## ELECTROCHEMICAL CHARACTERIZATION OF SCREEN-PRINTED CARBON ELECTRODE MODIFIED WITH GRAPHENE AND TYROSINASE FOR DIRECT DETERMINATION OF PARACETAMOL

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## Abstract

The aim of this study was to develop an amperometric biosensor utilizing mushroom (Agaricus bisporus) tyrosinase (EC 1.14.18.1) suitable for the selective determination of acetaminophen in human urine. The presented biological device was based on a commercial screen-printed carbon electrode covered with a thin graphene layer (transducer) with an enzyme (bioreceptor) immobilized with glutaraldehyde and Nafion.

Owing to the use of tyrosinase and presence of NFG, the developed analytical instrument is able to measure even at potentials of 0 V. Linear ranges differ according to choose of detection potential, namely up to 130  $\mu$ mol L<sup>-1</sup> at 0 V, up to 90  $\mu$ mol L<sup>-1</sup> at -0.1 V, and up to 70  $\mu$ mol L<sup>-1</sup> at -0.15 V. The first mentioned linear range is described by the equation Ip [ $\mu$ A] = 0.236 - 0.1984c [ $\mu$ mol L<sup>-1</sup>] and correlation coefficient r = 0.9987. The limit of detection of APAP was estimated to be 1.1  $\mu$ mol L<sup>-1</sup>. A recovery of 96.8% (c = 25  $\mu$ mol L<sup>-1</sup>, n = 5 measurements) was calculated. Best flow rate in flow injection analysis was 0.6 mL·min<sup>-1</sup>. It can be stated that this biosensor can be used to detect paracetamol in very complex samples such as urine, for the possibility of operation at potential OV.

## References

- [1] Ivey KJ, Settree P. Effect of paracetamol (acetaminophen) on gastric ionic fluxes and potential difference in man. Gut. 1976;17(11):916–9.
- [2] Hodis J. New facts about paracetamol, risks of overdose, intoxication and their management. Practical Pharm. 2015;11(3):90–2.
- [3] Luque de CastroMD, Valcárcel M. Flow injection analysis of pharmaceuticals. J Pharm Biomed Anal. 1989;7(12):1291–300.
- [4] Mičová K, Friedecký D, Faber E, Polýnková A, Adam T. Flow injection analysis vs ultra-high performance liquid chromatography coupled with tandem mass spectrometry for determination of imatinib in human plasma. Clin ChimActa. 2010;411(23-24):1957–62.
- [5] Luque de Castro MD, Cases MV. Simultaneous determinations in flow injection analysis. A review. Analyst. 1984;109(4):413–9.
- [6] Valero E, Varón R, García-Carmona F. Catalytic oxidation of acetaminophen by tyrosinase in the presence of L-proline: a kinetic study. Arch Biochem Biophys. 2003;416(2):218–26.
- [7] Rolff M, Schottenheim J, Decker H, Tuczek F. Copper–O2 reactivity of tyrosinase models towards external monophenolic substrates: molecular mechanism and comparison with the enzyme. Chem Soc Rev. 2011;40(7):4077–98.
- [8] Valero E, Varón R, García-Carmona F. Tyrosinase-mediated oxidation of acetaminophen to 4acetamido-o-benzoquinone. Biol Chem. 2002;383(12):1931–9.
- [9] Calas-Blanchard C, Istamboulié G, Bontoux M, Plantard G, Goetz V, Noguer T. Biosensor-based real time monitoring of paracetamol photocatalytic degradation. Chemosphere. 2015;131:124–9.

**Figures** 



Figure 1. Effect of flow rate

Figure 2. Preparation process of Tirosinase biosensor



**Figure 3.** Dependence of the amperometric response of pure human urine (blue) and that with an admixture of 50  $\mu$ mol L<sup>-1</sup> APAP (yellow column). Supporting electrolyte: non deaerated 0.1 mol L<sup>-1</sup> PBS of pH 7.0; injection volume: 100  $\mu$ L, flow rate: 0.6 mL min<sup>-1</sup> and temperature: 25°C.