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Green analytical determination of emerging pollutants in environmental waters using excitation–emission photoinduced fluorescence data and multivariate calibration

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ABSTRACT

An eco-friendly strategy for the simultaneous quantification of three emerging pharmaceutical contaminants is presented. The proposed analytical method, which involves photochemically induced fluorescence matrix data combined with second-order chemometric analysis, was used for the determination of carbamazepine, ofloxacin and piroxicam in water samples of different complexity without the need of chromatographic separation. Excitation–emission photoinduced fluorescence matrices were obtained after UV irradiation, and processed with second-order algorithms. Only one of the tested algorithms was able to overcome the strong spectral overlapping among the studied pollutants and allowed their successful quantitation in very interferent media. The method sensitivity in superficial and underground water samples was enhanced by a simple solid-phase extraction with C18 membranes, which was successful for the extraction/preconcentration of the pollutants at trace levels. Detection limits in preconcentrated (1:125) real water samples ranged from 0.04 to 0.3 ng mL^{-1}. Relative prediction errors around 10% were achieved. The proposed strategy is significantly simpler and greener than liquid chromatography-mass spectrometry methods, without compromising the analytical quality of the results.

1. Introduction

Emerging pollutants are compounds not currently covered by existing water-quality regulations, representing potential threats to ecosystems and human health because of their toxic effects [1,2]. They do not need to persist to negatively affect the exposed organisms, since their introduction into the environment is continuous, especially those belonging to the pharmaceutical group [1–7].

Pharmaceutically active compounds used in both human and veterinary medicine are excreted via feces and urine, partly transformed into glucuronides and sulphates or even unchanged, and are suspected to enter aquatic bodies through the effluents of sewage treatment plants [7–11]. Therefore, continuous efforts are devoted to develop appropriate methods for their monitoring and quantification in natural samples.

Although liquid chromatography–mass spectrometry (LC–MS) is one of the most commonly applied methods for the determination of pharmaceutical compounds and their degradation products in the aquatic environment [2,12,13], greener methodologies, i.e. without separations and clean up steps, and minimizing the use of organic solvents, are very welcome [14].

Abbreviations: A, antibiotics; CBZ, carbamazepine; CLC, capillary liquid chromatography; DAD, diode array detection; DICLO, diclofenac; DVB, divinylbenzene; DW, drinking water; EC, electrophoresis capillary; EEPIFM, excitation–emission photoinduced fluorescence matrix; EJCR, elliptical joint confidence region; EP, emerging pollutants; EW, environmental water; FLU, flufenamic acid; GC, gas chromatography; HLB, hydrophilic-lipophilic balance; Horm, hormones; IBU, ibuprofen; LC, liquid chromatography; LIF, laser induced fluorescence detection; LOD, limit of detection; LOQ, limit of quantification; MCR-ALS, multivariate curve resolution-alternating least-squares; MPs, surface-funcionalized magnetic particles; MS, mass spectrometry; MS/MS, tandem mass spectrometry; MWCN, multi-walled carbon nanotubes; MW, mineral water; NSAI, non-steroidal anti-inflammatory; OFL, ofloxacin; OP, organic pollutants; Pharm, pharmaceuticals; PARAFAC, parallel factor analysis; PIF, photoinduced fluorescence; PDS, polydimethylsiloxane; PX, piroxicam; QqLIT, quadrupole linear ion trap tandem mass spectrometry; QTOF, hybrid quadrupole time-of-flight; REC, recovery; REP, relative error of prediction; RMSEP, root-mean-square error of prediction; RSD, relative standard deviation; RSW, reservoir water; RW, river water; SAL, salicylic acid; SPE, solid-phase extraction; SPME, solid-phase microextraction; SW, sea water; TF, thin film; TOF, electrospray time-of-flight; TW, tap water; UPLC, ultra-high-performance liquid chromatography; U-PLS/RBL, unfolded-partial least-squares with residual bilinearization; UV, ultraviolet detection; UW, underground water; WW, Wastewater; WWE, wastewater effluent; WWI, wastewater influent

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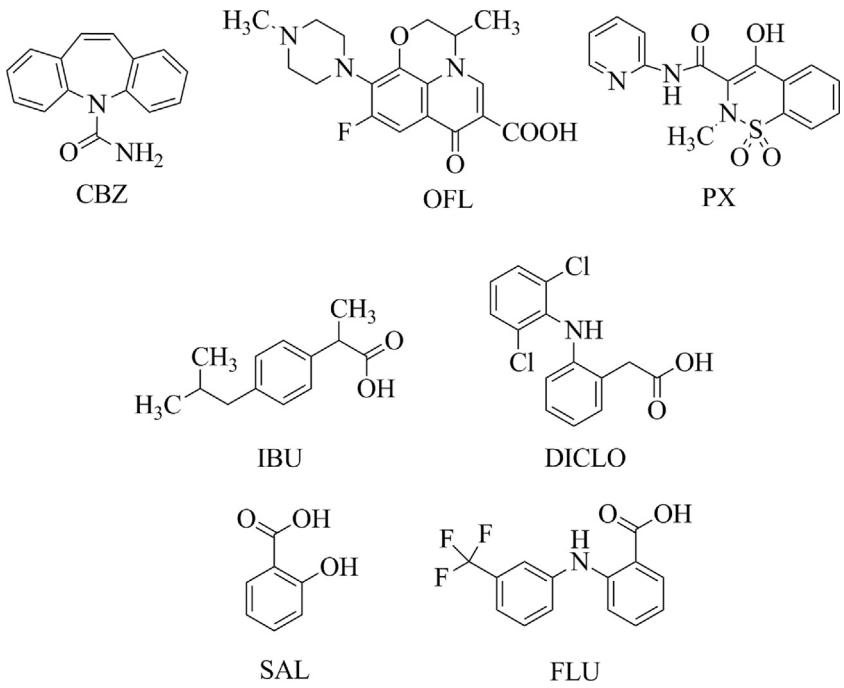

Scheme 1. Structures of carbamazepine (CBZ), ofloxacin (OFL), piroxicam (PX), ibuprofen (IBU), diclofenac (DICLO), salicylic acid (SAL) and flufenamic acid (FLU).

In the present work, three emerging pollutants, representative of different groups of therapeutic drugs, were investigated: the anticonvulsant carbamazepine (CBZ), the antibacterial fluoroquinolone ofloxacin (OFL), and the non-steroidal anti-inflammatory piroxicam (PX) (Scheme 1), because they are frequently found in environmental waters. They display photo-induced fluorescence (PIF) upon UV irradiation, which could allow their quantification. Relatively few molecules are fluorescent, and fluorescent photoproducts are even fewer, or parent compounds are photodegradated after UV irradiation. This may lead to the erroneous conclusion that PIF-based methods are free from interferences. However, as presently demonstrated, in multicomponent systems, the probability of the occurrence of interferences significantly increases and, in principle, clean-up and separation procedures are almost unavoidable.

Recently, our research group quantified CBZ, as a single analyte, in environmental waters using the PIF signals after UV irradiation of acidic solutions in a simple laboratory-constructed reactor [15]. The lack of selectivity was overcome by the second-order advantage of multi-way calibration [16] and pollutant was quantitated in the presence of unknown sample constituents. Second-order data were obtained as excitation–emission photoinduced fluorescence matrices (EEPIFMs) and processed by different algorithms, although successful results were obtained with multivariate curve resolution-alternating least-squares (MCR-ALS) [17].

The critical difference of the present report with the earlier work is that the simultaneous resolution of three usual emerging contaminants which strongly overlap their PIF spectra is presently intended, with the concomitant change in both data analysis and results interpretation. Further, the determinations are performed in solutions containing the analytes and additional pharmaceuticals, such as ibuprofen (IBU), diclofenac (DICLO), salicylic acid (SAL) and flufenamic acid (FLU) (Scheme 1). The latter are profusely employed in our geographical region and may thus be present in real waters, and showed fluorescence signals (either in native form or from their photoproducts) which significantly overlap those of the analytes.

Three chemometric algorithms achieving the second-order advantage, i.e., parallel factor analysis (PARAFAC) [18], MCR-ALS, and unfolded partial least-squares/residual bilinearization (U-PLS/RBL) [19,20], were applied to process the EEPIFMs. Noticeable differences in the prediction capabilities of the employed algorithms were found and discussed.

To the best of our knowledge, it is the first time that the selectivity offered by the chemometric analysis is evaluated for the simultaneous determination of several analytes using EEPIFMs in very interfering media. The feasibility of determining the three emergent pollutants in real water samples using sustainable resources is demonstrated.

2. Experimental

2.1. Reagents and solutions

CBZ, OFL and PX were purchased from Sigma (St. Louis, MO, USA). Methanol (MeOH), formic acid and hydrochloric acid (HCl) were obtained from Merck (Darmstadt, Germany). IBU, DICLO, SAL and FLU were of analytical grade and were used as received. Stock standard solutions of individual analytes (404.0 $\mu g\ mL^{-1}$ CBZ, 420.0 $\mu g\ mL^{-1}$ PX and 510.0 $\mu g\ mL^{-1}$ OFL) were prepared by dissolving an appropriate amount of each compound in methanol, and stored at 4 °C. Working analyte solutions of 2.0 $\mu g\ mL^{-1}$ were daily prepared by dilution of stock standard solutions in ultrapure water. Ultra pure Milli-Q water was used throughout the work.

2.2. Instrumentation

Fluorescence measurements were performed on an Aminco Bowman (Rochester, NY, USA) Series 2 luminescence spectrophotometer, equipped with a 150 W xenon lamp. EEPIFMs were measured in the ranges 246–333 nm (each 3 nm, excitation) and 380–480 nm (each 1 nm, emission), leading to 29 × 100 matrices. Excitation and emission slit widths were of 8 nm using 1.00 cm quartz cells. The photomultiplier tube sensitivity was 600 V and the cell temperature was regulated at 20 °C using a thermostatic bath (Cole-Parmer, IL, USA). EEPIFMs were saved and transferred to a PC for subsequent chemometric analysis.

For the reference chromatographic analysis, see Supplementary material.