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Determining Tolfenpyrad in Water Samples Using Liquid-Liquid Extraction with Low Temperature Purification (LLE-LTP)

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Tolfenpyrad is an insecticide and acaricide of the pyrazole class, which has been used to control pests in cereal, legume and vegetable crops. Despite its high efficiency, this insecticide is considered highly toxic to humans by Brazilian legislation. Therefore, this study aims to optimize and validate liquid-liquid extraction with low temperature purification followed by analysis by high-performance liquid chromatography with diode array detection to determine tolfenpyrad in water. The results showed that the optimal extraction conditions were achieved using only acetonitrile as extracting phase and 60 min as freezing time. Under these conditions, the extraction method was selective, accurate, and precise, with a recovery of 102.41% and a relative standard deviation of 11.29%. The method was linear from 2.0 to 150.0 μg L^{-1}, with a limit of quantification of 2.0 μg L^{-1}, and the matrix effect was –7.67%. The half-life was 23 days (with sunlight) and 30 days (no sunlight).

Keywords: insecticidal pyrazoles, heterocyclic pyrazole insecticide, extraction method, LLE-LTP

Introduction

Tolfenpyrad is a heterocyclic pyrazole insecticide and acaricide (Figure 1), which acts by contact and has a broad insecticidal spectrum against various types of pests.[1,2] This compound has also stood out for its ability to fight pests that are resistant to the most common agricultural pesticides, such as organophosphates and carbamates.[3]

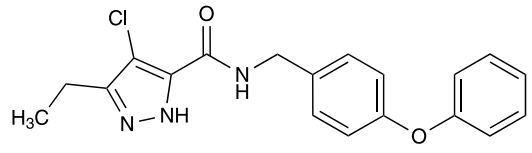

Figure 1. Chemical structure of the tolfenpyrad molecule.

This insecticide was authorized in Brazil in 2020 for use against pests present in cereals, legumes, and vegetables, among others. On the other hand, Brazilian legislation classified this insecticide as a very dangerous product to the environment and highly toxic to humans.[4] In this sense, monitoring this insecticide in environmental and food matrices such as water is very important.

To the best of our knowledge, only solid phase extraction (SPE) and magnetic solid phase extraction (MSPE) have been optimized and validated for monitoring this insecticide in a water matrix, but the recovery rates were less than 90%, even using high sample volumes.[5,6]

In contrast, the liquid-liquid extraction with low temperature partition (LLE-LTP) method has stood out for high recovery rates for several pesticides in water samples, using reduced sample and organic solvent volumes.[7-11] This methodology is based on partitioning the organic and aqueous phases by decreasing the temperature in the system, in which the target analyte is removed to the liquid organic phase and the matrix interferents are trapped in the solid aqueous phase, which also contributes to eliminate the clean-up step.[12] However, no studies employing this method have been conducted to determine tolfenpyrad in water samples.

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Therefore, the aim of this study was to optimize and validate the LLE-LTP method followed by high performance liquid chromatography analysis coupled with diode array detection (HPLC-DAD) to determine tolfenpyrad in water samples.

Experimental

Reagents and solutions

The HPLC-grade solvents used in the chromatographic analyzes were an acetonitrile from Dinâmica (Diadema, Brazil) and methanol from F. Maia (Belo Horizonte, Brazil). Formic acid from Sigma-Aldrich (St. Louis, USA) was also used. PA-grade acetonitrile from Êxodo Científica (Sumaré, Brazil) and ethyl acetate from Dinâmica (Diadema, Brazil) were used to develop the extraction method. The tolfenpyrad solutions were prepared from the standard with 99.4% purity from Sigma-Aldrich (St. Louis, USA), dissolved in HPLC-grade acetonitrile to obtain concentrations of 497 mg L^{-1} (stock solution), 20 mg L^{-1} (intermediate solution) and 5 mg L^{-1} (working solution), and kept at – 20 ºC. All extracts and solutions were filtered through a polytetrafluoroethylene (PTFE) membrane with pores of 0.22 µm (Filtrilo, Colombo, Brazil) before chromatographic analysis.

Equipment

A vortex mixer (Scilogex, Rocky Hill, NJ, USA), a vacuum pump (Prismatec, Itu, Brazil) and a Cary 50 UV-Vis spectrophotometer (Agilent Technologies, St. Clair, USA) were used to prepare the samples.

Chromatographic analysis

Chromatographic analyzes were performed on a high-performance liquid chromatograph coupled to a diode array detector (HPLC-DAD; model 1290 Agilent Technologies, St. Clair, USA). A Kinetex C18 column (100 Å, 150 mm × 4.60 mm, 5 µm, Phenomenex) was used in the chromatographic analyses, and the injection volume was 10 µL.

For optimization of the chromatographic conditions, two wavelengths were evaluated, 210 and 233 nm. The mobile phase compositions evaluated were methanol:water 100:0 (v/v); methanol:water 90:10 (v/v), acetonitrile:water 100:0 (v/v); acetonitrile:water 90:10 (v/v); acetonitrile:water 85:15 (v/v) and acetonitrile:water 80:20 (v/v), with or without acidification with 0.1% (v/v) of formic acid. Two mobile phase flow rates were evaluated: 0.5 and 0.3 mL min^{-1}. Three analysis temperatures were evaluated: 25, 30 and 40 ºC.

Optimization of the extraction method

The method consisted of adding 4 mL of the water sample into a 22 mL vial, followed by fortification with 73 µL of tolfenpyrad solution at 5 mg L^{-1}. The system was vortexed for 1 min to further integrate the analyte into the matrix. Then, 8 mL of the extraction phase were added, the system was vortexed again for 1 min and then refrigerated at –20 °C for 60 min.

Next, two phases were observed in the system after this period, namely the lower solid aqueous phase, and the upper liquid phase was the organic extract obtained. Then, 5 mL of the liquid extract were recovered, transferred to a 5 mL vial and subjected to airflow to evaporate the solvent. The obtained residue was resuspended with 400 µL of acetonitrile acidified with 0.1% (v/v) of formic acid, and stored in vial at –20 ºC for HPLC-DAD analysis.

Then, the LLE-LTP was optimized by evaluating three compositions of extractor phase: acetonitrile, acetonitrile acidified with 0.1% (v/v) of formic acid and 6.5 mL acetonitrile/1.5 mL ethyl acetate. The results were applied to the statistical means comparison test (the *F* test), and Tukey's test was performed when the means were considered different.

Validation of the extraction method

After optimizing the chromatographic conditions and the extraction parameters, the method was validated using the main figures of merit such as selectivity, limit of detection, limit of quantification, linear range, precision, accuracy and matrix effect. Data were evaluated according to SANTE guidelines.[13]

Selectivity

The method selectivity was evaluated by comparing the chromatograms obtained for the insecticide-free water matrix extract (blank extract) and for the tolfenpyrad-spiked matrix extract with 73 µL of tolfenpyrad solution at 5 mg L^{-1}. The method was considered selective when no chromatographic signal was detected in the blank extract chromatogram, in the same tolfenpyrad retention time.

Limit of detection (LOD) and limit of quantification (LOQ)

The limit of detection (LOD) and limit of quantification (LOQ) were determined by extraction experiments with spiked water samples with different tolfenpyrad concentrations. The LOD and LOQ

were appointed as the concentrations that reached chromatographic areas three and ten times greater, respectively, than the chromatographic area of the baseline noise present in the blank extract chromatogram in the same tolfenpyrad retention time.[13,14]

Linear range

The linear range was evaluated by constructing an analytical calibration curve with the chromatographic areas obtained for the matrix extracts spiked with tolfenpyrad at concentrations of 2, 30, 60, 90, 120 and 150 μg L^{-1}, with three independent replicates for each level.[13] The ordinary least squares method (OLSM) was applied to the results to estimate the linear regression parameters, and extreme values identified by the Jackknife test were excluded when necessary, without exceeding the limit of 22.2% of the data. To evaluate homoscedasticity, independence and normality of the regression residuals, the Ryan-Joiner test, the Brown and Forsythe test and the Dubin and Watson test were applied, respectively. Analysis of variance (ANOVA) was applied to verify the significance of the regression and linearity deviation.[15]

Precision and accuracy

The precision of the method was carried out to evaluate the agreement of a set of results obtained from the analysis of extracts of samples of the same concentration.[13] Therefore, fortification and recovery experiments were performed on seven identical extractions of water samples spiked with tolfenpyrad at 90 μg L^{-1} and the relative standard deviation (RSD) of the chromatographic areas obtained was calculated to evaluate the precision of the method. RSD values less than 20% indicate acceptable precision.[13,14]

The accuracy of the method was carried out to evaluate the closeness between the value obtained by the optimized method and the reference value (100%).[13,14] Therefore, accuracy was evaluated through fortification and recovery experiments, for which water samples spiked at 2, 90 and 150 μg L^{-1} of tolfenpyrad, with three independent repetitions for each level. Recovery rates between 70 and 120% were considered acceptable.[13]

Matrix effect

First, two analytical calibration curves were prepared to evaluate the matrix effect; one with tolfenpyrad solutions in acetonitrile (solvent) and the other with matrix extracts spiked with tolfenpyrad. Both analytical curves presented six concentration levels: 2, 30, 60, 90, 120 and 150 μg L^{-1}, with three independent repetitions for each level.[13,16,17] The OLSM was applied to the results to estimate the linear regression parameters.[15] The matrix effect was calculated according to equation 1.[16,17]

$$\text{Matrix effect}\,(\%) = \left(\frac{\alpha_{\text{matrix}} - \alpha_{\text{solvent}}}{\alpha_{\text{solvent}}}\right) \times 100 \qquad (1)$$

where α_{matrix} is the slope of the tolfenpyrad curve in the matrix extract; $\alpha_{solvent}$ is the slope of the tolfenpyrad curve in acetonitrile.

The matrix effect was classified as low, medium or high according to the result obtained, in which: values between –20% and +20% indicated a low matrix effect; values between +20% and +50% or –20% and –50% corresponded to a medium matrix effect; and values above +50% or below –50% pointed to a high matrix effect.[16,17]

Stability study of tolfenpyrad in water

This study was conducted in order to evaluate the environmental influence of sunlight on the compound. To do so, two flasks were prepared, each containing 120 mL of water sample spiked with tolfenpyrad at an initial concentration of 150 μg L^{-1}. The flasks were closed to prevent water evaporation throughout the study. One of the flasks was placed protected from sunlight, while the other was exposed to ambient sunlight. Then, three 4 mL aliquots were collected from each flask every five days for extraction by the optimized LLE-LTP method and analyzed by HPLC-DAD. The experiment was performed over 40 days.

Application in real samples

The optimized and validated extraction method was applied to 11 water samples, which seven samples were collected from groundwater and four from surface water in rural areas in the north of Minas Gerais State, Brazil, as shown in Table S1 (Supplementary Information (SI) section). The criteria for choosing the collection sites were the intense agricultural activity close to the collected water resources and the probable use of tolfenpyrad in vegetable crops.

Results and Discussion

Optimization of chromatographic conditions

First, a tolfenpyrad solution was analyzed in a UV-Vis spectrophotometer, and the spectrum obtained is shown in Figure S1 (SI section). The results revealed that the highest absorbances were observed at 210 and 233 nm. Thus,

the chromatographic analyzes were performed at these wavelengths. The chromatograms obtained are shown in Figure S2 (SI section).

The chromatogram obtained at 210 nm showed a more intense tolfenpyrad peak, however, with an interferent peak in the same retention time of the analyte. The chromatogram obtained at 233 nm showed less intense tolfenpyrad peak, but did not show interfering signals. Therefore, this wavelength was chosen for the next steps of this study. This result was similar to previous studies[18,19] that have used 230 and 245 nm for determining tolfenpyrad in other matrices.

Next, methanol and acetonitrile were evaluated as the mobile phase. The chromatograms obtained using methanol as mobile phase are shown in Figure S3 (SI section). Methanol has already been used in different proportions to determine tolfenpyrad in fruit,[20-22] vegetable,[19,21,23] and water,[5,6] samples, and therefore, it was evaluated as a mobile phase for this study. However, despite the mobile phase composed of 100% methanol presenting greater intensity, it was observed that an interfering signal very close to the analyte signal was observed. On the other hand, the methanol:water 90:10 (v/v) presented a tolfenpyrad peak with low intensity. Therefore, different proportions of acetonitrile and water were used as mobile phase, as can be seen in Figure S4 (SI section).

The presence of acetonitrile in the mobile phase resulted in an increase in the tolfenpyrad peak intensity, in which the acetonitrile:water 90:10 (v/v) ratio showed the highest chromatographic signal. However, when analyzing the tolfenpyrad-spiked matrix extract under optimized chromatographic conditions, an interfering peak was observed at the same analyte retention time (Figure S5b, SI section). Therefore, these chromatographic conditions were reevaluated using tolfenpyrad-spiked matrix extract, as can be seen in Figure S5.

Separation of the tolfenpyrad peak and the matrix interferent was observed using the mobile phase consisting of acetonitrile:water 80:20 (v/v) (Figure S5d). However, a reduction in the tolfenpyrad peak intensity was observed in this condition when compared to the other proportions. Therefore, mobile phases were acidified with 0.1% (v/v) of formic acid, as can be seen in Figure S6 (SI section). The results showed that tolfenpyrad retention time reduced and the peak intensity increased. Therefore, this mobile phase was chosen for the next steps of this study.

The next parameter evaluated was the chromatographic column temperature and the chromatograms obtained are shown in Figure S7 (SI section). The results show that the chromatogram obtained at 25 ºC showed a more intense peak and better separation. A temperature of 40 ºC has already been used for the analysis of tolfenpyrad in fruits,[18,22] however, the tolfenpyrad peak and the interferent peak became closer when this temperature was used in this study, which may compromise the method selectivity. Similar temperatures were used in previous studies[19,23] involving tolfenpyrad in other matrices.

The last chromatographic parameter evaluated was the mobile phase flow and the chromatograms obtained are shown in Figure S8 (SI section). It can be observed that the tolfenpyrad peak intensity was similar in both conditions, however, chromatographic separation was better with a flow of 0.3 mL L^{-1}. Therefore, the best chromatographic conditions were obtained with a tolfenpyrad retention time of 10.7 min.

Optimization of the LLE-LTP parameters

The extraction phase compositions evaluated in the present study were selected based on previous studies[7-11,24-26] and the solubility of the compound in each solvent. The recovery percentages obtained in each extracting phase, with the respective relative standard deviations, are shown in Figure 2.

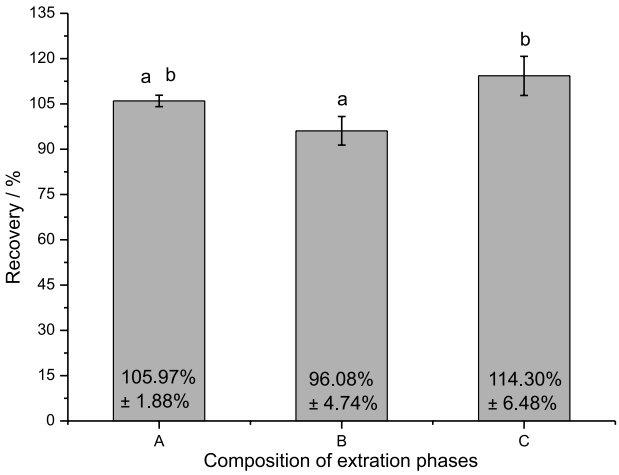

Figure 2. Tolfenpyrad recovery percentages in different extraction phase compositions. The bars presented by the same letter were considered statistically similar by Tukey's test with a 5% level of significance. (A) Acetonitrile; (B) acetonitrile acidified with 0.1% (v/v) of formic acid; (C) 6.5 mL acetonitrile/1.5 mL ethyl acetate.

The results showed that the extraction percentages obtained with acetonitrile and acetonitrile/ethyl acetate (6.5:1.5 v/v) did not differ statistically. Similarly, the extraction percentages obtained with acetonitrile and acidified acetonitrile did not differ statistically. Therefore, it was performed a comparison of the chromatograms obtained from the analyzes in each extracting phase. The obtained chromatograms are shown in Figure S9

(SI section). The results revealed that the addition of formic acid or ethyl acetate to the extractor phase did not promote a gain in peaks separation. Therefore, acetonitrile was chosen as the extractor phase for this study.

Validation of the extraction method

Selectivity

The chromatograms of the tolfenpyrad-free matrix extract (blank extract) and the tolfenpyrad-spiked matrix extract are shown in Figure 3.

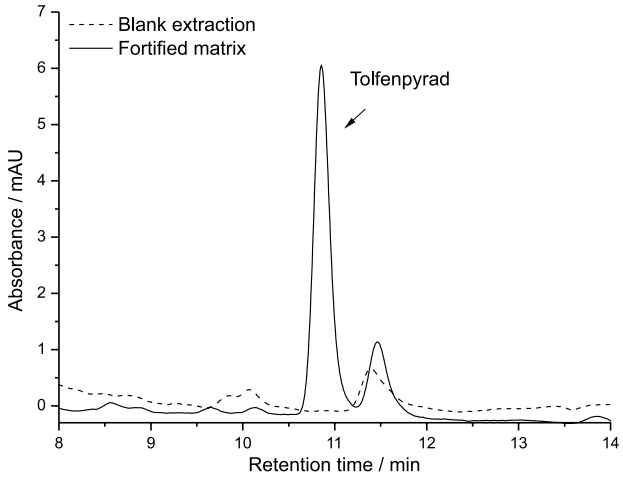

Figure 3. Chromatograms of water matrix extract with and without tolfenpyrad at 90 μg L^{-1}. Chromatographic conditions: Kinetex column, injection volume: 10 μL, flow rate: 0.3 mL min^{-1}, temperature: 25 ºC, λ: 233 nm, mobile phase: acetonitrile:water 80:20 (v/v) acidified with formic acid.

The results revealed that the blank extract chromatogram did not show interferents peak at the same tolfenpyrad retention time, and therefore, the methodology was considered selective.

LOD and LOQ

The LOD and LOQ values achieved in this study are shown in Table 1. In Brazil, the maximum residue limit (MRL) for water samples has not yet been defined. However, the MRL for tolfenpyrad in the European Union is 10 μg L^{-1} for water samples, whereas the MRL in Japan, China and the USA is 20 μg L^{-1}.[27]

Linear range

The linearity range was constructed with six concentration levels and the OLSM was applied to determine the regression parameters and residuals. Then, the Jackknife test was applied to the presented residuals, and two extreme values were excluded. The residual plot excluding the two extreme values is shown in Figure S10a (SI section).

After excluding the extreme values, the OLSM was applied again to the results, and the regression parameters and determination coefficient were estimated and described in Table 1, while the linear regression is shown in Figure S10b. With the obtained values, the use of the OLSM was evaluated by normality, homoscedasticity, independence and significance of the regression and deviation from linearity parameters.

Normality was assessed using the Ryan-Joiner test, for which a graph of residuals arranged in ascending order and expected values was constructed. This graph is shown in Figure S10c. Next, the correlation coefficient (R) and the critical correlation coefficient (R_{crit}) were calculated from the graph, in which the R value (0.96) was greater than the R_{crit} value (0.94). Thus, it is possible to conclude that the linear regression noise follows the normal distribution at a significance level of 0.05.

The Levene test with adaptation of Brown and Forsythe was used to evaluate homoscedasticity, in which the t_L value (0.995) found was lower than the t_{crit} value (2.14), calculated for a significance level of 0.05. The result showed no difference in the variances of the regression residuals, proving the homoscedasticity.

The third test applied to the regression residuals was the Durbin-Watson test to identify the presence of independence between their values. The test did not identify correlation between the regression residues. A Durbin-Watson graph was subsequently constructed (Figure S10d), and confirmed the result obtained with the random distribution of its values in the four presented quadrants.

Regression significance and deviation from linearity were evaluated by ANOVA. Linear regression proved to be significant and without linearity deviation for the analyzes in the range from 2 to 150 μg L^{-1}.

Table 1. Optimized method validation data for determination of tolfenpyrad by LLE-LTP

Linear range / (μg L^{-1})	Linear equation	R^2	Recovery mean ± RSD / %			LOD / (μg L^{-1})	LOQ / (μg L^{-1})
			2.0 μg L^{-1} [a]	90.0 μg L^{-1} [b]	150.0 μg L^{-1} [a]		
2.0-150.0	y = 87900x – 76200	0.9984	104.29 ± 16.5	102.41 ± 11.29	103.62 ± 1.68	0.50	2.00

[a]Mean of 3 replicates; [b]mean of 7 replicates; R^2: determination coefficient; RSD: relative standard deviation; LOD: limit of detection; LOQ: limit of quantification.

Precision and accuracy

The precision and accuracy of the method were evaluated simultaneously, and the data are described in Table 1. The recovery rates obtained in this study are between 70 and 120%; therefore, these recovery rates prove the method accuracy. Similarly, the RSD values obtained are below 20% as recommended in the SANTE validation protocols,[13] and these values confirm the method precision.

Matrix effect

The analytical calibration curves obtained for studying the matrix effect are shown in Figure S11 (SI section). The matrix effect calculated for the water samples was –7.67%, considered a low matrix effect for being in the range between –20 and +20%. Similar results were found in a previous study[5] which determined tolfenpyrad in water samples, whose matrix effect was –12% in surface waters, and no matrix effect in seawater samples.[6] On the other hand, previous studies in more complex matrices aimed at determining tolfenpyrad in fruits found a matrix effect of –61.7% in pears and –67.9% in oranges.[28] Tolfenpyrad determination in vegetables[29] revealed a matrix effect between –28 and –9%, and –26% in samples of seasonings.[30]

Comparison between extraction methods

Until now, SPE and MSPE have been applied to determine tolfenpyrad in water samples.[5,6] Therefore, a comparative study of these extraction methods with the optimized and validated LLE-LTP in this study was performed, as shown in Table 2.

Water has been considered a simple matrix with a reduced presence of interferents, justifying the absence of cleaning steps in the three extraction methods compared in Table 2. In addition, the low complexity of this matrix favors using extraction techniques with fewer steps, as can be seen by a similar number of steps between the three methods in Table 2.

Moreover, the methods which presented the smallest volume of extracting phase were MSPE and LLE-LTP, indicating a positive factor for these two methods. However, the main advantages observed for LLE-LTP are the higher recovery rate associated with the lower RSD value, using a significantly lower sample volume than the other two methods. These three parameters have been considered very important and determinants for an extraction method.

It is important to highlight that although MSPE and SPE presented LOD and LOQ lower than the LLE-LTP, all methods presented values lower than the LMR.

Table 2. Comparative study of extraction methods for determining tolfenpyrad in the water matrix

Parameter	This study	Reference 5	Reference 6
Detection technique	HPLC-DAD	LC-HRMS	LC-MS/MS
Extraction method	LLE-LTP	SPE	MSPE
Cleaning step	no	no	no
Number of steps	5	5	7
Solvent volume / mL	8	20	5
Sample volume / mL	4	200	500
LOD / (μg L^{-1})	0.50	–	0.00019
LOQ / (μg L^{-1})	2.00	0.0025	0.0010
Recovery rate / %	102-104	38-25	66-90
RSD	11.3	15.0	17.0

HPLC-DAD: high performance liquid chromatography with diode array detection; LC-HRMS: liquid chromatography with detection by high resolution mass spectrometry; LC-MS/MS: liquid chromatography with detection by tandem mass spectrometry; LLE-LTP: liquid-liquid extraction with low temperature purification; SPE: solid-phase extraction; MSPE: magnetic solid-phase extraction; RSD: relative standard deviation; LOD: limit of detection; LOQ: limit of quantification.

Stability study

The degradation of tolfenpyrad in water in the presence and absence of sunlight for 40 days is shown in Figure 4.

The half-life of tolfenpyrad in water exposed to sunlight was approximately 24 days. It was observed that the drop in concentration until day 10 was only 4.54%, but from that day on, the presence of tolfenpyrad reduced considerably, with a drop of 24.85% in just five days. On the other hand, the water protected from sunlight showed a reduction in concentration of 20.85% in the first five days, but with a half-life of approximately 30 days, being greater than in conditions exposed to the sun. A previous study[31] has shown that this degradation occurs over one year in the absence of sunlight, but in 11 days of sunlight.

Real samples

Tolfenpyrad was recommended in Brazil to combat the "cruciferous moth" (*Plutella xylostella*) in vegetable crops and the "tomato moth" (*Tuta absoluta*) in tomato crops.[32] Thus, the optimized and validated method was applied to 11 real samples, in which the presence of tolfenpyrad residue was not detected. These results may be associated with degradation in water by photolysis or by microorganisms. In addition, studies have reported the degradation of tolfenpyrad in some plants and soil,[1] which may decrease the amount of the compound that reaches the water. The non-detection of tolfenpyrad residues in water samples was also reported by Liu *et al.*[6] in an

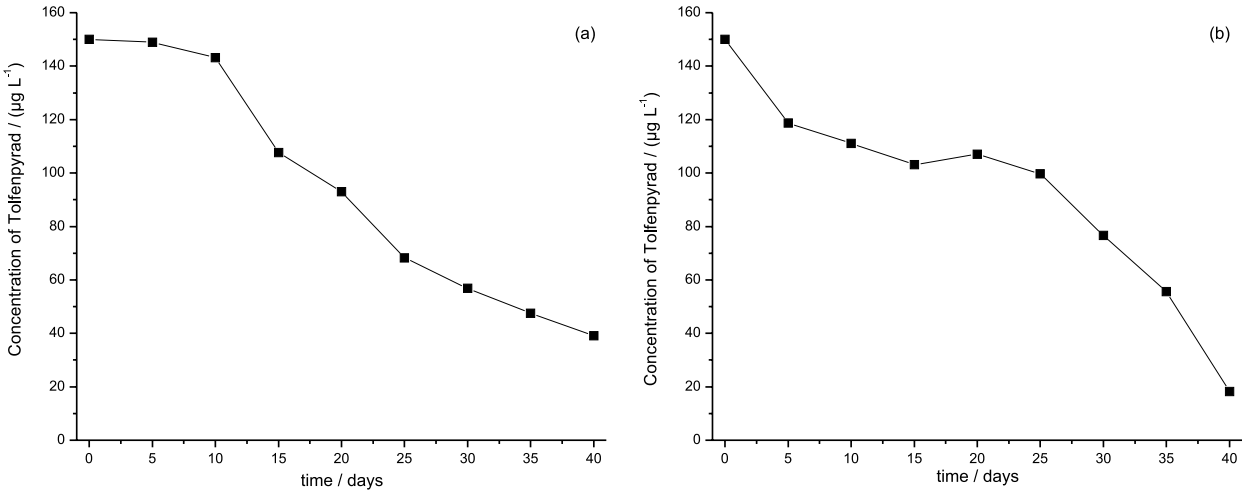

Figure 4. Graph of the concentrations obtained in the analyzes carried out on different days of a 150 µg L^{-1} tolfenpyrad solution with the (a) presence of sunlight and (b) absence of sunlight.

evaluation carried out in the Jiulong River estuary, China, in 2020, and in England,[5] with the evaluation of pesticides in four rivers located in the southwest of the country.

Conclusions

LLE-LTP was successfully optimized and validated in this work. This methodology involved only five steps, achieving high recovery percentages and reduced relative standard deviations. An important aspect of LLE-LTP is that the limit of quantification reached was lower than the MRL defined by international legislation. This methodology also stood out due to the reduced sample volume required for the extraction method when compared to other extraction methods already used for this insecticide in water. For all of these reasons, this extraction method is an important and advantageous alternative for monitoring this insecticide in water samples.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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References

1. Hikiji, W.; Yamaguchi, K.; Saka, K.; Hayashida, M.; Ohno, Y.; Fukunaga, T.; *J. Forensic Leg. Med.* **2013**, *20*, 962. [Crossref]
2. Jiao, Y.; Preston, S.; Song, H.; Jabbar, A.; Liu, Y.; Baell, J.; Hofmann, A.; Hutchinson, D.; Wang, T.; Koehler, A. V.; Fisher, G. M.; Andrews, K. T.; Laleu, B.; Palmer, M. J.; Burrows, J. N.; Wells, T. N. C.; Wang, Q.; Gasser, R. B.; *Parasites Vectors* **2017**, *10*, 272. [Crossref]
3. Yamaguchi, K.; Hikiji, W.; Takino, M.; Saka, K.; Hayashida, M.; Fukunaga, T.; Ohno, Y.; *J. Anal. Toxicol.* **2012**, *36*, 529. [Crossref]
4. Ministério da Agricultura, Pecuária e Abastecimento (MAPA); Ato No. 70, de 23 de dezembro de 2020; *Publicação do Resumo dos Registros de Agrotóxicos e Afins Concedidos, Conforme Previsto no Artigo 14 do Decreto No. 4.074, de 04 de janeiro de 2002*; Diário Oficial da União (DOU), Brasília, de 11/01/2021, p. 7. [Link] accessed December 2023
5. Casado, J.; Santillo, D.; Johnston, P.; *Anal. Chim. Acta* **2018**, *1024*, 1. [Crossref]
6. Liu, Z.; Qi, P.; Wang, J.; Wang, Z.; Di, S.; Xu, H.; Zhao, H.; Wang, Q.; Wang, X.; Wang, X.; *Sci. Total Environ.* **2020**, *708*, 135221. [Crossref]
7. Silvério, F. O.; Silva, J. G. S.; Aguiar, M. C. S.; Cacique, A. P.; de Pinho, G. P.; *Quim. Nova* **2012**, *35*, 2025. [Crossref]
8. Mesquita, T. C. R.; Santos, R. R.; Cacique, A. P.; de Sá, L. J.; Silvério, F. O.; Pinho, G. P.; *J. Environ. Sci. Health, Part B* **2018**, *53*, 199. [Crossref]
9. Sicupira, L. C.; Tiago, J. P. F.; de Pinho, G. P.; Silvério, F. O.; *J. Braz. Chem. Soc.* **2019**, *30*, 1284. [Crossref]
10. Freitas, L. V. P.; Sicupira, L. C.; Pinho, G. P.; Silvério, F. O.; *J. Braz. Chem. Soc.* **2020**, *31*, 1898. [Crossref]
11. Vieira, L. H. S.; Sicupira, L. C.; Cacique, A. P.; Silvério, F. O.; *J. Environ. Sci. Health, Part B* **2022**, *57*, 697. [Crossref]

12. Vieira, H. P.; Neves, A. A.; de Queiroz, M. E. L. R.; *Quim. Nova* **2007**, *30*, 535. [Crossref]
13. SANTE No. 11312/2021: *Analytical Quality Control and Method Validation Procedures for Pesticide Residues and Analysis in Food and Feed*, https://www.eurl-pesticides.eu/userfiles/file/EurlALL/SANTE_11312_2021.pdf, accessed in December 2023.
14. Bruce, P.; Minkkinen, P.; Riekkola, M. L.; *Mikrochim. Acta* **1998**, *128*, 93. [Crossref]
15. de Souza, S. V. C.; Junqueira, R. G.; *Anal. Chim. Acta* **2005**, *552*, 25. [Crossref]
16. Economou, A.; Botitsi, H.; Antoniou, S.; Tsipi, D.; *J. Chromatogr. A* **2009**, *1216*, 5856. [Crossref]
17. Tomasisni, D.; Sampaio, M. R. F.; Caldas, S. S.; Buffon, J. G.; Duarte, F. A.; Primel, E. G.; *Talanta* **2012**, *99*, 380. [Crossref]
18. Avuthu, M. R.; Rao, T. N.; Reddy, B. V.; Murthy, S.; Revathi, P.; *J. Agric. Vet. Sci.* **2016**, *3*, 358. [Link] accessed in December 2023
19. Qing-Qing, W.; Chuan-De, L.; *Adv. Sci. Eng.* **2017**, *9*, 7. [Link] accessed in December 2023
20. Sun, L.; Guo, Q.; Jacob, C. C.; Martins, C. P. B.; Fussell, R.; *Multi-Pesticide Residues Analyses of QuEChERS Extracts Using an Automated Online µSPE clean-up Coupled to LC-MS/MS*, https://lcms.cz/labrulez-bucket-strapi-h3hsga3/an_65684_lc_ms_multi_pesticides_residue_analysis_an65684_en_2e4988f8f5/an-65684-lc-ms-multi-pesticides-residue-analysis-an65684-en.pdf, accessed in December 2023.
21. Lopes, J. C. S.; Sicupira, L. C.; Silvério, F. O.; *J. Braz. Chem. Soc.* **2022**, *34*, 302. [Crossref]
22. Doug, M.; Wen, G.; Tang, H.; Wang, T.; Zhao, Z.; Song, W.; Wang, W.; Zhao, L.; *Food Chem.* **2018**, *269*, 136. [Crossref]
23. Bousova, K.; Sarikaya, E.; Godula, M.; Martins, C.; George, E.; *Fast Screening and Quantification of Pesticide Residues Using a Comprehensive LC-MS Solution: The Pesticide Explorer Collection - Standard Quantitation*, https://www.thermoscientific.com/content/dam/tfs/ATG/CMD/cmd-documents/sci-res/app/ms/lc-ms/solutions/AN-643-LC-MS-Pesticide-Explorer-Standard-AN64638-EN.pdf, accessed in December 2023.
24. Maia, M. R.; Arcanjo, A. L. P.; Pinho, G. P.; Silvério, F. O.; *J. Braz. Chem. Soc.* **2017**, *28*, 179. [Crossref]
25. Alves, I. M.; Melo, N. O.; Marinho, P. A.; Almeida, M. R.; *Vib. Spectrosc.* **2020**, *110*, 103112. [Crossref]
26. Pereira, N. G. F.; Silvério, F. O.; Pinho, G. P.; *Int. J. Environ. Anal. Chem.* **2020**, *100*, 968. [Crossref]
27. Food and Agriculture Organization of the United Nations (FAO); *Report of the Working Group on Maximum Residue Levels and on Maximum Residue Levels in the Brew*, https://www.fao.org/fileadmin/templates/est/COMM_MARKETS_MONITORING/Tea/IGG22/16-CRS2-MRLsChina.docx, accessed in December 2023.
28. Kmellar, B.; Fodor, P.; Pareja, L.; Ferrer, C.; Martínez-Uroz, M. A. M.; Valverde, A.; Fernandez-Alba, A. R. F.; *J. Chromatogr. A* **2008**, *1215*, 37. [Crossref]
29. Lan, T.; Yang, G.; Li, J.; Chi, D.; Zhang, K.; *Food Chem.* **2022**, *13*, 100241. [Crossref]
30. Ghosh, B.; Bhattacharyya, A.; Hingmire, S.; Aher, P.; Zende, P.; Banerjee, K.; *J. AOAC Int.* **2021**, *104*, 148. [Crossref]
31. Food Safety Commission Pesticides Expert Committee; *Evaluation Report Tolfenpirade*, https://www.fsc.go.jp/english/evaluationreports/pesticide/evaluationreport_tolfenpyrad.pdf, accessed in December 2023.
32. Nichino do Brasil Agroquímicos LTDA; *Tolfenpirade*, https://agrofit.agricultura.gov.br/agrofit_cons/agrofit.ap_download_blob_agrofit?p_id_file=422462&p_nm_file=F406451164/Bula_Ohkami%2010%20EW_Incl%20Culturas_05%2004%2022.pdf, accessed in December 2023.

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