

DLLME-GC/ECD Method for the Residual Analysis of Parathion-Methyl and its Application in the Study of the UV-Photodegradation Process

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A new method has been developed to determine trace levels of organophosphorus pesticide parathion-methyl in water samples by using dispersive liquid-liquid microextraction (DLLME), followed by gas chromatograph coupled with electron capture detector (GC/ECD) analysis. The optimized and validated method showed high extraction recovery (101.1%), high enrichment factor (57.3), low limits of detection and quantification, 0.083 and 0.250 $\mu\text{g L}^{-1}$, respectively. The established DLLME-GC/ECD method has been successfully applied for the evaluation of the photodegradation of the parathion-methyl by UV_{254nm} radiation in different conditions of pH and temperature. The parathion-methyl photodegradation at pH 3 and 35 °C achieved > 99.5% after 120 min of exposition. For this condition, it was observed the kinetic rate of 0.0515 min^{-1} , the quantum yield of $1.22 \times 10^{-5} \text{ mol Einstein}^{-1}$ and a half-life time of 13.46 min. All experimental conditions tested proved to be strongly influenced by pH and temperature. The application of the optimized process in distilled and drinking water spiked with parathion-methyl provided residues of this pesticide at levels below the maximum permitted by Brazilian legislation, which is 9.0 $\mu\text{g L}^{-1}$.

Keywords: pesticide, dispersive liquid-liquid microextraction, gas chromatography, UV radiation, degradation

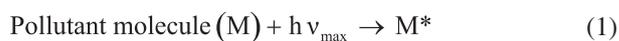
Introduction

Organophosphates (OPs) are used as pesticides in different cultures due to its efficiency in pests control.¹ Parathion-methyl (*O,O*-dimethyl-*O*-4-nitrophenyl phosphorothioate) is an insecticide and acaricide from OPs class. Because it is classified as extremely dangerous, it has been banned or had its restricted use in many developed countries like Japan, USA and Australia. In spite, it is still used in cultures of rice, garlic, wheat, beans in many other developing countries including Brazil.² The yearly large-scale use of parathion-methyl, as well as low decomposition rates in the environment cause the accumulation of these compounds in soils, from which they are subsequently washed out to enter groundwater and rivers.³

Many techniques have been investigated to eliminate this waste and other pesticides in the environment, such as photo-Fenton process, homogeneous and heterogeneous

photocatalysis, nanofiltration and photodegradation.⁴ The photodegradation has proven to be an important process of destruction of organic micro-pollutants in water and wastewater. In photodegradation, photo-oxidation reactions occur due to the excitation of electrons of the organic substance through absorption of radiant energy. UV radiation can initiate numerous chemical reactions, such as hydrolysis, oxidation and photolysis.⁵

At first, if the molecule of organic pollutant absorb energy emitted by the light photons, links can therefore be cleaved.⁶ The equations 1 and 2 represent the basic mechanism of photodecomposition reactions of organic pollutants. Equation 1 represents the photochemical excitation due to radiation of UV absorption at the maximum wavelength ($h\nu_{\text{max}}$) by the pollutant and equation 2 shows the photo-excited molecule becoming reaction product or intermediaries who can participate in subsequent reactions.^{5,7-9}



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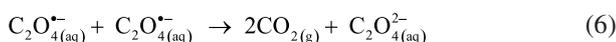
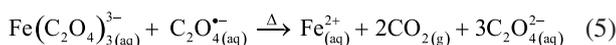
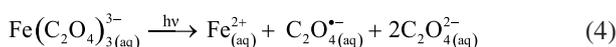
The most effective region of the electromagnetic spectrum for degradation of organic pollutants lies in the UV-C near 254 nm.¹⁰ The germicidal low pressure (LP) mercury lamps are the most common sources of ultraviolet radiation. These lamps emit 80 to 90% of the energy at a wavelength of 253.4 nm and can be considered monochromatic.¹¹

Typically the photobleaching studies are evaluated in terms of their kinetic behavior, but the efficiency of photodecomposition reactions can also be measured by the quantum yield (Φ_λ), which expresses the number of photons required to degrade certain amount of organic contaminant.⁶ On molar basis, Φ_λ is given in mol Einstein⁻¹, where 1 Einstein is equal to 1 mol of photon, according to the equation 3.

$$\Phi_\lambda = \frac{\text{number of mol of reacted molecules per time unit}}{\text{number of mol of absorbed photons per time unit}} = \left[\frac{\text{mol}}{\text{Einstein}} \right] \quad (3)$$

The number of moles of photons required for the reaction can be measured by actinometry. The actinometry allows the determination of the photons flow in a specific geometry and in a well-defined spectral domain; therefore, the most favorable case is when the incident light is monochromatic. In absolute actinometric measurements a physical device (such as a photomultiplier or a photodiode, e.g.) converts the energy or the number of incident photons in measurable electrical signal. However, the most commonly utilized method is based on a chemical actinometer; a reference substance undergoing a photochemical reaction whose yield is already known, calibrated against a physical device, well studied actinometers or calorimetric methods.¹²

The ferrioxalate chemical actinometer is the most reliable and practical actinometer to UV and visible light up to 500 nm and was initially proposed by Hatchard and Parker.¹³ Under the excitation light, the potassium ferrioxalate decomposes according to equations 4, 5 and 6.



The quantity of ferrous ions formed during a period of irradiation is monitored by conversion to the colored tris-phenanthroline complex (*o*-phenanthroline iron(II), $\epsilon = 11.100 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\max} = 510 \text{ nm}$). By this relation, it can be determined the number of moles of effective photons in the production of photochemical changes.¹²

Bhattacharjee and Shah¹⁴ and Teixeira and Jardim¹⁵ have suggested that the photolysis is influenced by several factors and should be highlighted the pH of the medium, the concentration of organic contaminants, light sources characteristics and the operating system, geometry and hydrodynamic parameters of the reactor, temperature, among others. Khaleel *et al.*¹⁶ showed the importance of assessing these parameters to examine the influence of the variation of the initial concentration, solution pH, and temperature on the photolysis of the antidepressant desipramine. Although the pH has shown a significant impact on the degradation rate, the temperature, contrary to expectations, showed no significant effect in the study.

Among some advantages of photolysis, Domènech *et al.*¹⁷ emphasize the increasing reaction rate compared with other techniques in the absence of light, the system flexibility by allowing the use of a variety of combined oxidants and the fact that this process does not require drastic pH changes.

For the determination of pesticides in water by gas chromatography methods, several simultaneous extraction and pre-concentration of the residues have been proposed. Among them, the dispersive liquid-liquid microextraction (DLLME) has shown powerful and can be applied appropriately to quantify the residual compound by gas chromatography (GC) or by high-performance liquid chromatography (HPLC). In DLLME, a mixture composite of an extraction solvent and of a dispersive solvent is rapidly injected into an aqueous solution containing the analyte of interest to form a cloudy solution. This solution is homogenized and then, centrifuged to separate the phases. Consecutively, the sedimented organic phase is removed and injected into the analytical instrument for quantitation.¹⁸

This research applied a chemometric experimental design to optimize DLLME- gas chromatography-electron capture method to analyze the residue of parathion-methyl and evaluate its UV-photodegradation at different conditions of pH and temperature.

Experimental

Reagents and solutions

Parathion-methyl ($\text{C}_8\text{H}_{10}\text{NO}_5\text{PS}$, 99.0%) was obtained from Chem Service® (West Chester, PA, USA) and bifenthrin ($\text{C}_{23}\text{H}_{22}\text{ClF}_3\text{O}_2$, 92.2%), used as internal standard (IS), was obtained from FMC® (FMC Brasil, Campinas, SP, Brazil). Toluene 99.5% HPLC grade (Vetec®, Rio de Janeiro, RJ, Brazil) was used as extraction solvent and

acetonitrile 99.9% HPLC grade (Sigma-Aldrich®, São Paulo, SP, Brazil) as dispersive solvent.

Stock solutions of parathion-methyl were prepared in acetonitrile 99.9% HPLC grade (Sigma-Aldrich®, São Paulo, SP, Brazil) in the concentration of 35.0 mg L⁻¹ and bifenthrin in the concentration of 1000.0 mg L⁻¹. From these pesticide standard solutions, work solutions were prepared in the concentrations of 100.0 µg L⁻¹ in distilled water of parathion-methyl and the IS in acetonitrile at the concentration 13.2 mg L⁻¹. These solutions were stored in a freezer at -20 ± 2 °C.

Instrumentation

The identification and quantification were performed in a gas chromatograph (Shimadzu® GC 2014) equipped with an electron capture detector (GC/ECD) and a split/splitless injection system with auto-injector (AOC-20i). The separation was performed using a capillary column ZB-5 (Zebron®), stationary phase of 5% phenyl and 95% dimethylpolysiloxane (30 m × 0.25 mm i.d. and 0.10 µm of stationary film thickness). Nitrogen (99.999% purity) was used as carrier gas at a flow rate of 1.2 mL min⁻¹ and the injection of 1.0 µL of sample was carried out in the split mode in the ratio 1:5. The temperatures of the injector and detector were 280 and 300 °C, respectively. The column was initially set at 180 °C for 0.22 min, and heated at a rate of 20 °C min⁻¹ to 205 °C and held at this temperature for 0.5 min. After, it was heated at 5 °C min⁻¹ to 217 °C and then, heated at 30 °C min⁻¹ to 290 °C, maintaining at this temperature for 1.2 min. The total analysis time was 8 min.

The determination of the quantum yield in photolytic reactions was performed using a UV-Visible spectrophotometer (Cintra® C-20). It was also used: analytical balance (Sartorius® EP 221S), centrifugal (Quimis® Q222-T28), pH meter (Digimed® DM-20), magnetic stirrer (Nova Ética® 114) and a thermostatic bath (Tecnal® TE-184).

Chromatographic analysis

The identification of analytes, parathion-methyl and bifenthrin (IS), was conducted by comparing the retention time (R_t) of the chromatographic peaks of pesticides standard solutions with the R_t of pesticides contained in the extracts of the samples. The quantification of pesticides was performed by internal standardization method with matrix-matched. The extracts were fortified with 1.0 µL of the work solution of IS 13.2 mg L⁻¹ getting a final concentration of 200.0 µg L⁻¹.

DLLME procedure

For optimization of the extraction method it was used a full factorial design 2³. The tests were performed in duplicate at 25 ± 2 °C and the variables evaluated were: ionic strength ([KCl] in mol L⁻¹); vortexing time (s); amount of extraction solvent (µL) (Table S1, Supplementary Information section).

The results were based on the effects of the factorial design at a confidence level of 95% (α = 0.05) using the Statistica® 12 software (StatSoft Corp., Tulsa, USA). The evaluation was conducted from the extraction efficiency (E).

The adapted DLLME extraction method^{18,19} consists of extracting the interest analyte in water samples (5.0 mL) free or fortified with parathion-methyl at concentration level of 5.0 µg L⁻¹ adding 600.0 µL of dispersing and extraction solvents mixture, acetonitrile:toluene (5:1). This mixture was rapidly injected into the sample by a microsyringe of 1000.0 µL. The resulting cloudy solution was vortex shaken for 30 seconds followed by centrifugation at 6,000 rpm for 5.0 min. The extract located in the supernatant (around 65.0 µL) was collected with an automatic pipette of 100.0 µL and transferred to a vial provided with an insert of 150 µL. This extract was fortified with 1.0 µL of work solution of IS at 13.2 mg L⁻¹ and then, injected into the GC/ECD to obtain the chromatographic responses.

Method validation

The method validation of DLLME-GC/ECD was carried out following the procedures adopted by our group,^{20,21} which are based on established criteria by leading regulatory agencies in Brazil: Agência Nacional de Vigilância Sanitária (ANVISA) through the Resolution No. 899/03,²² Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO)²³ through the guide document DOQ-CCGRE-008/2007, Ministério da Agricultura, Pecuária e Abastecimento (MAPA)²⁴ through the Validation Guide and Analytical Quality Control and by the Analytical Quality Assurance Manual of the Ministry of Agriculture, Livestock and Supply.

UV-photodegradation process

The irradiation experiments were conducted in batch in an aluminum cylindrical reactor with a total volume of 700.0 mL and surface area of 147.4 cm². The reactor was placed in a timber chamber of 60 × 55 × 40 cm size which was completely covered with aluminum foil to a better use of UV radiation. Samples of distilled water spiked

with parathion-methyl at concentration level of $50.0 \mu\text{g L}^{-1}$ were introduced into the reactor and submitted to UV irradiation, under magnetic stirring, for 180 min. Samples of 5.0 mL were collected every 30 min and were submitted to optimized and validated method (DLLME-GC/ECD) to determine the residual amount of parathion-methyl. The experiments as well as the chromatographic injections were performed in duplicate.

The medium temperature was monitored using a digital thermometer and kept constant through a handmade heat exchanger connected to a thermostatic bath. A TUV Sylvania® 15 W germicidal lamp was used as UV radiation source. For the determination of the quantum yield of the photolytic reactions, the average intensity of ultraviolet radiation (Einstein min^{-1}) was measured by a chemical actinometer of potassium ferrioxalate proposed initially by Hatchard and Parker.¹³

The UV-photodegradation assays were performed to achieve parathion-methyl degradation as a function of pH (3, 7 and 11) and temperature (15, 25 and 35 °C). To modify the pH of the reaction medium, appropriate quantities of nitric acid solution 1.0 mol L^{-1} or sodium hydroxide 1.0 mol L^{-1} were added.

The optimized degradation procedure was applied in drinking water samples collected after conventional treatment in a treatment plant (WTP, Viçosa, Brazil) and spiked with known concentrations of pesticides.

Results and Discussion

Optimization of the DLLME-GC/ECD method

The Table 1 shows the results of the factorial design 2^3 for the DLLME-GC/ECD method optimization. The term E is defined as the percentage of the total amount, by weight, of the analyte extracted to the organic phase; m_i ($0.025 \mu\text{g}$) corresponds to the initial amount of analyte in the aqueous phase and m_{org} corresponds to the amount of extracted analyte. The extraction efficiency was calculated according to equation 7.

$$E(\%) = \frac{m_{\text{org}}}{m_i} \times 100 = \frac{C_{\text{org}} \times V_{\text{org}}}{C_i \times V_{\text{aq}}} \times 100 \quad (7)$$

where C_{org} is the analyte concentration in the organic phase, C_i is the initial concentration of the analyte in the sample, V_{org} is the volume of organic phase recovered after extraction and V_{aq} is the volume of the sample solution.

The C_{org} was obtained by linear equation of the calibration graph constructed from the direct injections of standard solutions of parathion-methyl prepared in toluene

Table 1. Results of the full 2^3 factorial design for DLLME^a optimization based on the effects of the factors in extraction efficiency (E) of parathion-methyl in distilled water

Test	Factors ^b			E \pm SD ^c / %
	(1)	(2)	(3)	
1 and 2	0.0	15	80	71.1 \pm 0.9
3 and 4	1.5	15	80	81.5 \pm 3.2
5 and 6	0.0	30	80	73.3 \pm 1.7
7 and 8	1.5	30	80	80.4 \pm 0.1
9 and 10	0.0	15	100	86.1 \pm 0.2
11 and 12	1.5	15	100	101.8 \pm 2.5
13 and 14	0.0	30	100	100.6 \pm 0.8
15 and 16	1.5	30	100	101.5 \pm 2.5

^aOther extraction conditions: sample volume 5.0 mL of water; volume of dispersive solvent 500.0 μL ; centrifugation at 6,000 rpm for 5.0 min; $T = 25 \pm 2 \text{ }^\circ\text{C}$; concentration of parathion-methyl equal to $5.0 \mu\text{g L}^{-1}$; ^b(1) ionic strength (in mol L^{-1}); (2) vortex time (in s); (3) amount of extractor solvent (in μL); ^cSD: standard deviation.

at the range $100.0\text{-}1000.0 \mu\text{g L}^{-1}$. The injections were in triplicate. The equation of the linear regression curve was $y = 1,391.8x + 200,167.0$, with determination coefficient (R^2) equal to 0.995.

The Figure 1 shows the Pareto chart with the effects of the factors on extraction efficiency.

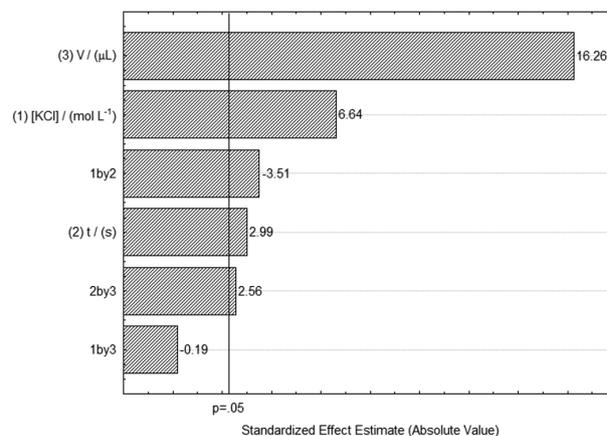


Figure 1. Pareto chart with the effects of the factors ionic strength (1), agitation time vortex (2) and volume of solvent extractor (3) on the extraction efficiency (E) of parathion-methyl.

Analyzing the main effects of the factors studied in extraction efficiency (E) (Figure 1), it was found that the volume of extraction solvent has significant influence ($p < 0.05$), with high volume of extractor solvent (3) the value of E increased. It was also found that the ionic strength and the vortex time influenced significantly the extraction efficiency ($p < 0.05$), because the higher values for these factors shown best results for E.

The Table 1 shows the conditions of the tests 11 to 16 offered the best experimental results for extraction

efficiency. However, fixing up the vortex time at 30 s (tests 13 to 16) it was found that the variation of the ionic strength has little influence in the extraction efficiency, once values close to 100% were obtained without any salt addition. Therefore, the experimental condition of tests 13 and 14 (Table 1) was selected as optimal parameters for the method application, since it offered high extraction efficiency ($100.6 \pm 0.8\%$), analytical and operational simplicity and rapidity. Then, the optimal condition for extraction of parathion-methyl in aqueous samples by DLLME was: add in 5.0 mL of water sample, without changing the ionic strength, the extractive mixture containing 500.0 μL of dispersive solvent (acetonitrile) and 100 μL of extractor solvent (toluene) and vortexing for 30 s.

The method also showed an enrichment factor (E_F) of 57.3 ± 1.5 and relative standard deviation (RSD) of 2.6%. E_F was calculated as the ratio of the analyte concentration in the organic phase (C_{org}) and the initial concentration of the analyte in the sample (C_i).

DLLME-GC/ECD method validation

All calibration curves used in the validation step were built from the internal standardization method with matrix-matched blank samples, and the extraction procedure was performed in triplicate for each concentration level with two injections for each replicate. Statistical tests were performed using software Statistica® 12 (StatSoft Corp., Tulsa, USA) at a 95% confidence level.

The selectivity of the method was evaluated by comparing the chromatographic responses obtained after submitting samples of distilled water, free and spiked with the pesticide under study, the method of DLLME-GC/ECD optimized. It was not detected any interference in the times of retention of parathion-methyl and IS (Figure S1, Supplementary Information section).

The limits of detection (LOD) and quantification (LOQ) were calculated according to Ribani *et al.*²⁵ and MAPA²⁴ (equations 8 and 9).

$$\text{LOD} = 3.3 \times \frac{s}{S} \quad (8)$$

$$\text{LOQ} = 10 \times \frac{s}{S} \quad (9)$$

where s is the estimated standard deviation of analytical response of the matrix blank in the characteristic R_i of parathion-methyl, S is the slope of the calibration curve. The values obtained are presented in Table 2.

It was found that both LOD and LOQ are below the maximum contaminant level (MCL) recommended by the Ministry of Health²⁶ which is $9.0 \mu\text{g L}^{-1}$.

The linearity of the method was evaluated analyzing the extracts obtained by spiking distilled water samples at concentrations levels of 0.25-60.0 $\mu\text{g L}^{-1}$ (8 points). The linear regression curve was obtained for $y = 0.215x + 0.774$ and the correlation coefficient (r) equal to 0.996. According to this parameter, the curve was linear in the concentration levels evaluated, once its value is above the minimum values recommended by ANVISA²² (0.99) and INMETRO²³ (0.90). The selected working range was 0.25 to 20.0 $\mu\text{g L}^{-1}$, because the most of the measurements performed on the degradation experiments were contemplated in this range.

To evaluate the accuracy of the proposed method, distilled water samples were spiked with parathion-methyl in four concentration levels: $1 \times \text{LOQ}$, $2 \times \text{LOQ}$, $40 \times \text{LOQ}$ and $80 \times \text{LOQ}$ (0.25, 0.50, 10.0 and 20.0 $\mu\text{g L}^{-1}$, respectively) and submitted to extraction procedure. Recovery factors ($f_{\text{rec}} \times 100$) obtained are shown in Table 3. It was found that the method provides results with high level of agreement with those regarded as real, since the f_{rec} values for all concentration levels are within the range recommended by the MAPA,²⁴ that is 50-120% for 1 and $2 \times \text{LOQ}$, and 80-110% for 40 and $80 \times \text{LOQ}$.

The precision was evaluated in terms of repeatability and intermediate precision in the same concentration levels used to determine the accuracy. It was found that the method is accurate, since the RSD values for all concentration levels are below the recommended by the MAPA²⁴ that is 23% for 1 and $2 \times \text{LOQ}$ and 13% for 40 and $80 \times \text{LOQ}$ (Table 3).

UV-photodegradation of parathion-methyl

The DLLME-GC/ECD optimized and validated method

Table 2. Estimated standard deviation of the matrix blank (s), the slope of the calibration curve (S), limits of detection (LOD) and quantification (LOQ) to the method

Pesticide	s^a	S^b	Linear range / ($\mu\text{g L}^{-1}$)	LOD / ($\mu\text{g L}^{-1}$)	LOQ / ($\mu\text{g L}^{-1}$)
Parathion-methyl	0.018	0.707	0.25-60.0	0.083	0.250

^aAverage of 7 reps of water samples free of pesticide submitted to DLLME-GC/ECD optimized method; ^banalytical curve obtained by spiking water samples with parathion-methyl at final concentrations of 0.1 to 0.5 $\mu\text{g L}^{-1}$ (5 points); $y = 0.707x + 0.040$; $R^2 = 0.998$ and residues standard deviation (s_R) = 0.006.

Table 3. Accuracy and precision of DLLME-GC/ECD method

Concentration / ($\mu\text{g L}^{-1}$)	Recovery factor ^a ($f_{\text{rec}} \times 100$) \pm RSD / %	Precision	
		Repeatability ^a (RSD) / %	Intermediate precision (RSD) / %
0.25 (1 \times LOQ)	100.2 \pm 4.2	2.5	5.5
0.50 (2 \times LOQ)	100.3 \pm 4.9	2.2	6.5
10.0 (40 \times LOQ)	102.2 \pm 5.9	2.6	4.0
20.0 (80 \times LOQ)	99.0 \pm 5.6	7.7	6.3

^aAverage triplicate. f_{rec} = product of the average concentration measured in the matrix spiked by the theoretical concentration of the blank matrix spiked;

^bcarried out on different days and not consecutive, by the same analyst.

was used to monitoring the photodegradation of parathion-methyl through UV_{254nm} radiation.

The kinetics of degradation of parathion-methyl under UV_{254nm} absorption can be represented by the integrated model expressed by first order (equation 10).

$$\ln\left(\frac{[\text{CPM}]_0}{[\text{CPM}]_t}\right) = k_{\text{UV}} \times t \quad (10)$$

where $[\text{CPM}]_0$ and $[\text{CPM}]_t$ correspond to the initial concentration and the residual concentration of parathion-methyl after a time t (min) of experiment, respectively, and k_{UV} corresponds to the kinetic rate constant of 1st-order degradation (min^{-1}).

The Figures 2 and 3 present graphs of the concentration decay of parathion-methyl during UV-photodegradation under different conditions of pH and temperature and the corresponding graphs to the kinetic behavior contemplating $\ln([\text{CPM}]_0/[\text{CPM}]_t)$ versus exposure time.

For Chelme-Ayala *et al.*²⁷ and Wu and Linden²⁸ the pesticide degradation in UV radiation water can also be represented by the 1st-order kinetic model.

It was found that parathion-methyl degradation is favored in acidic environment, once the pesticide was greater than 99.5% degraded in pH 3 during 180 min exposure (Figure 3). Bhattacharjee and Shah¹⁴ and Gogate and Pandit²⁹ also reported that greater efficiency in the degradation of organic contaminants can be achieved at low pH values in the range of 2.5 to 5. For the other pH values evaluated (7 and 11), it was observed an incomplete degradation of parathion-methyl and the pesticide residues remained above the MCL which is $9.0 \mu\text{g L}^{-1}$.²⁶

It was found that parathion-methyl degradation is favored by increasing the temperature once the degradation of >99.5% of the pesticide occurred at 35 °C during 120 min of exposure (Figure 4). According to Langlais *et al.*³⁰ an increment of 10 °C generally increases by a factor of 2 or 3 the rate of decomposition of an organic compound.

Although 35 °C present as the best temperature for direct UV-photodegradation of parathion-methyl in UV_{254nm} in pH 3, the other tested temperatures, 15 and 25 °C, also led to satisfactory results, once at the end of the total exposure time (180 min) the residual concentrations of pesticide at these conditions were below the MCL.²⁶

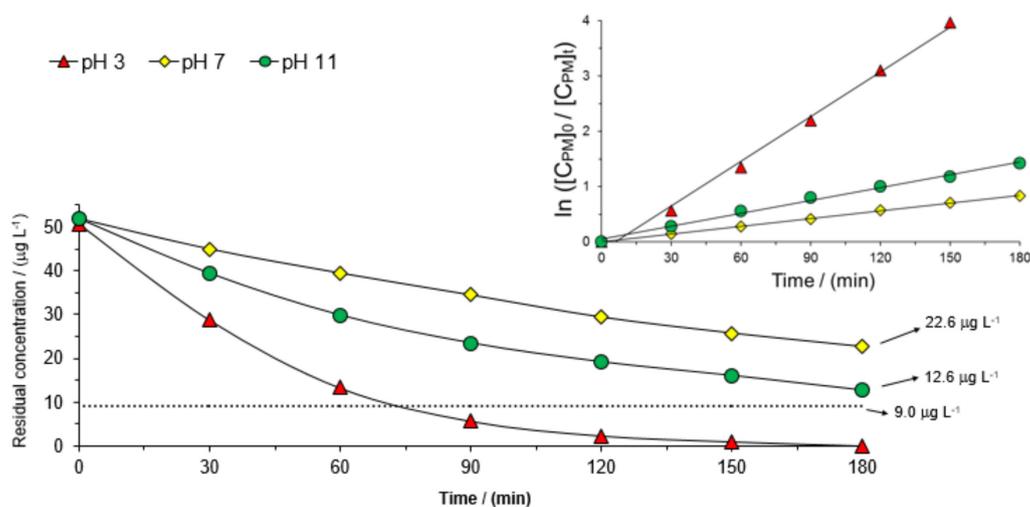


Figure 2. Concentration decay of parathion-methyl in distilled water for direct photolysis in UV_{254nm} at different pH values. The insert corresponds to the kinetic behavior under the same conditions. Each point of the curve represents the arithmetic average of the results of experimental repetitions. $[\text{CPM}]_0 = 50.0 \mu\text{g L}^{-1}$; $T = 25 \pm 1 \text{ }^\circ\text{C}$.

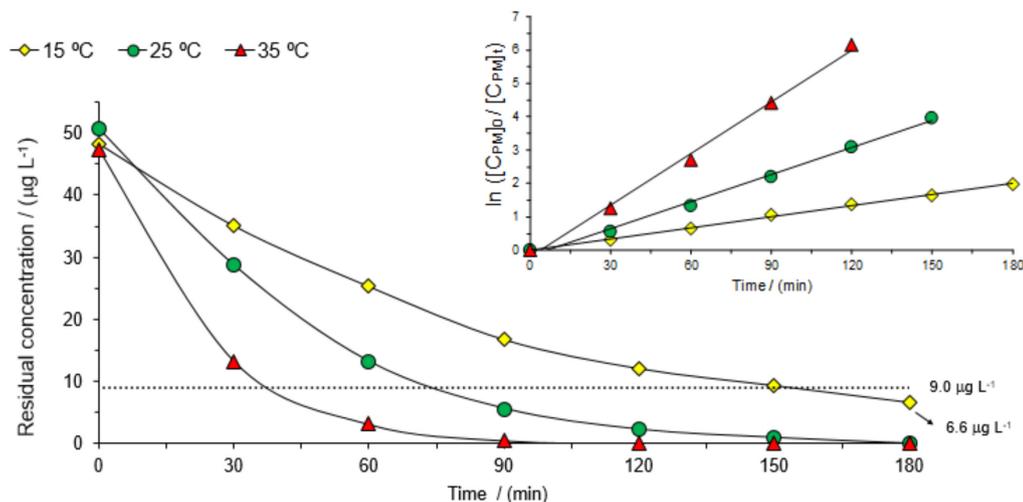


Figure 3. Concentration decay of parathion-methyl in distilled water for direct photolysis in UV_{254nm} at different temperatures. The insert corresponds to the kinetic behavior under the same conditions. Each point of the curve represents the arithmetic average of the results of experimental repetitions. $[C_{PM}]_0 = 50.0 \mu\text{g L}^{-1}$; $\text{pH}_i = 3$.

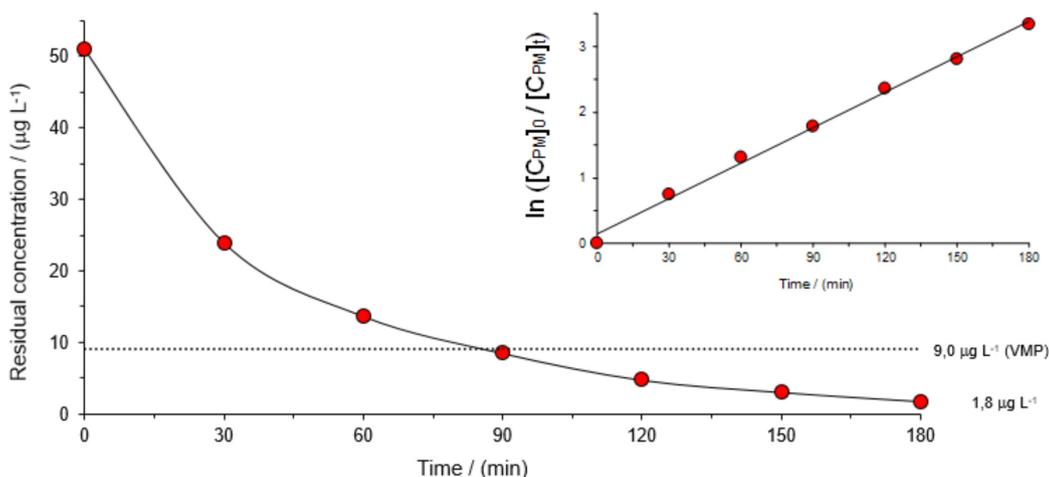


Figure 4. Concentration decay of parathion-methyl in potable water during the direct photolysis in UV_{254nm} at pH 3 at 35°C . The insert corresponds to the kinetic behavior under the same conditions. Each point of the curve represents the arithmetic average of the results of experimental repetitions. $[C_{PM}]_0 = 50.0 \mu\text{g L}^{-1}$.

Between the conditions evaluated, the best kinetics behavior was achieved in experiments carried out at pH 3 and 35°C , with an estimated k_{UV} 0.0515 min^{-1} .

The number of moles of photons required for the reaction was measured by chemical actinometry assuming the Φ_{254nm}

for potassium ferrioxalate equal to $1.25 \text{ mol Einstein}^{-1}$.¹³ Thus, the average radiation intensity obtained (I_{254nm}) was $8.53 \pm 0.34 \times 10^{-5} \text{ Einstein min}^{-1}$. The Φ_{254nm} values obtained for the photodegradation assays are described in Table 4. This parameter is important to reproduce this experiment

Table 4. Kinetics rate of degradation (k_{UV}), half-life ($t_{1/2}$) and quantum yield (Φ_{254nm}) determined for the experiments of direct photolysis of parathion-methyl under UV_{254nm} radiation in distilled water samples

EC (pH, $T \pm 1^\circ\text{C}$)	k_{UV} / min^{-1}	$t_{1/2} / \text{min}$	$\Phi_{254nm} / (\text{mol Einstein}^{-1})$
(1) pH 3, 25°C	0.0269 ± 0.0003	25.74 ± 0.30	$(8.78 \pm 0.17) \times 10^{-6}$
(2) pH 7, 25°C	0.0047 ± 0.0004	148.38 ± 11.8	$(5.09 \pm 0.22) \times 10^{-6}$
(3) pH 11, 25°C	0.0077 ± 0.0003	89.48 ± 3.84	$(6.81 \pm 0.51) \times 10^{-6}$
(4) pH 3, 15°C	0.0111 ± 0.0001	62.32 ± 0.24	$(7.21 \pm 0.40) \times 10^{-6}$
(5) pH 3, 35°C	0.0515 ± 0.0007	13.46 ± 0.18	$(1.22 \pm 0.01) \times 10^{-5}$

EC: experimental condition.

Table 5. Efficiency parameters calculated from the results of the application of the optimized process of direct photolysis in UV_{254nm} in samples of distilled and drinking water

	Parameter	k_{UV} / min^{-1}	$t_{1/2} / \text{min}$	$\Phi_{254nm} / (\text{mol Einstein}^{-1})$
Matrix	PW	0.0515 ± 0.0007	13.46 ± 0.18	$(1.22 \pm 0.01) \times 10^{-5}$
	DW	0.0181 ± 0.0001	38.37 ± 0.30	$(8.52 \pm 0.24) \times 10^{-6}$

k_{UV} : kinetics rate of degradation; $t_{1/2}$: half-life; Φ_{254nm} : quantum yield; PW: distilled water; DW: drinking water.

using other UV sources taking different photons emission rates. Table 4 also shows the average values of k_{UV} and half-lives ($t_{1/2}$) for all tests.

The experimental condition that provided the best quantum yield (Table 4), which showed the highest parathion-methyl degradation by UV_{254nm} power unit, was carried out at pH 3 at 35 °C with Φ_{254nm} equal to $1.22 \times 10^{-5} \text{ mol Einstein}^{-1}$. Accordingly, this condition showed the best reaction kinetic rate ($k_{UV} = 0.0515 \text{ min}^{-1}$) and the shorter half-life ($t_{1/2} = 13.46 \text{ min}$). Wu and Linden²⁸ reported a Φ_{254nm} of $7.14 \times 10^{-4} \text{ mol Einstein}^{-1}$ to parathion degradation at pH 5 using four monochromatic low-pressure lamps.

Thus, it was concluded that the proposed procedure of direct photolysis in UV_{254nm} for parathion-methyl degradation conducted at pH 3 at 35 °C was very efficient, being able to eliminate all the pesticide present in the sample in 120 min. The degradative process in these pH and temperature conditions was applied in spiked drinking water samples ($[C_{PM}]_0 = 50.0 \mu\text{g L}^{-1}$). The Figure 4 shows the graph of the concentration decay of parathion-methyl in drinking water during UV-photodegradation at pH 3 and 35 °C and the graph of their kinetic behavior.

After performing the measurements and calculated the efficiency parameters (k_{UV} , $t_{1/2}$ and Φ_{254nm}), the results obtained were compared with those determined from the application of the optimized process in distilled water. Table 5 shows these results.

A comparison of the results for each parameter was performed through the ANOVA test at a 95% confidence level. It was found that the results for the parameters evaluated (k_{UV} , $t_{1/2}$ and Φ_{254nm}) in parathion-methyl degradation in drinking water are statistically different from those obtained for the same process in distilled water samples. According to Bhattacharjee and Shah¹⁴ and Gálvez *et al.*³¹ the photodegradation process is strongly influenced by the presence of some interfering ions such as sulfates, phosphates, carbonates and bicarbonates. According to the authors, these species act as sequestrants, competing with the organic substrate by radiation absorption. This issue was probably the cause for significant difference observed between the results, once for drinking water the presence of several species able to exercise such interference is allowed at the national territory.

Conclusions

The method of DLLME optimized and validated for the quantification of parathion-methyl by GC/ECD was adequate and effective in the extraction of pesticides in water samples, distilled and drinking, with high extraction efficiency ($101.1 \pm 2.8\%$) and high enrichment factor (57.3 ± 1.5). The DLLME-GC/ECD method showed good linearity and repeatability, achieving low LOD and LOQ in the range of ppt (ng L⁻¹).

The established DLLME-GC/ECD method has been successfully applied for the evaluation of the photodegradation of the parathion-methyl in different conditions of pH and temperature. For the optimized conditions (pH 3 and 35 °C), direct photolysis in UV_{254nm} completely degraded parathion-methyl in distilled water at 120 min of exposure to the radiation. It was found that both k_{UV} and Φ_{254nm} are strongly dependent on the pH and on temperature of the reaction medium. The application of UV-photodegradation process in drinking water samples confirmed the efficiency and versatility of it, once the parathion-methyl residues achieved remained below the MCL ($9.0 \mu\text{g L}^{-1}$) at the end of the experiment. However, the obtained efficiency parameters were statistically different from those obtained in the tests in distilled water, suggesting the presence of interfering anions which competed with the pesticides by absorption of radiation.

Supplementary Information

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

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