Alternative to High Pressure Mercury Vapor Lamp for Photo Induced Fluorescence Analytical Methods; Application to the Determination of Pesticides in Water

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Notes

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The photo-induced fluorescence method is often applied to determine non-native fluorescent compounds. It typically uses UV irradiation from a high pressure mercury vapor discharge lamp to create photo-induced fluorescent compounds, which are then quantified by fluorescence spectroscopy. However, these mercury lamps require a high-voltage power supply and may accidentally induce electric shocks and the release of mercury vapors. As an alternative, we have evaluated in this technical note new UV-C germicidal lamps. These lamps exhibit a higher power at 254 nm and allowed us to obtain a far greater amount of photo-induced compounds in a shorter time. For the first time, this new irradiation system has been applied for the determination of pesticides in water and has shown a significant increase in the method sensitivity. These good results allowed us to conclude that the new UV-C lamps are a relevant alternative to high pressure mercury vapor discharge lamps for use with photo induced fluorescent methods.

Keywords Fluorescence, environment, water, PIF

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Introduction

The photo-induced fluorescent method (PIF) is used to transform by UV irradiation non-native fluorescent compounds into highly fluorescent photoproducts that may then be detected by fluorescence spectroscopy. The PIF method is often used to analyze pesticides in naturals water, *i.e.*, insecticides,[2–4] herbicides[5,6] and other pesticides[7–9] with limits of detection in the 1 to 25 ng mL^{-1} range. However, althouhg the method is efficient, its main drawbacks come from the use of a high pressure mercury vapor discharge lamp (HPHgV) to obtain sufficient UV irradiation. First of all, the glass protection around the lamp must be removed to let the UV rays pass; it is consequently dangerous to use and can sometimes induce accidental electric shocks. Secondly, this type of lamp requires a power supply transformer to obtain a high voltage of 380 V, and a ballast for ignition; all this adds additional costs. Thirdly, the case of an accidental lamp breakage, can lead to inhalations of mercury vapor.

An alternative to HPHgV lamps is now possible with new UV-C germicidal lamps. These low pressure mercury fluorescent lamps offer important advantages. Firstly, their cost is low. Secondly, they use a standard power supply (220 or 110 V), reducing the risk of electric shocks. Thirdly they contain a lower amount of mercury, reducing the risk of accidental mercury vapor inhalations.

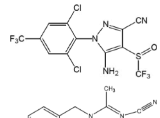
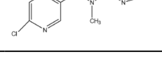
As these new UV-C germicidal lamps have never been used for the PIF method, we present in this technical note a comparative study. The spectral properties of the two lamps are compared, as well as the results obtained for the determination of fipronil and acetamipride pesticides by the PIF method in natural waters.

Experimental

Reagents

Technical-grade fipronil, acetamipride (Table 1) (purity > 99%) and spectroscopy solvent methanol (analytical reagent grade) were obtained from Sigma Aldrich. Ultra-pure water

Table 1 Chemical properties of fipronil and acetamipride

Pesticide	Chemical structure	Formula	Molecular weight/ g mol^{-1}	Water solubility (20°C)/ mg L^{-1}
Fipronil		$C_{12}H_4Cl_2F_6N_4OS$	437.15	3.78
Acetamipride		$C_{10}H_{11}ClN_4$	222.67	2950

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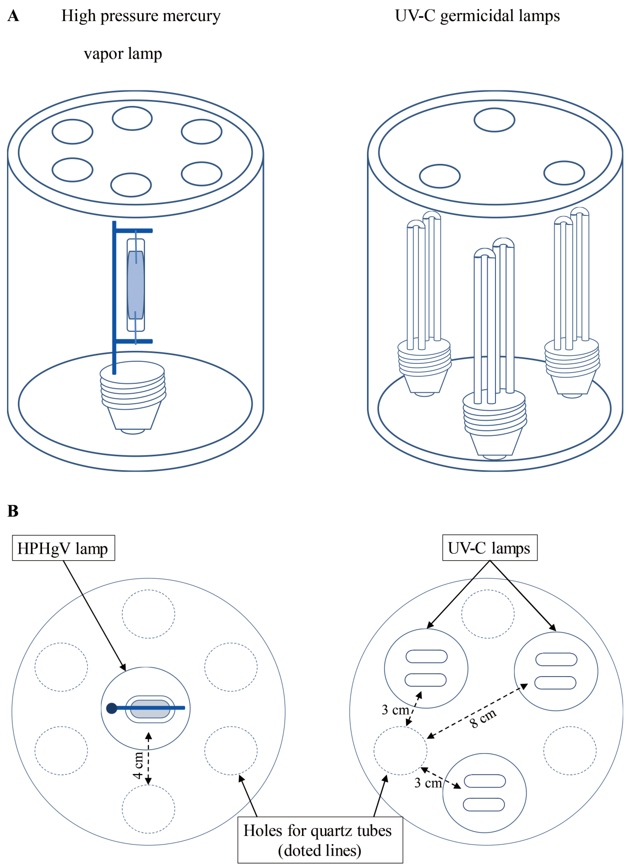

Fig. 1 Diagram of the irradiation systems: A, side view; B, top view.

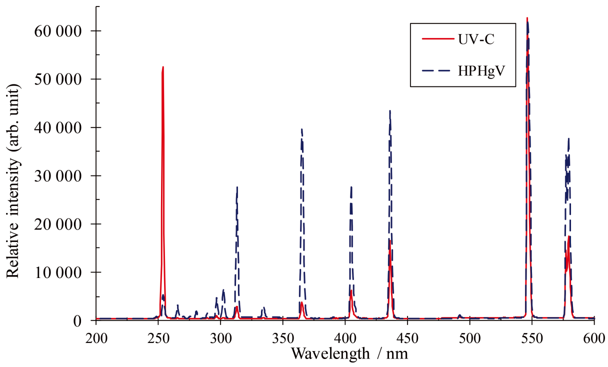

Fig. 2 Comparison of the spectra from the mercury discharge lamp and the fluorescent compact UV-C lamp.

(Millipore Mro-MQ System) was used for the working solutions. Stock standard solutions of the pesticides (in the range of 350 mg L^{-1}) were prepared by dissolving the compounds in methanol. The working solutions were prepared in water.

Apparatus

The following equipment was used in this study: 90 W, 380 V high pressure Mercury vapor discharge lamp (Philips, Amsterdam, Netherlands); UV-C fluorescent compact E27 15 W 240 V Germicide TUV HNS 55 × 230 mm (Bailey Electric & Electronics bv, Oosterhout, Netherlands); 30 mL quartz tubes photo-reactor (2 cm diameter); diode array spectrometer (200 – 800 nm), Flame, Oceans Insight (Geograaf, Netherland); Cary Eclipse spectrofluorimeter, Agilent (Santa Clara, USA); Statgraphics 18 Centurion software (Statgraphics Technologies, Inc; The Plains, Virginia, USA).

Results and Discussion

Development of the experimental setup

The irradiation chamber is a PVC cylinder with a diameter of 16 cm and a height of 24 cm, set up as follows (Fig. 1A: side view; and Fig. 1B: top view).

For HPHgV irradiation, the 90 W lamp (without its protective glass) is arranged in the center of the chamber. The chamber top is closed by a PVC circle with 6 holes allowing the quartz tubes to be placed 4 cm from the lamp. The irradiance (W cm^{-2}) can be computed by the following formula, where P is the lamp power (W) and r the distance (cm) between the lamp and the quartz tube.

$$\text{Irradiance} = \frac{P}{4\pi r^2}$$

The irradiance at the surface of a quartz tube lighted by the HPHgV lamp is equal to 0.45 W cm^{-2}.

For UV-C irradiation, three 15 W lamps are mounted in a triangle in the chamber. The upper part of the chamber is closed by a PVC ring with only 3 holes allowing to insert the quartz tubes at 3 cm from two adjacent lamps, and 8 cm from the third lamp. The total irradiance (sum of the irradiance from each UV-C lamp) at the surface of a quartz tube is equal to 0.28 W cm^{-2}.

Comparison of the lamp spectra

Both lamps exhibit a line spectrum. In Fig. 2, for an easier relative comparison the highest line of each spectrum has been adjusted to 65000 a.u., the maximal value of the spectrometer scale. The UV-C lamp presents fewer lines than mercury the lamp, moreover the main emission lines of mercury are present but at a lower intensity. In contrast, the most efficient line for breaking organic bonds at 254 nm is considerably more intense in the UV-C spectrum compared to the HPHgV one.

Regarding the integrated signal of each spectrum, the power emitted at 254 nm is equal to 3.49 W for the UV-C lamp and 1.39 W for the HPHgV lamp. As a consequence, the experimental set up associating three 15 W UV-C lamps reaches an irradiance of 66 mW cm^{-2} at 254 nm compared to only an irradiance of 6.9 mW cm^{-2} at 254 nm for one 90 W HPHgV lamp (Table 2A).

Spectroscopic properties

Acetamipride presents two intense absorption bands at 214 and 245 nm, while fipronil absorption bands are less intense at 223 and 285 nm (Table 3 and Fig. 3). These two pesticides were chosen to evaluate the efficiency of the UV-C: acetamipride which has an intense absorbance of 0.153 at 254 nm, and fipronil which has a low absorbance of only 0.022 at the same wavelength, both at the same concentration of 2.0 μg mL^{-1} in aqueous solution.

Acetamipride and fipronil exhibit no native fluorescence,[4] while UV irradiation yields the formation of strongly fluorescent photoproducts. Aqueous solutions of 20 mL containing the pesticides at 2 μg mL^{-1} were irradiated by the UV-C lamps. The photo induced fluorescent compound issued from acetamipride has two excitation bands (230 and 300 nm) and one emission band (370 nm); while the one from fipronil has only one excitation band (260 nm), and one emission band (470 nm), (Fig. 4 and Table 3). The same spectra where

Table 2 Comparison of high pressure mercury vapor discharge lamp and UV-C lamp

A: Technical characteristics

	High pressure mercury vapor discharge lamp	UV-C lamp
Life time[a]	900 h	1 000 h
Price[a]	200 €	30 €
Power supply[a]	380 V	220 V
Power[a]	90 W	15 W
Power at 254 nm	1.39 W	3.49 W

B: Experimental results

	High pressure mercury vapor discharge lamp	New experimental set up with three UVC lamps
Specific irradiance at 254 nm	6.9 mW cm^{-2}	66 mW cm^{-2}
Sensitivity for fipronil	181 a.u. mL μg^{-1}	500 a.u. mL μg^{-1}
Sensitivity gain for fipronil	Reference	2.7
Sensitivity for acetamipride	39 a.u. mL μg^{-1}	60 a.u. mL μg^{-1}
Sensitivity gain for acetamipride	Reference	1.5

a. Data from manufacturer.

Table 3 Fluorescence properties of fipronil and acetamipride photoproducts (2.0 μg mL^{-1}) in aqueous medium

Pesticide	Absorbance	Optimal irradiation time/s		Fluorescence	
		HPHgV	UV-C lamp	λ_{ex}/nm	λ_{em}/nm
Fipronil	223; 285	180	30	260	460
Acetamipride	214; 245	300	90	230; 300	370

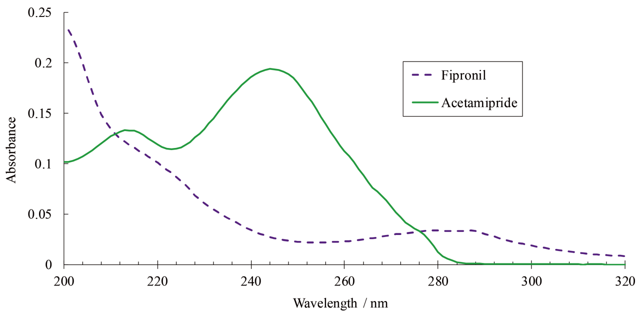

Fig. 3 Absorbance spectra of fipronil and acetamipride (2.0 μg mL^{-1}) in aqueous solution.

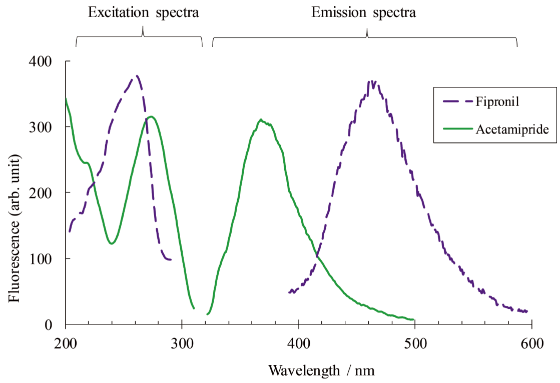

Fig. 4 PIF excitation and emission spectra of fipronil and acetamipride (2.0 μg mL^{-1}) in aqueous medium after 30 and 90 s of irradiation time, respectively.

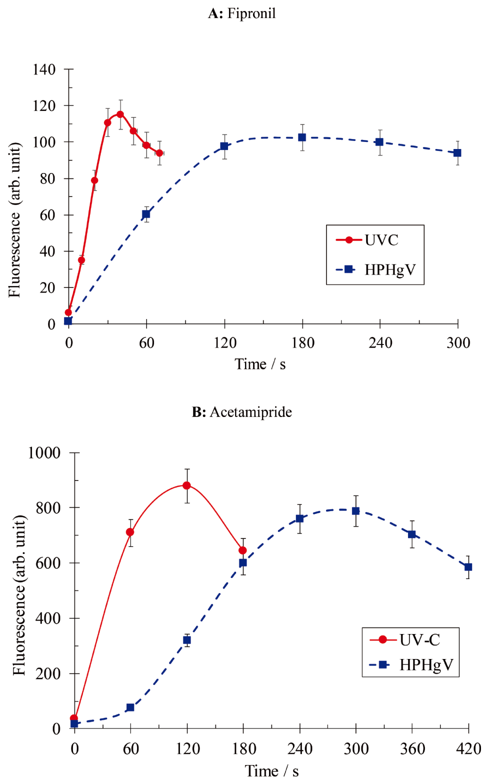

Fig. 5 Formation of the photo-induced compounds of fipronil (A) and acetamipride (B) at 2.0 μg mL^{-1} in aqueous medium as a function of irradiation time.

obtained after irradiation by the HPHgV lamp. It can be noted that Llorent-Martnez *et al.*[4] detected a similar photoproduct for FIP using the PIF method on a 0.01 M aqueous NaOH solution.

Analytical applications

The formation of the photoproduct is much faster with the UV-C lamp irradiation than with the HPHgV one. With UV-C irradiation, the maximum fluorescence emission of the photo-induced compounds is reached quickly after only 30 s for fipronil and 1.5 min for acetamipride. By comparison, with HPHgV irradiation, the maximum formation of the photo-induced compounds is obtained after a longer time of 2.5 min for fipronil and 4.5 min for acetamipride (Fig. 5 and Table 3).

Considering the optimized irradiation time for each lamp, the calibration curves were performed with pesticide concentrations ranging from 0.05 to 3.00 μg mL^{-1} (Fig. 6). The PIF measurements were done in triplicate for each concentration using the above-determined optimum excitation and emission wavelength. The curves obtained show good linearity with a correlation coefficient close to 0.98.

One can see that we obtained a higher sensitivity by UV-C irradiation for the two pesticides (Table 2B). For acetamipride, the sensitivity is almost three times higher with a slope of the

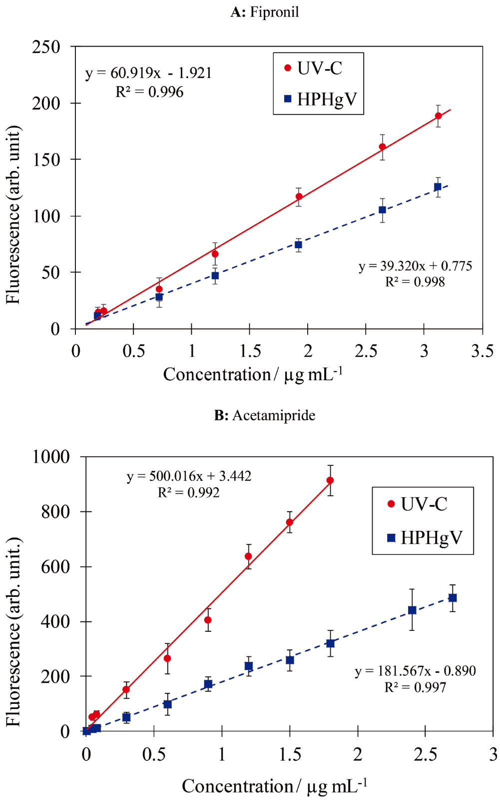

Fig. 6 Comparison of the calibration curves of fipronil (A) and acetamipride (B) photo-induced compounds after irradiation by classical high pressure mercury vapor lamp or new UV-C lamp.

calibration curve of 500 a.u. mL μg^{-1} after UV-C irradiation compared to 181 a.u. mL μg^{-1} by HPHgV irradiation. For fipronil, the sensitivity is also greater by UV-C compared to HPHgV but to a lesser extent (*i.e.*: 61 a.u. mL μg^{-1} compared to 39 a.u. mL μg^{-1}). This last result is logically due to its low absorbance at 254 nm, however the intensity of the 254 nm line of the UV-C lamp allows nevertheless to reach a better sensitivity. These good results were obtained firstly because the power at 254 nm is greater for each UV-C lamp (3.49 W) instead of 1.39 W for the HPHgV; and secondly because the experimental set up associates three 15 W UV-C lamps to reach a power of 10.47 W at 254 nm.

Conclusions

We have shown first that the new UV-C lamp exhibits a very high power at 254 nm compared to traditional high pressure mercury vapor discharge lamps.

Our results demonstrate secondly that this improves the formation of photo-induced compounds, which are obtained faster and in larger quantities even with compounds having a low absorbance at 254 nm. Consequently, it also provided a greater sensitivity in all cases. These results are obtained by an experimental set up that allows for a radiance ten times higher at 254 nm, even if the total power of the three UV-C lamps is lower than that of the HPHgV lamp. In addition, these new lamps are inexpensive and avoid the risks associated with mercury lamps such as electric shocks and mercury vapor release.

All these results show that the new UV-C lamps are a great alternative to HPHgV lamps for photo-induced fluorescence analytical methods.

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