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Development of a Bioelectronic Tongue Modified with Gold Nanoparticles for Dairy Analysis †

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Abstract: The objective of this work was to create an all-solid-state potentiometric bioelectronic tongue with an array of polymeric membrane-based sensors, which could be used, in the dairy sector. Membranes were modified with gold nanoparticles and enzymes were covalently linked to the sensor's surface to create an array of sensors with greater sensitivity. The responses of the sensors modified with gold nanoparticles and covalently associated enzymes showed higher sensitivities. Moreover, the bioelectronic tongue developed was able to perform the discrimination of milks with different nutritional characteristics applying principal component analysis. In addition, the results obtained showed that applying partial least squares analysis the system developed could be used as a prediction system for different chemical parameters (such as acidity, proteins, lactose, etc.)

Keywords: Electronic tongue; Biosensor; Potentiometric; Dairy industry; Nanoparticles

1. Introduction

The concept of electronic tongues has developed rapidly during recent years due to their large potential. E-tongues are based on sensor arrays with low selectivity and high cross-selectivity between multiple sensors [1]. Compared to other analytical methods, this type of device allows the acquisition of chemical information from different matrixes by applying suitable multivariate statistical qualitative or quantitative data processing techniques, targeting to overcome drawbacks such as the requirement of pretreatment of samples, noise issues and colinearity between variables [2].

E-tongues can implement a range of transduction principles, being electrochemical sensors (potentiometric, amperometric, voltammetric, or impedimetric sensors) the most common sensors applied in the development of e-tongues. Potentiometric sensors are based on the measurement of the differences in the interface potential created across a selective membrane. The interaction between the electrode and the solution determines this potential, which is related to the physicochemical properties of the solutions under inquiry [3].

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The objective of this work was to design an all-solid-state potentiometric bioelectronic tongue (bio-ET) dedicated to the dairy sector, using an array of biosensors based on polymeric membranes operating in parallel. The membranes were modified with gold nanoparticles (AuNPs) to create an array of sensors with greater sensitivity [4]. Moreover, to further improve the sensor's selectivity, enzymes including galactose oxidase, urease, and lactate dehydrogenase were covalently attached to the PVC surface. The bio-ET has beeb apllied to the analysisi of milk samples with different nutricional content.

2. Materials and Methods

The electronic tongue was constructed by combining sensors based on polymeric matrixes that differ in its composition. Polymeric membranes were made of PVC [poly(vinyl chloride)] mixed with an additive (oleyl alcohol), a plasticizer [(bis(1-butylpentyl)adipate, tris(2ethylhexyl)phosphate or 2-nitrophenyl-octylether] and gold nanoparticles creating an array of 27 sensors. Each of the polymeric mixtures were applied on solid conducting silver-epoxy supports. The bio-ET was composed of the sensor array, an Ag/AgCl reference electrode, and a data collecting multiplexer.

The effect of gold nanoparticles and the bioelectronic tongue performance was tested by analysing six standard solutions at concentrations ranging from 1×10^{-3} and 1×10^{-1} mol / L. Applying multivariate analysis technique a set of sensors was selected for the construction of a bio-ET that was applied to twelve commercial milk samples. Potentiometric signals obtained from the array of sensors were processess using Principal Component Abalyisis (PCA). Using Partial Least Squares (PLS), correlations between the responses of the sensors and chemical parameters were established.

3. Results

The results obtained in this research indicate that sensors with a higher percentage of gold nanoparticles in their composition showed higher sensitivities towards compounds found in milk, and example of the sensor behaivour is showed in Figure 1. This behaivour could de doue to an increase of the sensitivity of the sensors towards inespecif ions on the interface of the polymeric membrane when AuNPs are included in the matrix composition.

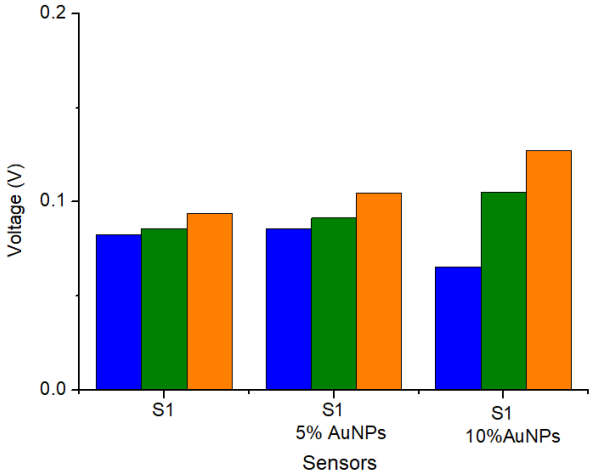

Figure 1. Sensors response to glucose at increasing concentrations (blue=10^{-4}M; green=10^{-3} M and orange=10^{-2} M depending in the percentage of AuNPs applied in the membrane matrix. .

Moreover, sensosor that combined gold nanoparticles with enzymes showed a greater ability to differentiate between increasing concentrations of products of interest found in milk such as urea, lactic acid, galactose, etc. With deviations of voltages up to 65 mV between different samples.

Furthermore, using statistical analysis (PCA), the bioelectronic tongue constructed was able to classify milk with various nutritional features, resulting in four distinct groups that were also sorted according to the fat content of the samples (Figure 2).

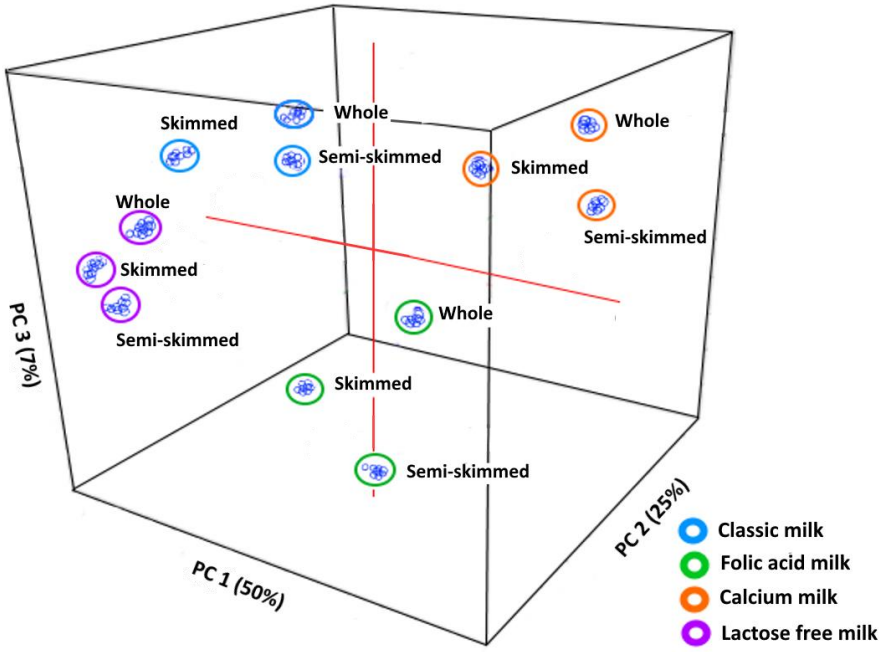

Figure 2. Classification of the milk samples studied according to the score diagram of the principal component analysis.

Additionally, the study's findings revealed that using partial least squares analysis (PLS) with regression coefficients above 0.85 for three variables in the physico-chemical parameters studied, the bioelectronic tongue developed could be used as a prediction system to determine parameters, such as density, acidity, lactose or fat content, of future milk samples (Table 1).

Table 1. Correlation parameters resulting from the regression of partial least squares analysis (PLS).

Parameters	$R2_C$	$RMSE_C$	$R2_P$	$RMSE_P$	Latent variables
Acidez	0.8683	0.2894	0.8483	0.2753	3
Density	0.8729	0.5172	0.8621	0.5736	3
%Proteins	0.8629	0.1027	0.8432	0.1251	3
%Fat	0.8512	0.4723	0.8404	0.4817	3
%Lactose	0.8895	0.0553	0.8813	0.0577	3

4. Conclusions

In this work, a bioelectronic tongue was developed and used to predict chemical characteristics of milks. Sensors with higher concentrations of gold nanoparticles in their composition showed greater sensitivity towards compounds of interest in milk (such as lactic acid, galactose and urea). The system using nine potentiometric sensors could be successfully used to discriminate between milks applying PCA based on their nutritional content. The bio-ET was successfully used to predict the acidity, density, %proteins, %lactose and %fat, with low errors and high correlation coefficients for three factors. This device could be adapted for its implantation in dairy industry.

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Conflicts of Interest: The authors declare no conflict of interest.

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