

VOLTAMMETRIC DETERMINATION OF
CHLORAMPHENICOL AT
ELECTROCHEMICALLY ACTIVATED CARBON
FIBER MICROELECTRODES

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Electrochemical activation of carbon fiber microelectrodes by repetitive square-wave voltammetric scans between 0.0 and +2.6 V has shown to increase dramatically the cathodic current of chloramphenicol (Fig.1), also producing a shift in the peak potential value of 220 mV. Moreover, the shape of the cyclic voltammograms changes from the cathodic wave observed at a non-activated fiber to a large peak-type signal. This behaviour is attributed to the increase of the carbon fiber surface area due to its fracture and the appearance of deep fisures (Fig.2). The current density/concentration ratio, calculated for the reduction of chloramphenicol at an activated fiber, was $6.5 \times 10^7 \mu\text{Acm}^{-2}\text{mol}^{-1}$, which is more than one order of magnitude higher than that observed for the electrooxidation of some organic compounds at activated fibers known as ultrahigh-surface area carbon fibers (UHSACF) [1].

This behaviour has led us to develop a method for the sensitive determination of chloramphenicol, a broad spectrum antibiotic whose toxic effects have led to restrict its use in both human and veterinary medicine. Then, analytical methods for the strict control of residues of chloramphenicol in food of animal origin are necessary.

Carbon fiber microelectrodes, $8 \mu\text{m}$ ϕ and 8-mm length were used and chloramphenicol cathodic responses were employed as the test signals to optimize the experimental conditions. Different techniques were checked for the activation of fibers. Potentiostatic electrooxidation using a potential of +2.6 V gave rise to non-reproducible results. Repetitive scans by CV or DPV between 0.0 and +2.6 V gave less sensitive responses than those observed with SWV activation. The effect of the experimental conditions used in the activation step, i.e. potential range, number of scans, pH value, type and concentration of electrolyte, as well as typical parameters of the square-wave voltammetry was studied. The best results were obtained using five scans between 0.0 and +2.6 V in a 0.05 mol l^{-1} phosphate buffer of pH 7.8. SWV was applied at $f=25\text{Hz}$, $\Delta E_s=4\text{mV}$ and $E_{sw}=50 \text{ mV}$. Under these conditions, a good reproducibility was reached by applying the activation procedure to various microelectrodes, with a RSD for i_p of 4.3% ($n=5$). Furthermore, repetitive measurements using a single activated microelectrode gave RSD values near to 3% ($n=10$).

Cyclic voltammograms of chloramphenicol at the activated carbon fibers showed a single sharp cathodic peak in the 0.0 to -1.3 V range scanned. No anodic peak appeared, indicating the irreversibility of the process. Furthermore, the peak potential shifted to more negative values as the scan rate increased. A linear i_p vs. $v^{1/2}$ plot was found in the 5 to 100 mV s^{-1} range, as corresponding to a diffusion-controlled process. However, for faster scan rates, i_p increased very rapidly with increasing v , this suggesting adsorption phenomena. Both E_p and i_p values depended on pH,

which agrees with a reduction process involving protons such as that of the nitro group of chloramphenicol. Calibration graphs were linear ($r=0.9990$) in the 1.0×10^{-7} – $1.0 \times 10^{-5} \text{ mol l}^{-1}$ concentration range, with a slope of $(2.69 \pm 0.03) \times 10^5 \mu\text{A mol}^{-1}$. Deviations from linearity were observed for higher concentrations, probably due to adsorption. A limit of determination (10s) of $1.6 \times 10^{-7} \text{ mol l}^{-1}$ and a limit of detection (3sb/m) of $4.7 \times 10^{-8} \text{ mol l}^{-1}$ (15 ppb) were found. These values are comparable to those obtained by GC using EC detection [2], thus demonstrating the suitability of the electroanalytical method using electrochemically activated carbon fibers for the determination of residues of chloramphenicol. The method is being used with good results for the analysis of this compound in milk samples.

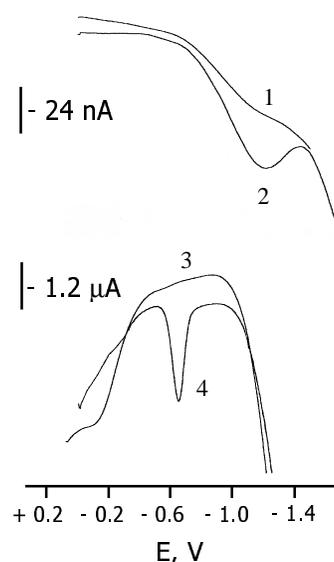


Fig. 1. Square-wave voltammograms at an unactivated (curves 1 and 2) and an activated (curves 3 and 4) carbon fiber microelectrode from: a $1.0 \times 10^{-5} \text{ mol l}^{-1}$ chloramphenicol in 0.05 mol l^{-1} phosphate buffer solution of pH 7.8 (curves 2 and 4); curves 1 and 3, background solution.

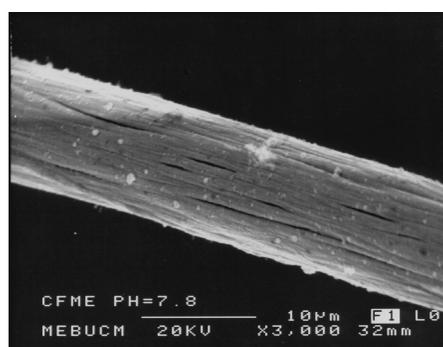


Fig.2. Scanning electron micrograph for an activated carbon fiber

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