COMPARATIVE STUDY OF TWO ELECTRONIC TONGUES FOR THE DETECTION OF ETHYLPHENOLS BY MIP-BASED AND CHEMICALLY MODIFIED VOLTAMMETRIC SENSORS

A. Herrera-Chacon, A. González-Calabuig and M. del Valle

Sensors and Biosensors Group, Department of Chemistry

Universitat Autònoma de Barcelona, Edifici Cn, 08193 Bellaterra, Barcelona, Spain

Universitat Autònoma de Barcelona

GRUP DE SENSORS I BIOSENSORS

INTRODUCTION

Volatile phenols are the main substances related to the Brett character in wine, produced by *Brettanomyces* fungi and providing the their beverage an unpleasant aroma and flavour, which ruins the production. Consequently its early detection during initial fermentation steps is required to save loses to the producers. In this direction, herein it is reported the applicability of two electronic tongues (ETs) for their identification, the detection and the quantification of main Brett-related volatile phenols: 4-ethylphenol (4-EP), 4-ethylguaiacol (4-EG) and 4-ethylcatechol (4-EC).

On the one hand, a sensor array based on Molecularly Imprinted Polymers (MIPs) was designed to be individually selective to each of the analytes responsible of the Brett character, i.e., 4-EP, 4-EG and 4-EC. These polymers were designed and synthesised using each of the analytes, respectively, as template molecules. Once obtained, these materials were characterised and integrated onto the Graphite Epoxy Composites sensors (GECs). Then, the readout was done by Differential Pulse Voltammetry (DPV), optimizing previously the measurement conditions. On the other hand, a voltammetric ET based on a chemically modified sensor array was formed by 5 modified-GECs and plus 1 GEC bare electrode. The different sensors were modified with Cu nanoparticles, WO_3 nanoparticles, Co phtalocyanine, Bi_2O_3 nanoparticles and polypyrrole. This choice was intended as to maximize the differences in the obtained voltammograms for the different sensors using cyclic voltammetry (CV) as electrochemical technique.

Once the sensor arrays were developed, Principal Component Analysis (PCAs) was used in order to discriminate the different phenols among them as well as from other interferent species. Finally, Artificial Neural Networks (ANNs) were used for the quantification of these analytes in aqueous samples in the case of the MIPs-based sensor array and in wine samples in the case of modified sensor array.

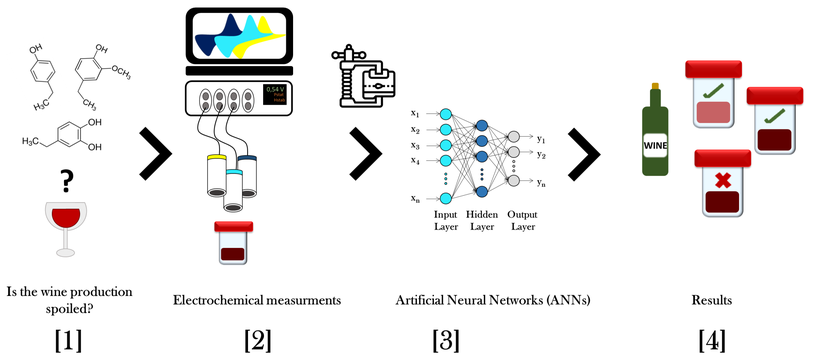

Figure 1. Electronic Tongue application diagram for the identification and quantification of the before-mentioned volatile phenols.

MOLECULARLY IMPRINTED POLYMER BASED SENSOR ARRAY

Molecularly imprinted polymers (MIPS), alternatively known as nanoplastics, are polymers furnished with supramolecular chemistry principles that have proven their potential as synthetic receptors, mimicking antibodies functionality. These materials are able to recognize biological and chemical species, based on the same principles as their biological counterparts: antibodies or aptamers. Non-imprinted polymers (NIPs) were also obtained under the same conditions but in absence of the template. Upon its synthesis, MIP/NIP particles were immobilized onto GEC surfaces by sol-gel.

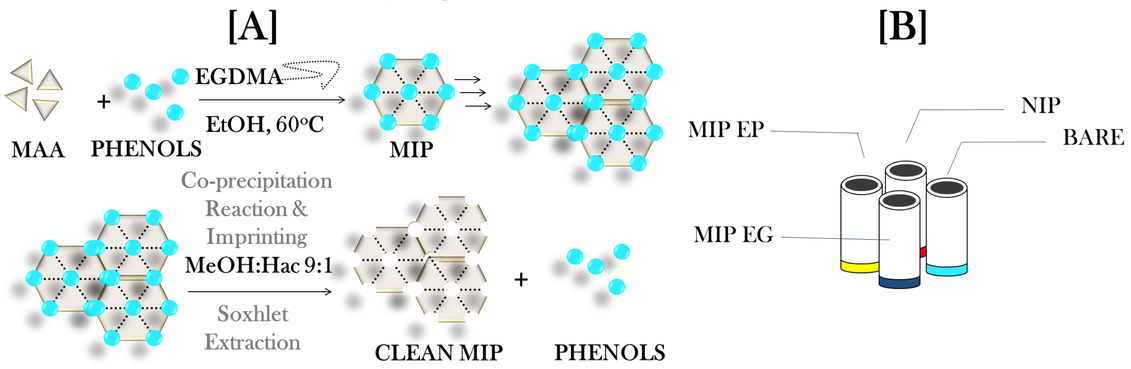

Figure 2A. [A] Schematic plot of molecularly imprinting synthesis and [B] sensory array performed in this work.

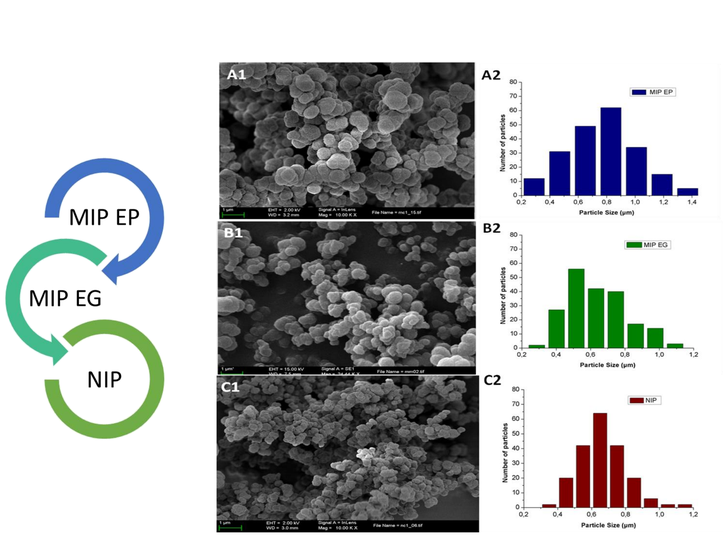

Figure 3A. (A1/B1/C1) Scanning electron microscopy (SEM) images of the obtained 4-EP MIP (top), 4-EG MIP (middle) and NIP (bottom). (A2/B2/C2) Histograms of the 4-EP MIP (top), 4-EG MIP (centre) and NIP (bottom).

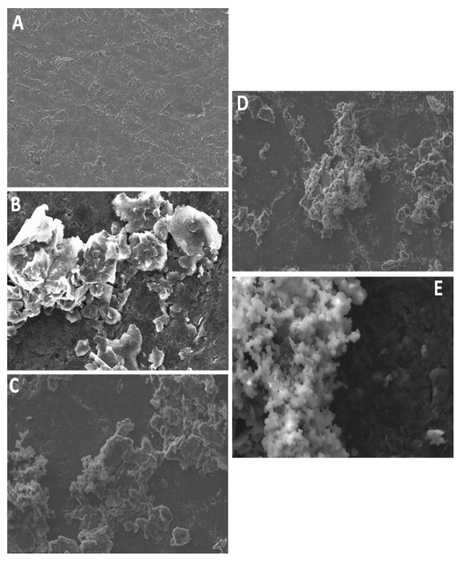

Figure 4A. SEM images of the sol-gel modified GEC surfaces: (A) before, (B) sol-gel, (C) 4-EP MIP , (D) 4-EG and (E) NIP.

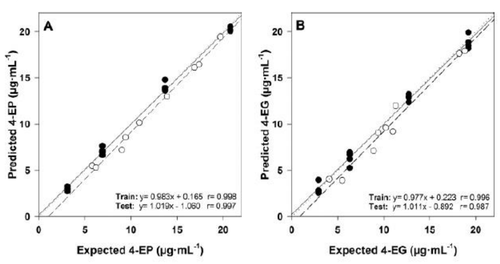

Figure 5A. (Left)Fittings of predicted vs. expected concentrations for (A) 4-EP and (B) 4-EG, both for training (•, solid line) and testing subsets (○ , dashed line). Dotted line corresponds to ideal behaviour (diagonal line).

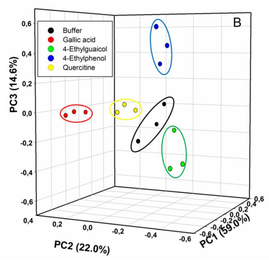

Figure 6A. Scores plot for then three first principal components for the analytes 4-EP, 4-EG, and two polyphenols present in wine, Quercitine and Gallic acid.

Table 1A. Results of the fitted regression lines for the comparison between obtained vs. expected values, both for the training and testing sets for the considered species (intervals calculated at 95% confidence level).

	Compound	Correlation	Slope	Intercept (mg L^{-1})	NRMSE	Total NRMSE
Train	4-EP	0.998	0.983 ± 0.075	0.162 ± 0.893	0.023	0.038
	4-EG	0.996	0.977 ± 0.106	0.223 ± 1.274	0.031	
Test	4-EP	0.997	1.019 ± 1.52	-1.060 ± 1.978	0.049	0.076
	4-EG	0.987	1.010 ± 0.299	-0.892 ± 3.537	0.059	

CHEMICALLY MODIFIED VOLTAMMETRIC SENSOR ARRAY

In the group of Sensors and Biosensors of UAB, there is a large experience in working on modified Graphite Epoxy Composites (GECs). Briefly, GECs were constructed by mixing 15% of graphite powder, 2% of the specific modifier and 80% of the epoxy resin. Then, they were cured in the oven for 72 hours and finally polished before used. In this manner, a large array different modified graphite epoxy composite (GEC) electrodes were prepared to be evaluated as the working electrodes that will form the ETs, from which a total of six was selected taking into account previous studies with ETs, and the electrochemical response of a larger set of sensors towards the considered compounds.

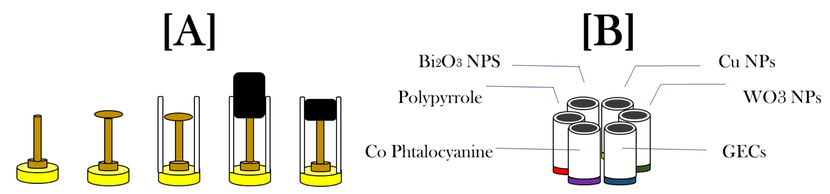

Figure 2B. [A] Schematic process of GECs construction and [B] sensory array employed in this work.

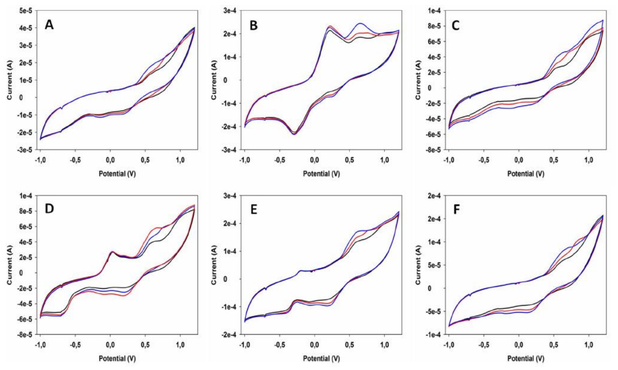

Figure 3B. Example of the different voltammograms obtained for 25 ppm of 4-EP (black), 4-EG (red) and 4-EC (blue) in a wine matrix for a (A) Bare GEC and electrodes modified with (B) Cu nanoparticles, (C) WO3 nanoparticles, (D) Bi_2O_3 nanoparticles, (E) Polypyrrole and (F) Co(II) phthalocyanine.

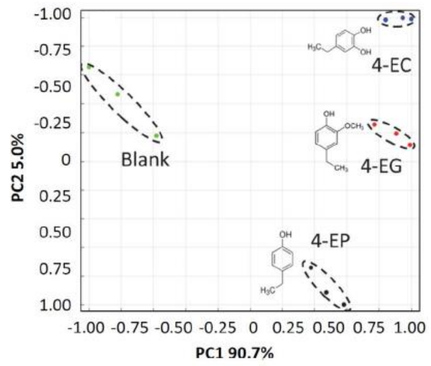

Figure 4B. (B) The PCA scores plot of the different electrodes for 25 ppm of 4-EP (black), 25 ppm of 4-EG (red) and 25 ppm of 4-EC (blue).

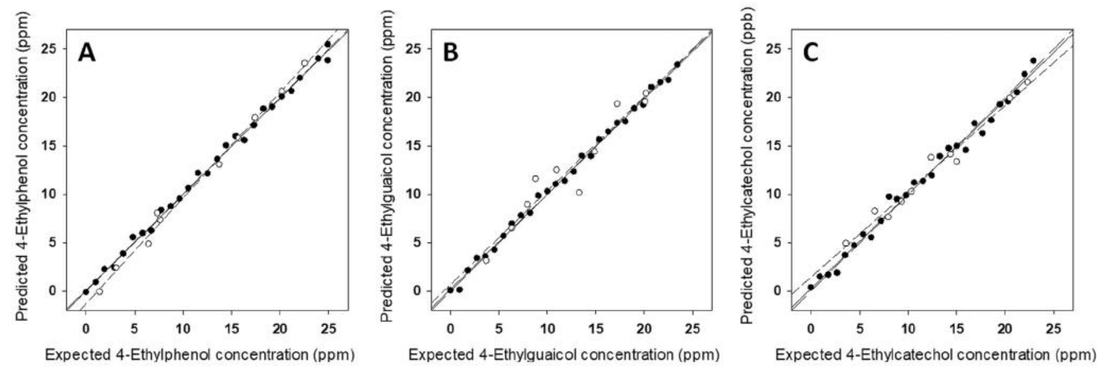

Figure 5B. Modeling ability of the developed DWT-ANNs response model. Adjustments of expected vs. predicted concentrations for (A) 4-EP, (B) 4-EG and (C) 4-EC, both for training (•, solid line) and testing subsets (○, dashed line). Dotted line corresponds to theoretical diagonal line.

		r	Slope	Intercept (mg L^{-1})	NRMSE	Total NRMSE
Train	*4-EP*	*0.998*	*0.990 ± 0.049*	*0.13 ± 0.72*	*0.019*	*0.022*
	4-EG	*0.998*	*0.981 ± 0.049*	*0.21 ± 0.67*	*0.018*	
	4-EC	*0.995*	*0.974 ± 0.082*	*0.28 ± 1.10*	*0.029*	
Test	*4-EP*	*0.997*	*1.089 ± 0.133*	*−1.24 ± 1.80*	*0.037*	*0.050*
	4-EG	*0.958*	*0.969 ± 0.474*	*0.7 ± 6.4*	*0.069*	
	4-EC	*0.988*	*0.886 ± 0.227*	*1.5 ± 3.1*	*0.043*	

NRMSE: Normalized Root Mean Square Error.

Table 1B. Results of the fitted regression lines for the comparison between obtained vs. expected values, both for the training and testing subsets of samples and the three considered species (intervals calculated at the 95% confidence level).

CONCLUSIONS

Two different approaches for the detection of volatile phenols based on the usage of ETs are compared. On the one hand, the use of a MIP modified sensor array that demonstrate its selectivity and specificity against its template molecules. On the other hand, a chemically modified array of sensors was used with the same purpose. Both approaches showed similar performance and have been demonstrated to be a versatile tool for the detection and quantification of volatile phenols even in the presence of other compounds or directly in wine simples.

ACKNOWLEDGMENTS

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