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Determination of phenylurea pesticides by direct laser photo-induced fluorescence

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ABSTRACT

A direct Laser Photo-Induced Fluorescence (DL-PIF) method is developed for the determination of two phenylurea pesticides, namely fenuron and diflubenzuron. The DL-PIF method uses a tunable Nd:YAG-OPO Laser to obtain the photoproduct(s) and to simultaneously analyse their fluorescence in a short acquisition time on an intensified CCD camera. Compared to classical PIF methods, the use of a tunable laser improves the selectivity (by choosing the suitable excitation wavelength), increases the sensitivity (due to the high energy of the beam) and also reduces the time of analysis. The analytical performances of this method for the determination of both pesticides are satisfactory in comparison to other classical PIF methods published for the determination of phenylurea pesticides. The calibration curves were linear over one order of magnitude and the limits of detection were in the ng mL^{-1} range. Satisfactory recoveries were obtained in the analysis of both pesticides in river and sea water spiked samples.

1. Introduction

Pesticides are widely used in agriculture to improve productivity and, consequently, they can produce residues in crops, soils and surface water. Their persistence is an important matter of concern due to their toxicity and possible carcinogenicity. The presence of pesticides could affect ground water or disrupt water treatment plants. Consequently, a European Union Directive (98/83/EC, 1998) advice for surface waters a maximum value of 5 μg L^{-1} for the total concentration of all pesticides and 1 μg L^{-1} for the maximum concentration of an individual pesticide.

Substituted ureas are an important group of pesticides that are used as herbicides (phenylureas and sulfonylureas) and insecticides (benzoylureas). In this work, we investigated fenuron, i.e., a phenylurea pesticide that acts as a photosynthesis inhibitor herbicide, and diflubenzuron, i.e., a benzoylurea that acts as a chitin inhibitor insecticide (Table 1).

Both pesticides under study are naturally non-fluorescent, but they can be photolysed into rapidly-formed strongly fluorescent photoproducts upon UV irradiation. This Photo-Induced Fluorescence (PIF) property can be used to determine these compounds by fluorescence detection. This corresponds to the classical PIF methods and it has been widely applied for the determination of pesticides and drugs [1,2]. As an alternative to classical PIF, we have developed a different method based on Direct Laser Photo-Induced Fluorescence (DL-PIF) [3], which is for the first time applied for the determination of phenylurea pesticides. We have used a tunable Nd:YAG-OPO Laser [4] to obtain the photoproducts and to simultaneously analyse their fluorescence in a short acquisition time on an intensified CCD camera. Here, we determine the fluorescence characteristics and the kinetic formation of the photoproducts obtained by DL-PIF for both pesticides, we expose the analytical performances obtained and we conduct an interference study.

2. Material and methods

2.1. Absorption and fluorescence spectrophotometer

UV–visible absorption spectra are recorded on an Eclipse UV–visible spectrophotometer (Varian). Excitation and emission fluorescence spectra are obtained on a Cary Eclipse Fluorescence spectrophotometer (Varian) with an arc-xenon lamp pulsed at 80 Hz as excitation source.

2.2. Laser system and detection device

For laser induced fluorescence measurements, the light source is a Powerlite Precision 9010 (Continuum, Santa Clara, USA) pulsed Nd:YAG pump laser beam at a 10 Hz repetition rate, with a Sunlite

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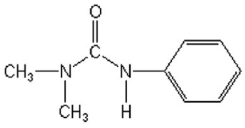
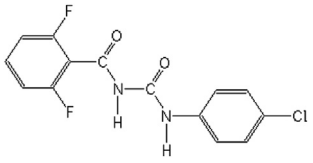
Table 1
Chemical properties of fenuron and diflubenzuron.

Fenuron	Formula	$C_9H_{12}N_2O$	
	Molecular weight	16,420 g/mol	
	Water solubility (20 °C)	3850 mg/L	
Diflubenzuron	Formula	$C_{14}H_9ClF_2N_2O_2$	
	Molecular weight	31,068 g/mol	
	Water solubility (20 °)C	0.08 mg/L	

EX OPO and FX-1 UV frequency extension system from Continuum, which permits continuous wavelength scanning from 225 to 1750 nm (LYOPO programme). The available energy in the UV domain ranges from 2 mJ at 225 nm to 10 mJ per pulse at 275 nm. It can be lowered by positioning a divergent lens in the optical path [5,14]. The detection device includes a spectrometer and an intensified CCD camera. The fluorescence was collected at a 90° angle from the excitation beam and focussed with a f/8 cm lens. The SpectraPro-550i spectrometer (Acton Research Corporation, Acton, MA, USA) has a 550 mm focal length and is equipped with a triple grating turret. The ICCD-MAX intensified CCD Camera (Princeton instruments, Trenton, NJ, USA) has a 512×512 pixel array optimised for the UV–visible domain. A 0.2 nm pixel resolution is reached with the 150 g mm^{-1} grating. The camera is operated with a ST-133 controller (RS Princeton Instruments, Trenton, NJ, USA) for data acquisition. Timing control is achieved with a DG 535 digital delay/pulse generator (Stanford Research System Inc., Sunnywale, CA, USA). The WINSPEC 32-bit Windows software package (Roper Scientific Inc., Trenton, NJ, USA) provides acquisition, display and processing functions. Fluorescence cells (10 mm light path), quartz Suprasil, are from Hellma.

2.3. Reagents

Fenuron and diflubenzuron were purchased from Sigma-Aldrich. Ethanol and methanol were obtained from Sigma. All the reagents were of analytical reagent grade. Ultrapure water (Millipore Mro-MQ System) was used for the experimental work.

Stock standard solutions of the pesticides (10^{-3} M) were prepared by dissolving the compounds in methanol. An ultrasonic bath is used to o obtain complete dissolution; then, solutions are stored in the dark. Serial dilutions were performed to obtain the working standard solutions. The working solutions were prepared either in ultrapure water (for fenuron) or in a 50/50 (v/v) methanol–water mixture (for diflubenzuron).

3. Results and discussion

3.1. Photo-induced fluorescence properties

Fenuron exhibited no native fluorescence, while the laser irradiation yielded the formation of strongly fluorescent photoproducts. The UV absorption spectrum of fenuron showed a main band in pure aqueous solution at 240 nm. Consequently, the laser beam was initially set at 240 nm so that the formation of the photoproducts could be maximised.

Fig. 1 shows the excitation–emission fluorescence matrices of a diluted aqueous solution of fenuron (EEFM) obtained, after 20 min (panel A) and 40 min (panel B) of laser irradiation at 240 nm. As can be seen, three photoproducts are formed. Their maximum excitation and emission wavelengths are shown in Table 2. Fig. 2 shows the evolution of the photoproducts fluorescence intensity with the irradiation time. PIF1 was quickly formed and showed a fluorescence intensity which remained practically constant over 40 min. The fluorescence intensity of PIF2 increased slowly with time and was found to be higher than that of PIF1 after 20 min of UV irradiation. Finally, the third photoproduct, PIF3 was also formed slowly, and showed the highest fluorescence intensity of all photoproducts after about 40 min of irradiation.

Some interpretation of the three PIF compounds spectra from fenuron has been conducted based on their fluorescent characteristics and on bibliographical data. The main photodegradation processes of fenuron correspond to the loss and the oxidation of its alkyl-chains and, as a secondary process, the hydroxylation of the aromatic ring [6]. Based on its fluorescent characteristics, PIF1 could be attributed either to benzene ($\lambda_{ex}=253$ and $\lambda_{em}=280$ nm, pure compound), or to phenol ($\lambda_{ex}=220$ and $\lambda_{em}=302$ nm, pure compound). PIF2 corresponded to aniline ($\lambda_{ex}=231$ and $\lambda_{em}=343$ nm, pure compound), and was confirmed after the analysis of an irradiated sample of fenuron by HPLC chromatography (C18 reverse phase, 30 °C column oven, methanol/water 60/40 v/v, 1.0 mL min^{-1}) followed by fluorescence detection. The analysis of the irradiated sample by GC–MS also indicated the presence of aniline. The photodecomposition of fenuron into aniline has been already demonstrated by Mazzochi and Rao [7]. Unfortunately, PIF3 could not be identified.

Similar to fenuron, diflubenzuron exhibited no native fluorescence, while laser irradiation yielded the formation of two fluorescent photoproducts. First, the UV absorption spectrum of diflubenzuron was measured. Since diflubenzuron did not absorb in water, all the experiments were conducted in a 50/50 (v/v) methanol–water mixture where it presented a strong absorbance band with a maximum at 260 nm. Consequently, the laser beam was initially set at 260 nm in order to maximise the formation of photoproducts. Fig. 1 shows the excitation–emission fluorescence matrix of the two photoproducts (PIF1 and PIF2) obtained, respectively, after irradiation times of 1 min and 7 min at 260 nm. The maximum excitation wavelengths for both photoproducts, PIF1 and PIF2, were respectively of 230 nm and 220 nm (Table 2).

The kinetic formation of the diflubenzuron photoproducts was studied by monitoring the evolution of the fluorescence of the photoproducts with irradiation time at an excitation wavelength of 240 nm and an emission wavelength of 342 nm (for PIF1) and 422 nm (for PIF2). Fig. 3 shows that the first photoproduct, PIF1, rapidly appeared and decreased after an 1-min irradiation time, while the second one, PIF2, continuously increased, becoming preponderant after an irradiation time of 6 min, and then stabilized.