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Determination of imidacloprid in water samples via photochemically induced fluorescence and second-order multivariate calibration

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ABSTRACT

This paper presents a new method for the determination of imidacloprid in water samples; one of the most widely used neonicotinoid pesticides in the farming industry. The method is based on the measurement of excitation–emission spectra of photo-induced fluorescence (PIF-EEMs) associated with second-order multivariate calibration with a parallel factor analysis (PARAFAC) and unfolded partial least squares coupled to residual bilinearization (U-PLS/RBL). The second order advantage permitted the determination of imidacloprid in the presence of potential interferences, which also shows photo-induced fluorescence (other pesticides and/or unexpected compounds of the real samples). The photoreaction was performed in 100-μl disposable micropipettes. As a preliminary step, solid phase extraction on C18 (SPE-C18) was applied to concentrate the analyte and diminish the limit of detection. The LOD was approximately 1 ng mL^{-1}, which is suitable for detecting imidacloprid in water according to the guidelines established in North America and Europe. The PIF-EEMs coupled to PARAFAC or U-PLS/RBL was successfully applied for the determination of imidacloprid in different real water samples, with an average recovery of 101 ± 10%.

1. Introduction

Neonicotinoid insecticides are a new group of pesticides with properties that allow for their systemic distribution within plants after being absorbed by the leaves or roots. The major modes of application of these compounds are spraying and seed dressing, especially to control pests in crops, such as cereals, soybeans, corn and several fruits and vegetables. Due to their high efficiency, good selectivity against a large number of pests and insects, low mammalian toxicity, and high versatility in a wide range of agricultural practices, they have become dominant pesticides [1]. Globally, 60% of neonicotinoids are used in seed dressing. However, the widespread adoption of these compounds is also due to their flexibility of use, including as foliar sprays on soft fruits; arable crops, such as soya; and in gardens as a flower spray [2].

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] belongs to a new group of active ingredients and was first introduced to the market by Bayer in 1991. It is currently the most widely used neonicotinoid in the farming industry. Due to its polarity, the extensive use of imidacloprid may cause pollution of surface or groundwater via runoff or percolation and also via the drainage of treated soil. In surface water, imidacloprid may degrade due to sunlight, pH, and temperature, producing several compounds that may be hazardous to the health of vertebrates, mammals and humans [3]. However, its transport into groundwater makes this compound more persistent and may affect several aquatic organisms [4]. Moreover, neonicotinoid pesticides could have an adverse effect on the population of bees, causing the so-called "colony collapse disorder", which is characterized by sudden depopulation of hives by worker bees and the subsequent death of the larvae and queen. Along with the decline in honey production, the loss of pollinators has had a negative impact on the reproduction of multiple crops [5,6]. Thus, the use of these pesticides in agriculture also has indubitable repercussions on the environment and the quality of natural waters, which has become a serious environmental concern.

Monitoring the environmental impact of neonicotinoid insecticides in matrix environments, such as natural water, requires sensitive analytical methods. The low concentration levels of imidacloprid that may be present in these types of samples make sample treatments that involve extraction and concentration steps necessary. The extraction of imidacloprid from aqueous samples has primarily been performed using liquid–liquid extraction (LLE) [7] and solid phase extraction (SPE) on C18 [7–10]. On the other hand, due to its low volatility and relatively high hydrophilicity, the determination of imidacloprid in environmental water samples

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has primarily been performed using liquid chromatography methods with UV or diode array detection [11–15], mass spectrometry detection [16–18], ion chromatography [19] and micellar electrokinetic chromatography [8].

The summarized conventional analytical approaches applied for imidacloprid determination in water samples require a large amount of solvent and produce a large amount of waste due to sample preparation and chromatographic analysis. Alternative methods based on the fluorimetry of a photoproduct of imidacloprid produced after the UV irradiation of an aqueous imidacloprid solution have been proposed for water analysis. In aqueous media, imidacloprid does not exhibit native fluorescence; however, its irradiation with UV light results in a fluorescent signal. The fluorescent photoproduct generated in a basic aqueous media has been previously isolated and identified as 1-(6-chloro-3-pyridylmethyl)-2-(hydroxyimino)-3,4-didehydroimidalozolidene, which exhibits native fluorescence [20]. In this work, the authors proposed a fluorimetric method for the determination of imidacloprid in water after its irradiation. Subsequently, Vílchez et al. [21] presented a flow injection alternative to the method using a homemade continuous photochemical reactor to irradiate the sample while it was circulated through a PTFE tube. In another study, López Flores et al. [22] proposed a method for determining imidacloprid in peppers and environmental water samples that combines photochemically induced fluorescence, performed in-line, with solid phase spectroscopy of the fluorescent compound retained on a C18 filled flow-cell. The reported limits of detection were 4.1 and 1.8 $\mu g\, l^{-1}$ for injection volumes of 100 and 640 μl, respectively. A similar method for the in-line determination of imidacloprid in water samples was developed more recently by Araujo et al. [23], who reported a limit of detection of 5.3 $\mu g\, l^{-1}$ with an injection volume of 100 μl. In a different approach, Subhani et al. [19] proposed the determination of imidacloprid and carbendazim in water samples using a post-column photochemical reactor with alkaline medium and fluorescence detection after the ion chromatography separation of analytes. The limit of detection reported for imidacloprid by the authors was 7.8 $\mu g\, l^{-1}$.

However, the relevance of these methods has been limited by their lack of selectivity, especially when chemically similar compounds must be analyzed in a complex matrix. One approach to improve the analytical selectivity in this matrix would be the use of excitation–emission fluorescence measurements (three-way data set), in conjunction with different chemometric algorithms as a parallel factor analysis (PARAFAC) and unfolded partial least square with residual bilinearization (U-PLS/RBL) to build a second-order calibration method. These methods permit the resolution of analytical signals without the use of chromatography and the resolution of spectra of target compounds from a complex background signal and overlapping spectral interferences that are not included in the calibration set (known as the second-order advantage) [24]. This characteristic helps minimize sample pretreatment, which is primarily used to concentrate the analyte and reduce the limit of detection. Moreover, the use of excitation–emission fluorescence data also improves this analytical characteristic and avoids increasing the volume of sample to be analyzed.

Despite the capability of chemometric methods, there are no available reports on the determination of imidacloprid in water samples through photochemically induced fluorescence spectroscopy coupled to multivariate calibration. In this work, PARAFAC and U-PLS/RBL methods were applied to determine imidacloprid in different water samples using photochemically induced fluorescence excitation–emission matrices (PIF-EEMs) in presence of other pesticides (clothianidin, thiamethoxam, fipronil, carbofuran, carbaryl, fenvalerate and atrazine) and/or dissolved fluorophores presents in water samples as potential interferences. The UV irradiation of samples was performed using disposable micropipettes. Solid phase extraction (SPE) on C18 was used as sample preparation step. The predicted PARAFAC and U-PLS/RBL concentrations were compared with those obtained using high-performance liquid chromatography (HPLC) with UV–vis detection. The method was applied for the analysis of different water samples (mineral, drinking, well and irrigation ditch).

2. Theory: figures of merit in multivariate calibration.

In multivariate calibration, figures of merit are related to the concept of multivariate net analyte signal (NAS) [25,26]. This concept involves the decomposition of the total spectrum of a given sample (x) into two orthogonal parts: one part that can be uniquely assigned to the analyte of interest (the net analyte signal, designated x^*) and the remaining part that contains the contributions from the other components, which may be different than expected or unexpected sample components (x_{other}), as indicated in Eq. (1):

$$x = x_n^* + x_{other} = c_n \cdot s_n^* + x_{other} \quad (1)$$

where x_n^* and s_n^* are the net analyte signals (vector signal) corresponding to a given sample and to a sample having the nth analyte at unit concentration, respectively, and c_n is the analyte concentration. If matrix-like net analyte signals are implied, Eq. (2) is applied

$$X_n^* = c_n \cdot S_n^* \quad (2)$$

The expressions for the sensitivity (S_n) are obtained from the norm of the net analyte signal at unit concentration $s_n = \|s_n^*\|$ or $S_n = \|S_n^*\|$. Conversely, for an inverse model the sensitivity is defined as $S_n = \|s_n^*\|^{-1}$ or $S_n = \|S_n^*\|^{-1}$.

When the second-order advantage is used, the sensitivity is sample-specific and cannot be defined for the multivariate method as a whole. In this case, an average value for the set of samples can be estimated and reported [25]. The analytical sensitivity, γ_n, appears to be more useful than S_n and is defined, analogous to univariate calibration, as the quotient between S_n and the instrumental noise level (s_x). Its inverse, γ_n^{-1}, establishes the minimum concentration difference that can be appreciated across the linear range and is independent of the instrument or scale [26]. Thus, the limit of detection (LOD_n) can be gathered from the expression $LOD_n = 3\ \gamma_n^{-1}$. In addition to S_n as an average value over a test sample set, LOD_n is also reported as an average figure of merit.

3. Experimental

3.1. Reagents and solutions

Imidacloprid, clothianidin, thiamethoxam and fipronil were of high purity grade and obtained from Sigma-Aldrich (St. Louis. MO, USA). NaCl, NaOH and Na_2HPO_4 were of analytical purity grade and obtained from Merck (Darmstadt, Germany). Acetonitrile, methanol and chloroform were of HPLC grade and purchased from Merck (Darmstadt, Germany).

Stock solutions of pure analytes (1000 $\mu g\, mL^{-1}$) and diluted solutions (100 $\mu g\, mL^{-1}$) were prepared in acetonitrile. The stock solutions were stored in amber vials at 4 °C in the dark. Under these conditions, the stock solutions were stable for almost two months.

3.2. Apparatus and software

A Varian Cary-Eclipse luminescence spectrometer (Mulgrave, Australia) equipped with a xenon flash lamp was used to obtain excitation–emission fluorescent measurements. A Hellma