



Rapid determination of bisacodyl in flow injection system combination by a novel sensitive adsorptive square-wave voltammetry

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ABSTRACT

A continuous square-wave voltammetric study of bisacodyl at gold microelectrode was carried out. The drug in phosphate buffer (pH 2.0) is adsorbed at -300 mV, giving rise to change in the current of well-defined oxidation peak of gold. Signal-to-noise ratio has significantly increased by application of discrete fast Fourier transform (FFT) method, background subtraction and two-dimensional integration of the electrode response over a selected potential range and time window. Also in this work some parameters such as SW frequency, eluent pH, and accumulation time were optimized.

The monitored adsorptive current was directly proportional to the concentration of bisacodyl and it shows a linear response in the range from 0.008 to 14.5 nM (correlation coefficient = 0.9995) and the detection limit ($S/N=3$) is 1.0×10^{-12} mol l⁻¹ at an accumulation time of 700 ms. The developed adsorptive stripping voltammetry (AdSV) procedure shows a good reproducibility, the relative standard deviation R.S.D.% ($n=10$) at a concentration level of 5.0×10^{-8} mol l⁻¹ was 0.94% . Possible interferences by other pharmaceutical drugs and surfactants have been also evaluated. The applicability of this approach was illustrated by the determination of bisacodyl in pharmaceutical preparation and biological fluids such as serum and urine.

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1. Introduction

Bisacodyl, [4-[(4-acetyloxyphenyl)-pyridin-2-yl-methyl]phenyl] acetate, a laxative, is used on a short-term basis to treat constipation. It also is used to empty the bowels before surgery and examinations such as X-ray procedures using barium enemas.

Several screening procedure for detection of stimulant laxatives and/or their metabolites in human urine using gas chromatography–mass spectrometry [1], high-performance liquid chromatography [2–5], high-performance thin-layer chromatography [6,7], have been reported. HPLC [8,9], and spectrophotometric assay [10], methods for the quantitative determination of biperiden in pharmaceutical dosage forms have also been published. Also, current compendial (USP) methods [11], of assay for the analysis of bisacodyl in bulk form and pharmaceutical dosage forms involve the use of titrimetric and HPLC procedures, respectively.

The combination of microelectrode (ME) with square-wave voltammetry (SWV) has recently been shown to be advantageous

for environmental detection of several compounds [12]. The adaptation of this technology to adsorptive stripping voltammetry (ASV) of bisacodyl on a gold ME could provide a substantial improvement for rapid analysis [13,14]. This paper describes a fundamentally different approach to SWV measurement, in which the detection limits are improved, while preserving the information content of the SW voltammogram. The approach is designed to separate the voltammetric signal and background signal in frequency domain by using discrete fast Fourier transformation (FFT) method. The purpose of this work is to introduce a new technique which combines the square-wave voltammetry technique and ac voltammetry. Experiments are carried out under condition similar to the traditional square-wave voltammetry but the electrode response at each dc scans converted into the frequency domain via fast Fourier transform. Therefore, FFT square-wave voltammetry measures the admittance of the electrode as a function of potential (since the electrode response under ac voltammetric condition is represented as admittance because of frequency domain). The admittance of electrode is calculated at each potential step by Fourier transformation method. FFT-SW produce results similar to those obtained using a traditional ac voltammetry set-up with a phase-sensitive lock-in amplifier. This method allows digitally filtering of some of the noises and decreasing the bandwidth of the measurement. Theoretically, if 32 current values are measured

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per cycle the admittance of the electrode for eight odd harmonic can be calculated together with eight even harmonics generated by the non-linear response of the electrode. Filtering the signals help to eliminate the noise and improve the S/N ratio [15].

Further improvement in the signal was gained by two-dimensional integration of the electrode response over a selected potential range and time window of the signal. Although at sufficiently high scan rates cyclic voltammetry (CV) can approximate an ac voltammetric technique and can be used to investigate electrode surface phenomena such as physical adsorption, FFT-SWV may be a more appropriate technique for monitoring analyte adsorption, as the potential dependence of analyte adsorption may be more clearly characterized. SWV measures the current response while rapid alternating potentials are applied during a staircase scan, whereas CV, which uses only a forward and reverse linear dc scan, is not sensitive to the potential dependence of changes that occur in the double layer.

2. Experimental

2.1. Flow injection set-up

The equipment for flow injection analysis included a 10 roller peristaltic pump (home made) and a four-way injection valve (Supelco Rheodyne Model 5020) with a 100- μ l sample loop. Solutions were introduced into the sample loop by means of a plastic syringe. The used electrochemical cell in this work is in the same scheme of our previous reports [16–20]. In all experiments, the eluent flow rate was 0.5 ml/min.

2.2. Procedure

The general procedure adopted for obtaining adsorptive stripping voltammograms was as follows: a 0.05-M of phosphate buffer at desired pH was flowing in a clean voltammetric cell and the required standard solutions of bisacodyl were injected in the eluent after filling the loop by opening it. The surface of electrode always is clean because of potential wave form. By using a high potential and then a low potential for a while the fouling of the electrode would be inhibited and the electrode would be clean. Following the pretreatment the accumulation potential of -300 mV versus Ag/AgCl was applied to electrode while the solution was passed for 500 ms. The solutions do not need to purge nitrogen, the stripping was stopped and after 20 s had elapsed, anodic scans were carried out over the range -400 to 1600 mV. All measurements were made at room temperature.

2.3. Assay sample preparation

Twenty tablets were weighed, finely powdered and portions equivalent to 0.4 mg bisacodyl were transferred into 100 ml volumetric flask; 50 ml BGE was added, shaken thoroughly to dissolve, made up to volume and mixed well. Suitable aliquots of solution were filtered through a Millipore filter (0.45 μ m). 1 ml of the filtered solution was diluted with background electrolyte (BGE) in a 100-ml volumetric flask. Then 1 ml of the resulting solution was added to a 100-ml volumetric flask and made up to volume with 0.05 M phosphoric acid to yield starting concentration of 4 ng/ml.

2.4. Determination of bisacodyl in human urine and plasma

Drug free human plasma was obtained from the Iranian blood transfusion service (Tehran, Iran) and stored at -20 °C until use after gentle thawing. Urine was also collected from healthy volunteers (males, around 35-year-old).

For the determination of bisacodyl in human urine, 1 ml of untreated urine containing 2 ng/ml bisacodyl was placed into a 10-ml volumetric flask and diluted with pH 2 buffer solution to the mark. Then 50 μ l aliquot was injected into the FIA system.

For the determination of bisacodyl in plasma, a 100- μ l aqueous bisacodyl solution (1 ng/ml) was added to 100 μ l of untreated plasma. The mixture was vortexed for 30 s. In order to precipitate the plasma proteins, the plasma samples were treated with 20 μ l of 20% (v/v) HClO₄. After that, the mixture was vortexed for a further 30 s and then centrifuged at 6000 rpm for 5 min. Then 50 μ l aliquot of the obtained supernatant was injected into the FIA system.

The voltammograms were recorded according to the above recommended procedure. The voltammograms of samples without bisacodyl do not show any signal that can interfere with the direct determination, so external calibration can be used.

2.5. Electrode preparation

Gold microelectrodes (MEs) (with a 25- μ m, in diameter) were prepared as reported before in our previous work [15–20]. Before each experiment, the electrode surface was polished for 1 min using extra fine carborundum paper and then for 10 min with 0.3 μ m alumina. Prior to being placed in the cell, the electrode was washed with water. In all measurements, an Ag (s) | AgCl (s) | KCl (aq, 1 M) reference electrode was used. The auxiliary electrode was made of a Pt wire, 1 cm length and 0.5 mm in diameter. All electrochemical experiments were done using a set-up comprised of a PC PIV equipped with a data acquisition board (PCL-818H, Advantech Co.) was used to output an analog waveform to the working electrode and acquire current readings from the working electrode that connected to a custom made potentiostat. The card and accompanying dynamic link libraries allowed waveform generation and current sampling to be synchronized, which was essential in interpreting SWV current response. The data could be interpreted in real time, or stored data could be loaded and reanalyzed to generate voltammogram. The algorithms used to interpret the current response from each waveform cycle were discussed before. Most of the waveform parameters could be modified from within the software; including the pre- and post scan potential/time, square-wave frequency/amplitude, dc ramp initial/final potential, and ramp time.

2.6. Electrochemical set-up

In this new method to improve the detector sensitivity, the FFT-SWV technique was modified in the potential excitation waveform and current sampling and data processing Fig. 1. The potential waveform consisted of three sections: (a) electrode conditioning; $E_{c1} - E_{c2}$ (for cleaning the electrode surface); (b) accumulation part; E_s (for accumulation of bisacodyl) and (c) application of square wave potential for determination of current. As is shown in Fig. 1, the measurement part of the waveform contains multiple SW pulses with amplitude of E_{sw} and frequency of f_0 , were superimposed on a staircase potential function, which was changed by a small potential step of ΔE . The values of potential pulse of SW (E_{sw}) and ΔE were in a range of few mV (10–50 mV). In potential ramp, the currents sampled four times per each SW polarization cycle.

3. Results and discussion

Fig. 2 shows the changes in the electrode admittance of the gold electrode in 0.05 M H₃PO₄ into the eluent solution caused by the injection of a 50- μ l of 1.0×10^{-6} M bisacodyl. The FFT-SW modulation had amplitude of 20 mV and a frequency of 600 Hz. Before each scan, the electrode was held at E_{c1} potential (1400 mV) for 60 ms,

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