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Rapid Method for the Quantification and Identification of Emerging Compounds in Wastewater Based in Nir Spectroscopy and Chemometrics

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ABSTRACT
The typical methods to quantify emerging compounds in wastewater are time and reagent consuming and new methods for its quantification are welcome. This work describes the development and validation of a Fourier transform near-infrared (FT-NIR) spectroscopy methodology for the quantification of emerging compounds in wastewaters. For this purpose, 180 samples obtained from an activated sludge wastewater treatment process were analyzed in the range of 200 cm^{-1} to 14000 cm^{-1}, and further treated by chemometric techniques to develop and validate the quantification models. The obtained results were found adequate for the prediction of atrazine, paracetamol, and desloratadine with coefficients of determination (R^2) from 0.93 to 0.98 and residual prediction deviation (RPD) values above three, for the overall (training and validation) data points. These results are very promising and confirm that this technology can be seen as an alternative for the quantification of emerging compounds in wastewater.

Keywords: Chemometrics; emerging compounds; NIR spectroscopy; PCA; PLS

1. INTRODUCTION
Intensive studies during the last decades have found that contamination of the aquatic environment by emerging pollutants is wide-spread. The traditional methods used for the quantification of these compounds, as titrimetric techniques, chromatographic techniques, high-performance liquid chromatography (HPLC), gas chromatography (GC), electrochemical and electrophoretic methods, are time or reagent consuming and faster, effortless and environmental friendly methods are welcome. In this context, this work presents a very simple, non-destructive, inexpensive and green strategy applied to the determination of atrazine (ATR), desloratadine (DSL), and paracetamol (PRC) concentrations using FT-NIR spectroscopy, in wastewater. This technique presents, as most interesting advantages, the absence of reagents use, its nondestructive character allowing to reuse the sample after measurement [1], speed and the possibility of online monitoring. The main difficulty of this technique is the complexity of the spectra due to their nature, and for this reason FT-NIR is not usually used as a direct analysis technique. Recent developments in chemometrics allowed overcoming these difficulties and the combination between FT-NIR and chemometrics is now considered as a promising technology able to quantify a wide range of organic compounds. The Y dataset employed in the chemometric analyses consisted of emerging compounds concentrations, measured by HPLC, monitored throughout the time length of the different experiments in this work, whilst the X dataset consisted of the collected FT-NIR spectra (ranging from 14000 to 200 cm^{-1}). Kolmogorov–Smirnov test and boxplot analysis were used for normal distribution check and outliers' rejection, followed by principal component analysis (PCA) for cluster analysis and outliers' rejection, and partial least squares (PLS) regression for the pharmaceuticals concentrations prediction [2].

2. RESULTS AND DISCUSSION
A principal components analysis (PCA) was performed and is present in Fig. 1. As can be observed, three different clusters were found corresponding to the three different emerging compounds studied. These results show that this method can be used for the rapid identification of emerging compounds.

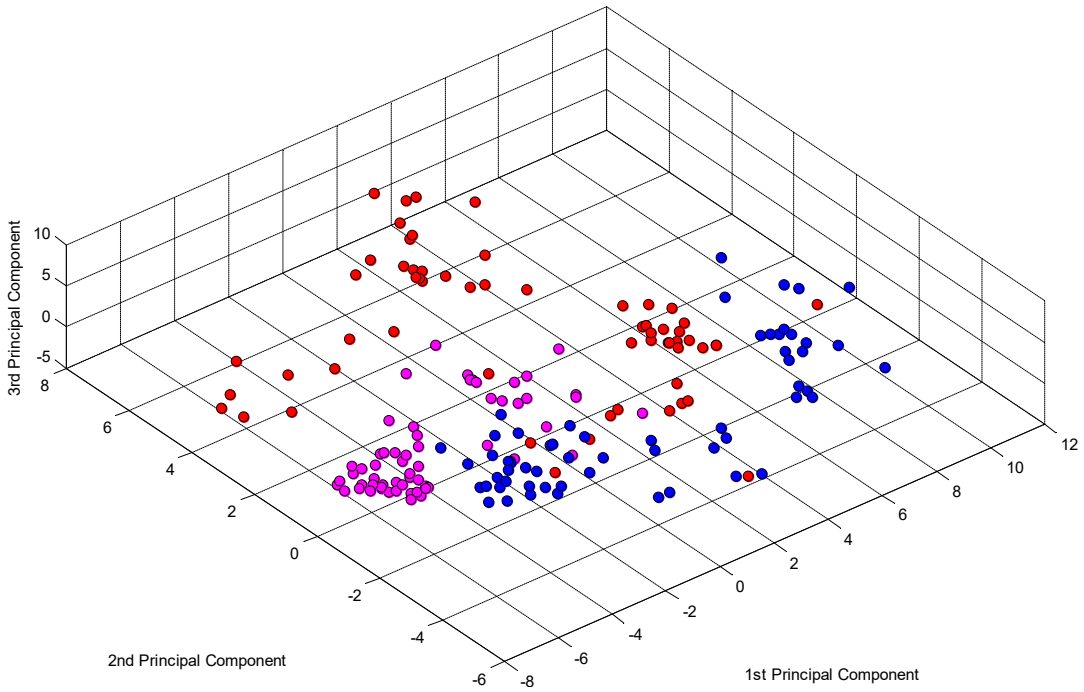

Figure 1. Principal component analysis: blue circles represent atrazine; rose circles represent paracetamol; and red circles represents desloratadine.

A PLS analysis was then performed in order to obtain a prediction model suitable for the emerging compounds quantification purposes. This procedure resulted in high coefficients of determination (R^2), and low root mean square errors (RMSE), for the prediction ability of all the studied compounds. Furthermore, the residual prediction deviation (RPD) for the overall (training and validation) samples was above three, configuring its adequacy towards these compounds monitoring (Table 1). The proposed method is not only a simple procedure, non-expensive and fast technique, but also it has relatively high sensitivity for the studied emerging compounds. Therefore, this methodology can be considered as promising towards the replacement of HPLC and GC analysis for routine emerging compound quantification in wastewater, decreasing costs in reagents and analysis time.

Table 1. Main results of the PLS analysis

	Eq. (tr+val)	R^2 (tr+val)	RMSE % (tr+val)	RMSE % (val)	RPD (tr+val)	RPD (val)	n
ATR	y = 0.998x	0.982	2.37	4.29	7.94	4.38	15
DSL	y = 0.995x	0.963	4.77	8.11	5.20	3.06	12
PRC	y = 1.001x	0.925	6.72	11.57	3.87	2.24	11

tr – training; val – validation; R^2 – coefficient of determination; RMSE – root mean square error (in percentage of the studied range); RPD – residual predictive deviation; n – number of PLS components

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