https://dx.doi.org/10.21577/0103-5053.20220132

J. Braz. Chem. Soc., Vol. 34, No. 4, 582-589, 2023

Article

Optimization and Validation of the Miniaturized Solid-Liquid Extraction with Low Temperature Purification (SLE-LTP) Method for Determining Fluopyram in Sandy, Clayey and Medium-Textured Soil

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Fluopyram is a fungicide which can also be used as a nematicide in agricultural areas. The Brazilian Ministry of Agriculture authorized the commercialization and use of this molecule in Brazilian agriculture in 2019, but studies involving the development of an extraction and quantification method of this compound in environmental matrices such as soil are still scarce. Therefore, the present study aimed to optimize and validate the miniaturized version of the solid-liquid extraction with low temperature purification (SLE-LTP) method for determining this compound in sandy, clayey and medium-textured soil samples. All analyzes in this study were performed by gas chromatography coupled to mass spectrometry (GC-MS). The results revealed that the analyte recovery percentages in the three soil types ranged from 86 to 114% with a relative standard deviation of less than 15%. In addition to employing smaller amounts of reagents and sample, the miniaturized SLE-LTP method was selective, precise, exact, and linear in the range from 3 to 210 μg kg^{-1}, and reached a limit of quantification lower than 3.00 μg kg^{-1} for the three soil types. The extraction method was applied to 30 real samples collected in coffee growing regions, but no residue of this compound was detected in these samples.

Keywords: fluopyram, miniaturized SLE-LTP, benzamide pyramidal fungicide

Introduction

Fluopyram (*N*-[2-[3-chloro-5-(trifluoromethyl)-2-pyridin-2-yl]ethyl]-2-(trifluoromethyl)benzamide) is a fungicide and nematicide, which has a broad action spectrum and belongs to the group of pyramidal benzamides. This fungicide acts by inhibiting the succinate dehydrogenase enzyme in complex II of the electron transport chain of mitochondria.[1,2] Although the fluopyram molecule is already well known in several countries in Europe, the United States and also Australia, this compound was only authorized for marketing and use in Brazil in 2019.

The Brazilian Institute for the Environment and Renewable Natural Resources (Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis-IBAMA) classified this fungicide as a very dangerous product for the environment which can affect the microbiological activity of the soil and consequently its productivity.[3,4] In this sense, recent study[5] have revealed that this compound is persistent and can be detected in the soil up to 80 days after application in pepper crops.

Due to its recent insertion in Brazilian agriculture, there are still no studies related to the extraction and detection methodologies of this compound in Brazilian soils. To the best of our knowledge, only the QuEChERS (quick, easy, cheap, effective, rugged and safe) method and solid-liquid extraction have been optimized and validated for this compound in soil.[6-12] Although these methodologies have proven to be very efficient and sensitive, the development of new extraction methods which can be simpler, easier to perform, sensitive, efficient

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Editor handled this article: Eduardo Carasek

and cheaper is recommended. In this sense, previous works[13-16] have shown that solid-liquid extraction with low temperature purification (SLE-LTP) has gathered these characteristics when applied to other environmental contaminants. Therefore, a miniaturized variation of this methodology was recently optimized and validated to monitor pesticides in biological matrices. High analyte recovery rates were observed using less reagents and samples in this study, in addition to maintaining the main advantage of this methodology, which is extracting and cleaning extracts in a single step.[17]

In a previous study,[18] the Empresa Brasileira de Agropecuária (Embrapa) defined that there are at least 13 types of soil classes in Brazil which differ in their chemical, physical and morphological characteristics. This complexity of the soil matrix can influence the recovery rate of chemical contaminants, as verified in a previous work by Đurović *et al*.[19] Therefore, we chose three soil types with different textures and organic matter contents in this study in order to ensure the applicability of the extraction method.

In view of the above, this study aimed to optimize and validate the miniaturized version of the SLE-LTP method followed by analysis by gas chromatography coupled with mass spectrometry (GC-MS) to determine fluopyram in sandy, clayey and medium-textured soils.

Experimental

Reagents and solutions

Fluopyram standard with 98% purity was purchased from Sigma-Aldrich (St. Louis, USA). Fluopyram stock solution at 100 mg L^{-1} and intermediate and working solutions at concentrations 20, 5, 1 and 0.5 mg L^{-1} were prepared in high performance liquid chromatography (HPLC) grade acetonitrile and stored in amber bottles at −20 ºC. HPLC grade acetonitrile was purchased from Merck (Darmstadt, Germany). PA grade acetonitrile was purchased from Êxodo Científica (Sumaré, Brazil). HPLC grade ethyl acetate was purchased from Dinâmica (Indaiatuba, Brazil). Sodium sulfate (Na_2SO_4) anhydrous was purchased from Vetec (Rio de Janeiro, Brazil).

Soil samples

Sandy, clayey and medium-texture soil samples were respectively collected in the rural area of Montes Claros (16º52'47''S 43º50'49''W), rural area of Francisco Sá (16º29'55''S 43º31'35''W) and in an experimental area of the Institute of Agricultural Sciences of the Federal University of Minas Gerais (16º40'59''S 43º50'16''W) at a depth of 30 cm. The soils were homogenized, sieved in a 1 mm sieve and stored in the laboratory in glass jars. The physical-chemical characterization of the three soils is presented in Table S1 (Supplementary Information (SI) section).

Equipment

A Shimadzu analytical balance (São Paulo, Brazil), a Scilogex vortex (Rocky Hill, USA), a Kindly centrifuge (São Paulo, Brazil) were used to prepare the samples and the analyzes were performed in a gas chromatograph (GC-7890A model) coupled to a mass spectrometer (MS-5975C model), both from Agilent Technologies (St. Clair, USA).

Optimization of chromatographic conditions

Extract analyzes were performed based on the chromatographic conditions described by Dong and Hu.[6] The chromatographic analysis time was the only parameter optimized in this step. The analyzes were performed in a GC-MS from Agilent Technologies (St. Clair, USA), and an SLB-5 MS capillary column (St. Louis, USA) with stationary phase 5% diphenyl and 95% dimethylpolysiloxane (30 m long × 0.25 mm inner diameter × 0.25 µm inner film thickness). Helium (99.9999%) at a flow of 1 mL min^{-1} was used as the carrier gas. The inlet temperature was maintained at 260 °C, and 1 µL of the extract was injected in splitless mode using the CombiPAL autoinjector. The initial column temperature was 120 °C increasing at a rate of 20 °C min^{-1} to 220 °C, remaining at this temperature for 1 min. Then, the temperature was raised at a rate of 5 °C min^{-1} to 250 °C. Total chromatographic analysis time was 12 min. The interface and ion source temperatures were 280 and 230 ºC, respectively. The mass spectrometer detector was used in electron impact ionization mode at 70 eV. A standard of 5 mg L^{-1} was initially analyzed in the scan mode and the selective ion mode (SIM) was adopted after selecting the most abundant ions. The selected ions were *m/z* 145, 173, 195, 223.

Optimization of the extraction method

First, two extracting phases were evaluated (acetonitrile and acetonitrile/ethyl acetate 6.5:1.5) in order to optimize the sample preparation, the traditional version of the SLE-LTP method uses 4 g of sample, 4 mL of water and 8 mL of organic solvent,[13] while the miniaturized version of this method used 1 g of sample, 1 mL of water and 2 mL of organic solvent.

The extraction methodology used in this study was the one that obtained the best experimental results and is in agreement with the study by Silva *et al*.[17] who miniaturized liquid-liquid extraction with low temperature partition (LLE-LTP) for pesticide determination in biological samples. Thus, 1 mL of distilled water was added to a 5 mL vial containing 1 g of soil and vortexed for 30 s. Then, 2 mL of acetonitrile were added and homogenized again for 30 s. After 15 min of rest, the samples were frozen at –20 ºC for 1 h. Next, 1.1 mL of the supernatant organic phase was transferred to a 15 mL Falcon tube containing 130 mg of anhydrous sodium sulfate and vortexed for 30 s. The anhydrous sodium sulfate was dried in a muffle oven for two hours at 300 ºC to remove water and possible interferences. After this step, the tubes containing the extracts were centrifuged at 4000 rpm for 5 min, and 800 µL of the supernatant was transferred to an injection vial and analyzed by GC-MS.

Validation of the extraction method

The criteria recommended by SANTE[20] were followed to validate the extraction method. Thus, the selectivity, limit of detection (LOD), limit of quantification (LOQ), linearity range, accuracy, precision and matrix effect parameters were studied. The selectivity was studied by comparing chromatograms of fluopyram-free matrix extract (blank extract) with chromatograms of fluopyram-fortified matrix extract at a concentration of 90 µg kg^{-1}. The absence of chromatographic signals in the retention time of fluopyram in the chromatogram of the blank extract ensures the selectivity of the method. The limits of detection and quantification were considered to be the lowest concentration of fluopyram in the matrix that resulted in a chromatographic signal with 3 and 10 times the signal to noise ratio at the retention time of fluopyram, respectively.

The linearity range of the method was studied through the analytical calibration curve using fortified matrix extracts and in triplicate at concentrations of 2, 10, 50, 90, 130, 170 and 210 µg kg^{-1} for sandy soil, and 3, 10, 50, 90, 130, 170 and 210 µg kg^{-1} for clayey and medium-textured soils. Data were submitted to linear regression analysis using the ordinary least squares method and statistical tests described by Souza and Junqueira.[21]

The accuracy and precision were studied with recovery tests at concentrations of 2, 90 and 170 µg kg^{-1} for sandy soil and 3, 90 and 170 µg kg^{-1} for clayey and medium-textured soils. Triplicates were performed at concentrations of 2, 3 and 170 µg kg^{-1} and seven replicates were adopted at concentrations of 90 µg kg^{-1}. The recovery percentage must be within the range of 70 to 120% for acceptability of the method, and the relative standard deviation (RSD) must be less than 20%.

The matrix effect was studied as described by Chamkasem and Harmon,[22] by analyzing the analytical calibration curves of fortified extracts with the analytical curves prepared with the standard in pure solvent at the same concentrations. The matrix effect was calculated as the ratio between the slope of the analytical calibration curve in the fortified matrix extract and the slope of the analytical curve prepared in solvent, multiplied by 100, as can be seen in the equation 1:

$$\text{Matrix effect } (\%) = \frac{\alpha_{\text{matrix}}}{\alpha_{\text{solvent}}} \times 100 \quad (1)$$

In which α_{matrix} is the slope on the analytical curve in the matrix extract; $\alpha_{solvent}$ is the slope on the analytical curve in solvent.

Real sample application

Fluopyram is authorized in Brazil for use in coffee crops. Therefore, in this study, we collected 30 soil samples from different coffee producing regions in the southern region of the State of Minas Gerais to evaluate the presence of fluopyram traces in the soil. Table S2 (SI section) presents the geographic coordinates of the sample collection locations.

Results and Discussion

Optimization of chromatographic conditions

A standard solution of fluopyram at 5 mg L^{-1} was analyzed following the chromatographic condition described by Dong and Hu[6] in scan mode to determine the compound retention time and the most abundant ions in the spectrum of masses (Figure S1, SI section) in order to optimize the chromatographic conditions. The retention time found was 8.86 min and the most abundant ions, as in the cited article, were 173, 145, 223, 195 and 396 respectively. Then ions 145, 173, 195, 223 were selected and analysis of a standard solution at 0.5 mg L^{-1} in SIM mode was performed.

The analysis time in the study performed by Dong and Hu[6] was 17 min, but in this study fluopyram was eluted in 8.86 min and the total analysis time was 12 min due to the post run to ensure that no matrix interference was retained in the chromatographic column.

Optimization of the extraction method

The first step in optimizing the extraction method was to define the best extraction method (traditional or miniaturized version of SLE-LTP) and the best extractor phases (acetonitrile or acetonitrile:ethyl acetate 6.5:1.5). The chromatogram obtained for each experiment can be seen in Figure 1.

As can be seen in Figure 1, the fluopyram signal intensity was higher when using acetonitrile as the extractor phase and when using SLE-LTP in the miniaturized version. In addition to reducing the signal intensity of the analyte studied, the use of ethyl acetate in the extractor phase also intensified the matrix effect, as evidenced by the high recovery percentages, as shown in Table 1. These results are in agreement with those found by Silva *et al.*[17] who achieved high recovery rates using acetonitrile in the miniaturized version of liquid-liquid extraction with low temperature partition to determine pesticides in biological matrices; and Mesquita *et al.*,[14] who used acetonitrile in SLE-LTP to study various pesticides in soil samples.

After showing that the miniaturized version of SLE-LTP using acetonitrile generated recovery rates close to 100% and relative standard deviation below 6%, we proceeded to the validation step of the extraction method.

Validation

Selectivity

The selectivity was studied by comparing chromatograms of matrix extracts fluopyram-free (blank extract) with the chromatograms of matrix extracts fortified at 90 μg kg^{-1}. The method was considered selective for the three types of soils because there were no peaks of matrix interferences in the same fluopyram retention time, as can be seen in Figure 2.

LOD and LOQ

The LOD and LOQ were considered as the lowest concentration that generated a signal with an area that corresponded to three and ten times the area of the noise signal at the fluopyram retention time. In this study, the LOD of 0.5 μg kg^{-1} was reached for the three soils and the LOQ of 2 μg kg^{-1} for the sandy soil and 3 μg kg^{-1} for the clayey and medium-textured soils. The LOD and LOQ values found are lower than those of other published studies such as those by Mahdavi *et al.*,[11] Dong and Hu[6] and Katna *et al.*,[10] who found 8.3, 10 and 50 μg kg^{-1},

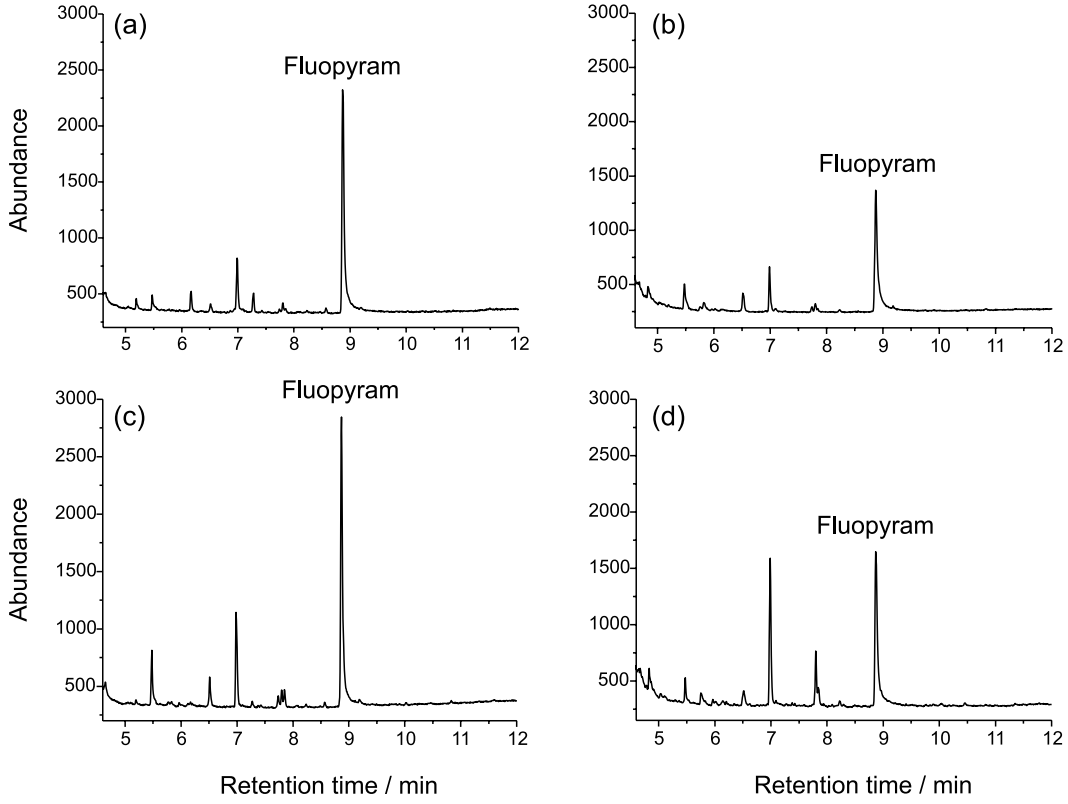

Figure 1. Chromatograms of matrix extracts fortified with fluopyram at 90 μg kg^{-1} in sandy soil. (a) Traditional SLE-LTP with acetonitrile extracting phase; (b) traditional SLE-LTP with acetonitrile + ethyl acetate extractor phase; (c) miniaturized SLE-LTP with acetonitrile extractant phase; (d) miniaturized SLE-LTP with acetonitrile + ethyl acetate extractor phase.

Table 1. Fluopyram recovery in optimization tests in different soil types

Technique	Extraction phase	Soil type	Recovery / %	Relative standard deviation / %
Traditional SLE-LTP	acetonitrile	sandy	119	5
		clayey	106	2
		medium-texture	118	2
Traditional SLE-LTP	acetonitrile + ethyl acetate	sandy	133	11
		clayey	121	3
		medium-texture	131	5
Miniaturized SLE-LTP	acetonitrile	sandy	94	3
		clayey	104	6
		medium-texture	100	1
Miniaturized SLE-LTP	acetonitrile + ethyl acetate	sandy	107	5
		clayey	109	7
		medium-texture	120	0

SLE-LTP: solid-liquid extraction with low temperature purification.

respectively, as the LOQ. There is still no legislation in Brazil which determines the maximum residue limit of fluopyram in soil, but the results obtained revealed that the LOD and LOQ values were lower than the maximum residue limits established for pesticides by the European Union for several foods of plant origin, such as bananas, apples and watermelon with residue limits of 800, 600 and 400 μg kg^{-1}, respectively.[23]

Linearity

The linearity curve was prepared on matrix extracts fortified with fluopyram in triplicate at concentrations ranging from 2 to 210 μg kg^{-1} for sandy soil and from 3 to 210 μg kg^{-1} for sandy, clayey and medium-textured soils. The statistical linear regression parameters were performed by the ordinary least squares method following the procedures described by Souza and Junqueira.[21]

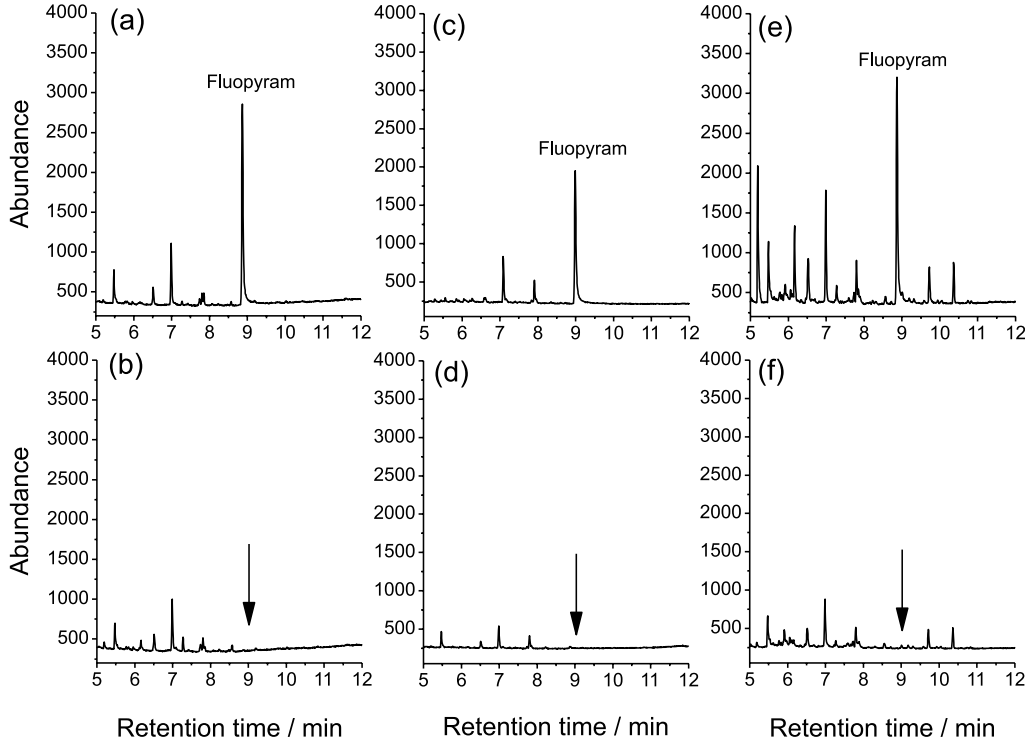

Figure 2. Chromatograms of extracts fortified with fluopyram and of blank extracts. (a) Chromatogram of fortified sandy soil extract; (b) chromatogram of the blank sandy soil extract; (c) chromatogram of fortified clayey soil extract; (d) chromatogram of the blank clayey soil extract; (e) chromatogram of fortified medium-texture soil extract; (f) chromatogram of blank medium texture soil extract.

Table 2. Recovery percentage and relative standard deviation of accuracy and precision tests

Sample	Recovery / %			
	2 μg kg^{-1}	3 μg kg^{-1}	90 μg kg^{-1}	170 μg kg^{-1}
Sandy soil	89.0 ± 12.0	–	93.0 ± 15.0	111.0 ± 4.0
Clayey soil	–	96.0 ± 8.0	86.0 ± 13.0	109.0 ± 8.0
Medium-texture soil	–	88.0 ± 8.0	106.0 ± 10.0	114.0 ± 10.0

Outliers (critical values) were identified and excluded using the Jackknife test, as shown in Figure S2 (SI section). Moreover, three critical values in sandy soil were excluded so that the data met the statistical criteria. Despite clayey soil having four critical values, only three were excluded in order to meet the statistical criteria. Lastly, only one value was excluded in the medium-textured soil.

The normality of the regression residuals was assessed using the Ryan-Joiner test. The regression residuals in the three soils followed normality at 5% significance, as shown in Figure S3 (SI section).

The Brown and Forsythe test confirmed homoscedasticity and homogeneous distribution of the regression residuals. The independence of residuals was studied using the Durbin and Watson test. The test showed that there is no autocorrelation of the residuals for the 5% significance level and they are randomly distributed in the four quadrants, as can be seen in Figure S4 (SI section).

Analysis of variance (ANOVA) indicated that the regression is significant and that there is no linearity deviation for the 5% significance level for the three soil types. Therefore, the proposed method was considered linear. Figure 3 shows the graphs of linearity curves for the three soil types.

Accuracy and precision

The accuracy and precision of the method was evaluated by recovery studies at concentrations of 2, 90 and 170 μg kg^{-1} for sandy soil and 3, 90 and 170 μg kg^{-1} for clayey and medium-textured soils. The obtained results can be seen in Table 2.

The method was considered accurate because it presents average recoveries within the range of 70 to 120%, and accurate because it presents a relative standard deviation of less than 20%, as recommended by SANTE.[20]

Matrix effect

The matrix effect was studied with calibration curves prepared on fluopyram-fortified matrix extracts and solvent-prepared standard solutions at the same concentrations as presented above. Table 3 presents the angular coefficients of the calibration curves prepared in solvent and in extracts from the three soils and the calculated matrix effect.

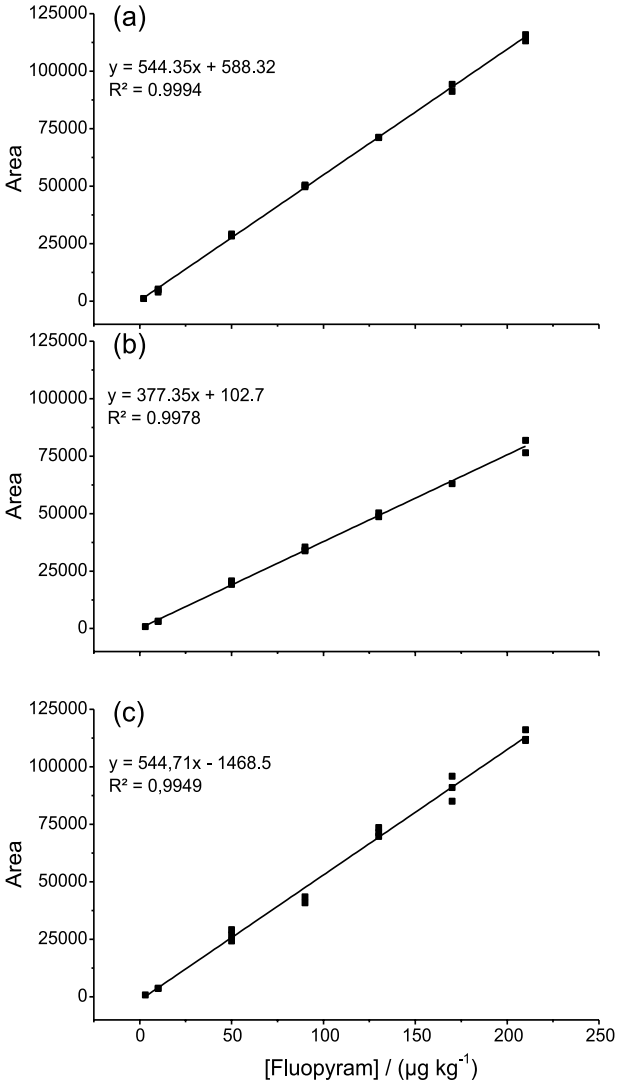

Figure 3. Linear regression graphs for the three soil types. (a) Sandy soil; (b) clayey soil; (c) medium-texture soil.

Table 3. Matrix effect on different soils

Sample	Angular coefficient on the curve in solvent	Angular coefficient in the matrix extract curve	Matrix effect / %
Sandy soil	550.70	545.91	99.13
Clayey soil	548.40	377.35	68.81
Medium-texture soil	548.40	544.70	99.33

Table 4. Comparison of the results of this study and other results from the literature for determining fluopyram in soil samples

Method	Analysis technique	Organic solvent volume / mL	Clean up	Recovery / %	LOQ / (μg kg^{-1})	Reference
QuEChERS	LC-MS/MS	20	C18	80.6-93.5	8.3	Mahdavi *et al.*[11]
QuEChERS	GC-MS	10	PSA	88.6-98.0	10	Dong and Hu[6]
QuEChERS	GC-MS	20	PSA	73.6-103.6	10	Mohapatra *et al.*[8]
QuEChERS	LC-MS/MS	20	PSA	86.6-92.7	50	Chawla *et al.*[9]
QuEChERS	GC-MS	20	PSA	96.0-107.0	50	Katna *et al.*[10]
Miniaturized SLE-LTP	GC-MS	2	–	86.0-114.0	2 and 3	this study

QuEChERS: quick, easy, cheap, effective, rugged and safe; SLE-LTP: solid-liquid extraction with low temperature purification; LC-MS/MS: liquid chromatography coupled with tandem mass spectrometry; GC-MS: gas chromatography coupled with mass spectrometry; C18: octadecylane; PSA: primary secondary amine; LOQ: limit of quantification.

The matrix effect in sandy and medium-textured soils was less than 1% (99.13 and 99.33%), which means that the matrix has little interference in the analytical response of the proposed method. There was suppression in the analytical response with a matrix effect of 68.81% in the clayey soil. However, in clayey soil, the matrix effect generated a ca. 31% suppression in the analytical response. This may have happened because the clayey soil has higher organic matter content, as shown in Table S1. A study by de Sousa *et al.*[24] which evaluated the matrix effect of 11 pesticides in soil showed that soil organic matter has molecules with high molecular mass that can form active sites in the injection liner in which analytes can bind and suppress the analytical response.

Real sample application

A total of 30 soil samples from coffee plantations in the southern region of the State of Minas Gerais were analyzed in the application in a real sample, however, traces of fluopyram were not detected in any of these samples. This result may be associated with its recent approval in the country and it has not yet been applied to crops, or it may have been used, but was degraded under environmental conditions, as occurred in studies by Mohapatra *et al.*[8] and Matadha *et al.*[5]

Comparison with other methods

Table 4 presents a comparison between the results of this study and other works already published.

As can be seen in Table 4, the miniaturized version of the SLE-LTP optimized and validated for soil samples showed lower solvent consumption for extraction, it was not necessary to use adsorbents for clean up, and reached limits of quantification 25 times lower than works already published in the literature. Therefore, the optimized and validated method in this work proved to be easy to perform, with few steps, efficient and sensitive.

Conclusions

In this study, a miniaturized version of SLE-LTP was optimized and validated, followed by analysis by GC-MS in SIM mode to determine fluopyram in three soil types. In addition to the reduced use of solvent and sample, this extraction method was fast, easy to perform and sensitive. The miniaturized SLE-LTP version showed high recovery rates and reduced relative standard deviation, proving to be efficient and reliable. The LOQ value achieved in this study was lower than that of published studies and that of European legislation. For all these reasons, the miniaturized version of the SLE-LTP is a suitable alternative for monitoring fluopyram in different soil types.

Supplementary Information

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

Acknowledgments

The authors thank the National Council for Scientific and Technological Development (CNPq) (308480/2019-8) for the financial support for the research grants, the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) (APQ-02736-21), the Coordination for the Improvement of Higher Education Personnel (CAPES), and the Federal University of Minas Gerais (UFMG) for the infrastructure made available.

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Submitted: June 30, 2022
Published online: October 21, 2022