

# PAPER-BASED ELECTROCHEMICAL PLATFORMS FOR EMERGING CONTAMINANT ANALYSIS: PRECONCENTRATION AND DETECTION OF DICLOFENAC AND AZITHROMYCIN

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## 1.- Objectives

In the last years, pharmaceuticals such as antibiotics and anti-inflammatory drugs, have become important environmental contaminants due to their massive use and their persistence. Furthermore, conventional wastewater treatment plants are not specifically designed for their elimination. Consequently, they are widely distributed in the environment and, although found at very low concentrations, their presence has been associated with damage on human and animal health.

Diclofenac (DCF) is a common anti-inflammatory drug that is broadly used as analgesic for acute joint inflammation and mild to moderate pain. Azithromycin (AZI) is a semisynthetic antibiotic derived from erythromycin and is widely prescribed to treat infections of the respiratory tract, skin and soft tissues. DCF and AZI are frequently found in environmental waters, which is a serious problem since several studies associate harmful effects to different organisms after their exposure to trace levels of these substances.

Therefore, the development of innovative devices that allow the analysis of DCF and AZI in a cost- and time-efficient way is an important challenge. Moreover, the portability of these devices is also a highly-interesting characteristic since they are aimed for environmental analysis.

## 2.- Methods

In this context, a simple electroanalytical device for the detection of DCF and AZI was developed by combining a paper-based carbon working electrode (WE) with gold-plated metallic wires as pseudoreference- and counter electrodes [1,2]. The WE's area was wax-delimited and the metallic wires of a standard header connector were used.

The electrochemical behaviour of DCF and AZI on this paper-based device was studied. To improve the sensitivity, several preconcentration strategies were evaluated. The procedure for preconcentrating the pharmaceuticals on the paper-based WE was very simple: an aliquot of the analyte solution was deposited onto the WE and left to dry. The volumes of the aliquots and the drying temperature were optimized in order to achieve the best analytical signal.

### 3.- Results

As can be seen in Fig. 1, the preconcentration provides a significant increase in the current intensity of the anodic peak for both pharmaceuticals (32.5  $\mu\text{A}$  vs. 2.1  $\mu\text{A}$  for DCF (75  $\mu\text{M}$ ) and 35.6  $\mu\text{A}$  vs. 7.1  $\mu\text{A}$  for AZI (250  $\mu\text{M}$ )). Once the procedure was optimized, linear calibration plots were obtained between 0.10 and 100  $\mu\text{M}$  for DCF and between 5 and 1000  $\mu\text{M}$  for AZI. The preconcentration step provides a huge increase in the sensitivity of the electrochemical detection and the limits of detection were *ca.* 800-fold lower for DCF (70 nM vs. 55  $\mu\text{M}$ ) and 49-fold lower for AZI (4  $\mu\text{M}$  vs. 205  $\mu\text{M}$ ) respectively. The developed platform and preconcentration procedure were used for the determination of both pharmaceuticals in spiked tap water.

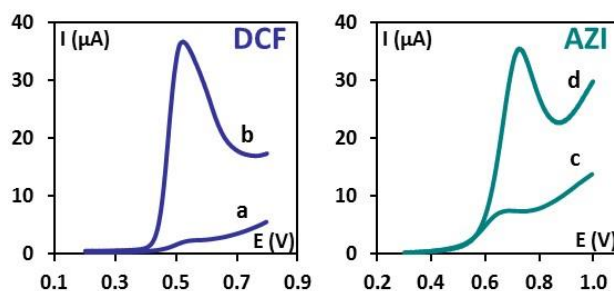


Fig. 1: LSVs recorded in: (a) 10  $\mu\text{L}$  of a 75- $\mu\text{M}$  DCF solution; (b) 10  $\mu\text{L}$  of 0.1 M PB pH 7.0 after preconcentration of 40  $\mu\text{L}$  of a 75- $\mu\text{M}$  DCF solution; (c) 10  $\mu\text{L}$  of a 250- $\mu\text{M}$  AZI solution; (d) 10  $\mu\text{L}$  of 0.1 M PB pH 7.0 after preconcentration of 20  $\mu\text{L}$  of a 250- $\mu\text{M}$  AZI solution.

### 4.- Conclusions

A user-friendly paper-based device for the electrochemical analysis of DCF and AZI was developed. The porous matrix of the paper was explored for on-site preconcentration which considerably improved the sensitivity of the analysis without the need of external preconcentration systems that increase the final cost of the analysis and the amount of waste generated. Moreover, the preconcentration procedure allowed to decouple the sample from the detection volume, as well as the possibility to change the medium. Due to the versatility and simplicity of the platform, another advantage of its design is that multiplexed platforms with independent electrochemical cells can be easily be constructed.

**Keywords:** Paper-based devices, Electroanalysis, Preconcentration, Pharmaceuticals, Contamination.

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