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Enhanced simultaneous electroanalytical determination of two fluoroquinolones by using surfactant media and a peak deconvolution procedure

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ABSTRACT

The use of anionic surfactants and the application of a deconvolution procedure were investigated as suitable methods to provide electrochemical peak separation in the simultaneous detection of the fluoroquinolones levofloxacin (LEVO) and norfloxacin (NOR). Concurrently, an electroanalytical methodology was developed based on the simultaneous determination of both fluoroquinolones using a mathematical treatment via baseline correction. We also developed a deconvolution procedure to separate overlapping peaks. These methods provided satisfactory peak separation and intensification of peak current, allowing efficient quantification of analytes in both tablets and biological samples with recovery values ranging from 88.1%–107.5%.

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1. Introduction

The use of antibiotics such as fluoroquinolones in human and veterinary medicine is very common and is often used to treat a wide variety of diseases. As a result of their widespread applicability, highly effective antibacterial agents are in demand, resulting in the introduction of a variety of broad-spectrum drugs in the market. In this sense, fluoroquinolones are an interesting class of antibiotics as they show enhanced in vitro activity against Gram-positive and Gram-negative bacteria [1–4]. The pharmaceutical industry has devoted significant research to the development of new fluoroquinolones and improved production processes over the past decade in order to meet the demand for new antibiotics [1–3,5].

In medicinal chemistry, antibiotics exhibiting a broad activity spectrum can be almost as damaging as the disease itself due to adverse reactions and toxicities. Therefore, it is necessary to ensure that the use of fluoroquinolones is rigorously controlled [5–8]. Moreover, some fluoroquinolones can be absorbed in non-metabolized form by animal tissues and/or excreted in milk, urine, and other biological samples, reaching up to 80% of the total of impurities present [5–10]. Residual fluoroquinolone contamination in food is a significant health problem worldwide [11]. The problem is specially significant when the residues occur in foods of animal origin as it can cause resistance to the drug via indirect ingestion by the healthy public [6,9,11]. To deal with this concerning situation, foods of animal origin and related biological samples must be analyzed to determine the levels of the accumulated non-metabolized drug present. Thus, it is necessary to develop reliable analytical methods to precisely monitor the final concentration of the active content. Addressing such needs, electroanalytical methods employing square-wave voltammetry (SWV) have been developed by our research group and successfully applied to the quantification of the fluoroquinolone antibiotic, moxifloxacin, in tablets and biological samples [12,13]. The methodologies developed are simple, fast, and suitable for the quantification of target analytes in real samples with satisfactory recovery test results.

Varieties of electroanalytical methods have been reported for fluoroquinolones determination in different biological and tablet samples. These methods employ different working electrodes such as glassy carbon [14–16], mercury drop electrodes [17–20], electrochemical sensors [21,22], modified carbon paste [23], multi-walled carbon nanotube composite film modified electrodes [24], and screen-printed carbon electrodes [25]. However, despite the large number of studies on biological samples and analyses of a variety of fluoroquinolones, no attention has been devoted to using electroanalytical methods for the analysis of urine and tablets. There has also been no effort directed at peak deconvolution procedures for the simultaneous determination of levofloxacin (LEVO) and norfloxacin (NOR). To this end, we report the development of an electroanalytical methodology for the simultaneous determination of LEVO and NOR (Fig. 1) in tablets and spiked biological samples using surfactants. We also develop a deconvolution procedure to satisfactorily resolve the peaks of the fluoroquinolones being studied.

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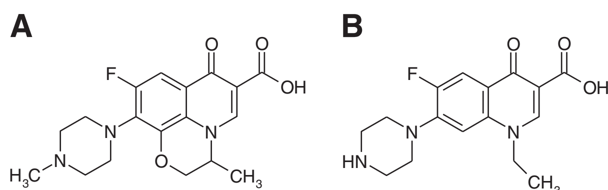

Fig. 1. Chemical structures of levofloxacin (LEVO, **A**) and norfloxacin (NOR, **B**).

2. Experimental

2.1. Instrumentation

Electrochemical measurements were performed using a potentiostat/galvanostat (DropSens®, model μStat 400) connected to a microcomputer controlled by Drop View® software. The measurements were performed using an electrochemical cell with capacity of 5 mL, and the three-electrode system was composed of Pt wire as the auxiliary electrode, Ag/AgCl as the reference electrode, and a glassy carbon electrode (GCE) as the working electrode.

The pH measurements of a Britton–Robinson (BR) buffer solution were obtained using a combined glass electrode (eltex combination electrode) connected to a digital pH-meter (ION, model pHB 500). High-purity water (R ≥ 18.2 MΩ cm) was obtained from a Milli-Q Plus system (Millipore®) and was used for stock solution preparation and supporting electrolyte solutions. A sonicator (Unique®, model USC 800) was used for the dissolution of LEVO, NOR, and the constituents of the BR buffer solution. A centrifuge (Excelsa® II, model 206 BL) was used to separate the precipitated protein before biological sample analysis, and to separate excipients in tablet composition studies.

2.2. Reagents and solutions

A standard LEVO stock solution (1.00×10^{-3} mol L^{-1}) was prepared in a water/methanol (99.8%, Vetec®) mixture (7:3, v/v). A standard NOR stock solution (1.00×10^{-3} mol L^{-1}) was prepared in high-purity water (R ≥ 18.2 MΩ cm) containing 5.0% (v/v) of acetic acid (99.7%, Vetec®); both solutions were stored in dark bottles in a refrigerator.

BR buffer solutions, used as supporting electrolytes, were prepared in the usual way from 0.04 mol L^{-1} acetic acid (99.7%, Vetec®), 0.04 mol L^{-1} boric acid (Merck) and 0.04 mol L^{-1} phosphoric acid (Merck) solutions. Phosphate buffer solutions (0.04 mol L^{-1}) were prepared using disodium hydrogen phosphate dihydrate (Merck®) and sodium dihydrogen phosphate monohydrate (Merck®) as supporting electrolytes. The pH of all buffer solutions was adjusted by the addition of 0.20 mol L^{-1} sodium hydroxide solution (Merck®). The surfactants sodium dodecyl sulfate (SDS), tetraethylammonium chloride (TEAC), dioctyl sodium sulfosuccinate (DSS), tetra-n-butylammonium bromide (TBAB), cetyltrimethylammonium bromide (CTAB), and Triton X-100 were purchased from Sigma/Aldrich; stock solutions of 1.00×10^{-3} mol L^{-1} concentration were prepared by dissolving the appropriate amount of surfactant in high-purity water (R ≥ 18.2 MΩ cm).

2.3. Procedures

2.3.1. Procedure for plotting calibration graphs

A 5.0 mL aliquot of the supporting electrolyte solution was added to the electrochemical cell and deoxygenated by purging with pure nitrogen for approximately 60 s; after purging ceased and a subsequent 10-second delay, cyclic or square-wave voltammograms were recorded. After the background voltammograms were obtained, appropriate concentrations of target analytes and surfactants were introduced into the cell, and the corresponding voltammogram was recorded. Between each measurement, the GCE surface was renewed by polishing with an alumina suspension (0.5 μm).

2.3.2. Deconvolution procedure

Due to the observed overlapping of the oxidation peaks when both fluoroquinolones were detected in the mixture, a mathematical peak deconvolution procedure via Microcal Origin® software (version 6.0) was necessary for satisfactory separation and simultaneous determination. For the deconvolution process, the baselines of all voltammograms were adjusted, and subsequently, the "analysis-Gaussian" tool was used to select the number of peaks, the peak width at a half height ($W_{1/2}$, fixed at 75 mV), and peak potential values. The deconvolution procedure when carried out as described above allowed the satisfactory separation of the fluoroquinolones target peaks and their subsequent quantification.

2.3.3. Procedure for sample preparation and analysis

The human and bovine urine samples were collected from a consenting healthy individual and healthy animal, transferred to calibrated 25 mL volumetric flasks, and spiked with LEVO and NOR at concentrations of 50, 100, and 200 μg mL^{-1}. Before use, the samples were collected in glass bottles and stored in a refrigerator. For analysis of the target samples by spike-and-recovery tests, 3.0 mL aliquots of urine samples were treated with 0.20 mL of methanol to precipitate proteins. After stirring for approximately 20 s, the precipitated protein was separated by centrifuging for 30 min at 2800 rpm (relative centrifugal force = 1575). Supernatant aliquots of 80, 40 and 20 μL with concentrations of 50, 100, and 200 μg mL^{-1}, respectively, were placed in the voltammetric cell containing 5.0 mL of BR buffer (pH 5.0), followed by purging with pure nitrogen for 10 min. The SWV voltammograms were recorded under the optimized experimental and instrument conditions. The sample preparation and dilution steps, in conjunction with the use of a surfactant (at suitable concentration), were essential to avoid matrix effects due to the diversity of interfering species present in the biological samples. The quantification of LEVO and NOR was then performed via standard addition methods and carried out in triplicate.

2.3.4. Procedure for tablet analysis

Tablets containing LEVO (500 mg) and NOR (400 mg) were weighed, powdered and the average mass per tablet was determined. A quantity of the powder equivalent to 0.3661 mg (±0.001 mg) of LEVO and 0.2641 mg (±0.001 mg) of NOR was accurately transferred to a calibrated 250 mL volumetric flask containing the appropriate solvent (Section 2.2) and dissolved in the ultrasonic bath for 30 min; the volume was made up with high-purity water (R ≥ 18.2 MΩ cm). Prior to use, the resultant solutions were separated by centrifugation for 30 min at 2800 rpm to isolate the insoluble excipients. The desired concentration of both drugs was obtained by accurate dilution of the prepared solutions to a voltammetric cell containing 5.0 mL of the supporting electrolyte solution. The SWVs were recorded and the content of the respective drugs in the tablets was determined via standard addition methods, and carried out in triplicate.

3. Results and discussion

3.1. Voltammetric studies of LEVO and NOR at GCE

The ability to distinguish between the peaks obtained during the simultaneous detection of LEVO and NOR on the GCE surface was initially tested by studying the voltammetric behavior of the analytes using differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), and SWV. Fig. 2 displays the voltammograms carried out to verify the fluoroquinolones' electroactivity and also to compare the simultaneous detection of the electrochemical oxidation of LEVO and NOR (1.00×10^{-4} mol L^{-1}) in 0.10 mol L^{-1} BR buffer (pH 7.0) as the supporting electrolyte with SDS as the surfactant.

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