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On the performance of multiway methods for simultaneous quantification of two fluoroquinolones in urine samples by fluorescence spectroscopy and second-order calibration strategies

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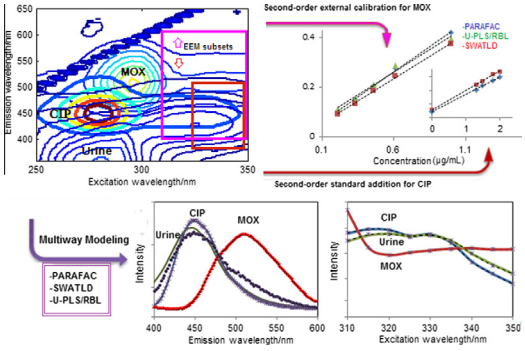
HIGHLIGHTS

- Multiway methods were compared for analysis of MOX and CIP in urine using EEM data.
- Performance of the methods depends on the EEM subset and the calibration strategy.
- UPLS/RBL allows for the successful determination of both analytes in all conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, the analytical performance of three multi-way algorithms has been evaluated. The proposed analytical problem was the simultaneous determination of moxifloxacin and ciprofloxacin in human urine samples using fluorescence spectroscopy. Parallel factor analysis (PARAFAC), self-weighted alternating trilinear decomposition (SWATLD) and unfolded partial least squares combined with the residual bilinearization procedure (U-PLS/RBL) have been compared, regarding their ability to solve the proposed problem. In this study, "second-order advantage" was also exploited for the mentioned algorithms through different calibration strategies. The three-way data was obtained via fluorescence spectroscopy, so that excitation–emission matrices (EEM) of the samples were recorded as the analytical signals. The accuracy and precision of each individual algorithm for analyzing the drugs in urine samples were compared using root mean square error of prediction (RMSEP), recovery and elliptical joint confidence region (EJCR) plots. The results revealed that each of the three algorithms could be applied for determination of moxifloxacin and ciprofloxacin, despite different EEM subsets and calibration strategies. However, better analytical performances were observed through PARAFAC and U-PLS/RBL modeling for MOX and CIP, respectively. So, by coupling the multi-way decomposition algorithms with fluorescence spectroscopy, a main part of preliminary sample preparation steps can be eliminated and experimental procedure might be significantly simplified, while achieving desirable analytical performance.

Introduction

Moxifloxacin (MOX) is a fourth generation 8-methoxyquinolone derivate of fluoroquinolones with enhanced activity in vitro against gram positive bacteria and also maintenance of activity

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against gram negative bacteria [1–3]. MOX is one of the most important and successful synthetic antibacterials, which is frequently used in treatment of various cases, such as lung and respiratory tract infections, skin allergy, pneumonia, and urinary tract infections [4,5]. The administrated dose of this drug is usually 400 mg daily and as a consequence its final concentrations in the treated patients' serum and urine range between 2.00–5.00 and 30.00–60.00 μg mL^{-1}, respectively [6].

High-performance liquid chromatography with ultraviolet detection has been one of the most frequently used techniques in determination of moxifloxacin as well as other fluoroquinolones, in plasma, urine and pharmaceutical preparations [7–16]. Determination of moxifloxacin in human plasma [17,18] and dried blood spots [19] have also been carried out, using liquid chromatography–tandem mass spectrometry method. Spectrofluorimetric determination of moxifloxacin in tablets, human urine and serum, as a single target analyte [20] or simultaneously with other fluoroquinolones in pharmaceutical preparations [21], has been also reported. In a study, micellar-enhanced spectrofluorimetry has been applied for determination of moxifloxacin in pharmaceutical formulations, human urine and plasma samples [22]. Spectrophotometric methods have been also used in some studies for the estimation of moxifloxacin in bulk and pharmaceutical formulations and simultaneous determination of moxifloxacin and cefixime, by first derivative of ratio spectra [23–24]. Capillary electrophoresis with laser-induced fluorescence has been also proposed for determination of moxifloxacin in very small sample volumes of human body fluids [25].

Ciprofloxacin (CIP) is a low toxicity fluoroquinolone antibiotic which is highly active against a broad spectrum of microbial pathogens [26]. It acts effectively in case of infections, such as pneumonias, bone infections, diarrhea, skin infections and urinary tract infections. It can be administered both parenterally and orally. Its main excretion pathway is urinary [27] with usual concentrations in the range of 100–200 mg L^{-1}. CIP is a weak diprotic acid and has several prototropic forms and in some acidity conditions, like the present work, has a single acid–base form in the solution. Several methods have been reported for the quantification of CIP including spectrophotometry and spectrofluorimetry [28,29], high-performance liquid chromatography (HPLC) [30,31], micellar liquid chromatography [32], flow-injection chemiluminescence [33], capillary electrophoresis with diode-array detection [34] and Rayleigh light scattering technique [35].

All of the above mentioned methods, when used for analyzing complex biological matrices, may demand for several preliminary steps, such as extraction into a suitable organic solvent, clean-up and pre-concentration procedures and also proteins precipitation in some cases. This problem can be overcome through combining spectrofluorimetry and multivariate calibration techniques, so that interferences can be removed mathematically [36–39]. Several studies have explored the use of fluorescence spectroscopy combined with second-order calibration and second-order standard addition methods (SOSAM). In this field, successful determination of drugs, such as naproxen [40], ibuprofen [41], piroxicam [42], doxorubicin [43], daunorubicin [44], carbamazepine [45], ciprofloxacin [39], folic acid and methotrexate [46], fluoroquinolone antibiotics [47,48] and phenylanthranilic acid derivatives [49,50], in plasma, serum and urine matrices, has been reported.

In the present study, the analytical performance of three algorithms; parallel factor analysis (PARAFAC), self-weighted alternating trilinear decomposition (SWATLD) and unfolded partial least-squares (U-PLS) combined with residual bilinearization procedure (RBL), has been compared, as second-order data analysis strategies for simultaneous determination of moxifloxacin and ciprofloxacin in human urine samples. Particularly, the second-order advantage can be exploited with the mentioned algorithms through different strategies. In fact, the proposed method can be used (with minimum sample preparation effort) for analysis of any of these analytes in a batch of samples from different donors, without any need to change or adjust the instrumental and operational settings.

Materials and methods

Chemicals

Stock standard solutions of MOX and CIP (1000 μg mL^{-1}) were prepared by dissolving the compounds in deionized water (Milli-Q, USA) and stored in the dark at 4 °C. Working solutions were prepared prior to use, through proper dilutions of the stock solutions with deionized water. The 0.1 M buffer solution (pH = 4.00) was prepared using acetic acid (Fluka, USA) and sodium acetate (CDH, India). Urine samples were obtained from fasting and healthy two individuals in the morning. Since no drug usage had been proclaimed by the donators, the samples were considered as blank for MOX and CIP. Urine samples were centrifuged at 3000 rpm for 10 min and clear supernatants were separated and used in further analytical procedures.

Apparatus and software

All fluorescence measurements were carried out on a Jasco (Japan) FP-6500 spectrofluorimeter equipped with 1.00 cm quartz cells and a 150 W Xe lamp. EEMs were obtained in the excitation range of 250–350 nm (at 5 nm steps) and in the emission range of 360–650 nm (at 2 nm steps), yielding a total of 21 × 146 = 3066 data points per sample matrix. The excitation and emission monochromator slit widths were both 3.0 nm, and the scanning rate was 1000 nm min^{-1}. Centrifugation of the urine samples was carried out on a Hettich320 R (Germany) at 4000 rpm. A 744 pH meter Metrohm (Switzerland) equipped with a combined glass/saturated calomel electrode was used for pH measurements. All calculations were carried out by MATLAB R2009a, using the MVC2 routine, an integrated MATLAB toolbox for second-order calibration, developed by Olivieri et al. [51].

Calibration and validation sets

A set of 15 samples was constructed for calibration using a random design, where the analyte concentration values were in the range of 0.00–1.00 μg mL^{-1} for MOX and 0.00–2.00 μg mL^{-1} for CIP (see Table 1 for detailed composition of these samples). For preparing a given calibration sample, predetermined aliquots of MOX and CIP stock solutions were added into the 10.0 mL

Table 1
Composition of the calibration set.

Calibration set	MOX (μg mL^{-1})	CIP (μg mL^{-1})
C1	0.46	0.38
C2	0.21	0.13
C3	1.00	0.90
C4	1.00	0.58
C5	1.00	2.00
C6	0.21	0.58
C7	0.33	0.38
C8	0.61	2.00
C9	0.61	0.13
C10	0.61	0.13
C11	0.33	0.38
C12	0.46	2.00
C13	0.21	0.58
C14	0.46	0.90
C15	0.33	0.90