerically resulting in an input vector with three values for each sample. Before being submitted to the neural network, the input vectors were normalized per min max so that all input variables presented the same order of magnitude thus avoiding the neural network attributed more importance to certain variable only due to its magnitude [1].
The first database consisted of 40 samples. The bootstrap resampling allowed to obtain new input vectors by generating random data with the same mean and standard deviation than original, in all were created over 160 samples, it facilitated the neural network training without the need to perform new measures. Overall, 70% of samples were used for training, 15% for validation and 15% for the test.

4.4 Multilayer Perceptron (MLP)
Using the Neural Network Toolbox, available tool in Matlab a neural network type Multilayer Perceptron was prepared. The model of a neuron for this type of network is given in Figure 2.

Figure 2. Model of a neuron in an MLP.

The sum realized in each neuron \( N^l \) of a network of \( L \) layers is called induced local field Eq(1), subsequently it is applied in a non-linear activation function Eq(2) that will produce the neuron output [8].

\[
V^l_k = \sum_{m=0}^{m=l-1} W^l_{km} V^l_m , \text{where } k=1,2\ldots N^l , e \ l=1,2\ldots, L. \tag{1}
\]
\[
Y^l_k = \varphi(V^l_k) , \text{where } k=1,2\ldots N^l , e \ l=1,2\ldots, L \tag{2}
\]

For \( m = 0, V^{l-1}_m = 1 \) and \( W^{l-1} \) is called bias, its function is to increase or decrease the liquid entry activation function. The activation function used here was the sigmoid logistics Eq(3).

\[
\varphi(V^l_k) = \frac{1}{1+e^{-V^l_k}} , \ k = 1,2\ldots N^l , e \ l = 1,2\ldots, L \tag{3}
\]

The inclination of the logistic function \( \alpha \) is one of the network parameters to be optimized.

For network training we used the backpropagation algorithm where the weights are adjusted according to the output provided by the network. Each interaction network response is subtracted from the desired response generating an error signal which is backpropagated through synaptic connections adjusting the weights Eq(4).

\[
W^{l+1}_{km}(n+1) = W^{l+1}_{km}(n) + \rho \Delta W^{l+1}_{km}(n-1) + \eta \delta^l_{m+k} \tag{4}
\]

where \( k=1,2\ldots N^l; l=1,2\ldots, L; m=1,2\ldots,j_k; n=0,1,2\ldots \)

Be:

\[
\delta^l_k = \begin{cases} e_k \varphi_k'(V_k) & \text{ (I)} \\ \varphi_k'(V_k) \sum_m \delta^{l+1}_m W^{l+1}_{km}(n) & \text{ (II)} \end{cases} , \text{where } k = 1,2\ldots, N^l; l = 1,2\ldots, L; m = 1,2\ldots, j_k \tag{5}
\]
\[
e_k = d_k - o_k , \ k = 1,2\ldots N^l \tag{6}
\]

I - For the neuron \( k \) of output layer.
II - For the neuron \( k \) of the layer \( l \).
The term $W_{lm}^{k}(n + 1)$ is the new synaptic weight applied to the subsequent interaction and $\Delta W_{lm}^{k}(n + 1)$ is the correction of weights held in the previous interaction, $\rho$ is the time constant and $\eta$ is the learning rate. The local gradient of each neuron is given by $\delta k^l$, the error signal $e_k^l$ is equal to the desired response $d_k^l$ less produced by the network $o_k$. The learning process is repeated several times until the synaptic weights and bias become approximately constant and the mean square error Eq (7) converge to a minimum.

$$EQM = \frac{1}{2N} \sum_{n=1}^{N} \sum_{k=1}^{C} e_k^l(n)$$  

(7)

In the above equation $N$ is the training set size and $C$ the number of neurons in the output layer.

In order to maximize the percentage of correct classification and consequently minimize the mean square error the sequential simplex method was applied to the optimization of the following parameters: slope of activation function, learning rate, constant time and the number of neurons in the intermediate layer.

5. Results and Discussion

In MOS sensors the detection of a given substance occurs when catalyzed reactions occurring on the sensor surface altering its resistance inversely proportional to the concentration of analyte. The following figure shows the response of the sensory array to four samples (pure milk, urea, milk with sodium hydroxide and milk with formaldehyde) to 200 °C.

![Figure 2. Response of sensors: 10ml of pure milk (a), 10 ml of pure milk with 0.064g of urea (b), 10 ml of pure milk with 0.060g of sodium hydroxide (c), 10 ml of pure milk 0.05 ml of formaldehyde (d).](image)

It was observed that all sensors showed rapid adsorption and desorption kinetics with a variation of its conductance by 50% over two and a half minutes. For all measurements it was verified that a single sensor shows different response for each type of dopant used and measurements in the same environment without considerable temperature variation and humidity variation of conductivity for each sample remained constant demonstrating that the sensors have good repeatability.

In relation to the optimization of the neural network parameters by applying the sequential simplex method the best classification performance with lower mean square error was obtained with learning rate equal to 0.93, the time constant of 0.6 and inclination of the activation function equal to unity.
The network architecture was defined according to the size of the input vectors and the number of output classes being used, therefore, three neurons in the input layer, and four neurons in the output layer, the sufficient number of neurons in the middle layer it was set between 3-5 neurons. It was observed that the use of more than 5 neurons in the intermediate layer while result in a smaller mean square error to the training set, the network generalization capacity for new input vectors was reduced, such behavior is known as overtraining. The sequential mode of training was more appropriate to the problem in question in relation to the batch mode, because once the presentation of standards to the network is performed in random order the synaptic weights search space is made more widely, in addition, this mode was able to circumvent redundant patterns in the database, all this has reduced the possibility of training algorithm getting stuck in a local minimum.

The application of optimized parameters and sequentially training allowed a correct rating of 100% of the test set, for the validation samples the percentage of correct classification stood at around 95.7% and the training set this rate reached to 97.1% on average. These and other performance variables such as the mean square error and the number of training epochs are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Performance of the neural network.</th>
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<tr>
<td>Mean square error</td>
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<td>Number of epochs</td>
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<td>Correct classification of validation samples</td>
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<tr>
<td>Correct classification of training samples</td>
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<tr>
<td>Correct classification of test samples</td>
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These results were made possible by the use of sequential simplex optimization of parameters, the application of bootstrap in generating a broad and diverse set of training and the proper normalization of input vectors. A highly positive point of the incorporation of the neural network to the electronic nose is that it allowed soften the effect of noisy signals and interferences to which the electrical measurements are subject by the fact of allow previous inclusion of information throughout its development simplifying the design and increasing the response speed.

6. Conclusions

The incorporation of neural network Multilayer Perceptron to electronic nose resulted in the development of a relatively new and extremely effective tool which greatly will assist in the control of milk quality. Their portability allows the monitoring of the entire production cycle of milk substantially reducing product fraud rates; its low cost, easy operation and non-use of chemicals does not require skilled labor or the need for confinement in laboratories; all this related to possible of real production cycle of milk substantial improvements to the control of milk quality. Their portability allows the monitoring of various types of contaminants which makes it an innovative tool for the dairy industry.

7. Acknowledgments

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8. References


