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Article

Development of a Fast Method for the Determination of the Insecticide Fipronil and its Metabolites in Environmental Waters by SPE and GC-ECD

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Um método eficiente e sensível para a determinação simultânea do inseticida fipronil e seus principais metabólitos fipronil desulfinil, fipronil sulfeto e fipronil sulfona em águas superficiais foi desenvolvido e validado. Fipronil e seus metabolitos foram determinados por cromatografia gasosa com detecção por captura de elétrons (GC-ECD) após uma etapa de pré-concentração empregando extração em fase sólida (SPE). Os parâmetros de validação avaliados incluíram curva analítica e linearidade, limites de detecção (LOD) e de quantificação (LOQ), precisão e exatidão. GC-ECD apresentou uma boa resposta para fipronil e seus metabólitos, e todas as curvas analíticas apresentaram coeficientes de determinação superiores a 0,995. Os LODs do método foram 2,5 ng L^{-1} para fipronil e 2,0 ng L^{-1} para cada metabólito. Todos os valores de recuperação variaram de 81,3 a 112,3%, com valores de desvio padrão relativo (RSD) inferiores a 14,2%. O método proposto foi aplicado com sucesso em amostras de água de lavoura de arroz irrigado.

An efficient and sensitive method for simultaneous determination of the insecticide fipronil and its main metabolites fipronil desulfinyl, fipronil sulfide and fipronil sulfone in surface water was developed and validated. Fipronil and its metabolites were determined by gas chromatography with electron capture detection (GC-ECD) after a preconcentration step using solid phase extraction (SPE). The evaluated validation parameters included analytical curve and linearity, limit of detection (LOD) and quantification (LOQ), precision and accuracy. GC-ECD presented a good response for fipronil and its metabolites, and all analytical curves showed determination coefficients higher than 0.995. The LOD values of the method were 2.5 ng L^{-1} for fipronil and 2.0 ng L^{-1} for each metabolite. All recovery values were between 81.3 and 112.3%, with relative standard deviation (RSD) values lower than 14.2%. The proposed method was successfully applied to the analysis of water samples from flooded rice fields.

Keywords: pesticide residues, fipronil, metabolites, solid phase extraction

Introduction

The rice cultivation in flooded paddy fields generates great environmental impact in terms of the amount and the quality of water resources. Both the reduction in availability and the contamination of water resources are current problems. Rice crops, especially irrigated ones, have great social and economic importance in Brazil, which is the 10th greatest rice producer in the world, responsible for 1.8% of the worldwide rice production and 50% of the Latin American rice production. Brazil is the most important non-Asian producer, followed by the United States.[1]

Pesticides are used for controlling harmful plants, illnesses and plagues. Insecticides are normally applied in at least one phase of plant development. Although pesticide use contributes to an increase in production, there are growing concerns related to its adverse effects on surface and ground water.[2,3] Pesticides present different routes of degradation in the environment and can be transferred to different environmental compartments.[4] A fraction of the pesticides is transferred to the environment through draining of flood irrigation water and leaching into

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the ground.[5] Pesticides can be transferred to the atmosphere during spraying treatment or through processes posterior to application, such as volatilization and resuspension of solid particles containing pesticides.[6] Moreover, some transformations of pesticides in the hydrological system result in metabolites whose chemical properties, such as toxicity and behavior, are not well known.[7]

The pesticide fipronil (5-amino-1-(2,6-dichloro-α,α,α-trifluoro-*p*-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile) is a highly effective insecticide of contact from the phenylpyrazole class with a wide spectrum commonly used in agricultural insect control as well as non-agricultural uses such as wood preservation and sanitizer. Fipronil is mainly used against ground insects and is recommended for foliar or seed application. In flood irrigated rice crops, it is applied to control root.[8] Fipronil degradation route was established by Fenet *et al.*,[9] who detailed that the compound can undergo a number of processes, including reduction in the soil generating the metabolite fipronil sulfide, oxidation producing fipronil sulfone, and photodegradation in the presence of solar light either in the water or soil, generating fipronil desulfinyl. Figure 1 presents the structures of the compounds studied in our work.

Fipronil is an extremely active molecule and a powerful disruptor of the central nervous system of insects via chloride channels regulated by the gamma-aminobutyric acid (GABA). It is highly toxic for birds, fish, aquatic invertebrates, bees and ants.[10] Currently, there is a great concern with the toxicity of the fipronil, mainly with respect to bees.[11] Like fipronil, its metabolites also act in the GABA receptor and are biologically active. Fipronil desulfinyl and fipronil sulfide are about two times more toxic for aquatic invertebrates than fipronil. Fipronil sulfone is about six times more toxic for certain trout species, aquatic invertebrates and birds and three times more toxic for some species of fish.[10] Laboratory tests with fipronil and its metabolites have revealed acute lethal toxicity at very low concentrations for aquatic macroinvertebrates, with LD50 (lethal dose, 50%) below 0.5 μg L^{-1}.[12]

For many years, pesticide analysis in environmental samples has attracted attention due to the wide use and serious impacts of such compounds. High standards for water quality imposed by the regulatory agencies demanded the development of analytical methods of high sensitivity, selectivity, accuracy and precision for quantitative pesticide determinations compatible with increasing restrictions.[13] The determination of fipronil, sometimes together with its metabolites, in different matrices is commonly performed by gas chromatography (GC) with mass spectrometric (MS) detection,[14-19] electron capture detection (ECD)[15-20] or nitrogen phosphorus detection (NPD).[21] Liquid chromatography (LC) also has been used with tandem mass spectrometry (MS/MS) detection.[22,23]

Several works describe the determination of fipronil residues in different matrices. Using GC-ECD and GC-MS techniques, Jimenez *et al.*[15] determined fipronil in pollen using extraction with solvent, Smalling *et al.*[16] determined 85 current-use pesticides, including fipronil and its metabolites, in sediment sample after microwave-assisted extraction, Bichon *et al.*[17] quantified fipronil residue in ovine plasma and Sánchez-Brunete *et al.*[18] and Jiménez *et al.*[19] determined fipronil residues in honey samples after solvent extraction.

Brennan *et al.*[20] compared different cleanup methods for the determination by GC-ECD of fipronil and its degradation products in sediment samples. Morzycka[21] described a simple method for the determination by GC-NPD of trace levels of fipronil in honeybees using matrix solid-phase dispersion. LC-MS/MS, after an extraction with solvent, was applied for the determination of traces of fipronil in pollen[22] and in honey[23] samples. Llorent-Martínez *et al.*[24] described a photo-induced fluorimetric determination of

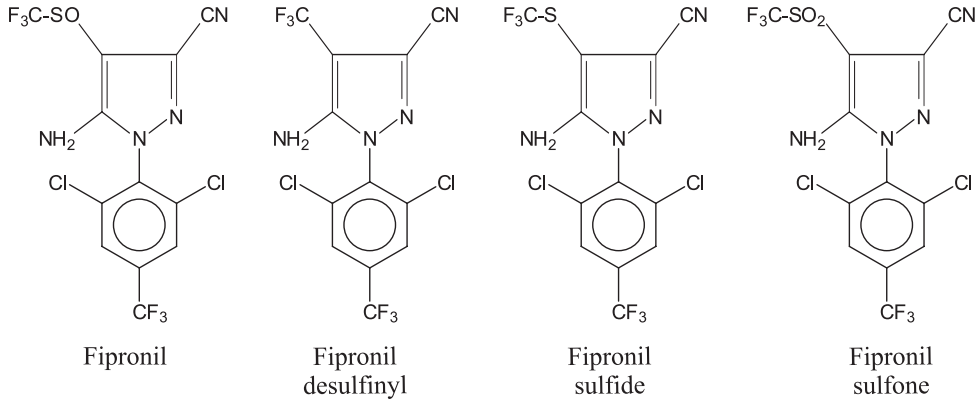

Figure 1. Structural formulas of the compounds studied.

fipronil in phytosanitary and veterinary products using a sequential-injection flow assembly.

Some works described the determinations of fipronil residues in water samples using different sample preparation and analysis techniques. Yang *et al.*[25] proposed an efficient and sensitive method for simultaneous determination of 38 pesticides, including fipronil, in agricultural drainage waters and soils by GC-MS. Water samples were extracted using solid-phase extraction (SPE) with C_{18} cartridges with recoveries from 98 to 105%. The limit of detection (LOD) of the method for fipronil in water samples was 52 ng L^{-1}. Harman-Fetcho *et al.*[14] developed a method for the determination of several pesticides in water samples from canals using SPE with styrene-divinylbenzene as sorbent and GC-MS. Fipronil presented average recovery of 79% and LOD value of 0.2 ng L^{-1}. Vílchez *et al.*[26] described the determination of fipronil in water, soil and urine samples carried out by solid phase microextraction (SPME) and GC-MS. Fipronil was extracted with a fused-silica fiber coated with 85 mm polyacrylate and a LOD value of 80 ng L^{-1} was achieved for water samples. A method using liquid-liquid extraction (LLE) and analysis by GC-ECD of pyrethroid and phenylpyrazole pesticides in emulsion-prone surface water samples was described by Wu *et al.*[27] Fipronil, fipronil sulfide and fipronil sulfone presented average recoveries of 115.5, 82.8 and 103.5%, respectively, and LOD values of 0.31, 0.36 and 0.29 ng L^{-1}, respectively. Besides good detectability, it requires a laborious step for sample preparation by LLE, with a considerable consumption of solvents.

The determination of fipronil residues in water was carried out using LLE and HPLC with UV detection achieving LOD value of 100 μg L^{-1}.[14] Liu *et al.*[28] applied the ionic liquid dispersive liquid-liquid microextraction (IL-DLLME) for the determination of fipronil in water by HPLC-DAD (diode-array detection) with LOD of 530 ng L^{-1}. Donato *et al.*[29] and Demoliner *et al.*[30] described multiresidue methods for the determination of pesticide residues in water based on SPE and LC-MS/MS. For both works, the LOD value for fipronil was 10 ng L^{-1}.

However, to the best of our knowledge, no method for the determination of fipronil and its three more important metabolites fipronil desulfinyl, fipronil sulfide and fipronil sulfone in water samples has been reported until now. Therefore, the objective of this study was to develop and validate a fast and accurate method using SPE and GC-ECD for the determination of these compounds in surface water samples. The method suitability was evaluated by applying the method in the determination of fipronil and its metabolites in water samples from experimental flooded rice fields to study the degradation of fipronil.

Experimental

Chemicals

Fipronil standard (96.5%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Individual standards of the metabolites fipronil desulfinyl (98%), fipronil sulfide (99.6%) and fipronil sulfone (100%) were purchased from AccuStandard (New Haven, USA), in the concentration of 100 mg L^{-1} in acetone. The stock solution of fipronil, in the concentration of 1000 mg L^{-1}, was prepared in acetone. The working standard solutions were prepared by the dilution of these solutions in acetone. Cartridges SPE Strata C_{18}-E 500 mg *per* 3 mL (Phenomenex, USA) were used. Acetone and *n*-hexane were Nanograde® degree (Mallinckrodt, USA), isopropyl alcohol and phosphoric acid were analytical reagent grade (Merck, Brazil) and water was purified in a Milli-Q® system (resistivity 18.2 MΩ cm).

Instrumentation and chromatographic conditions

The GC-ECD system used was a gas chromatograph 3800 (Varian, USA) equipped with autosampler, split/splitless injector, electronic flow control, electron capture detector, Star Workstation 6.6 version and capillary column DB-5 (5% phenyl, 95% methylpolysiloxane) of fused silica with 30 m length, 0.25 mm i.d. and 0.25 μm of film thickness (J&W Scientific, Foster City, CA, USA). The chromatographic conditions used were: injector temperature of 280 ºC; volume of injection of 1.0 μL splitless, with split vent opened (1:10) at 3 min; carrier gas helium, constant flow of 1.3 mL min^{-1}; column oven temperature program at 80 ºC (1 min), increasing 25 ºC min^{-1} up to 215 ºC, followed by 3 ºC min^{-1} up to 250 ºC; detector temperature at 300 ºC, N_2 as make-up gas at 60 mL min^{-1}. Helium and nitrogen were 5.0 grade.

Optimization of the SPE procedure

The SPE preconcentration system used a vacuum pump (Tecnal, Brazil) and a SPE manifold (Varian, USA). The SPE procedure was optimized in terms of pH and sample volume and the type and volume of solvent used for elution. As solvent for elution of the compounds, ethyl acetate and a mixture of *n*-hexane:isopropyl alcohol (3:1, v/v) were evaluated. The influence of the use of 1 or 2 mL of eluent was also investigated. The sample volume was chosen as a function of the breakthrough volume, which occurs when the pesticides are not strongly retained by the sorbent or when the capacity of the sorbent is exceeded.[31] Sample

volumes varying between 50 and 500 mL were studied with a constant mass of 2.5 ng for each compound, at pH 3.0 and 6.0, adjusted with a solution of phosphoric acid:water (1:1, v/v).

Sample preparation procedure for SPE

The samples, placed in volumetric flasks, were transferred to the SPE cartridges through PTFE tubes at a flow rate of about 5 mL min^{-1}. The optimized procedure for analysis of fipronil and metabolites began with the conditioning of the C_{18} cartridge with 3 mL of methanol followed by 6 mL of purified water. An aliquot of 100 mL of sample or "blank" surface water spiked with the analytes was then percolated through sorbent. After the preconcentration step, 10 mL of purified water were used to rinse the sample volumetric flask, and then it was transferred to the cartridge, followed by 15 min of vacuum for water removal from sorbent bed. The analytes were then eluted with two aliquots of 1.0 mL of a mixture of hexane:isopropyl alcohol (3:1, v/v). The eluate was collected in vial and the volume was evaporated to dryness using a N_2 flow. For the GC-ECD analysis, a redissolution in 500 μL of acetone was carried out.

Method validation

With the optimized conditions for analysis of the compounds, a method validation was performed with the following parameters: analytical curve and linearity, limits of detection (LOD) and of quantification (LOQ), precision (repeatability and intermediate precision) and accuracy (recovery).[32] Solutions for the analytical curve and for spiking were prepared by the dilution of the stock solutions in acetone. The analytical curves were obtained with 7 different levels of concentration (1 to 1000 μg L^{-1}) for each analyte with 6 replicates each. Linearity of the analytical curve was evaluated according to the IUPAC, that considers that points whose signal/concentration ratio does not differ more than 5% from the angular coefficient of the calibration line are considered to be inside of the linear range. The limits of detection and quantification were established considering the concentration that produced a signal-to-noise ratio of 3:1 and 10:1, respectively. For the recovery assays, "blanks" of surface water samples spiked at 12.5, 25.0 and 250 ng L^{-1} for fipronil and 5.0, 12.5, 25.0 and 250 ng L^{-1} for each metabolite were used, which corresponded to 1.8, 3.6 and 36 times the LOQ value for fipronil and 1, 2.5, 5 and 50 times the LOQ values for the metabolites. The precision of the method, in terms of repeatability, was evaluated by carrying out extraction and analysis of the fortified samples in six replicates. To evaluate the intermediate precision of the method, different days and analysts were used.

Sampling of environmental water samples to evaluate the method applicability

To evaluate the method developed, water samples were collected from experimental flooded rice fields from 1 to 70 days after application of the insecticide fipronil at the recommended dose. Samples were collected by submerging amber glass bottles (1 L) below the water surface to a depth of 0.3 m. All water samples were held on ice until transported back to the laboratory where they were stored in refrigerator at 4 °C. Extraction and analysis of the water samples occurred within 24 h of collection.

Results and Discussion

Quantitative analysis of fipronil and its metabolites

The technique GC-ECD proved to be a good option for the determination of fipronil and its metabolites, allowing an analysis with good sensitivity in a total time of 12 min. Figure 2 shows the chromatograms of a "blank" surface water spiked with fipronil and its metabolites at the limit of quantification of the method. Figure S1 (in the Supplementary Information (SI) section) presents a chromatogram of the second point for the analytical curve containing fipronil and metabolites at the concentration of 5 μg L^{-1}. The selectivity of the method can be evaluated considering these chromatograms, in which no interferences from the matrix were observed in the retention times of the compounds. The use of SPE permits the reduction of sample handling, labor, and solvent consumption.[33] Sample preparation using SPE was very effective for the analysis of fipronil and metabolites at trace level.

Analytical curve and linearity

The parameters for linear regression ($y = ax + b$) obtained for the seven concentration levels, each level injected 6 times, are shown in Table 1. From the analytical curve, the linearity of the method was evaluated in the range of the LOQ values to 1000 μg L^{-1}. All analytical curves presented linearity in all evaluated interval. Considering a preconcentration factor of 200 times (100 mL of sample and a final volume of 500 μL), it results in a linear working range in the samples from the LOQ (7.0 and 5.0 ng L^{-1} for fipronil and metabolites, respectively) to 20 μg L^{-1}.

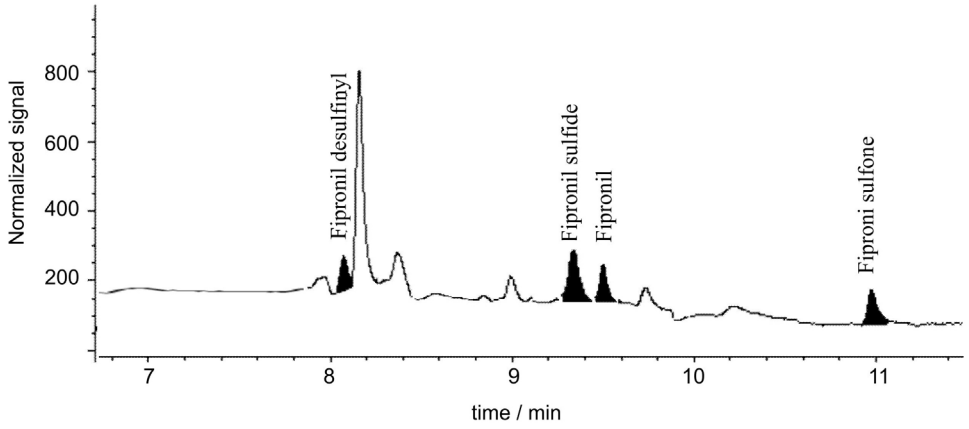

Figure 2. Chromatogram of a "blank" surface water spiked at the limit of quantification of the method.

Table 1. Analytical curve parameters and limits of the method for fipronil and its metabolites

Pesticide	Linear regression $y = ax + b$	r^2	Linear interval / (μg L^{-1})	Limits of the method / (ng L^{-1})	
				LOD	LOQ
Fipronil desulfinyl	$y = 14.651x - 100.130$	0.9952	1.0-1000	2.0	5.0
Fipronil sulfide	$y = 22.165x - 118.510$	0.9971	1.0-1000	2.0	5.0
Fipronil	$y = 5.627x + 48.688$	0.9970	1.4-1000	2.5	7.0
Fipronil sulfone	$y = 24.240x - 209.850$	0.9964	1.0-1000	2.0	5.0

LOD: limit of detection; LOQ: limit of quantification; r^2: determination coefficient.

Limits of detection (LOD) and quantification (LOQ)

The LOD and LOQ values obtained for the instrument ranged from 0.4 to 0.5 μg L^{-1} and 1.0 to 1.4 μg L^{-1}, respectively. The LOD and LOQ values of the method are shown in Table 1. Despite the great structural similarity between the compounds, the LOD and LOQ values showed that fipronil presents a little lower sensitivity than its metabolites.

The LOQ values obtained are suitable for the determination of residues of these compounds in surface water, considering that the values are even below the tolerance level of 0.1 μg L^{-1} established in the European Union (Directive 98/83/EC) for pesticide residues in drinking water,[34] showing that the proposed method is useful for the determination of fipronil and metabolites in water samples.

Accuracy (recovery) and precision (repeatability and intermediate precision)

Table 2 presents the results of recovery and precision, in terms of repeatability and intermediate precision, obtained through the analysis of "blank" surface water spiked with the compounds in study. For environmental matrices, precision is dependent on the sample matrix, the concentration of the analyte and the technique of analysis. Considering the criteria for acceptability for recoveries between 70 and 120% with precision of up to 20%,[35] it can be concluded that the method is in accordance with the required parameters because all the obtained values were within these ranges.

Application of the developed method

The validated method was applied to the analysis of water samples from experimental flooded rice fields where a study of degradation of fipronil was carried out. The compound was applied at the recommended dose and sampling was carried out from 1 to 70 days after application. Despite the high complexity of this type of samples, these analyses presented no interferences or difficulties. Figure 3 presents a chromatogram obtained with GC-ECD of a surface water sample collected 3 days after the application of fipronil at the recommended dose. Fipronil desulfinyl was the compound that presented the highest concentrations of all metabolites, being detected in the maximum concentration of 6.9 μg L^{-1}. This indicates that the photocatalytic decomposition of fipronil, with consequent formation of fipronil desulfinyl, is fast. Fipronil sulfone appeared in all the collected samples, presenting maximum concentration of 0.5 μg L^{-1}. Fipronil sulfide was

Table 2. Recovery, precision (n = 6) in terms of repeatability (RSD_R) and intermediate precision (RSD_{IP}) for fipronil and its metabolites

Compound	Spike level / (ng L^{-1})	In repeatability conditions		In intermediate precision conditions	
		Recovery / %	RSD_R / %	Recovery / %	RSD_{IP} / %
Fipronil desulfinyl	5.0	83.8	9.0	109.8	5.2
	12.5	98.9	4.8	94.3	10.9
	25.0	103.3	7.4	88.7	3.1
	250	102.2	5.5	82.6	6.2
Fipronil sulfide	5.0	89.6	12.4	81.3	2.3
	12.5	92.5	9.8	95.3	2.8
	25.0	103.4	8.9	98.1	13.2
	250	97.8	10.7	105.4	8.6
Fipronil	12.5	90.4	14.2	112.3	11.2
	25.0	99.4	3.3	100.7	5.8
	250	102.3	6.6	95.8	7.1
Fipronil sulfone	5.0	105.5	13.9	83.4	3.4
	12.5	91.3	6.2	98.4	9.4
	25.0	95.5	13.3	109.9	2.3
	250	106.2	9.7	95.7	10.5

RSD: relative standard deviation.

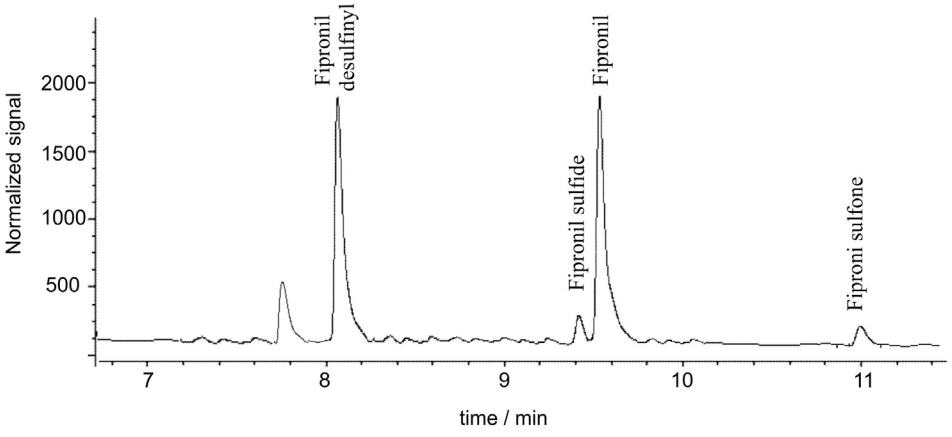

Figure 3. Chromatogram of a surface water sample collected 3 days after the application of fipronil at the recommended dose.

not detected in the first days after application of fipronil and its presence was only detected in the samples collected between 7th and 21st days with concentrations that had varied from 0.01 to 0.2 μg L^{-1}, with the maximal concentration observed on the 12th day. This appearance in a period subsequent to the maximum concentration of the fipronil is consistent with the degradation process, considering that this metabolite is a product of the reduction of fipronil frequently detected in soil samples.[20]

Conclusion

The proposed method is simple to perform and expensive or toxic materials are not required. The results show that SPE extraction method reflects its main advantages of speed, simplicity, low consumption of organic solvents, in addition to the simplification of laborious steps sometimes employed in water sample preparation. Using SPE cartridges containing 500 mg of C_{18}, it was possible to extract fipronil insecticide and its metabolites fipronil desulfinyl, fipronil sulfide and fipronil sulfone quickly and efficiently. The determination by GC-ECD proved to be sufficiently sensitive and selective, allowing a chromatographic analysis of the compounds in 12 min. Satisfactory results were obtained for the proposed method during the validation step. Analytical curves presented r^2 values (determination coefficients) above 0.995 for a wide range of concentrations. The recovery presented values between 81.3 and 112.3%, with RSD lower than 14.2%, which is considered to be adequate for the proposed method. The limits of quantification of the method, 5.0 ng L^{-1} for each metabolite and 7.0 ng L^{-1} for

fipronil, were satisfactory for the analysis of fipronil and its metabolites in water samples. These limits are several times lower than maximum permissible levels set by the legislations for surface and drinking water. This method was successfully applied for the determination of residues of fipronil and its metabolites in environmental water samples.

Supplementary Information

Supplementary chromatogram of the second point of the analytical curves containing fipronil and all studied metabolites at the concentration of 5 μg L^{-1} is available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgments

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