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Inclusion Complex of *O*-phthalaldehyde-Buprofezin with Dimethyl-β-Cyclodextrin Using Thermochemically-Induced Fluorescence Derivatization (TIFD) Method and its Analytical Application in Waters

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Abstract

Improvement of the TIFD method to determine buprofezin (BUP) founded on the *O*-phthalaldehyde (OPA)-thermoproduct complex of buprofezin (OPA-BUP) with dimethyl-β-cyclodextrin (DMβCD) was investigated at 25 °C. The TIFD method developed in DMβCD medium, was optimized with respect to the reaction time, DMβCD concentration and pH. Based on the inclusion reaction, the OPA-BUP: DMβCD inclusion complex was developed in two aqueous media pH 7 and pH 13. A 1:1 stoichiometric ratio of OPA-BUP: DMβCD complex was obtained. The binding constants (K) and Gibbs energy (ΔG°) values increasing and decreasing with pH, respectively, show the spontaneous and thermodynamically favorable at 25 °C of the inclusion complexes formation. Normalized TIFD spectra were measured at 425 nm for emission and at 345 nm for excitation. Limits of detection (LOD) and quantification (LOQ) obtained, according to the pH, were in the ranges 0.05–0.1 ng mL^{-1} and 0.2–0.4 ng mL^{-1}, respectively. Relative standard deviation (RSD) values, less than 1.3% corroborated TIFD method repeatability in DMβCD medium. Solid phase extraction (SPE) procedure which was used for quantitative analysis of natural water samples collected from Niayes area, led to satisfactory recovery rates values 99.5–117.3%.

Introduction

To protect the human food supply chain, pesticides with complex properties develop miscellaneous mutations to combat the target of harmful insects. Buprofezin also named [(Z)-2-tert-Butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one], is a commonly used chemical, with satisfactory biological activities against sucking insect pests [1, 2] with various characteristics, including its toxicity [3, 4], its growth regulator [5–7] and its production of "bioresidual" effect by preserving natural enemies in cotton [8, 9]. However, for several reasons, buprofezin seems to dress a dualistic nature between its biological and chemical effects. Thereby, the literature reports the studies that have been conducted of buprofezin degradation kinetics in grapes [10], its photodegradation in organic and aqueous solutions [6, 11, 12]. As a result, the controlling procedure of risk level in environmental matrices within various conditions requires varied and adapted methods for the determination of buprofezin. For this purpose, sensitive analytical methods of agrochemical [13–17] and biological [4, 18–20] interests have been used for this insecticide.

In Senegal, for horticultural crops protection, the highly hydrophobic buprofezin [21] is widely used mainly in Niayes area. And, owing to the unsolved outlines of buprofezin metabolites from biodegradation and chemical reactions, the quality of foods as water or fruits and vegetables may be compromised. Yet, far from the expected results, this dynamic research paper is intended to be a reduction of metabolites in environment. In addition to cyclodextrins complexes that frequently improve the resistance of guest molecules to thermal degradation and increase the solubility and biological activity [22, 23], fluorescence spectroscopy is a powerful tool to study the host-guest molecular systems with both high sensitivity and high selectivity [24]. Therefore, the

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sensitivity enhancement of the TIFD method for the determination of buprofezin based on the reaction of its thermoproducts with O-phthalaldehyde (OPA) in usual aqueous solutions [25] was done in organized media of DMβCD. For that, the processing of experimental data associated with Job's [26], Scatchard's [27] and Benesi-Hildebrand's [28] methods makes it possible to establish both stoichiometry and important thermodynamic parameters. Cyclodextrins (CDs) are organized environments with proven benefits. And hence, several thermochemical methods [29] investigated the effect of CDs on fluorescence properties of substrates. And, generally, CD-complexed reagents can exhibit photochemistry which is quite different from that observed in homogeneous solution [30, 31]. From an analytical standpoint, among the cyclodextrins (α-; β-; γ-CD; HP-γ-CD and β-CD hydrate) used, DMβCD (Fig. 1) offers an improved reactivity and high sensitivity. Indeed, several studies have shown that DMβCD has greater affinity for different hosts as well as greater solubilization capacity compared to natural cyclodextrines [32–34].

As a result, in this document we have studied the enhancement of TIFD method on the complexes formation OPA-thermoproducts of BUP [25] at pH 7, and pH 13, using DMβCD. The introduction of DMβCD leads to the formation of a new inclusion complex OPA-BUP: DMβCD. Our aim is to improve the sensitivity of the TIFD method through complexation of the OPA-thermoproduct complex of BUP with DMβCD. On the other hand, the TIFD method developed in cyclodextrin aqueous media permitted to analyse the BUP residues in spiked natural waters collected in the Niayes area using solid-phase extraction (SPE) procedure.

Materials and Methods

Chemicals and Reagents

Buprofezin (99% m/m) was purchased from Cluseau (Paris, France) and used without further purification. Sodium hydroxide pellets (97% m/m), hydrochloric acid (37% m/v), potassium chloride (KCl ≥ 99% m/m), potassium hydrogen phosphate (K_2HPO_4, 98% m/m), potassium dihydrogen phosphate (KH_2PO_4, 98% m/m), 1,2-benzenedicarboxaldehyde (*O*-phthalaldehyde: OPA 97% m/m), spectroscopic solvents (methanol and acetonitrile), heptakis (2,6-di-*O*-methyl)-β-cyclodextrine (dimethyl-β-CD: DMβCD) were obtained from Sigma Aldrich (Taufkirchen, Germany). DMβCD was purchased in purities no less than 98%. The chemical structure of buprofezin, OPA, and DMβCD are shown in Fig. 1.

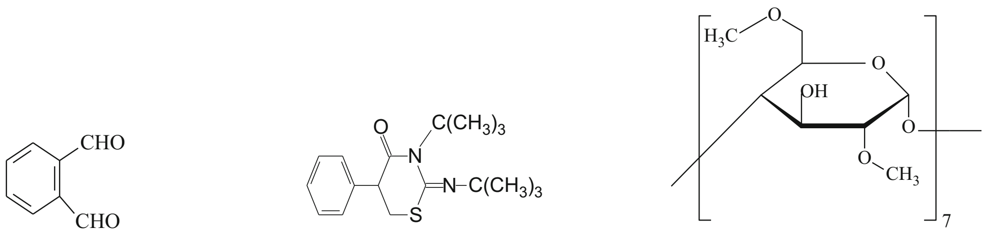
A stock standard solution of buprofezin (1.0×10^{-3} mol L^{-1}) was freshly prepared by dissolving the compound in acetonitrile. Serial dilutions were performed to obtain working solutions. OPA (1.0 mol L^{-1}) and DMβCD (0.5 mol L^{-1}), respectively in 50-mL volumetric flasks with distilled water, were used for serial dilutions. Buffer solutions of different compositions were: KCl + HCl for pH 2, K_2HPO_4 + KH_2PO_4 for pH 7 and KCl + NaOH for pH 13. These solutions were protected against light with aluminum foil and stored in a refrigerator at 6 °C for further use.

Instruments

Fluorescence spectra have been registered using Perkin-Elmer LS-55 luminescence spectrophotofluorimeter interfaced with a microcomputer and processed through software FL WinLab and thermostated bath. Standard quartz fluorescence cuvettes with a 1 cm path length (Labo Moderne, France) were used for measurements and, 20–1000 mL micropipettes (Gilson, France) were used for several dilutions. Every analytical measurement was carried out under the same conditions of spectrophotofluorimeter sensitivity (slits width = 10 nm / 10 nm, excitation / emission). The conductivity was recorded using a CDM 92, two-electrode Conductivity Cells Radiometer Analytical, and the pH measurements were performed with a Consort pH meter Model P 107. The statistical analysis of data was performed with Origin Pro 8. 5. 1 software.

General Analytical Procedure

OPA-thermoproduct of BUP complex was prepared as described for the TIFD method [25]. First, aqueous solutions containing 0.5 mL of OPA (5×10^{6} mol L^{-1}) and 0.5 mL of BUP (5×10^{6} mol L^{-1}) were introduced in 5-mL volumetric flask of distilled water and brought to 80 °C in a thermostatic bath for 25 min to form the OPA-BUP complex.



OPA (1) Buprofezin (2) DMβCD (3)

Fig. 1 Chemical structures of OPA (**1**), buprofezin **(2)** and DMβCD **(3)**

Then, inclusion complexes were obtained by introducing into a fluorimetric cuvette an appropriate mixture of 1-mL OPA-BUP (5×10^{-7} mol L $^{-1}$) with 1.5 mL buffered solutions of DMβCD at pH 2, pH 7 and pH 13 with maximum concentration of 13 mmol L ^{1}. All fluorescence spectra are registered at room temperature (25.0 ± 1.0 °C).

Nevertheless, in all experiments, in order to determine the binding constants, each of the buffer solution of DMβCD (0–30 mmol L ^{1}) was added at stable OPA-BUP concentration. A portion of OPA-BUP: DMβCD working solution was transferred into the quartz cell with a cover and the TIFD spectra of inclusion complex were recorded data scanning at speed of 500 nm / min. The excitation and emission wavelengths were set at 345 nm and 425 nm respectively. TIFD intensities were monitored by wavelengths for emission and excitation spectra of the OPA-BUP: DMβCD inclusion complexes by measuring their height signals, respectively. All fluorescence measurements were corrected by the solvent blank signal (background). Binding constants measurements are also acquired at room temperature (25.0 ± 1.0 °C). OPA-BUP (2×10^{-7} mol L $^{-1}$) solution previously obtained at different pH values [25] was used as reference for the respective fluorimetric measurements with the DMβCD. Binding constants (K) were measured in order to analyze interactions between OPA-thermoproduct of BUP complex and the DMβCD at different pH.

Job's [26], Scatchard's [27] and Benesi-Hildebrand's [28] methods were performed for determining both the stoichiometry and the binding constant of the inclusion complex. The composition ratio of OPA-BUP: DMβCD inclusion complex was determined using Job's continuous variation method and molar ratio method. Job's method, equimolar solutions (2.0×10^{-3} mol·L ^{1}) of the OPA-BUP and DMβCD were mixed in which the total moles of reactants were kept at 2×10^{-7} mol. Total volume of reaction medium was kept constant at 2.5 mL; then, steps were completed as described under the second paragraph of this section 2.3.

Both plots of $\Delta I_{TIFD} = I_{TIFD} - I_{TIFD_0}$ (normalized TIFD intensity changes of OPA-thermoproduct complex of BUP in the absence and presence of DMβCD) have been represented as a function of the mole fraction X of reagent DMβCD such that X = [DMβCD] / ([DMβCD] + [OPA-BUP]).

TIFD Method Extraction Conditions

Spiked samples of BUP (20, 50 and 100 ng mL $^{-1}$) were prepared with a known buprofezin concentration included in the linear dynamic range of the calibration curves. From preparation to experimental results we used SPE procedure described elsewhere in slightest methodological details [25]. After dissolving dry residue in a 5 mL volume of analytical medium in presence of OPA aqueous solutions, each mixture was kept in a water bath at 80 °C for OPA-BUP. After 25 min of heating OPA-BUP, half of mixture was used for the preparation of OPA-BUP: DMβCD complex in buffer solutions at pH 7 and pH 13 with the strongest concentration (14 mmol L $^{-1}$). The satisfactory recovery results were obtained by using standard addition procedure.

Results and Discussion

Complexation of OPA-BUP Complex with DMβCD

DMβCD effect on OPA-thermoproduct complex of BUP was investigated by recording their excitation and emission spectra at the three pH (Fig. 2). The TIFD parameters of BUP in DMβCD were also reported in Table 1. Despite the transition from classical [25] to organized media of DMβCD at pH 2, pH 7 and pH 13 (Table 1), no shift of the maxima emission wavelengths of the maxima normalized TIFD intensity has been recorded (Table 1). In contrast, excitation wavelengths indicate a hypsochromic offset at 339 nm, 345 nm and 345 nm in ascending pH order, respectively (Table 1) with a higher spectral resolution than that obtained in water at different pH [25]. Furthermore, the normalized TIFD intensity enhancement produced by buffer solutions of DMβCD (13 mmol L ^{1}) with maximum concentration is ranged in the following order: I_{TIFD} (pH 13) ≥ I_{TIFD} (pH 7) ≥ I_{TIFD} (pH 2) with higher sensibility than OPA-BUP complex in water solutions [25] (Table 1). Moreover, following the relative normalized TIFD intensity, the method is more sensitive at pH 7: I_{TIFD} / I_{TIFD0} (pH 7) ≥ I_{TIFD} / I_{TIFD0} (pH 2) and I_{TIFD} / I_{TIFD0} (pH 7) ≥ I_{TIFD} / I_{TIFD0} (pH 13) (Table 1). These changes in fluorescence were attributed to the inclusion complexes formation OPA-BUP: DMβCD in acidic, neutral and basic buffer media used in accordance with the literature data [34]. Therefore, it is more convenient to examine the effects of reaction time on TIFD signal intensity of OPA-BUP complex in each DMβCD

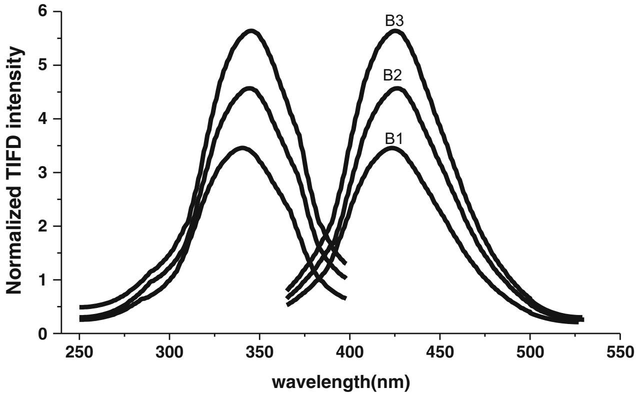


Fig. 2 Excitation and emission TIFD spectra of OPA-BUP: DMβCD inclusion complex at pH 2 (B1), pH 7 (B2) and at pH 13 (B3). DMβCD and OPA-BUP concentrations are 13 mmol L^{-1} and 2×10^{-7} mol L^{-1}, respectively

Table 1 TIFD parameters of OPA-BUP complex in various pH media

Solvent	pH	$I_{TI\ FD}$	$^{b}I_{TI\ FD}/\ ^{a}I_{TIFD0}$	^{c} $\lambda_{ex}/\ \lambda_{em}$(nm)
DMβCD	2	3.5^{b} $(0.5)^{a}$	7	339/423 ^{b} $(364/424)^{a}$
DMβCD	7	4.6^{b} $(0.55)^{a}$	8.4	345/425 ^{b} $(364/424)^{a}$
DMβCD	13	5.6^{b} (0.8) ^{a}	7	345/425 ^{b} $(360/424)^{a}$

[a] normalized TIFD intensity and wavelength excitation (λ_{ex}) and emission (λ_{em}) maxima of OPA-BUP complex in water at pH 2, pH 7 and pH 13 [25], selected as reference

[b] normalized TIFD intensity and wavelength excitation (λ_{em}) and emission (λ_{em}) maxima when all of OPA-BUP complex has been complexed in DMβCD at pH 2, at pH 7 and at pH 13

[c] Experimental measurements were performed at room temperature of 25.0 ± 1.0°C

Table 2 TIFD parameters of the kinetic study of OPA-BUP: DMβCD inclusion complex at various pH

$[\text{DM}\beta\text{CD}]_{max}$	pH	$\lambda_{ex}/\ \lambda_{em}$(nm)	kinetic
13	2	339/423	unstable
13	7	345/425	stable
13	13	345/425	stable

DMβCD concentrations in mmol L $^{-1}$

media, since in the cyclodextrin cavity; the movement is reduced so that the probability of radiation transition can decrease.

Effect of Reaction Time

The stability of OPA-BUP DMβCD inclusion complex has been studied at different pH over a time ranged 0.00–30.00 min (Fig. 3). OPA-BUP complex showed a relative stability behavior in each DMβCD medium (Fig. 3). Spectral and thermochemical data are shown in Table 2.

The stability of OPA-BUP: DMβCD inclusion complex has been studied at different pH, for fixed temperature for 80 °C. For the quantitative TIFD method analysis, the pH 7 and 13 buffer solutions of DMβCD for the determination of buprofezin residues yielding a very stable fluorescence signal seem to be the most convenient for a better sensitivity and reproductibility of the TIFD method (Table 2). The TIFD value of complex at pH 2 was significantly smaller than obtained at pH 7 and 13. The TIFD intensity of the complex formation, is high and stable at pH 7 and 13, we decided to choose these both media for analysis the insecticide in spiked natural water samples.

DMβCD Concentration Effect

A typical set of maxima normalized TIFD intensities of emission spectra of the OPA-thermoproduct complex of BUP was plotted against DMβCD concentrations (Fig. 4). The increased normalized TIFD intensities of the OPA-BUP complex with an increase concentration of DMβCD was materialized at pH 7 and pH 13. While rather high DMβCD concentrations are needed to yield a conceivable increase of normalized TIFD intensity, a saturation behavior is materialized for high DMβCD concentrations (Fig. 4). Saturation results show that normalized TIFD intensity remains constant over a range of DMβCD concentrations from 9 to 13 mmol L^{-1} at pH 7 and from 11 to 14 mmol L $^{-1}$ at pH 13. Thus, with the fixed wavelengths, the data retained as ideal experimental conditions to further expand TIFD studies are 13 mmol L $^{-1}$ at pH 7 and 14 mmol L $^{-1}$ at pH 13 of DMβCD concentration and will be used in subsequent experiments of BUP analysis in environmental samples taken from natural areas suitable to agriculture.

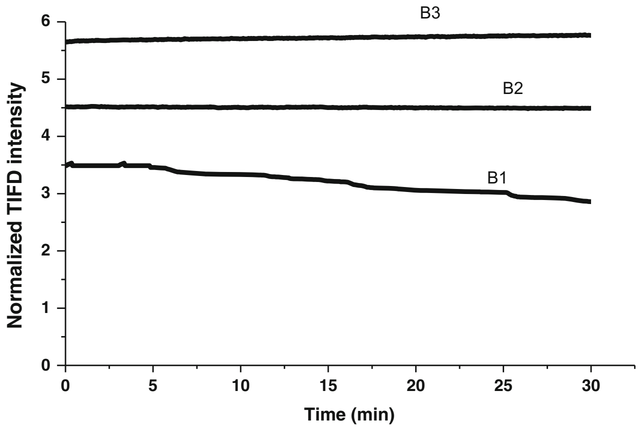


Fig. 3 Kinetic of the OPA-BUP: DMβCD inclusion complex at pH 2 (B1), pH 7 (B2) and at pH 13 (B3). DMβCD and OPA-BUP concentrations are 13 mmol L^{-1} and 2×10^{-7} mol L^{-1}, respectively

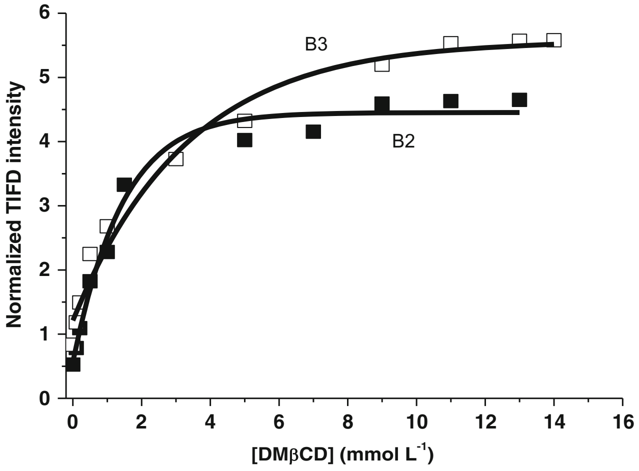


Fig. 4 Normalized TIFD intensity of OPA-BUP complex as a function of DMβCD concentrations at pH 7 (■) and at pH 13 (□)

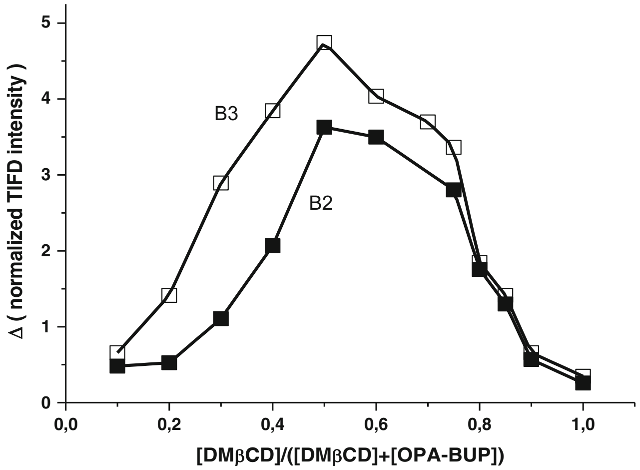


Fig. 5 Continuous variation plots of the complexation between OPA-BUP complex and DMβCD at pH 7 (■) and at pH 13 (□)

Stoichiometry of the Inclusion Complexes

Spectroscopic analysis based on cited methods and transverse equations (Eq. (1)–(4)); whole data was summarized as follows:

- Job's method

Provided the described conditions, we used the Job's method of continuous variation in order to determine the stoichiometry of inclusion complex~~es~~. The maximum normalized TIFD intensity occurred at 0.5 mol fraction for OPA-BUP: DMβCD species at pH 7 and at pH 13. This datum-point indicates a 1:1 ratio for inclusion complex formation (Fig. 5).

According to the formation of a 1:1 host-guest complex [28], the following writing can be adapted:

$$\mathrm{OPA{-}BUP} + \mathrm{DM\beta CD} \overset{K}{\rightleftharpoons} \mathrm{OPA{-}BUP : DM\beta CD} \tag{1}$$

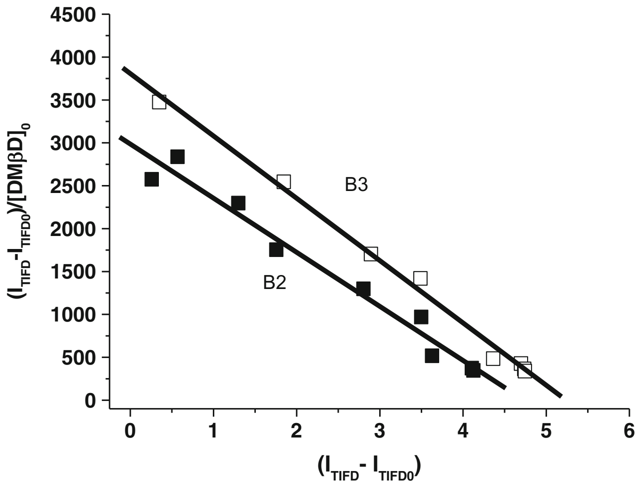


Fig. 6 Scatchard plots for the OPA-BUP: DMβCD inclusion complex at pH 7 (■) and at pH 13(□)

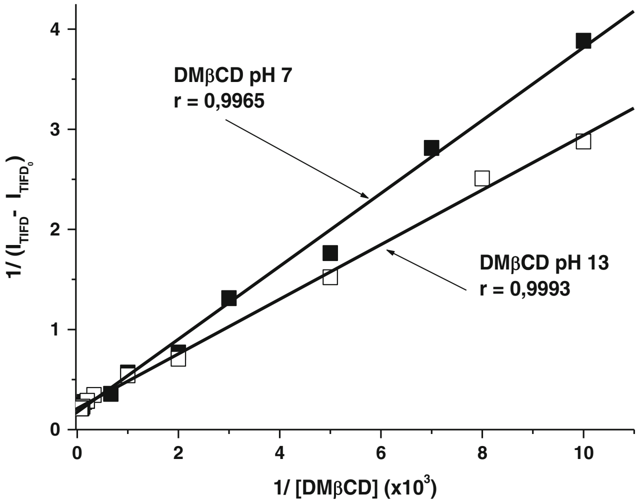


Fig. 7 Benesi-Hildebrand plot of $1/[I_{TIFD} - I_{TIFD0}]$ versus $1/[DM\beta CD]$ for OPA-BUP concentration of 2×10^{-7} mol L^{-1} at pH 7 (■) and at pH 13(□)

The expression of the formation constant (K) of the complex is written as follows:

$$K = \frac{[\mathrm{OPA{-}BUP : DM\beta CD}]}{[\mathrm{OPA{-}BUP}][\mathrm{DM\beta CD}]} \tag{2}$$

[DMβCD], [OPA-BUP] and [OPA-BUP: DMβCD] are equilibrium concentrations. Scatchard's [27] and Benesi-Hildebrand's [28] methods allowed to calculate the stoichiometry and binding constant of the inclusion complex [34].

- Scatchard's method

With $[DM\beta CD]_0$ >> ≫[OPA-BUP], the writing below can be applied:

$[DM\beta CD] = [DM\beta CD]_0$ - [OPA-BUP].

And like $[DM\beta CD]_0$ >> [OPA-BUP]

then $[DM\beta CD] \approx [DM\beta CD]_0$.

The following relationship between the observed TIFD intensity improvement (I_{TIFD} I_{TIFD0}) and the DMβCD concentration is given [35]:

$$\frac{I_{TIFD}-I_{TIFD0}}{[DM\beta CD]_0} = (I_{TIFD\infty}-I_{TIFD0})K-(I_{TIFD}-I_{TIFD0})K \tag{3}$$

Table 3 TIFD thermodynamic parameters for OPA-BUP: DMβCD inclusion complex at various pH

medium	K (L mol $^{-1}$)	ΔG° (kJ mol $^{-1}$)
DMβCD (13 mmol L^{-1}) pH 7	246 ± 27	13.640
DMβCD (14 mmol L^{-1}) pH 13	317 ± 53	14.268

K (binding constant) and ΔG° (Gibbs energy) acquired at room temperature (25.0 ± 1.0 °C)

Table 4 TIFD analytical parameters of OPA-BUP: DMβCD inclusion complex at different pH

Solvent	LDR (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)	r^2
$[\text{DM}\beta\text{CD}]_{\text{max}}$ pH 7	10–580	0.05	0.2	1.2	0.998
$[\text{DM}\beta\text{CD}]_{\text{max}}$ pH 13	10–580	0.1	0.4	1.0	0.997

LDR: Linear dynamic range

LOD: Limit of detection was defined as the amount of analyte giving a signal to noise ratio of, 3

LOQ: Limit of quantification was defined as the amount of analyte giving a signal to noise ratio of 10

RSD: Relative standard deviation (*n* = 6)

r^2 : Correlation coefficient

DMβCD concentration maximal is 13 mmol L^{-1} at pH 7 and 14 mmol L^{-1} at pH 13

- Benesi-Hildebrand's method

According to the formation of a 1:1 host-guest complex [28], the following expression can be adapted:

$$\frac{1}{I_{TIFD}-I_{TIFD_0}}=\frac{1}{(I_{TIFD_\infty}-I_{TIFD_0})K[DM\beta CD]}+\frac{1}{I_{TIFD_\infty}-I_{TFD_0}} \qquad (4)$$

[DMβCD]: DMβCD concentration tested;

I_{TIFD0}: Normalized TIFD intensity of OPA-BUP at pH 7 and at pH 13 in absence of DMβCD;

I_{TIFD}: Normalized TIFD intensity of OPA-BUP observed at each DMβCD concentration tested at pH 7 and at pH 13;

$I_{TIFD\infty}$: Normalized TIFD intensity when all of OPA-BUP complex has been complexed in.

DMβCD at pH 7 and at pH 13;

The representation of Scatchard (Eq. 3) and Benesi-Hildebrand (Eq. 4) equations gives the linear curves (Figs. 6 and 7), which indicates 1:1 stoichiometry. By use of a nonlinear regression program, the data are directly fitted into (Eq. 4) [34]. According to the 1:1 ratio, the binding constants values (K) of OPA-BUP: DMβCD complex~~es~~ at room temperature at pH 7 and at pH 13 are summarized in Table 3.

The K values obtained at room temperature, are (246 ± 27) L mol $^{-1}$ at pH 7 and (317 ± 53) L mol $^{-1}$ at pH 13, respectively (Table 3). Indeed, both of the DMβCD develop varied effects on the magnitude of the bindings with the OPA-BUP complex, despite the same number of glucose units of DMβCD. In this dynamic, the simultaneous auto-combination of several actions (driving forces of different nature) can make effective specific inclusion and seems more important quantitatively.

The binding constant (K) higher value obtained at pH 13 confirms a stronger association between DMβCD and OPA-thermoproduct. Gibbs equation (ΔG° = RTlnK) was used to calculate the Gibbs energy (ΔG°) at 25 °C. Negative obtained values at both pH indicates that complex formation is spontaneous i.e. thermodynamically favorable at 25 °C (Table 3).

Analytical Parameters

In assessing the analytical interest of TIFD method in DMβCD, the calibration curves have been presented under optimum analytical conditions for the complex formed. The correlation coefficient values close to unity, which indicates a good linearity of the TIFD analytical curves (Table 4). The analytical parameters obtained in the linear dynamic range (LDR) of the linear calibrations curves of TIFD intensity vs. BUP concentrations were presented in Table 3.

The limits of detection (LODs) significantly varied with the pH medium, ranging from low values of 0.05 and 0.1 ng

Table 5 Recoveries rate of buprofezin by related SPE TIFD methods

Water sample	[a,b] Added (ng mL 1)	Found (ng mL 1)	Recovery (%)
Well water [c]	20	20.1 [a] (19.9) [b]	100.5 [a] (99.5) [b]
	50	49.8[a] (51.0) [b]	99.6 [a] (102.0) [b]
	100	103.6 [a] (99.7) [b]	103.6 [a] (99.7) [b]
Sea water [d]	20	19.9 [a] (21.0) [b]	99.5 [a] (100.5) [b]
	50	50.7 [a] (49.9) [b]	101.4 [a] (99.8) [b]
	100	101.7 [a] (117.3) [b]	101.7 [a] (117.3) [b]

[a] buffer solution at pH 7 of DMβCD (14 mmol L^{-1})

[b] buffer solution at pH 13 of DMβCD (14 mmol L^{-1})

[c] physicochemical parameters =2.82 mS cm^{-1} , pH 8.24

[d] physicochemical parameters =387 mS cm^{-1} , pH 9.76

mL^{-1}, demonstrated the sensitivity of the TIFD method. Limits of quantification (LOQs) are in the ranges 0.05 0.1 ng mL^{-1}. The reproducibility of measurements is satisfactory, as indicated by the relative standard deviation (RSD) values less than 1.3%. (Table 4). We can worthwhile emphasizing that LOD values (0.05 0.1 ng mL^{-1}) obtained with TIFD method in DMβCD media at pH 7 and pH 13, were lower than those reported by TIFD method in water pH 13 (0.8 ng mL^{-1}) [25]. Which clearly indicates that the sensitivity of the TIFD method which has been improved in cylodextrin medium (DMβCD). Moreover, the obtained LOD data in DMβCD are the same order of magnitude as those reported previously in the literature [36, 37]. Also these results show that TIFD method using DMβCD is appropriate for the analysis of BUP in natural water collected in the agricultural Niayes area.

Analytical Applications

For verifying the applicability of the proposed TIFD method in DMβCD medium to water samples, Solid-Phase Extraction (SPE) procedure [25] was used to determine the BUP in spiked, well water and sea water collected in the Niayes area. Both organized media of DMβCD (pH 7 and 13) allowed to analyze the insecticide after SPE extraction. The recovery rate obtained in the different water samples varies between 99.5 and 117.3% (Table 5). The physicochemical properties, conductivity ( ) and pH of the measured natural waters samples have influence on the recovery rate (Table 5). TIFD method improved in DMβCD medium, has been successfully realized to determine buprofezin in natural waters used for agriculture mainly in horticultural crops practice.

Conclusion

In this study, we have improved in DMβCD medium the TIFD method of analysis developed in aqueous media [25]. The TIFD method is sensitive and efficient with low detection limits and satisfactory recovery rates of buprofezin measured in the presence of DMβCD. Therefore, DMβCD has significantly improved, the TIFD method developed in aqueous medium. This method will ease the elimination of insecticides in environmental matrices mainly in surface and groundwater. In perspective, the evaluation of the method on more complex environmental samples (soil and vegetables) is being embodiment.

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