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Enhanced fluorescence sensitivity by coupling yttrium-analyte complexes and three-way fast high-performance liquid chromatography data modeling

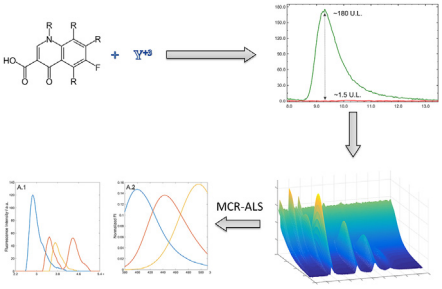
Mirta R. Alcaraz, María J. Culzoni**, Héctor C. Goicoechea*

Laboratorio de Desarrollo Analítico y Quimiometría (LADAQ), Cátedra de Química Analítica I, Facultad de Bioquímica y Ciencias Biológicas, Universidad Nacional del Litoral-CONICET, Ciudad Universitaria, 3000, Santa Fe, Argentina

HIGHLIGHTS

- Highly sensitive method for the analysis of seven fluoroquinolones.
- Coupling of yttrium-analyte complex and three-way modeling.
- Complex or tedious sample treatments or enrichment processes are nor required.
- Accuracy on the quantitation of fluoroquinolones in real water river samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study reports a sensitive chromatographic method for the analysis of seven fluoroquinolones (FQs) in environmental water samples, by coupling yttrium-analyte complex and three-way chromatographic data modeling. This method based on the use of HPLC-FSFD does not require complex or tedious sample treatments or enrichment processes before the analysis, due to the significant fluorescence increments of the analytes reached by the presence of Y^{3+}. Enhancement achieved for the FQs signals obtained after Y^{3+} addition reaches 103- to 1743-fold. Prediction results corresponding to the application of MCR-ALS to the validation set showed relative error of prediction (REP%) values below 10% in all cases. A recovery study that includes the simultaneous determination of the seven FQs in three different environmental aqueous matrices was conducted. The recovery studies assert the efficiency and the accuracy of the proposed method. The LOD values calculated are in the order of part per trillion (below 0.5 ng mL^{-1} for all the FQs, except for enoxacin). It is noteworthy to mention that the method herein proposed, which does not include pre-concentration steps, allows reaching LOD values in the same order of magnitude than those achieved by more sophisticated methods based on SPE and UHPLC-MS/MS.

1. Introduction

The imminent increase of research activities concerning environmental issues is mainly related to the frequent occurrence of new pharmaceuticals, both veterinary and human, in several environmental sources, i.e., surface water, groundwater, wastewater

* Corresponding author.
** Corresponding author.
E-mail addresses: mculzoni@fbcb.unl.edu.ar (M.J. Culzoni), hgoico@fbcb.unl.edu.ar (H.C. Goicoechea).

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and even drinking water [1,2]. Evaluation and monitoring of traces of these so-called "emerging" contaminant are imperative for human health protection as well as environmental control [2]. Therefore, sensitive, fast, and simple analytical methods are demanded. Over the last years, analytical methods based on fluorometric techniques have attracted considerable attention due to their ability to combine the three characteristics aforementioned.

By virtue of their selectivity and sensitivity, luminescent probes have demonstrated to be a good alternative to measure different compounds in diverse matrices. Metal ions, especially rare-earth ions, such as Terbium (Tb^{3+}) and Europium (Eu^{3+}) [3–5], as well as metal nanoparticles [6,7] are usually used as luminescent probes due to their singular luminescence characteristics: 1 – narrow spectral width, 2 – long luminescence life-time, 3 – large Stokes shift, and 4 – strong combination ability [8,9]. Recently, it has been demonstrated that Yttrium (Y^{3+}), a non-lanthanide element, could remarkably enhance the native fluorescence of several fluoroquinolones [9–13]. Y^{3+} in solution does not have native fluorescence by itself, but in presence of certain pharmaceuticals, i.e., fluoroquinolones (FQs), is able to enhance the native fluorescence of the analytes [9–11]. These Y^{3+} based systems for the analysis of pharmaceuticals would not require complicated or tedious treatment procedure (sample clean-up or pre-concentration steps) to achieve lower limits of detection, due to the fact that the increment of the native fluorescent of the analytes is giving in a quasi-selective way. Here, FQ reacts as a bidentate ligand to the Y^{3+} through the pyridine oxygen and carboxylate oxygen forming a strong and stable complex [10,14], leading both an increase of native fluoresce intensity as a change in the maximum wavelength position [11].

In the 1980s, FQs were developed as an effective group of antibiotics for the treatment of bacterial infections in humans, animals, poultry, and fish [15]. Since these compounds are not fully metabolized by the body and are not fully removed in wastewater treatment plants, they are discharged into surface water supplies as parent compound or as sub-product of the parent compound [16]. Besides, considering they are administrated in large quantities and do have high resistance to biodegradation, these compounds are of public and ecological health concern [15,16], mainly because is not well-known the health effect if they persist in the environment even at very low levels [17]. Hereof, simple and fast analytical methods capable of measuring trace concentrations of fluoroquinolones in several aqueous matrices are required.

A large number of methods for the determination of FQs in environmental water samples could be found in the literature, including chromatographic methods with fast-scanning fluorescence (FSFD) detection, mass spectrometry detection (MS) or diode-array detection (DAD), obtaining second-order data [18]. Recently, a high-performance liquid chromatographic (HPLC) method coupled to fluorescence detection, recording excitation-emission matrices as a function of elution time generating third-order data, has been published [19,20]. Also, a recent report proposes a method for quantitation of FQs in drinking water using capillary electrophoresis with DAD [21]. In this regard, multivariate calibrations can be implemented to model these data achieving considerable improvement in analytical properties [18] as well as a decrease of costs and time of analysis, contributing to the green analytical chemistry principles [22].

Due to the low concentration of FQs found in environmental waters and the complexity of these matrices, suitable sample pretreatments and enrichment processes are crucial steps in these analyses. It has been demonstrate that solid-phase extraction (SPE) is the technique most widely used both as pre-concentration processes as a technique to remove matrix effects associated with the composition of the sample [16]. Nevertheless, several enrichment techniques have been reported with the aim to reach increasingly low limits of FQs is several environmental matrices, e.g., ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction (DLLME) [23] and salting-out assisted liquid–liquid extraction (SALLE) [1], but increasing the complexity of the entire procedure with an increase of costs and time of analysis.

The present study reports a sensitive chromatographic method for the analysis of seven fluoroquinolones, including enoxacin, ofloxacin, norfloxacin, ciprofloxacin, enrofloxacin, sarafloxacin, and difloxacin, in environmental water samples, by coupling yttrium-analyte complex and three-way chromatographic data modeling. This method based on the use of HPLC-FSFD does not require complex or tedious sample treatments or enrichment processes before the analysis, due to the significant fluorescence increments of the analytes reached by the presence of Y^{3+}.

With the purpose of evaluating the application of the method to environmental water samples, determination of FQs in surface water, well water and wastewater was carried out.

2. Experimental section

2.1. Chemicals and reagents

All standards were of analytical grade. Enoxacin (ENO), norfloxacin (NRF), ofloxacin (OFL) and sarafloxacin (SRF) were provided by Sigma–Aldrich (Steinheim, Germany). Ciprofloxacin (CPF), difloxacin (DIF) and enrofloxacin (ENF) were purchased from Fluka (Buchs, Switzerland). Acetonitrile (ACN) LC grade was obtained from LiChrosolv (Merk Millipore Co., Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q purification system from Millipore (Bedford, USA). Glacial acetic acid (HAc) was purchased from Merk (Darmstadt, Germany) and sodium acetate trihydrate (NaAc) was provided by Anedra (La Plata, Argentina). Yttrium (III) nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$) was purchased from Sigma–Aldrich (Steinheim, Germany).

Stock standard solutions of each FQ were prepared by dissolving the appropriate amount of each FQ in alkalinized methanol (pH 9.00) to reach concentration levels of 200.00 $\mu g\ mL^{-1}$, and stored at 4 °C in the dark.

A stock standard solution of yttrium (Y^{3+}) was prepared by dissolving the appropriate amount of $Y(NO_3)_3{\cdot}6H_2O$ in ultrapure water in order to obtain a concentration of 0.1 mol L^{-1}.

A 0.02 mol L^{-1} acetic acid/acetate buffer solution (AcYB) was prepared by dissolving the appropriate amount of NaAc in ultrapure water, and adjusting the pH to 4.00 with glacial HAc. The solution was transferred to a 1000.00 mL volumetric flask and 1.00 mL of the standard solution of Y^{3+} was added in order to obtain an Y^{3+} final concentration of 1.0×10^{-4} mol L^{-1}. Then, the volume was completed to the mark with ultrapure water.

2.2. Instrumentation and procedure

The experiments were performed on an Agilent 1100 LC instrument (Agilent Technologies, Waldbronn, Germany), equipped with degasser, quaternary pump, auto-sampler, oven column compartment, UV–Vis Diode Array Detector (DAD), fast-scanning fluorescence detector (FSFD) and ChemStation software package (Agilent Technologies, Waldbronn, Germany) to control the instrument, the data acquisition and the data analysis.

The separation was performed on a 3.5 μm Zorbax Eclipse XDB-C18 analytical column (75 mm × 4.6 mm) (Agilent Technologies, Waldbronn, Germany) in isocratic mode at 2.20 mL min^{-1} flow rate during 16.0 min at 45 °C. The mobile phase consisted in a mixture of AcYB and ACN (91:9).

All pH measurements were carried out with an Orion (Massachusetts, United States) 410A potentiometer equipped with a Boeco BA 17 (Hamburg, Germany) combined glass electrode.