Photo-induced fluorescence properties of the propanil herbicide and analytical usefulness

O.M.A. Mbaye [a,b], M.D. Gaye Seye [a,b], A. Coly [b], A. Tine [b], M.A. Oturan [a], N. Oturan [a], J.J. Aaron [a,*]

[a] LGE, Université Paris-Est Marne-la-Vallée, 5 boulevard Descartes, Champs-sur-Marne, 77454 Marne-la-Vallée Cedex 2, France
[b] Laboratoire de Photochimie et d'Analyse, Département de Chimie, Faculté des Sciences et Techniques, Université C. A. Diop, Dakar, Senegal

ARTICLE INFO

ABSTRACT

The photo-induced fluorescence (PIF) spectral properties of propanil, a contact anilide herbicide were investigated. In the PIF approach, non-fluorescent propanil was transformed by UV irradiation into strongly fluorescent photo-product(s). The effect of solvents, including water, methanol, methanol-water binary mixtures and cyclohexane, on the propanil PIF properties was studied, and several PIF parameters (irradiation time, excitation and emission wavelengths, medium) were optimized. As a result, the analytical usefulness of a simple, sensitive and precise PIF analytical method was demonstrated for the determination of propanil. The best PIF analytical performances were obtained in an 80/20% v:v methanol/water mixture, with a wide linear dynamic range (LDR) of nearly three orders of magnitude, low limit of detection (LOD) and limit of quantification (LOQ) values of, respectively, 1.3 and 4.7 ng mL^{-1}, and a small relative standard deviation (RSD) of 1.3%. The optimized PIF method was applied to the estimation of propanil residues in various spiked natural water samples, collected in the Senegal River valley, with satisfactory recovery percentage values (97–117%). An interference study of several foreign species, including pesticides and inorganic ions, likely to be present in the Senegal natural waters, was also performed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Pesticides are widely used in agriculture, and, as a consequence, they are dispersed at the trace level in the environment, causing serious pollution problems in the atmosphere, soils and natural waters, which can considerably affect the aquatic ecosystems. Also, since pesticide residues persist in the environment, they may be incorporated and bio-accumulated through the food chain, and become a source of concern for human health. Therefore, it is very important to develop simple, rapid, sensitive, and precise analytical methods, allowing to measure and monitor these pesticide residues, especially in natural waters.

Propanil, a post-emergence contact anilide herbicide, is one of the most applied pesticides, often in combination with other herbicides, to protect paddy fields and improve grain yields in Senegal and in many other countries [1,2], as well as to control weeds in irrigated wheat crops [3]. Because of its rather high solubility in water, propanil (molecular structure in Fig. 1) can pollute environmental waters, where it is degraded by micro-organisms and is also known to cause acute toxicological effects on aquatic organisms [4–6].

Most reported analytical methods for the determination of propanil, are chromatographic ones with different detection systems. High performance liquid chromatography (HPLC) with UV–visible absorption spectrometry, preceded by on-line solid-phase extraction (SPE), has been applied to quantitative analysis of propanil in several matrices, such as surface and agricultural waters [7–9]. SPE-HPLC and solid-phase microextraction (SPME)-HPLC with photo-induced fluorimetric detection were also developed for the separation and determination of propanil and phenylurea herbicides at the μg L^{-1} level in river water and groundwater [2,10]. In another study, propanil was determined in surface water by liquid chromatography, with UV detector and positive ion electrospray ionization mass spectrometry [11]. Moreover, HPLC combined with mass spectrometric (MS) techniques was recently applied with success as a multi-residue method to the separation, identification and simultaneous determination of propanil and many other pesticides [12–17]. For example, Ferrer and Thurman [14] analyzed 101 pesticides, including propanil, and their degradation products in food and water samples by a LC/time of flight (TOF)-MS method, with LODs ranging from 0.04 to 150 μg kg^{-1}, according to the compound. In another study, Fenoll et al. [15] determined 48 pesticides in water samples by using sonication and LC–tandem mass spectrometry (LC–MS/MS), and obtained LODs around 0.05 ng mL^{-1}. The Indian research group of Sinha [16,17] developed a very selective and sensitive LC–MS/MS technique for the quantification of several organophosphate pesticides and propanil in drinking water samples with LODs at the ng L^{-1} level, and in vegetable samples with LODs in the 0.006–0.091 μg kg^{-1} range. In some instances, gas chromatographic (GC) techniques with detectors such as flame thermo-ionic, MS and MS/MS detection, were used for the analysis of water samples of propanil and other volatile and/or thermally stable pesticides [18–22].
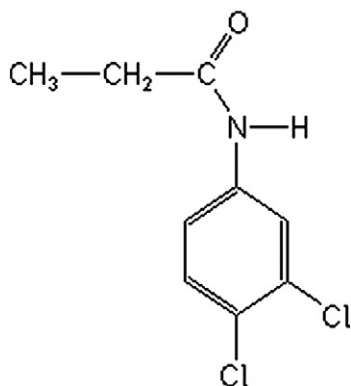
Fig. 1. Molecular structure of propanil.

Several non-chromatographic analytical methods were also reported for propanil determination [23–26]. Albert-Garcia et al. [23] proposed an elegant, analytical strategy, based on coupling photodegradation, chemiluminescence and a multicommutation continuous-flow system, for the quantification of propanil together with other herbicides, in various natural water samples. The method was sensitive and relatively rapid, with a LOD of 8 μg L^{-1} and a sample throughout of 20 samples h^{-1} in the case of propanil. Also, different types of immunoassays were described. Pichon et al. [24] developed and characterized an immunoaffinity solid-phase-extraction sorbent, and applied it to the trace analysis of propanil and structurally-related phenylurea herbicides in river waters and beverages. A rapid, homogeneous polarization fluorescence immunoassay was reported for propanil, a preliminary SPE step allowing to enrich low-concentration water samples at a propanil level of 0.1 ng mL^{-1} [25]. Moreover, an indirect enzyme-linked immunosorbent assay (ELISA) was optimized by Krikunova et al. [26], with a LOD of 0.2 ng mL^{-1}, which permitted to detect propanil in rice grains at levels above 1 μg g^{-1}.

The aim of this paper was to present the photo-induced fluorescence (PIF) spectral properties of propanil, and to optimize and develop a simple and rapid PIF analytical method, allowing to easily determine propanil in stationary solutions. As reported in a number of previous studies, the PIF method is based on the photo-transformation of naturally non-fluorescent pesticides into fluorescent photoproduct(s) under UV irradiation [27–30]. Our PIF method was optimized by fixing convenient excitation and emission wavelengths, and by investigating the effect of solvent and irradiation time on the propanil PIF properties. The PIF analytical performances were established. PIF was also applied to the quantitative analysis of propanil residues in spiked natural waters of Senegal, by means of the standard addition procedure. Moreover, in order to estimate the selectivity of the PIF method, an interference study of foreign chemical species, including pesticides and inorganic ions, was carried out. To show the interest of PIF for the propanil determination, we also compared our analytical results and applications with those of other literature analytical methods.

2. Experimental

2.1. Reagents

The standard pesticide propanil (analytical grade, PESTANAL®) was purchased from Riedel-de-Haën (Germany). The organic solvents (methanol, cyclohexane-spectroscopic grade) were obtained from VWR International (Prolabo). Distilled water was used for preparing aqueous solutions and binary mixtures.

2.2. Apparatus

All spectrofluorimetric measurements were performed on a Kontron SFM-25 spectrofluorimeter, interfaced with a microcomputer. An Osram 200-W high-pressure mercury lamp with an Oriel 8000 power supply was utilized for the photolysis reactions. The photochemical set-up included a light box consisting of a fan, the mercury lamp and a quartz lens. A standard Hellma (Mullheim, Germany) 1-cm path-length quartz fluorescence cell was placed on an optical bench at 30 cm from the mercury lamp.

2.3. Procedure

2.3.1. Preparation of solutions

10^{-3} M stock standard solutions of propanil were freshly prepared by exactly weighting and dissolving the herbicide in methanol. The working standard solutions were obtained by diluting the stock standard solutions in the appropriate solvent or binary mixture. All solutions were protected against light with aluminum foil to avoid any decomposition and stored in a refrigerator.

2.3.2. Photolysis reaction and PIF analytical measurements

During the photolysis reaction, a 3-mL volume of the working standard solution was placed in a quartz cell and irradiated with UV light at room temperature for increasing periods of time. The PIF intensity values were recorded in organic solutions (methanol, cyclohexane), aqueous solution or methanol-water binary mixtures, at the analytical excitation (λ_{ex}) and emission (λ_{em}) wavelengths, and at the optimum irradiation time (t_{irr}^{opt}) of the propanil photoproduct. In order to evaluate the t_{irr}^{opt} value, corresponding to the maximum PIF signal, plots of the PIF intensity vs. the UV irradiation time were constructed, in the appropriate solutions or methanol-water binary mixture. In all cases, the PIF intensity measurements were corrected for the background signal using the suitable blank. PIF signals were carried out in triplicate and expressed as mean values.

2.3.3. Preparation of natural water samples and standard addition procedure

600- to 900-mL water samples were collected in 1.0-L amber, glass bottles from natural waters (well, river or draining waters), located in an agricultural area of the Senegal River valley (paddy fields of Dagana, close to Saint-Louis), during June 2012. All samples were filtered through a quartz filter to eliminate the suspended organic matter, and stored at 4 °C.

For the standard addition procedure, 10 mL of filtered natural water samples were initially spiked with an appropriate volume of the 10^{-3} M propanil stock standard methanol solution, in order to obtain a solution of concentration 2×10^{-6} M (436 ng mL^{-1}). Then, aliquots of 1.0-mL portions of water samples were introduced in six 5-mL flasks, and increasing volumes of propanil standard solution (corresponding to the propanil concentrations of the calibration curve) were added to five of the six flasks, and the flasks completed with methanol to the mark, in order to obtain an 80/20% v:v methanol/water mixture. For the blank, the sixth flask containing the spiked natural water sample was simply completed with methanol. After a 6-min irradiation time for each solution, the PIF signals were measured. The classical standard addition procedure was applied to estimate the recovery percentage values.

In the case of some water samples (draining water), there was no parallelism between the standard addition and calibration curves, probably due to matrix effects. Therefore, we proceeded for these samples to a preliminary liquid–liquid extraction, using cyclohexane as extraction solvent. An 11-mL filtered natural water sample was initially spiked with a propanil stock standard solution, to obtain a concentration of 3.10^{-6} M (654 ng mL^{-1}). Then, a 10-mL portion of this spiked solution was extracted with a separating funnel, by successively shaking up three times the spiked water sample, after adding, each time, a 10-mL