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Simultaneous determination of five fluoroquinolones by the selective high performance liquid chromatography associating with sensitive resonance light scattering and mechanism study

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ABSTRACT

A novel and selective high performance liquid chromatography (HPLC) technique incorporating resonance light scattering (RLS) detection approach was developed for the determination of five fluoroquinolones (FQS) synchronously for the first time, including enoxacin (ENO), ofloxacin (OFLX), lomefloxacin (LMLX), gatifloxacin (GFLX) and sparfloxacin (SPLX). In pH 4.4 Britton - Robinson (BR) buffer medium, the ENO, OFLX, LMLX, GFLX, SPLX separated by HPLC reacted with erythrosine (ERY) to form 1:1 ion-association complexes, which led to significant enhancement of RLS. The maximum RLS wavelength of the ion-association complexes located at 330 nm. The detection limits of ENO, OFLX, LMLX, GFLX, SPLX were 5.1 $ng \cdot mL^{-1}$, 3.1 $ng \cdot mL^{-1}$, 4.2 $ng \cdot mL^{-1}$, 3.8 $ng \cdot mL^{-1}$, 17.5 $ng \cdot mL^{-1}$ respectively at a signal-to-noise ratio of 3. In this work, the optimum experimental conditions and reaction mechanism were investigated in detail. The proposed method could be applied to the determination of ENO, OFLX, LMLX, GFLX, SPLX in water samples synchronously and the results were satisfactory.

1. Introduction

The ENO, OFLX, LMLX, GFLX, SPLX (Fig. 1) belong to synthetic antibiotics of FQS, they are bactericidal and have broad-spectrum activity against both gram-positive and gram-negative bacteria [1]. Best of all, the FQS are very effective so that they are currently widely used to treat systematic infections in humans and animals [2–3]. However, production volume also increase continually with the increasing needs of FQS and the principal entry route of human pharmaceuticals into the environment is via receiving surface waters [4–5]. Therefore, FQS are of particular environmental concern because their entry into the environment has been continuous during the last decade [6–7]. Given that the chemicals increased level can not only contaminate water, but also make the aquatic vertebrates and organisms increase drug resistance, the potential dangerous on human health and aquatic ecosystem gets more and more attention [8]. Therefore, a variety of analytical techniques such as Plate Diffusion Method [9], CE - FLD [10], Enzyme - linked immunosorbent assays (ELISAs) [11], ultra performance liquid chromatography - tandem mass spectrometry (UPLC - MS/MS) [12], fluorescence immunoassay, HPLC - UV, HPLC - FLD, HPLC - RRS [13–16] have been put forward to determine FQS.

In 1993, resonance light scattering (RLS) phenomenon is first proposed by Pasternack as a new analytical technique [17]. It is generally known that RLS is the special application of RS. When the wavelength of Rayleigh scattering (RS) is located at or close to the molecular absorption band, the frequency of the electromagnetic wave absorbed by the electron is equal to the frequency of RS and re-scattering takes place, then, RLS produce, it is stronger than RS because of re-scattering [18, 19]. RLS technique has received extensive attention and application because of its high sensitivity, accuracy, and speed in recent years. For example, it has been widely applied to determine inorganics [20–22], pharmaceuticals [23], microRNA - 21 [24] and so on. However, RLS cannot detect multiple drugs synchronously on account of its inherently low selectivity. It is well known that HPLC - UV has been widely used in many fields by virtue of its reproducibility, accuracy, and selectivity, however, its sensitivity is low. Fortunately, high performance liquid chromatography - resonance light scattering (HPLC - RLS) method successfully incorporates the sensitivity of RLS and the selectivity of HPLC, up to now, HPLC - RLS has been successful to achieve simultaneous determination of target analytes by forming complexes between the separated target analytes and probe, such as amino acid [25], fluoroquinolones [16], six psychotropic drugs [26], procaine and lidocaine [27], even the proteins [28] and so on.

In the present work, we used HPLC - RLS analysis technique to determine ENO, OFLX, LMLX, GFLX, SPLX in water samples. Compared with other methods, ERY used for the assay is cheap, easy to get and can meet the routine analysis. Various experimental parameters for HPLC separation and post-column RLS detection were investigated in order to achieve accurate assay and high sensitivity, for example, detection

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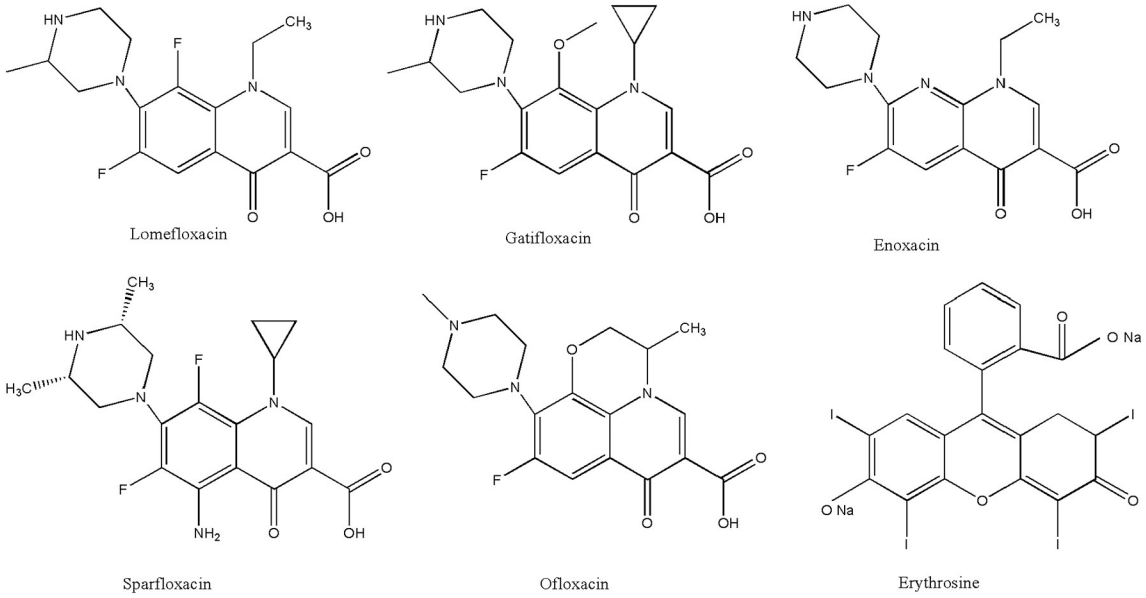

Fig. 1. The structures of the investigated enoxacin, ofloxacin, lomefloxacin, gatifloxacin, sparfloxacin and erythrosine.

wavelength, pH values, flow rate, reaction temperature, reaction tube length and so on. Scanning electron microscope (SEM), UV absorption spectra and the distribution fraction (δ) were utilized to discuss the mechanism, combination mode and binding sites of the system. To the best of our knowledge, this is the first report on simultaneous detection of ENO, OFLX, LMLX, GFLX, SPLX in water samples, in addition, the mechanisms of reaction were studied deeply for the first time. Obtained results demonstrate the applicability of the developed method for the detection of fluoroquinolones in water samples.

2. Experimental

2.1. Apparatus

A HPLC (Shimadzu, Japan) consisting of a DGU-20A5R degassing unit, two LC-20AD pumps and RF-20A fluorescence detector was used to separate the analytes. A PCX-BT post-column derivatization instrument was purchased from Tian Mei Da Scientific Instruments Co. Ltd. (Shenyang, China). A F-2500 fluorescence spectrophotometer (Tokyo,

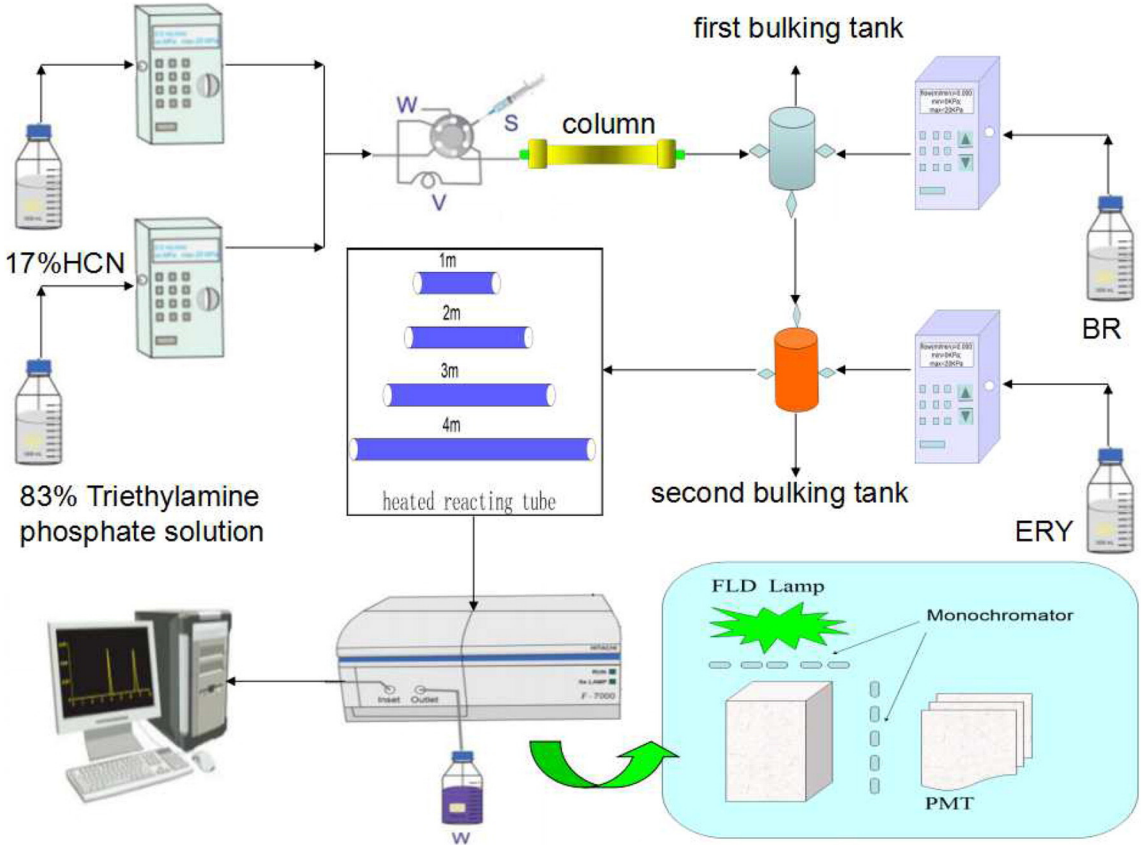

Fig. 2. Schematic diagram of HPLC - RLS system for the determination of enoxacin, ofloxacin, lomefloxacin, gatifloxacin, sparfloxacin.

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