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Sequential injection analysis for the determination of fluoroquinolone antibacterial drug residues by using eosin Y as complexing agent

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ABSTRACT

A sequential injection analysis (SIA) method was developed for the rapid and sensitive determination of fluoroquinolone residues, including norfloxacin, ciprofloxacin and enrofloxacin, in fish samples. The method is based on the reaction between fluoroquinolone drug and eosin Y in Britton-Robinson buffer (pH 2.0), forming pink colored complexes with maximum absorptions at 522, 525 and 527 nm for norfloxacin, ciprofloxacin and enrofloxacin, respectively. Linearity ranges were found to be 0.05–10.0 mg L^{-1} ($r^2 = 0.9996$), 0.1–10.0 mg L^{-1} ($r^2 = 0.9995$) and 0.05–10.0 mg L^{-1} ($r^2 = 0.9997$) for norfloxacin, ciprofloxacin and enrofloxacin, respectively. The detection limit was found to be in the range of 0.013–0.019 mg L^{-1}. The method was tested and validated for various parameters according to main guidelines. The proposed SIA method was successfully applied for the determination of fluoroquinolone drug residues in fish samples with the sampling rate of 47 h^{-1}. The results demonstrated that the method is accurate, precise and reproducible, while being simple, rapid, economical and less time consuming. It can be suitably applied for the estimation of fluoroquinolone drug residues in routine quality control.

1. Introduction

Fluoroquinolone are amphoteric quinolones. Their structures contain fluorine at C-6 position and piperazinyl at C-7 position, such as norfloxacin (NOR), ciprofloxacin (CIP), enrofloxacin (ENR) and ofloxacin (OFL) etc. Their chemical structures are presented in Fig. 1.

These drugs are used for the prophylaxis and treatment of veterinary diseases in most types of farm animals and aquaculture. Their broad antibacterial spectrum against gram-negative bacteria, gram-positive bacteria and mycoplasma generated a considerable interest in using fluoroquinolone as antibiotic in food production animals. Its use can enable antibiotic resistance in intestinal bacteria and this resistance can be transmitted to the general population, causing treatment-resistant illness [1]. Their side effects usually relate to central nerve system including gastrointestinal discomfort, dizziness, insomnia and headache. Nowadays, the usage of quinolone antibiotics in fish farming has increased. The main hazards are antibiotic residues and development of antimicrobial resistance in bacteria that may be transferred to consumers. To protect human health, the European Union, the US Food and Drug Administration (FDA) and other regulatory agencies have established safe maximum residue limits (MRLs) for these drugs, using as veterinary drugs in animal products entering the human food chain.

Several methods have been described for the determination of fluoroquinolones in various biological samples include thin layer chromatography (TCL)-fluorescence [2], high performance liquid chromatography (HPLC) with ultraviolet (UV) or fluorescence detection [3,4], capillary electrophoresis [5] and liquid chromatography-tendem mass spectrometry [6]. A multi-residue LC method for 13 quinolones in feeds using photodiode-array and fluorescence detection was described [7]. Quinolones in animal and fishery products by using multi-residue HPLC method were reported [8]. For the United States Pharmacopeia (USP34) and the British Pharmacopeia:fluoroquinolones in biological and other samples are determined using liquid chromatography with UV and/or detection by mass spectrometry [9,10]. Orbifloxacin was determined by sequence analysis of samples sensitized with luminescent terlium [11]. The widely used methods for fluoroquinolones determination in various biological samples were based on liquid chromatography (LC) coupled with ultraviolet (UV), fluorescence (FL) or mass spectrometric (MS) detection [12]. Flow injection analysis (FIA) is an

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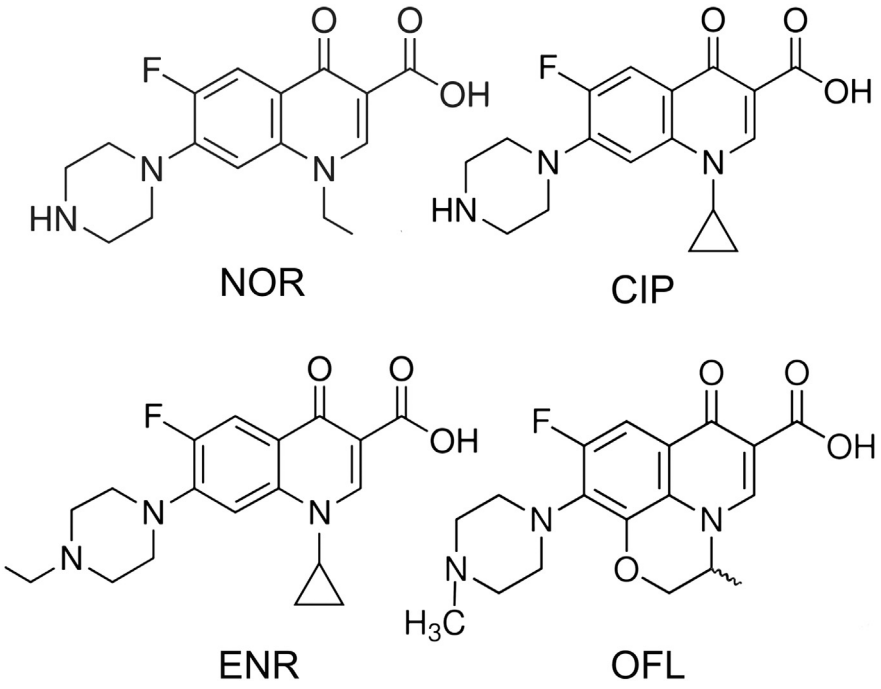

Fig. 1. Chemical structures of NOR, CIP, ENR and OFL.

automated or semiautomated analytical sample processing technique which is based on injection of a definite volume of liquid sample solution into a continuously flowing unsegmented carrier stream, followed by the quantitation of species of interest at a downstream detection area [13,14]. FIA has many advantages over other conventional methods in that high selectivity, good reproducibility, higher sampling rate, simplicity, flexibility and economical. The concept of sequential analysis was reported by Ruzicka et al. [14]. It is simpler than conventional FIA, the complexity of gradients formed by zone penetration with reverse flow.

In this investigation, a novel sequential injection analysis (SIA) method with lab-at-valve (LAV) has been described for fluoroquinolone determination, using eosin Y as complexing agent to obtain a greener analytical procedure to reduce reagent and sample consumption with minimum waste release. This method was tested for the determination of fluoroquinolone drugs residues in fresh water fish samples cultivated in fishing farm under the policy of King Rama the 9th project.

2. Material and Methods

2.1. Chemical and Reagents

Most chemicals were of analytical-reagent grade and used without any further purification (unless otherwise specified). De-ionized distilled water was used throughout the whole experiment. Ciprofloxacin, enrofloxacin, norfloxacin, ammonia and formic acid were obtained from Sigma-Aldrich (USA), eosin Y (Merck, Damstat, Germany), boric acid, glacial acetic acid (Carlo-Erba, Italy), disodium hydrogen phosphate, dihydrogen potassium phosphate (Ajax-Finechem, New Zealand), methanol, ethanol, phosphoric acid and sodium hydroxide (Merck, Germany).

2.1.1. Preparation of Standard Fluoroquinolones Stock Solutions

Stock standard solutions of the above fluoroquinolone drugs at concentration of 200 mg L^{-1} were prepared by dissolving approximately 0.0200 g (accurately weighed) of each fluoroquinolone in the minimum volume of 0.1 mol L^{-1} acetic acid and made up to 100 mL with deionized water. The working standard solutions of each drug containing 0.1–100 mg L^{-1} were prepared daily by suitable dilution from the above stock.

2.1.2. Preparation of 3.0×10^{-4} mol L^{-1} Eosin Y Solution

The 3.0×10^{-4} mol L^{-1} eosin Y solution was prepared by dissolving approximately 0.1000 g (accurately weighed) of eosin Y in 500 mL deionized water in a volumetric flask.

2.1.3. Preparation of Britton-Robinson Buffer Solution (pH 2.0)

Britton-Robinson buffer solution (pH 2.0) with a concentration of 0.02 mol L^{-1} was prepared by adding mixed acid, containing 0.02 mol L^{-1} of each boric acid (0.6184 g), phosphoric acid (0.68 mL) and acetic acid (0.56 mL) into 250 mL of deionized water, then the pH was adjusted to 2.0 with 0.2 mol L^{-1} of sodium hydroxide solution. Finally, its volume was diluted with deionized water to 500 mL volumetric flask.

2.2. Instrumentations

The developed SIA manifold (Fig. 2) was designed using the following equipment: a FIAlab® 3000 system (FIAlab® Instruments, USA) consisting of a syringe pump (syringe reservoir 2.5 mL) and a six-port selection valve (Valco Instrument Co., USA), which is connected to a four-port switching box. The four ports undergo the following function: Port A is connected to a syringe control (CAVROXL 3000 stepper motor-driven syringe pump). Port B is available for other instruments. Port C is connected to a valve control unit and Port D is connected Cecil CE 1010 Spectrophotometer.

A Cecil CE 1010 Spectrophotometer (Cecil Instruments, USA) equipped with a model QS 1.000 Hellma flow cell (10-mm path length, 120 μL inner volume) over the wavelength range of 325–1000 nm. The syringe pump was connected to the holding coil. The holding coil was constructed by winding the PTFE tubing (Cole-Parmer, USA) around the small test tubes. Upon flow reversal sample and reagent zones continued to mix and react. The reaction mixture reached the flow-through cell where the reaction product was monitored by using a spectrophotometer via the RS232 interface. All electrical devices of the manifold were connected to a personal computer using FIALAB for WINDOWS (version 5.0) for fluid control, data collection and analysis.