

Resolution of galactose, glucose, xylose and mannose in sugarcane bagasse employing a voltammetric electronic tongue formed by metals oxy-hydroxide/MWCNT modified electrodes

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ABSTRACT

Second generation ethanol is produced from the carbohydrates released from the cell wall of bagasse and straw of sugarcane. The objective of this work is the characterization and application of a voltammetric electronic tongue using an array of glassy carbon electrodes modified with multi-walled carbon nanotubes containing metal (Paladium, Gold, Copper, Nickel and Cobalt,) oxy-hydroxide nanoparticles (GCE/MWCNT/MetalsOOH) towards a simpler analysis of carbohydrates (glucose, xylose, galactose and mannose). The Artificial Neural Network (ANN) based prediction model has resulted satisfactory for all carbohydrates and the obtained response had shown an adequate accuracy. In this manner 192 architectures were evaluated. The final architecture of the back-propagation ANN model had 36 input neurons, a hidden layer with 5 neurons and the *tansig* transfer function, an output layer with 4 neurons and the *purelin* transfer function. All species a comparison correlation coefficient of $r \geq 0.99$ for the training subset and of $r \geq 0.96$ for the test subset, being close to the ideal value.

Keywords: Electronic Tongue, Carbohydrates, Artificial Neural Network, Multi-walled carbon nanotubes, Metal nanoparticles, Second generation ethanol.

1. INTRODUCTION

The biomass consisting of sugarcane bagasse is a by-product of the production process for sugar and ethanol. New applications for the bagasse have been developed and among them we can highlight the production of second generation biofuels (ethanol) [1, 2]. Second generation ethanol is produced from the carbohydrates that are released from the cell walls of sugarcane bagasse and straw [3, 4].

Biomass as sugarcane bagasse is formed in its majority by lignocellulosic materials, in other words composed of carbohydrate polymers with crystalline and amorphous structures, formed of three main fractions: cellulose, hemicellulose and lignin [3, 4]. The most abundant fraction is cellulose (32-44%), a linear homopolysaccharide, formed by glucose units strongly bound. The hemicellulose (27- 32%), consists of different carbohydrates, mainly xylose, configured in an easily hydrolysable chain. Finally, there is a series of aromatic alcohols polymerized, called lignin fraction, 19-24%, that linked to hemicellulose wraps up the cellulose and protects it from chemical or enzymatic hydrolytic attack [3, 4].

Hemicelluloses are a heterogeneous class of polymers configured in an easily hydrolysable chain formed by carbohydrates as, pentoses (β -D-xylose, α -L-arabinose), hexoses (β -D-mannose, β -D-glucose, α -D-galactose) and uronic acids (α -D-glucuronic, α -D-4-O-methylgalacturonic and α -D-galacturonic) [5, 6]

Abundant applications of enzymatic sensors for carbohydrates are reported in literature, with the majority dedicated to glucose in contrast to non-enzymatic ones. In their description, there is a balance of advantages and disadvantages of which both are significant. Despite dominating the glucose sensor market, enzymatic systems have a number of critical flaws such as high oxygen dependency, and can be therefore questioned for maximum reliability. Furthermore, the sensory ability of enzymatic sugar biosensors may be highly impacted by the presence of other electroactive interferences in the sample that are always commonplace in real industrial samples and it is still constrained by usage of mildly enzymic conditions, such as pH ranges of 2-8, temperatures below 44°C, and ambient humidity levels [7, 8].

Sensitive and selective carbohydrate sensors are relevant for use in blood sugar monitoring, food industry, bio-processing and in the development of renewable and sustainable fuel cells. Non-enzymatic carbohydrate electrodes used in direct oxidation may show considerably greater sensitivity, with high oxidation currents being reported over the past decade [8].

The development of non-enzymatic carbohydrates sensors has risen at a considerable rate, many efforts have been made to find new electrocatalytic materials for oxidation of glucose and carbohydrates such as: cobalt hydroxide nanoparticles electrodeposited on the surface of glassy carbon electrode [9], multi-wall carbon nanotubes containing copper oxide nanoparticles [10], copper hydroxide nanotubes [11], nickel hydroxide nanoparticles on boron-doped diamond electrodes [12], carbon nanotubes/copper composite electrodes [13], copper(II) oxide nanorod bundles [14], gold nanoparticle-constituted nanotube array electrode [15], palladium nanoparticles supported on functional carbon nanotubes[16], palladium nanoparticles distributed on surfactant-functionalized multi-wall carbon nanotubes [17], Nickel/cobalt alloys modified electrodes [18], nickel hydroxide deposited indium tin oxide electrodes [19], Au–CuO nanoparticles decorated reduced graphene oxide [20] and glassy carbon electrode decorated with multi-wall carbon nanotubes with nickel oxy-hydroxide [21].

Accurate measurement of the carbohydrate content in the samples of sugarcane bagasse is very important, because the quantification of these sugars is directly linked to what type of microorganism has to be used in fermentation and is also extremely important in the evaluation and optimization of different processes for the production of second generation ethanol [2].

The use of non-enzymatic chemically modified electrodes represents an attractive alternative to classical analytical methods for detection of carbohydrates; unfortunately, these sensors exhibit lower selectivity than those enzymatic ones, discriminating with difficulties individual carbohydrates. Although this can be as the possibility to predict total carbohydrates present, the only alternative to the lack of selectivity seen can be the use of chromatographic stages [22-25]. Besides that to such specific equipment are high cost, laboratory conditions and trained personnel.

A new methodology in the sensors field is the use of sensors in arrays coupled with complex data treatment, that is, the use of electronic tongues; these are

versatile sensor systems capable to simultaneously monitor the level of different analytes, or analytes in presence of their interferents, or to resolve mixtures of similar analytes [26-31].

An electronic tongue is a multisensor system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on Pattern Recognition and/or Multivariate data analysis – Artificial Neural Networks (ANNs), Principal Component Analysis (PCA), etc. [32]. Therefore, the electronic tongue is an analytical system applied to liquid analysis formed by a sensor array in order to generate multidimensional information, plus a chemometric processing tool to extract meaning from these complex data [27, 33].

From the beginning of this technique, there are electronic tongue devised using potentiometric sensors, but also using of the voltammetric type. In these original works, originated at the laboratories of Prof. Winquist in Linköping (Sweden), the sensor array was formed by an array of different metallic disc electrodes, and a scanning voltammetric technique was used to generate the analytical information [30]. The voltammetric principle has also been applied to develop electronic tongues since its early years, such as simultaneous identification and quantification of nitro-containing explosives by advanced chemometric data treatment of cyclic voltammetry at screen-printed electrodes [28], instrumental measurement of wine sensory descriptors using a voltammetric electronic tongue [33], evaluation of red wines antioxidant capacity by means of a voltammetric e-tongue with an optimized sensor array [34], voltammetric electronic tongue for the qualitative analysis of beers [27] and cava wine authentication employing a voltammetric electronic tongue [35].

The present work reports the characterization and application of a voltammetric electronic tongue using glassy carbon electrode modified with multi-wall carbon nanotubes decorated with metal (Copper, Cobalt, Paladium, Gold and Nickel) oxy-hydroxide nanoparticles (GCE/MWCNT/MetalsOOH) towards the analysis of carbohydrates (galactose, glucose, xylose and mannose). As such, it combines the responses from voltammetric electronic tongue formed by GCE/MWCNT/MetalsOOH modified electrodes, plus an advanced response model employing a specifically trained Artificial Neural Network (ANNs), with pretreatment of the data employing standard compression methods (Wavelet transform) and pruning step. This preprocessing is needed given the high dimensionality of the considered data.

2. MATERIALS AND METHODS

2.1. Reagent and Instruments

Purified multiwalled carbon nanotubes (MWCNTs) with an outer diameter of 30 nm were purchased from SES Research (Houston, Texas, USA). Cobalt (II) chloride hexahydrate ($\text{Cl}_2\text{Co}\cdot 6\text{H}_2\text{O}$), nickel(II) sulfate hexahydrate ($\text{NiSO}_4\cdot 6\text{H}_2\text{O}$), palladium chloride (PdCl_2), ammonium fluoride (NH_4F), boric acid (H_3BO_3), sodium borohydride (NaBH_4), N-N-Dimethylformamide 99.8% ($\text{C}_3\text{H}_7\text{NO}$), D-Glucose, D-Galactose, D-Mannose, D-Xylose and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulphuric acid 96% (H_2SO_4), nitric acid 69% (HNO_3) and ammonia 32% (NH_3) were purchased from Merck (Darmstadt, Germany). All solutions were made using MilliQ water from MilliQ System (Millipore, Billerica, MA, USA). The buffer used for formation of nickel and cobalt nanoparticles was phosphate buffer ($0.1 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$ and 0.1 mol L^{-1} mono-hydrated NaH_2PO_4 pH 7.0).

2.2. Characterization by scanning electron microscopy.

Transmission electron microscopy (TEM) images and microanalysis patterns were recorded with a JEOL JEM-2011 microscope equipped with an energy dispersive spectroscopy (EDS) detector. Scanning electron microscopy (SEM) images were performed on JSM 7500F model Brand Jeol FE-SEM microscope.

2.3. Measuring procedure

The amperometric measurement cell was formed by the 5 (five) GCE/MWCNT/MetalsOOH modified electrodes plus a reference double junction Ag/AgCl electrode (Thermo Orion 900200, Beverly, MA, USA) and a commercial platinum counter electrode (Model 52-67, Crison Instruments, Barcelona, Spain). Cyclic voltammetry measurements were taken using a 6-channel AUTOLAB PGSTAT20 potentiostat (Ecochemie, Netherlands), in multichannel configuration, using the GPES Multichannel 4.7 software package. For this, potentials were cycled between -0.7 V and $+0.8 \text{ V}$ vs. Ag/AgCl, with a scan rate of 50 mV s^{-1} . Electroanalytical experiments were carried out at room temperature (25°C) under

quiescent conditions. Briefly, samples were measured as described with the GCE/MWCNT/MetalsOOH sensor voltammetric array, and afterwards obtained responses were analysed by means of the different chemometric tools described below.

2.4. Experimental design for the quantification model

In order to prove the capabilities of the ET to achieve the simultaneous quantification of different carbohydrates mixtures, resolution of Galactose, Glucose, Xylose and Mannose a response model using ANNs was prepared. To this aim, a total set of 46 samples were manually prepared with a concentration range of 0.5 to 2.5 mM for each carbohydrate. The set of samples was divided into two data subsets: a training subset formed by 36 samples (78%) which were distributed based on a L36 Taguchi design [36], with 4 factors and 3 levels, and used to build the response model, plus 10 additional samples (22%) for the testing subset, distributed randomly along the experimental domain and used to evaluate the model predictive ability.

2.5. Data processing

In order to reduce the large dataset generated for each sample (5 sensors x 336 current values at different potential) a preprocessing stage was necessary to compress the original data. The objective of this step was to reduce the complexity of the input data while preserving the relevant information, the compression of the data allows also to reduce the training time, to avoid redundancy in input data and to obtain a model with better generalization ability.

The data was compressed using the Discrete Wavelet Transform (DWT) [37]: each voltammogram was compressed using Daubechies 4 wavelet mother function and a fourth decomposition level. In this manner, the original data was reduced to 135 coefficients without any loss of relevant information; additionally Causal Index pruning strategy [38] was employed to further refine the model by eliminating the inputs that make relatively small contributions to the model. With this, the 135 inputs per sample were further reduced down to 36 coefficients, achieving a total compression ratio up to 97.9%.

2.6. Preparation of electrodes for electronic tongue

2.6.1. Decoration of MWCNTs with Pd, CuO and Au nanoparticles

Before the modification with metal nanoparticles MWCNTs were purified with an acidic pre-treatment. Briefly, the MWCNTs were dispersed in a 3:1 mixture of concentrated H₂SO₄/HNO₃ acids using an ultrasonic bath for 90 min [39]. Purified MWCNTs were then used for further modification with different metal nanoparticles.

2.6.2. Palladium decorated multi-wall carbon nanotubes (MWCNT/Pd)

This modification was performed following the protocol reported by Cipri et al. [39]. Briefly, a flask was prepared with a solution consisting of PdCl₂ (14.0×10^{-3} mol L⁻¹), H₃BO₃ (1.57×10^{-1} mol L⁻¹) and NH₄F (6.67×10^{-2} mol L⁻¹). Then, purified MWCNTs (100 mg) were dispersed in the above solution via ultrasonication for approximately 1 h and the pH was adjusted to 8–9. A solution of NaBH₄ (17 mL) was added dropwise under vigorous stirring and followed by another 8h of stirring to complete the reaction. The MWCNT/Pd were filtered, washed and then dried under vacuum at 50°C.

2.6.3. Gold decorated multiwalled carbon nanotubes (MWCNT/Au)

The decoration with Gold was performed following and slightly modifying the procedure reported by Shi et al. [40]. Briefly, a flask was prepared with a solution of 0.5 mL of HAuCl₄·3H₂O (1.0×10^{-2} mol L⁻¹), 0.5 mL of an aqueous solution of trisodium citrate (1.0×10^{-2} mol L⁻¹) and 18.4 mL of double distilled water. Purified CNTs (20 mg for a Au loading ratio of 10% wt%) were added to the above solution and then 10-12 mL of ethanol were immediately introduced under vigorous stirring and the mixture was ultrasonicated for 10 min. Ice-cold freshly prepared NaBH₄ aqueous solution (0.6 mL, 0.1 mol L⁻¹) was then added to the above mixture while stirring and leaving it overnight. The MWCNT/Au were separated by centrifuging, washed with double distilled water for several cycles and then dried under vacuum overnight at 50 °C.

2.6.4. Carbon nanotubes integrated with copper oxide nanoleaves (MWCNT/CuO)

The modification with copper was performed by modifying the procedure reported by Yang et al. [41]. Briefly, in a flask sodium dodecyl sulfate (SDS) was dissolved (0.1 mol L^{-1}) in 300.0 mL of distilled water stirring at 60°C ; Then 50 mg of purified MWCNTs were ultrasonically dispersed in 25.0 mL of DMF and then added to the SDS solution and ultrasonicated for 10 min, then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.5 g) was added to the above solution and ultrasonicated for 10 min. The solution of 100 mL of NaOH (0.5 mol L^{-1}) was slowly dropped into the above solution and then stirred for 10.0 min. The resulting solution was then centrifuged, washed with doubly distilled water for few cycles and then dried at 60°C .

2.6.5. Glassy carbon surface modification GCE/MWCNT/PdOOH

All surfaces of the GC electrodes were polished with $0.3 \mu\text{m}$ alumina powder (Merck) and cleaned in ethanol and Milli-Q water.

2.0 mg MWCNT/Pd were dispersed in 1.0 mL N,N-dimethylformamide (DMF) with a ultrasonic bath to give a 2.0 mg mL^{-1} black solution. 3 steps of $10 \mu\text{L}$ of the black solution were dropped on the GC electrode surface to prepare the GCE/MWCNT/Pd electrode surface at the end of each step, the electrode was allowed to dry at 50°C for 3.0 hours. After modification, the glassy carbon electrode modified with carbon nanotubes containing palladium nanoparticles (GCE/MWCNT/Pd) was passivated to form palladium oxy-hydroxide using a solution of NaOH 0.1 mol L^{-1} in the potential range of -0.8 to 0.8 V at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$ for 20 cycles in cyclic voltammetry. Then, the GCE/MWCNT/PdOOH was washed thoroughly with deionized water and dried. The electrochemical behavior of the GCE/MWCNT/PdOOH electrode was evaluated in aqueous solutions with supporting electrolyte NaOH 0.1 mol L^{-1} .

2.6.6. GCE/MWCNT/AuO

2.0 mg MWCNT/Au were dispersed in 1.0 mL N,N-dimethylformamide (DMF) with a ultrasonic bath to give a 2.0 mg mL^{-1} black solution. 3 steps of $10 \mu\text{L}$ of the black solution were dropped on the GC electrode surface to prepare the GCE/MWCNT/Au electrode surface. At the end of each step the electrode was allowed to dry at 50°C for 3.0 hours. After each modification the glassy carbon

electrode modified with carbon nanotubes containing gold nanoparticles (GCE/MWCNT/Au) was passivated to form gold oxide using a solution of NaOH 0.1 mol L⁻¹ in the potential range of -0.4 to 0.5 V at a scan rate of 50 mV s⁻¹ for 20 cycles in cyclic voltammetry. Then, the GCE/MWCNT/AuO was washed thoroughly with deionized water and dried. The electrochemical behavior of the GCE/MWCNT/AuO electrode was evaluated in aqueous solutions with supporting electrolyte NaOH 0.1 mol L⁻¹.

2.6.7. GCE/MWCNT/CuOOH

2.0 mg MWCNT/Cu was dispersed in 20.0 mL N,N-dimethylformamide (DMF) with an ultrasonic bath to give a 0.1 mg mL⁻¹ black solution. 2 steps of 10 µL of the black solution were dropped at the GC electrode surface to prepare the GCE/MWCNT/Cu electrode surface at the end of each step, the electrode was dried at 50°C for 3.0 hours. After each modification the glassy carbon electrode modified with carbon nanotubes containing copper nanoparticles (GCE/MWCNT/Cu) was passivated to form copper oxy-hydroxide with a solution of NaOH 0.1 mol L⁻¹ in the potential range of -0.5 to 0.3 V at a scan rate of 50 mV s⁻¹ for 20 cycles in cyclic voltammetry. Then, the GCE/MWCNT/CuOOH was washed thoroughly with deionized water and dried. The electrochemical behavior of the GCE/MWCNT/CuOOH electrode was evaluated in aqueous solutions with supporting electrolyte NaOH 0.1 mol L⁻¹.

2.6.8. GCE/MWCNT/CoOOH

1.0 mg MWCNT was dispersed in 10.0 mL N,N-dimethylformamide (DMF) with an ultrasonic bath to give a 0.1 mg mL⁻¹ black solution. 5.0 µL of the black solution was deposited at the GC electrode surface to prepare the GCE/MWCNT electrode surface. Immediately after the glassy carbon electrode was modified with carbon nanotubes (GCE/MWCNT) cobalt nanoparticles were electrodeposited using 1.0×10⁻³ mol L⁻¹ of CoCl₂ in phosphate buffer 0.1 mol L⁻¹ (pH 6.5). The electrodeposition was carried out by cyclic voltammetry in a potential range of -1.1 to 1.2 V at a rate of 100 mV.s⁻¹ for 30 cycles [42]. To complete the modification, the glassy carbon electrode

modified with carbon nanotubes containing cobalt nanoparticles (GCE/MWCNT/Co) was passivated to form cobalt oxy-hydroxide at NaOH 0.1 mol L⁻¹ in the potential range of -0.3 to 0.7 V at a scan rate of 50 mV s⁻¹ for 45 cycles in cyclic voltammetry. Then, the GCE/MWCNT/CoOOH was washed thoroughly with deionized water and dried. The electrochemical behavior of the GC/MWCNT/CoOOH electrode was evaluated in aqueous solutions with supporting electrolyte NaOH 0.1 mol L⁻¹.

2.6.9. GCE/MWCNT/NiOOH

1.0 mg MWCNT was dispersed in 10.0 mL N,N-dimethylformamide (DMF) with a ultrasonic bath to give a 0.1 mg mL⁻¹ black solution. 5.0 μL of the black solution was deposited at the GC electrode surface to prepare the GC/MWCNT electrode surface. Immediately after the glassy carbon electrode was modified with carbon nanotubes (GCE/MWCNT) a solution of NiSO₄ (5.0×10⁻³ mol L⁻¹), in phosphate buffer 0.1 mol L⁻¹ (pH 6.5), was used for the electrodeposition of nickel nanoparticles. The electrodeposition was carried out by chronoamperometry at a potential of -1.3 V for 30 seconds. To complete the modification, the glassy carbon electrode modified with carbon nanotubes containing nickel nanoparticles (GCE/MWCNT/Ni) was passivated to form nickel oxy-hydroxide at NaOH 0.5 mol L⁻¹ in the potential range of -0.5 to 1.0 V at a scan rate of 100 mV s⁻¹ for 30 cycles in cyclic voltammetry [43]. Then, the GCE/MWCNT/NiOOH was washed thoroughly with deionized water and dried. The electrochemical behavior of the GCE/MWCNT/NiOOH electrode was evaluated in aqueous solutions with supporting electrolyte NaOH 0.1 mol L⁻¹.

3. RESULTS AND DISCUSSION

3.1. Characterization of GCE/MWCNT/Metals oxy-hydroxide modified electrodes

TEM characterization of the MWCNT/Pd is displayed in Figure 1-A, as can be observed the size of the nanoparticles is below 10 nm. The quasi-homogeneous distribution may be due to the small longitudinal size in comparison to the diameter of the nanotubes and to the in-situ growth of the palladium nanoparticles. This quasi-homogeneous distribution is expected to give better catalytic properties to the nanocomposite compared to its native properties. The morphology of the MWCNT/Au

composites was further characterized with TEM (Figure 1-B) and confirmed that the Au-NPs were attached on the MWCNT and ends, showing a diameter of about 4-7 nm. The TEM Figure 1-C shows that each leaf-like CuO polycrystalline is composed of several single-crystalline pieces, which suggest the coexistence of CuO and MWCNTs. Therefore, MWCNTs and CuO nanoleaves do indeed form a nanocomposite, and are not simply mixed together. In Figure 1-D it can be observed regular and spherical particles with size about 32 nm and their homogeneous distribution over the MWCNT. This better distribution and uniform sizes may be responsible for lower limits of detection in the analysis of sugars by the electrode modified with MWCNT/Ni. In Figure 1-E it can be observed that the particles are in a wire shape. Some of the particles are in vertical position taking a representative wire; the average particle size is around 20 nm for particles in an upright position as in the case of wire and 185 nm for the particles in horizontal position.

<Figure 1>

3.2. GCE/MWCNT/Metals oxy-hydroxide modified electrodes response

The voltammetric responses for each of the electrodes towards individual compounds was the first response feature checked. That is, to ensure that enough differentiated signals were observed for the different electrodes, generating rich data that might be a useful departure point for the multivariate calibration model.

To this aim, and under the described conditions in Section 2.5, individual standard solutions of galactose, glucose, xylose and mannose were analyzed and their voltammograms inspected, in Figure 2 displays the voltammetric behavior from the different GCE/MWCNT/MetalsOOH modified electrodes in the electrooxidation study of carbohydrates.

In Figure 2 (A) the selected is shown the voltammogram of GCE/MWCNT/PdOOH electrode during electro-oxidation of carbohydrates that occurs at potentials around -0.1 V vs. Ag/AgCl associated with an anodic peak current and also the decrease in cathodic peak current, the results suggest that Pd^(II)/Pd^(I) redox couple in form of PdOOH [44] can catalyze the electro-oxidation of carbohydrates.

In Figure 2 (B) is shown the voltammogram of GCE/MWCNT/AuO electrode during electro-oxidation of carbohydrates that occurs at potential around 0.25 V vs. Ag/AgCl, with the appearance of the anodic peak current and cathodic peak current of reoxidation at potentials -0.07 V vs. Ag/AgCl. This can be state as typical behavior of gold electrodes, which electrocatalytic activity of can be rationalized by the incipient hydrous oxide/adatom model can catalyze the oxidation of carbohydrates [15, 45, 46].

The voltammogram of GCE/MWCNT/CuOOH is shown in Figure 2(C), for which in electro-oxidation of carbohydrates occurs at a potential of around 0.60 V vs. Ag/AgCl, with the appearance of the anodic wave. During the positive scan, the Cu nanoparticles can be oxidized to CuOOH. The $\text{Cu}^{(\text{III})}/\text{Cu}^{(\text{II})}$ redox couple can catalyze the oxidation of carbohydrates [11, 47, 48].

The electro-oxidation of carbohydrates on GC/MWCNT/NiOOH electrode, as shown in the Figure 2 (D), occurred at a potential of around 0.52 V vs. Ag/AgCl associated with increased anodic peak current and decrease in cathodic peak current. The results suggest that $\text{Ni}^{(\text{III})}/\text{Ni}^{(\text{II})}$ redox couple can catalyze the electro-oxidation of carbohydrates [21].

The voltammogram of GCE/MWCNT/CoOOH shown in Figure 2(E) demonstrated electro-oxidation of carbohydrates occurring at potential around 0.65 V vs. Ag/AgCl, with the appearance of the anodic wave. This fact suggests that carbohydrates are oxidized by CoOOH species through $\text{Co}^{(\text{IV})}/\text{Co}^{(\text{III})}$ redox couple moiety and through a cyclic mediation redox process [9, 49].

The observed results as a whole, indicate the different GCE/MWCNT/MetalsOOH modified electrodes forming the electronic tongue can catalyze the electro-oxidation of carbohydrates (galactose, Glucose, Xylose and Mannose) to ketones, forming galactonolactone, gluconolactone, xylonolactone and mannonalactone, respectively [21]. Besides, clearly differentiated curves are obtained for each modified electrode and each considered sugar giving the desirable condition for an Electronic Tongue (ET) study.

This cross-response nature of the voltammograms can be summarized when plotting max currents (sensitivities) and oxidation peak potential observed for the 5 MWCNT/Metals NPs modified electrodes. This representation is shown in Figure 3, where it can be observed that carbohydrates anodic peak current (I_{pa}) is different

according to each metal nano-composite of the ET formed by GCE/MWCNT/Metals oxy-hydroxides modified electrodes and was also observed that the oxidation potentials (Epa) showed different behaviors according to each metal, this is a desirable condition for any ET study.

<Figure 2>

<Figure 3>

The Principal Component Analysis (PCA) is one of the most important methods used in chemometrics and it is the basis for many standards recognition, is a way of reducing a large multivariate data matrix into a matrix with a much smaller number of variables, without losing important information within the data. The principle behind PCA is that the multivariate data can be decomposed by linear projections onto a new co-ordinate system. The new axes, known as principal components (PCs), are orientated so that the first PC captures the largest amount of common variance [50]. PCA can be one way to demonstrate the complementarity of the generated information by each electrode, if electrodes are redundant they would appear superimposed, while different response will manifest in their separation. In Figure 4 is shown the PCA for the five GCE/MWCNT/MetalsOOH modified electrodes (metals = gold, palladium, copper, nickel and cobalt); the PCA was prepared by treatment of the sensitivities of carbohydrates and was observed that each sensor showed performance in different regions this is very positive because that is a desirable condition for any ET study, justifying the inclusion of the five prepared electrodes in the sensor array.

<Figure 4>

The analytical reproducibility (%RSD) for the sensors was estimated using standard solutions of 2×10^{-3} mol L⁻¹ glucose measured along 3 different days, obtaining values for GCE/MWCNT/AuO of 3.28%, for GCE/MWCNT/PdO 6.89%, for GCE/MWCNT/CuOOH 3.85%, for GCE/MWCNT/NiOOH 1.73% and for GCE/MWCNT/CoOOH 6.35%. The analytical reproducibilities shown seem

reasonable values, because the electrodes are subjected to analysis of many samples thus requiring maintain its reproducibility and stability.

Complete calibrations of considered sugars were conducted in 0.1 mol L⁻¹ NaOH solution with scan rate of 50 mV s⁻¹ in order to fully characterize the used sensors. It was observed in all cases an increase of anodic peak current which was linear with the increase of concentration of sugars; Table 1 shows the electrochemical parameters for all carbohydrates studied. We observed that the electronic tongue formed by GCE/MWCNT/MetalsOOH modified electrodes has good amperometric sensitivity. The values of limit of detection and quantification are very close, meaning that the behavior of the different sugars on the electrode is comparable. Therefore we may apply the electronic tongue in the same concentration range for all sugars considered.

<Table1>

3.3 Building of the ANN Model

For the electronic tongue study, a total set of 46 carbohydrate standard mixtures were manually prepared (shown in Figure S1 supplementary material), 36 corresponding to the train subset and 10 to the testing subset with concentrations ranged from 0.5 to 5.0 mM for each compound. These standards were first analyzed and used to build and validate the ANN model under the conditions previously described, the training and testing sets of samples were measured employing the GCE/MWCNT/MetalsOOH modified electrodes array, obtaining a complete voltammogram for each of the electrodes, and each sample. Because of the dimensionality and complexity of descriptive information generated (5 voltammograms per each sample), a double compression strategy with wavelet transform and causal index pruning was used.

Once the optimal set of coefficients was selected through Wavelet compressing and pruning the ANN final architecture was optimized. The parameters that were optimized were the 4 transfer functions employed in the hidden and output layers, the functions evaluated were *tansig*, *logsig*, *satlins* and *purelin*, and the number of neurons in the hidden layer, from 1 to 12 neurons.

In this manner 192 architectures were evaluated. The final architecture of the back-propagation ANN model had 36 input neurons, a hidden layer with 5 neurons and the *tansig* transfer function, an output layer with 4 neurons and the *purelin* transfer function.

The representation of the modeling performance of the system is illustrated in Figure 5. This figure shows the comparison graphs of predicted vs. expected concentrations for the four carbohydrates and for training and testing subsets, that were built to check the prediction ability of the ANN model. It may be seen that a satisfactory trend was obtained, with the regression line almost indistinguishable from the theoretical one for the training subset. From these data it appears that all species demonstrate very good correlation coefficients with an R value ≥ 0.99 on the training subset. The model prediction is satisfactory for all carbohydrates and the accuracy of the obtained response is adequate. The results obtained for external test subset with much more significance than the latter, are close to the ideal values, with 0 intercepts, 1 slopes and good correlation coefficients R values ≥ 0.96 .

<Figure 5>

With the aim of contrasting the goodness of these data, results were compared with those obtained from the most widely used in the chemometrics field data processing, PLS-1, with linear fittings from the comparison regression in Table S1 (supplementary material), and comparison plots, Figure S2 (supplementary material). Both with the numeric data and with the represented plots, a slightly worst performance is evidenced from PLS treatment, from the comparison slopes more discrepant to 1.0, correlation coefficients different from 1.0, and more evidenced scatter of points in the comparison graphs. Probably the non-linear features present in the sensors result better modeled with use of the ANN than with PLS.

After optimizing its performance, the electronic tongue was assessed through studies on synthetic samples of sugars shown in table 2, with three different sugar mixtures. As it can be seen results found are in good agreement with those expected.

<Table 2>

4. CONCLUSIONS

In this work, the application of an electronic tongue formed by GCE/MWCNT/MetalsOOH nanoparticle modified electrodes is described for detection and quantification of carbohydrates in sugar test samples. The complex response obtained from the electronic tongue was successfully processed employing a multilayer ANN and wavelet compressed information which proved to be especially suited for building the response model. Therefore this electronic tongue has enormous potential to be applied in hydrolyzed samples from sugarcane bagasse. Merit of the proposed system is to achieve resolution of mixtures of carbohydrates, with performance equivalent to HPLC equipment, without need to use any biosensor component thus permitting more stable responses.

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Table 1. Analytical parameters for various carbohydrates at electronic tongue formed by GCE/MWCNT/Metals oxy-hydroxide nanoparticle modified electrodes in 0.1 mol L⁻¹ NaOH by Cyclic Voltammetry ($v = 50 \text{ mV s}^{-1}$; $n = 3$).

Palladium				
Carbohydrate	Limit of Detection (mM)	Limit of Quantification (mM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Concentration range (mM)
Glucose	0.32	1.05	25.5	0.4 - 5.0
Xylose	0.38	1.25	11.9	0.4 - 5.0
Galactose	0.87	2.97	14.1	0.9 - 5.0
Mannose	0.08	0.27	14.3	0.2 - 5.0
Gold				
Glucose	0.64	2.11	7.3	0.8-5.0
Xylose	0.62	2.04	5.8	0.8-5.0
Galactose	0.57	1.88	5.5	0.6-5.0
Mannose	1.00	3.33	6.0	1.0 - 5.0
Copper				
Glucose	0.10	0.33	51.1	0.2 - 5.0
Xylose	0.06	0.19	49.5	0.2 - 5.0
Galactose	0.38	1.26	41.5	0.4 - 5.0
Mannose	0.36	1.19	7.18	0.4 - 5.0
Nickel				
Glucose	0.23	0.76	32.0	0.4 - 5.0
Xylose	0.38	1.26	39.2	0.4 - 5.0
Galactose	0.41	1.36	46.7	0.5 - 5.0
Mannose	0.47	1.56	42.0	0.5 - 5.0
Cobalt				
Glucose	0.31	1.03	83.6	0.4 - 5.0
Xylose	0.10	0.33	67.9	0.2 - 5.0
Galactose	0.25	0.83	75.7	0.4 - 5.0
Mannose	0.38	1.26	69.2	0.4 - 5.0

Table 2: Results in synthetic samples obtained from the electronic tongue formed by GCE/MWCNT/MetalsOOH modified electrodes in the analysis of Glucose, Xylose, Galactose and Mannose

Samples	Glucose / mmol L⁻¹	Glucose found / mmol L⁻¹
1	4.0	4.5
2	2.7	3.2
3	4.2	4.7
	Xylose / mmol L⁻¹	Xylose found / mmol L⁻¹
1	3.6	3.6
2	2.9	2.2
3	3.5	3.6
	Galactose / mmol L⁻¹	Galactose found / mmol L⁻¹
1	2.0	2.6
2	2.0	2.2
3	1.0	1.0
	Mannose / mmol L⁻¹	Mannose found / mmol L⁻¹
1	4.0	4.7
2	4.6	4.9
3	0.3	0.4

Figure Captions

Figure 1: TEM characterization of (A) MWCNT/PdO, (B) MWCNT/AuO and (C) MWCNT/CuO. SEM characterization of (D) MWCNT/NiOOH and (E) MWCNT/CoOOH composite materials.

Figure 2: Example of the different voltammograms obtained with (A) GCE/MWCNT/PdOOH, (B) GCE/MWCNT/AuO, (C) GCE/MWCNT/CuOOH, (D) GCE/MWCNT/NiOOH and (E) GCE/MWCNT/CoOOH for 0.1 mol L^{-1} NaOH and stock solutions $5.0 \times 10^{-3} \text{ mol L}^{-1}$ of each of the five carbohydrates (blank) Absence, (glu) Glucose, (xyl) Xylose, (gal) Galactose and (man) Mannose.

Figure 3: Studies of response (A) anodic peak current (I_{pa}) and (B) potential oxidation (E_{pa}) for $5.0 \times 10^{-3} \text{ mol L}^{-1}$ of each of the four carbohydrates (glucose, xylose, galactose and mannose) for electronic tongue formed by GCE/MWCNT/Metals oxy-hydroxide nanoparticle modified electrodes (metals = gold, palladium, copper, nickel and cobalt).

Figure 4: PCA analysis score plot for five GCE/MWCNT/Metals oxy-hydroxide nanoparticle modified electrodes (metals = (□) gold, (▽) palladium, (○) copper, (◇) nickel and (○) cobalt)

Figure 5: Modelling ability of the optimized electronic tongue formed by GCE/MWCNT/MetalsOOH modified electrodes. Comparison graphs of predicted vs. expected concentrations for (A) Glucose, (B) Xylose, (C) Galactose and (D) Mannose, both for training (•, solid line) and testing subsets (◦, Dashed line). Dotted line corresponds to theoretical $Y=X$.

Biographies

Acelino Cardoso de Sá received his degree in Chemistry in 2007, received his Master in Condensed Matter Physics at Science Materials program at the Paulista State University-UNESP working on the themes: electroanalytical, copper nitroprusside, cobalt nitropursside, 3-aminopropyl silica gel and electrodes chemically modified. Ph.D. student in Analytical Chemistry. His main research field is the biofuels (second generation ethanol) at Institute of Chemistry–UNESP, Araraquara, Brazil. Ph.D. student at the Universitat Autònoma de Barcelona working in the analysis of sugars from cane sugar bagasse using electronic tongues.

Andrea Cipri studied Chemistry at the University of Sassari, Italy. He received his Master degree in 2011. At the beginning of 2012 he joined the group of Manel del Valle at the Universitat Autònoma de Barcelona (UAB), Spain, as a Marie Curie fellow for his PhD. He is currently a PhD fellow in Manel del Valle group and his research interests include the study of nano-materials and bio-materials for sensing applications and devices.

Andreu González-Calabuig received his M.Sc. degree in Chemistry in 2013 from the Universtitat Autònoma de Barcelona, where he is at the moment completing his Ph.D. in Analytical Chemistry. His main research topics deal with the application of Electronic Tongues as a tool for security and food safety analysis.

Manel del Valle received his Ph.D. in Chemistry in 1992 from the Universitat Autònoma de Barcelona, where he got a position of associate professor in Analytical

Chemistry. He is a member of the Sensors & Biosensors Group where he is a specialist for instrumentation and electrochemical sensors. He has initiated there the research lines of sensor arrays and electronic tongues. Other interests of his work are the use of impedance measurements for sensor development, biosensors and the design of automated flow systems.

Nelson Ramos Stradiotto graduated from the University of Sao Paulo, Brazil with a PhD degree in chemistry in 1980 for studies on “the kinetics and mechanism of tin reduction in aprotic media”. He spent 2 years at The University of Southampton as a fellow researcher (1983–1984) and 2 years at The Loughborough University (1992–1994). Presently, he is a professor at the Institute of Chemistry—UNESP, Araraquara, Brazil. His research interests include Analytical Chemistry and Physical Chemistry in the specialties of Electrochemistry and Electroanalysis. The theme of current research is related to Sensors, Electrochemical Detectors coupled with chromatographic techniques and electroanalytical methods in Bioenergy, with emphasis on Biofuels, Bioproducts, Biomass and Biorefineries.

Figure 1

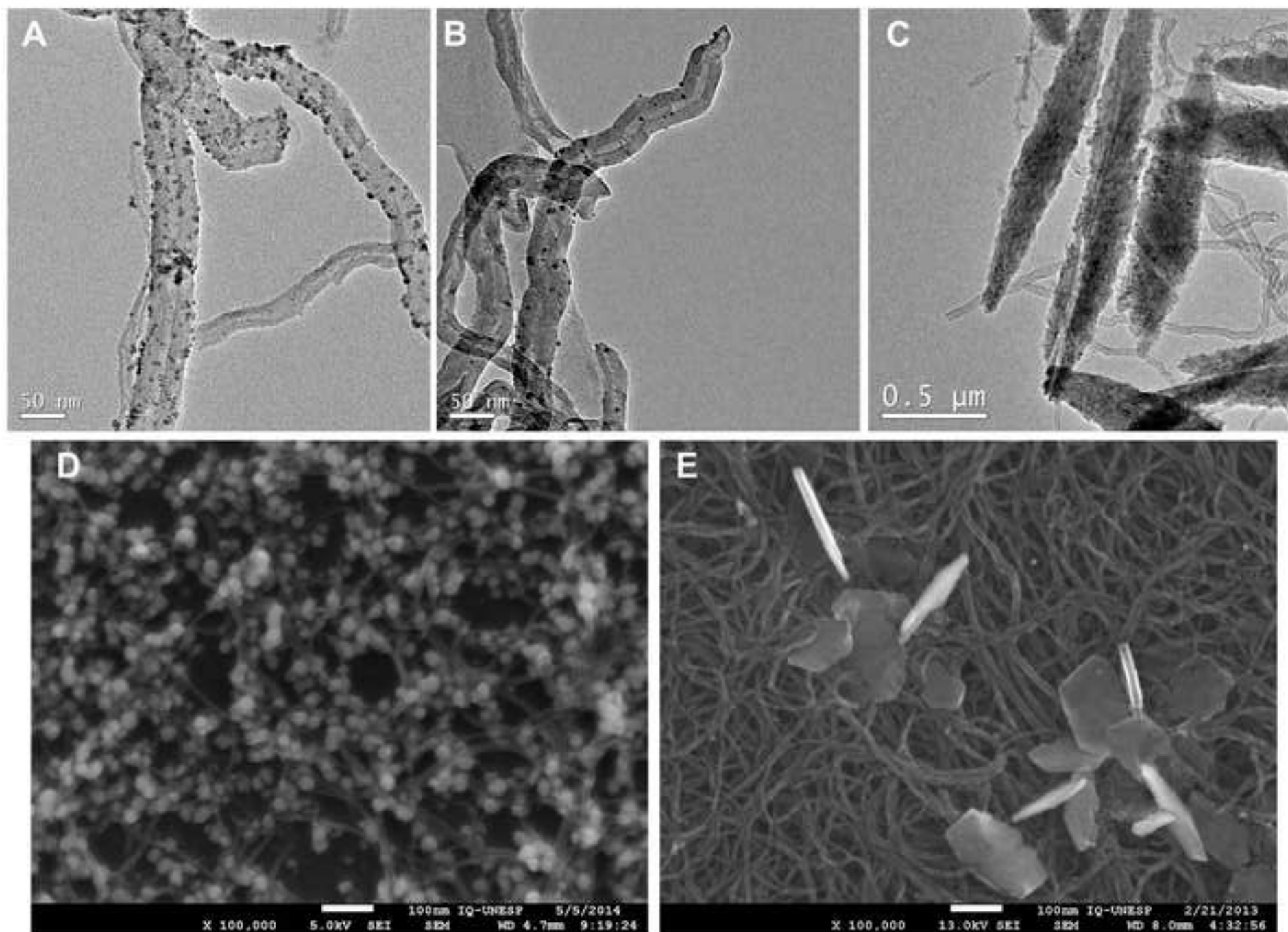


Figure 2

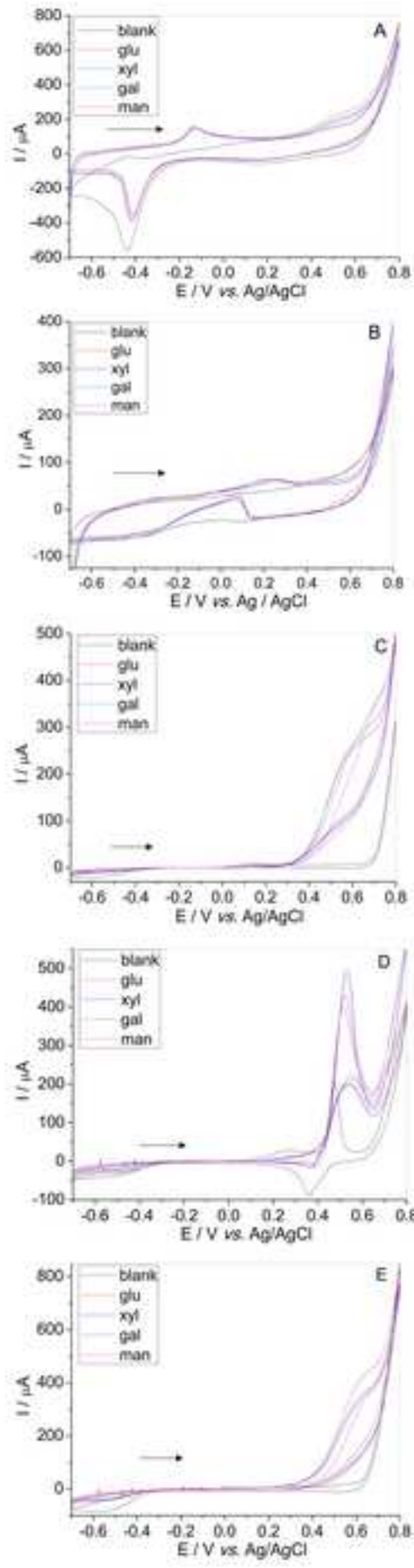


Figure 3

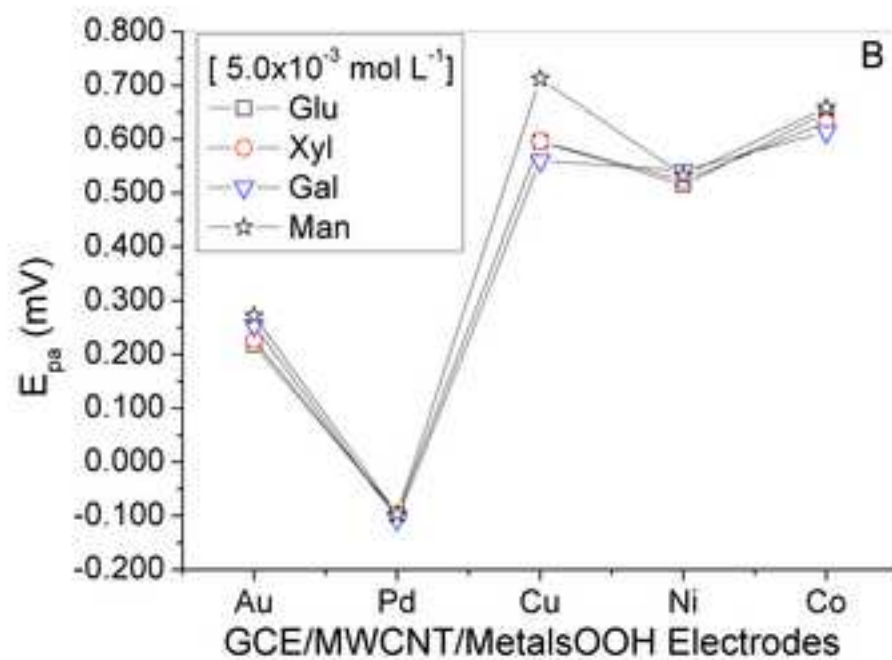
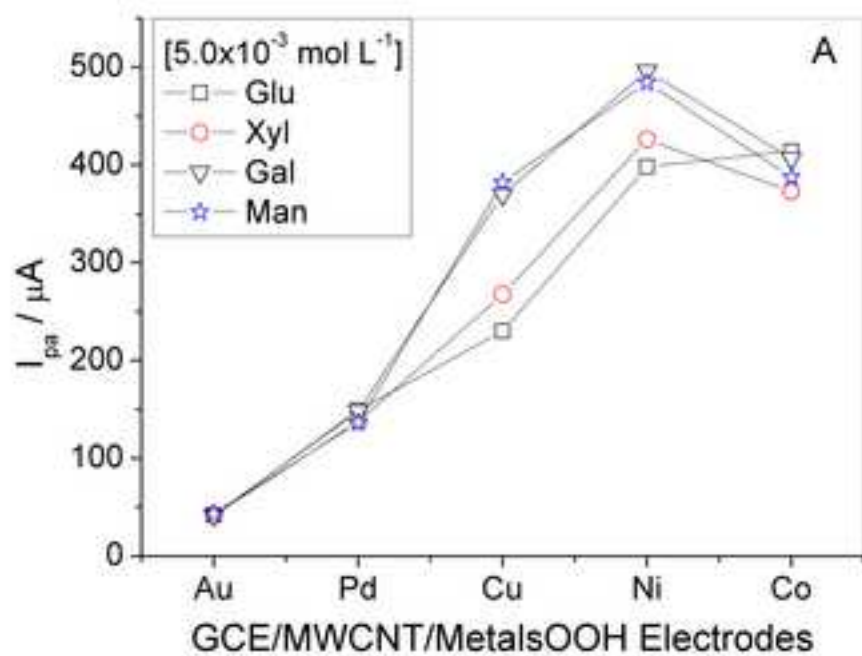


Figure 4

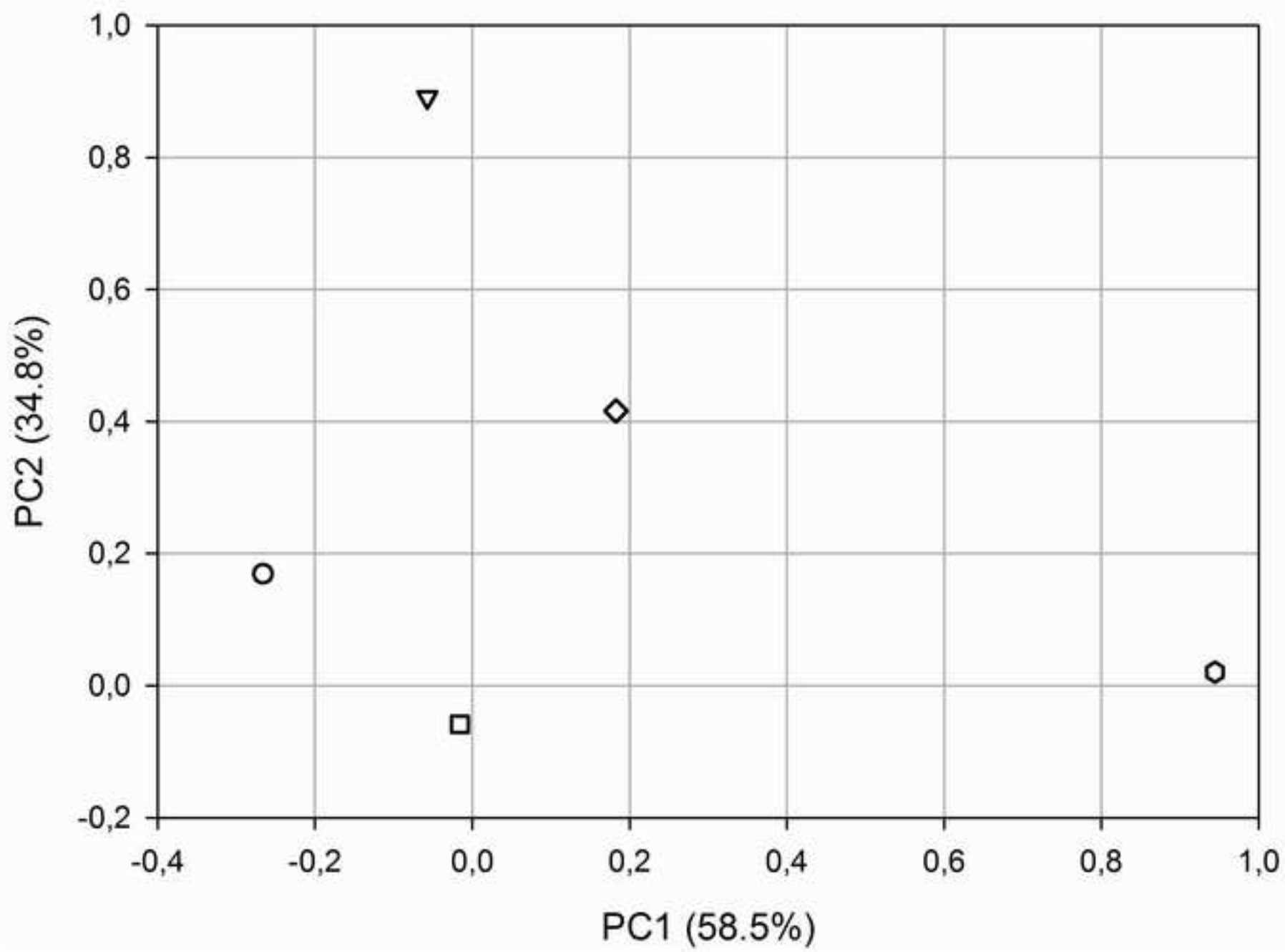


Figure 5

