DEVELOPMENT OF NEW METHODS FOR DETERMINATION OF SUGARS, FURANIC ALDEHYDES AND URONIC ACIDS FROM LIGNOCELLULOSIC MATERIALS DERIVATIVES OF CANE SUGAR

Nelson Ramos Stradiotto
Araraquara Institute of Chemistry / São Paulo State University (UNESP)
FAPESP Process 2012/00258-5 | Term: Jun 2012 to May 2014

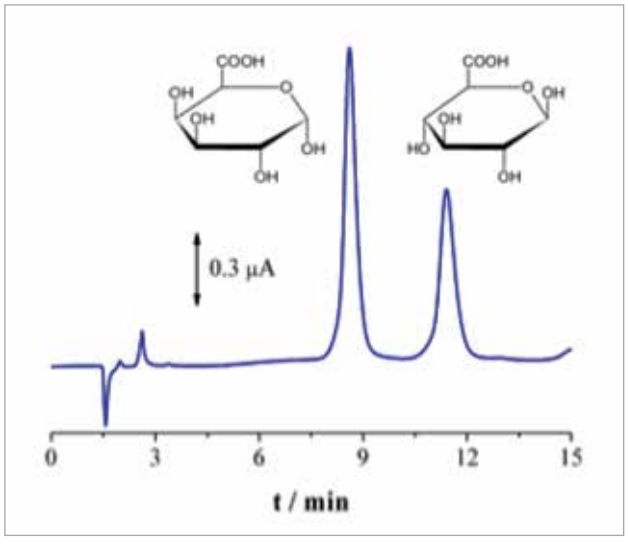

Figure 1. Isocratic separation chromatogram of standard solution D-galacturonic acid, and D-glucuronic acid in the CuNP detector. Mobile phase 0.1 mol L^{-1} NaOH plus 280 mmol L^{-1} CH_3COONa, detection potential of 0.45 V vs. Pd and flow rate of 1.0 ml min^{-1}

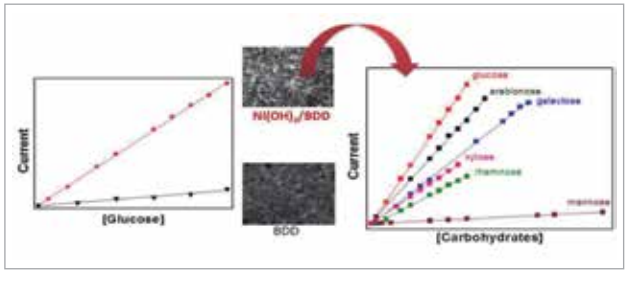

Figure 2. Detection of several carbohydrates using boron-doped diamond electrodes modified with nickel hydroxide n anoparticles

The energy needs of modern society are based primarily on the use of fossil fuels, which besides being finite cause numerous environmental problems. Due to this situation, the search for alternative renewable energy sources has intensified exponentially in order to meet the rising demand of energy. In this scenario, the lignocellulosic materials are presented as one of the viable alternatives in relation to fossil fuels, because it is a material rich in carbon and renewed availability. Among these materials, sugar cane bagasse, a residue of sugar mills, is a promising source for generating biofuels. The process of conversion of biomass to ethanol involves several steps such as pretreatment, hydrolysis, fermentation and distillation. During these steps is very important to know the composition of the different compounds participants to assess the efficiency and optimization of the steps involved in this process. The development of new methods of determination that are fast, sensitive and selective for specific compounds is highly essential in order to perform this conversion with yields economically competitive. Among these new methods of determination, one that uses the technique of liquid chromatography (HPLC) with electrochemical detection is presented as one of the most promising, since this technique stands out for being sensitive and selective, small display limits detection and a wide applicability to different substances. Therefore, this project aims to develop new methods for the determination of sugars, uronic acids and furanic aldehydes using HPLC with electrochemical detection technique aimed at producing lignocellulosic ethanol. The development project includes the preparation and characterization of modified electrodes, as well as the methodology for determining these compounds and their application in the determination of lignocellulosic materials derived from sugar cane.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The glassy carbon electrode modified with carbon nanotubes decorated with nickel oxy-hydroxide (GC/MWCNT/NiOOH) was used to studied electro-oxidation of glucose, galactose, xylose, arabinose and mannose in alkaline medium. Kinetic parameters such as, charge-transfer coefficient, electrocatalytic rate constant and diffusion coefficient were determined for sugars. Galactose exhibited a higher charge-transfer coefficient (0.37) with a diffusion coefficient of $1.3x10^{-6}$ cm^2 s^{-1} and showed the higher electrocatalytic rate constant of $2.1x10^4$ L $mol^{-1}s^{-1}$. The modified electrode exhibited a linear response to sugars concentration in the range around of $2.5x10^{-4}$ mol L^{-1} to $5.6x10^{-3}$ mol L^{-1} and limits of detection around of $1.9x10^{-4}$ mol L^{-1}-$4.3x10^{-4}$ mol L^{-1}.

In a similar study, the electrooxidation of glucose, galactose, mannose, rhamnose, xylose and arabinose was studied at of nickel hydroxide nanoparticle modified boron-doped diamond electrode and compared to unmodified electrode. Limits of detection were $5.3x10^{-5}$, $6.8x10^{-5}$, $2.7x10^{-4}$, $6.9x10^{-5}$, $8.8x10^{-5}$ and $2.6x10^{-5}$ $molL^{-1}$ for glucose, galactose, mannose, rhamnose, arabinose, xylose, respectively.

In another study an analytical method was development for iron and copper determination in ethanol fuel. This method was developed using stripping voltammetry with a glassy carbon electrode modified with Nafion/Carbon-nanotubes. With linear sweep stripping voltammetry was achieved a limit of detection of $7.1x10^{-7}$ mol L^{-1} for Fe^{3+} and $5.1x10^{-8}$ mol L^{-1} for Cu^{2+}. The amperometric sensitivities were $2.0 x10^6$ mA mol^{-1} L for Fe^{3+} and $2.8 x 10^7$ mA mol^{-1} L for Cu^{2+}.

A detector was modified with copper nanoparticles electrodeposited on the surface of the glassy carbon for determination of uronic acids in chromatography with pulsed amperometric detection in wall-jet cell. The separation of the acids was complete within 15 min. The method was applied to real samples of hydrolyzate bagasse and the value found in this sample was 15.8±0.5 g/kg of D-galacturonic acid and 12.5±0.5 g/kg of D-glucuronic acid. The results demonstrate that the proposed method can be used to detect these acids without the need for derivatization with the advantage of having fewer interfering, considerable accuracy.

For determination of furanic aldehydes a glassy carbon electrode chemically modified with nickel nanoparticles coupled to reverse phase chromatography with pulsed amperometric detection was used for the quantitative analysis in a real sample of sugarcane bagasse hydrolyzate. The values obtained in this sample by the standard addition method were 1.54 ± 0.02 g kg^{-1} for HMF and 11.5 ± 0.2 g kg^{-1} for furfural. The results demonstrate that the new proposed method can be used to quickly detect furanic aldehydes without the interference of other electroactive species, besides having excellent peak resolution, analytical reproducibility, sensitivity and accuracy.

MAIN PUBLICATIONS

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Nelson Ramos Stradiotto

Instituto de Química de Araraquara
Universidade Estadual Paulista (Unesp)
Departamento de Química Analítica
Rua Francisco Degni, s/n – Caixa Postal 355
CEP 14800-060 – Araraquara, SP – Brasil

+55-16-3301-9621
nrstradi@iq.unesp.br