

Single Drop Microextraction: a Sensitive Multiresidue Method for Determination of Pesticides in Water Using GC/ECD

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O monitoramento de pesticidas em amostras ambientais em baixas concentrações é necessário devido aos riscos que estes compostos representam a saúde humana e ao meio ambiente. Neste trabalho, o método microextração em gota única (SDME) foi otimizado e validado para a determinação das concentrações traço de oito pesticidas em água utilizando cromatografia gasosa com detector por captura de elétrons (GC/ECD). A cinética de transferência de matéria da fase aquosa para a fase orgânica durante o processo de extração também foi avaliada. O método mostrou recuperações entre 89,5 e 122,7%, com coeficientes de variação menores que 22,9%, e os limites de detecção entre 5,9 e 58,9 ng L⁻¹. O método foi aplicado a amostras fortificadas em diferentes níveis de concentração, e recuperações entre 50,5 e 148% foram obtidas. O processo de extração pode ser descrito pelo modelo de difusão de Noyes-Whitney, e a parationa metílica apresentou a maior taxa de transferência entre as duas fases.

The monitoring of pesticides in environmental samples at low concentrations is needed due to the risks that these compounds can pose to human health and the environment. In this work, a single drop microextraction (SDME) method was optimized and validated for the determination of trace concentrations of eight pesticides in water, using gas chromatography with electron capture detector (GC/ECD). The kinetics of the transfer of material from the aqueous phase to the organic phase during the extraction process was also evaluated. The method showed recoveries between 89.5 and 122.7%, with coefficients of variation smaller than 22.9%, and detection limits between 5.9 and 58.9 ng L⁻¹. The method was applied to spiked samples at different concentration levels, and recoveries between 50.5 and 148% were obtained. The extraction process could be described by the Noyes-Whitney diffusion model, and methyl parathion showed the highest rate of transfer between the two phases.

Keywords: single drop microextraction, pesticides, sensitive method, kinetics

Introduction

The contamination of aquatic systems by pesticides can occur in several ways, including leaching from soil^{1,2} and surface run-off during precipitation.³ When present in contaminated water, these pollutants can easily reach the human population because conventional water treatment stations are unable to eliminate pesticides.⁴ The World Health Organization (WHO) has established concentration limit values for a range of substances including some

pesticides (Table 1). In Brazil, these values are set out in Ordinance No. 2914 MS (December 2011), and are equal to the values established by WHO.⁵

In order to meet the increasing demands of legislation, pesticide research has focused on developing methods of analysis that are sufficiently sensitive to quantify these compounds at very low concentrations. The techniques used to extract pesticides from water include liquid-liquid extraction, solid phase extraction,^{6,7} bar sorptive extraction,⁸ solid phase microextraction,^{9,10} dispersive liquid-liquid microextraction,¹¹ liquid-liquid extraction with low temperature partitioning,¹² and single drop microextraction (SDME).¹³

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Table 1. Maximum allowable values for some pesticides in water established by the World Health Organization and Ordinance No. MS 2914

Pesticide	Maximum allowable values / ($\mu\text{g L}^{-1}$)
Trifluraline	20.0
Alachlor	20.0
Lindane	2.0
Methyl parathion	9.0
Endosulfan	20.0
Endrin	0.6
Dieldrin	0.03
4,4'-dichloro-difhenylo-trichloroethane (4,4'-DDT)	1.0

In SDME, the extraction phase is a small drop of a water-immiscible solvent, which is suspended on the tip of the needle of a syringe and immersed in a solution (usually the sample itself).¹⁴ The SDME procedure consists of two steps. In the first step, the analytes are extracted from the matrix into the drop. In the second step, the analytes present in the drop are injected into the instrument for detection.¹⁴

The process of SDME is simple and inexpensive once no sophisticated device is needed for the formation of the single drop. It can be applied for determination of different analytes in different samples, such as pesticides in vegetables^{15,16} and fruit,¹⁷ chlorobenzenes, trihalomethane and metals in water^{13,18-20} and organophosphate in soil.²¹ This technique shows some advantages over conventional liquid-liquid extraction as a low consumption of organic solvents and high enrichment factor.²² In addition, the procedure allows for their combination with various analytical techniques such as gas chromatography, high performance liquid chromatography, capillary electrophoresis, among others. On the other hand, a limitation of this technique is the instability of the single drop at high agitation speeds.¹⁴

The aim of this study was to adapt the SDME extraction technique for the extraction of the pesticides trifluraline, alachlor, lindane, methyl parathion, endosulfan, dieldrin, endrin, and 4,4'-DDT present in water samples. Evaluation was also made of the kinetics of pesticide transfer during the extraction.

Experimental

Standards, samples and reagents

The standards used in this work were trifluraline (99.3%, m/m), alachlor (99.0%, m/m), lindane (99.8%, m/m), methyl parathion (99.9%, m/m), dieldrin (97.9%, m/m), endrin (99.3%, m/m), and 4,4'-DDT (98.8%, m/m),

all obtained from Sigma-Aldrich. The physico-chemical properties of these pesticides are listed in Table 2. The HPLC-grade solvents used for extraction were acetonitrile, ethyl acetate, and *n*-hexane, all purchased from Vetec (Brazil). The water used in the experiments was obtained from a Milli-Q system (Millipore).

Preparation of standard solutions and samples

Stock 1000.0 mg L⁻¹ standard solutions of each pesticide were prepared by solubilization of the standards in acetonitrile. Working solutions containing all the pesticides were prepared at a concentration of 10.0 mg L⁻¹ by dilution of the stock standard solutions in acetonitrile. These solutions were stored in a freezer at a temperature of approximately -20 °C.

The analytical curves were constructed from dilutions of the working solution in acetonitrile.

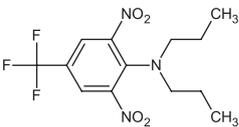
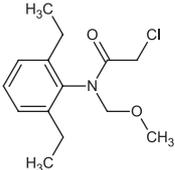
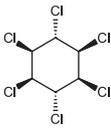
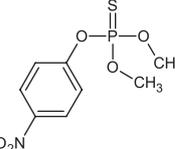
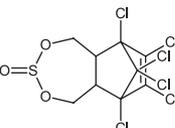
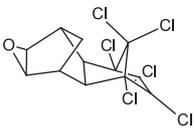
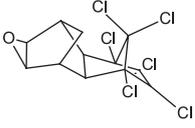
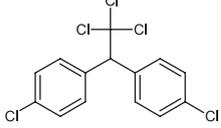
Chromatographic analysis

A gas chromatograph (Shimadzu GC-17A) fitted with an electron capture detector (ECD) and a manual injector was used. The capillary column used to separate the compounds was an Agilent HP-5 (30 m length, 0.25 mm internal diameter, and 0.1 μm film thickness), with a stationary phase consisting of 5% diphenyl and 95% dimethyl siloxane. Nitrogen was used as the carrier gas, at a flow rate of 1.2 mL min⁻¹. The column temperature program was an initial temperature of 150 °C, maintained for 1 min, an increase at 40 °C min⁻¹ to 200 °C, a hold at this temperature for 2 min, then an increase at 5 °C min⁻¹ to 210 °C, a hold at 210 °C for 3 min, then an increase at 3 °C min⁻¹ to 220 °C followed by an increase at 40 °C min⁻¹ to 290 °C and a hold for 2 min. The total analysis time was 16.5 min. The injector and detector temperatures were maintained at 280 °C and 300 °C, respectively. A volume of 1 μL of organic extract was injected into the chromatograph, using a split ratio of 1:5. Figure 1 shows a chromatogram of a 30 $\mu\text{g L}^{-1}$ standard solution, identifying the compounds according to the retention times.

Extraction of pesticides in water by single drop microextraction

The extraction method consisted of placing the aqueous sample in contact with one microdrop of organic solvent that had low miscibility in the aqueous phase. Several variables can interfere in the efficiency of extraction of active compounds from the aqueous phase to the organic phase. Here, univariate analysis was made of the effects of the time of contact between the phases, the aqueous

Table 2. Physical and chemical properties of the pesticides

Pesticide	Chemical structure	Chemical group	log K_{ow} pH = 7 20 °C	Solubility in water 20-25 °C / (mg L ⁻¹)
Trifluraline		dinitroaniline	5.27	0.194
Alachlor		chloroacetanilide	3.09	148
Lindane		organochlorine	3.61	7.3
Methyl parathion		organophosphate	3.0	55
Endosulfan		organochlorine	4.75	0.32
Endrin		organochlorine	5.06	0.25
Dieldrin		organochlorine	5.37	0.19
4,4'-DDT		organochlorine	6.53	0.025

phase stirring speed, and the volume of the microdrop. A 2³ factorial design was used to evaluate the effects of temperature (17 °C and 25 °C), salt (with and without the addition of Na₂HPO₄), and extraction solvent (toluene and *n*-hexane). The experiments were performed in triplicate.

The optimized and validated direct extraction method consisted of placing a 30.00 mL sample of water spiked with pesticides in a glass jar (40 mL) fitted with a polytetrafluoroethylene (PTFE) and silicone septum cap. The dimensions of the vessel were 10 cm (height) by

2.5 cm (diameter), and the height of the water column was 6.5 cm. A 10 µL microsyringe with a steel needle (RN 701, Hamilton, USA) containing *n*-hexane was introduced into the flask, and the tip of the needle was immersed in the aqueous sample at a depth of 2.5 cm. The piston was depressed slowly in order to produce a 1.6 µL microdrop in the solution. The microdrop was maintained in contact with the sample and the flask was shaken at 155 rpm for 30 min at 17 °C. The drop was then retrieved and a 1.0 µL volume was injected into the gas chromatograph. Prior

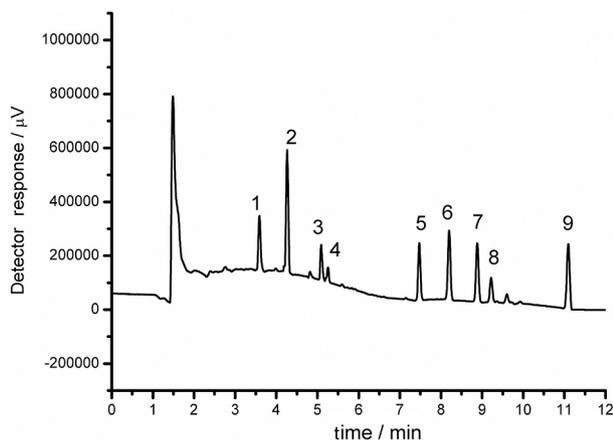


Figure 1. Chromatogram of a $30 \mu\text{g L}^{-1}$ standard solution of pesticides in acetonitrile: trifluraline (1); alachlor (2); lindane (3); methyl parathion (4); alpha- endosulfan (5); endrin (6); dieldrin (7); beta- endosulfan (8) and 4,4'-DDT (9).

to each extraction, the microsyringe was washed with extraction solvent to ensure thorough cleaning and the removal of air bubbles.

Validation of the analytical method

The figures of merit evaluated for the SDME-GC/ECD method were: selectivity, linearity, limits of detection (LOD) and quantification (LOQ), accuracy and precision (repeatability and intermediate precision), and enrichment factors.

Kinetics of transfer of compounds between the aqueous phase and the microdrop

The behavior and kinetics of transfer of the compounds from the aqueous phase to the organic phase was investigated by fortifying contaminant-free water samples with the pesticides. The exposure time of the microdrop in the samples was varied (5, 10, 15, 20, 25, and 30 min), and the agitation speed was kept constant at 155 rpm. After each exposure time, the extracts were injected into the GC/ECD and the peak areas were measured for each compound. The data obtained were then fitted using first and second order models, the intraparticle diffusion model, and the Noyes-Whitney diffusion model in order to identify the model that best explained the extraction of the analytes into the organic phase. The best model was then used to determine the diffusion constant and the saturation concentration.

Water samples

The optimized and validated SDME technique was applied in the analysis of three water samples from the

St. Bartholomew River. These samples were collected at two locations at the Federal University of Viçosa (Viçosa, Minas Gerais) and one location on the BR 482 highway between the towns of Viçosa and Porto Firme (Minas Gerais). Sample 1 was obtained at the capture point of the city's water treatment station, sample 2 was collected at a point outside the city, and sample 3 was from an artificial stabilization pond along the course of the river. The water samples were fortified at two concentration levels (LOQ and $3\times\text{LOQ}$) for each pesticide, and the percentage recoveries were calculated.

Statistical analyses

The statistical analyses were performed using the Statistica software (version 8, StatSoft Corp., Tulsa, EUA).

Results and Discussion

Optimization of SDME experimental conditions

The SDME procedure was optimized by univariate evaluation of the agitation rate, the microdrop volume, and the microdrop exposure time. Agitation speeds of between 60 and 250 rpm were used with an exposure time of 30 min, in order to assess the stability of the microdrop at the needle tip. The microdrop was lost from the end of the needle at speeds exceeding 155 rpm. A speed of 155 rpm was therefore used in all subsequent experiments, because the extraction efficiency increases with the stirring speed. The pH variable was not evaluated, once pesticides studied did not present acid-base behavior. The absence of acid-base character of the compounds was confirmed through software online ACD-Lab²³ and SPARC.²⁴ Thus, the extraction of these analytes were not significantly influenced by this variable.

Different microdrop volumes (1.4, 1.6, 2.0, and 2.4 μL) were exposed for a time of 20 min for extraction of the compounds. The extracts were then injected into the GC/ECD and the areas obtained for each compound were compared. No significant differences were observed in the chromatographic responses, using ANOVA at a 95% confidence level (Figure 2), and a volume of 1.6 μL was selected for use in the subsequent experiments, as described previously.^{25,26}

The effect of the exposure time of the drop was evaluated using deionized water samples spiked with pesticides at a concentration of $100 \mu\text{g L}^{-1}$. This concentration was selected in order to ensure a good chromatographic response for each analyte. The 1.6 μL microdrop was exposed for different times (10, 20, 25,

30, and 35 min) in an attempt to determine the time required to achieve equilibrium between the organic and aqueous phases. However, it was observed that the areas of the chromatographic peaks increased progressively as the contact time was increased (Figure 3), showing that equilibrium was not reached. At exposure times ≥ 35 min, there was loss of the microdrop in the aqueous phase, so the maximum time was restricted to 30 min in all subsequent studies.

These results are in agreement with the findings of Carlos *et al.*,¹³ Cortada *et al.*,²⁵ and Ahmadi *et al.*,²⁶ who found that the chromatographic response increased as a function of the exposure time of the microdrop.

Optimization of extraction solvent type, salt addition, and temperature, in terms of the chromatographic response, was carried out using the full 2^3 factorial design, in triplicate. Analysis using Pareto charts (Figure 4) revealed that for most of the compounds, the effects of ionic strength and temperature were significant at the 95% confidence level ($\alpha < 0.05$), while the effect of solvent type was not significant for any of the compounds studied. The efficiency of extraction decreased when the ionic strength was changed by adding NaH_2PO_4 , and was also poorer at the higher temperature (25 °C). The results for the addition

of salt to the sample are consistent with the findings of Carlos *et al.* for analysis of organochlorine,¹³ Ahmadi *et al.* for analysis of organophosphorus,²⁶ and Cordata *et al.* for analysis of organochlorine compounds in water.²⁵

The addition of salt to the sample usually increases the efficiency of extraction of polar compounds due to the increased ionic strength of the solution.²⁷ However, adverse effects have been observed for SDME.^{25,29} It is likely that in addition to the “salting-out” effect, the presence of salt causes changes in physical properties such as the surface tension of the extraction phase, which could reduce the rate of diffusion of the analyte into the organic phase.

Analyte extraction was not significantly affected by the type of extraction solvent (*n*-hexane or toluene), so *n*-hexane was selected due to its lower solubility in water, which increases the stability of the microdrop. Similar findings were reported by Carlos *et al.*,¹³ for the determination of trihalomethanes in water.

In the case of 4,4'-DDT, there was a significant positive effect of the second order interaction between the variables added salt and temperature, indicating that both factors should be used at the same level, whether positive or negative. Since there were significant negative (–) main effects, all subsequent tests used (–) levels of each factor.

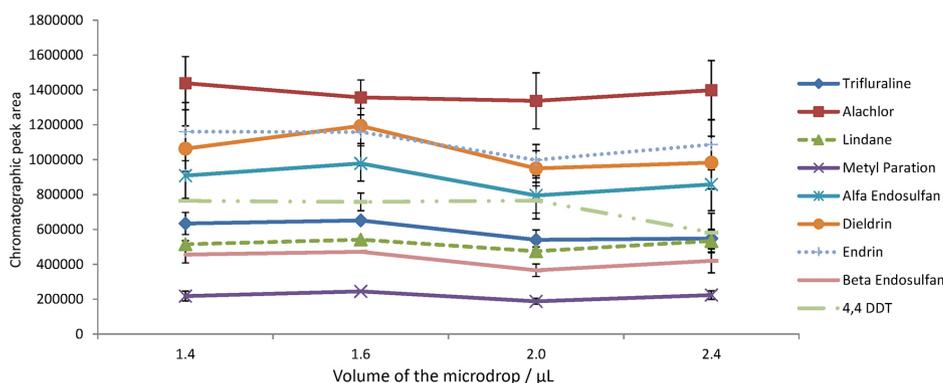


Figure 2. Variation of the chromatographic peak area for each pesticide, according to the volume of the microdrop used in the SDME extraction.

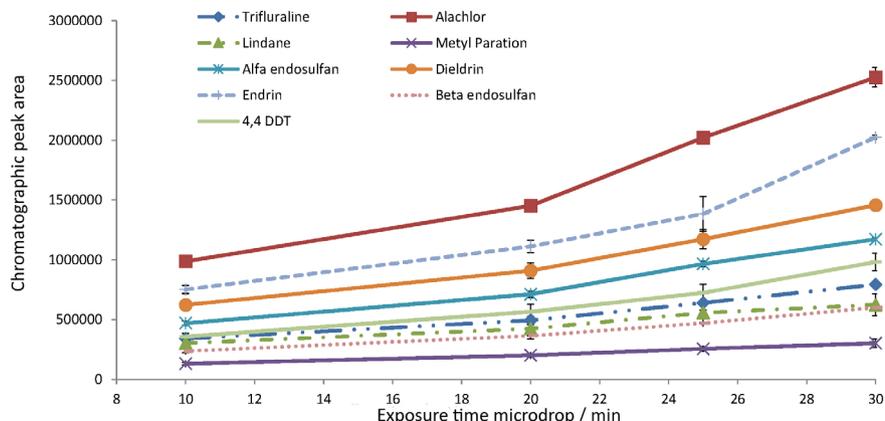


Figure 3. Chromatographic peak areas obtained for the pesticides, as a function of microdrop exposure time.

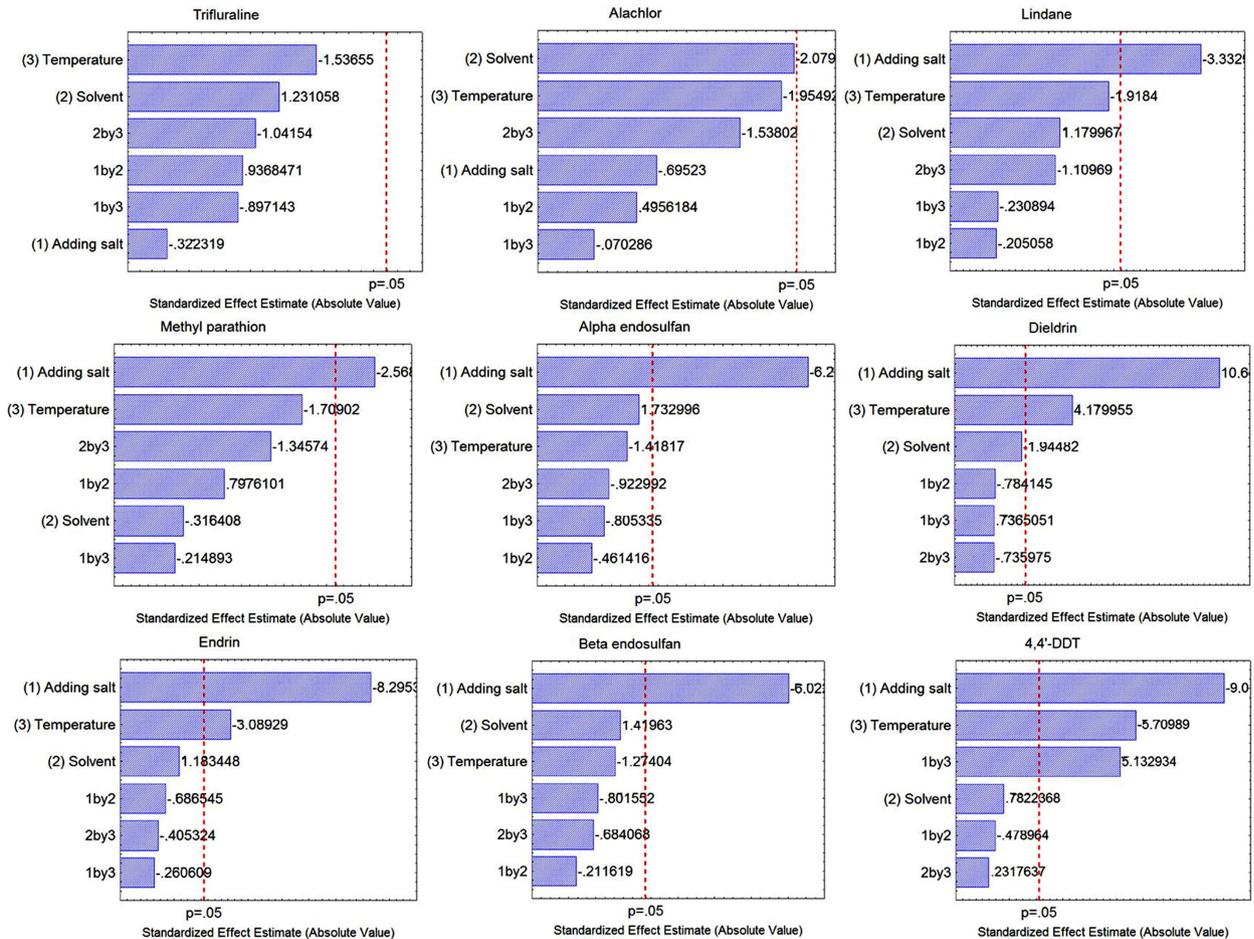


Figure 4. Pareto diagram for the factors adding salt, solvent extractor, and sample temperature for the pesticides.

Validation of the analytical method

Selectivity

About the chromatographic conditions used, the chromatograms obtained for the samples showed no interfering peaks at the retention times of the pesticides (Figure 5), when compared with the chromatograms for spiked sample at a concentration of $20 \mu\text{g L}^{-1}$, which confirmed the satisfactory selectivity of the proposed method.

Linearity

The linearity of the analytical method was evaluated by constructing curves with 5 points, measured in triplicate ($n = 15$). The linear regression correlation coefficients (r) ranged from 0.985 (dieldrin) to 0.994 (methyl parathion), indicating a good correlation between concentrations and peak areas (Table 3). Evaluation of the residuals graph confirmed the good fit.

Limits of detection and quantification

The minimum detectable concentrations were obtained from the signal/noise ratio by comparing the signals

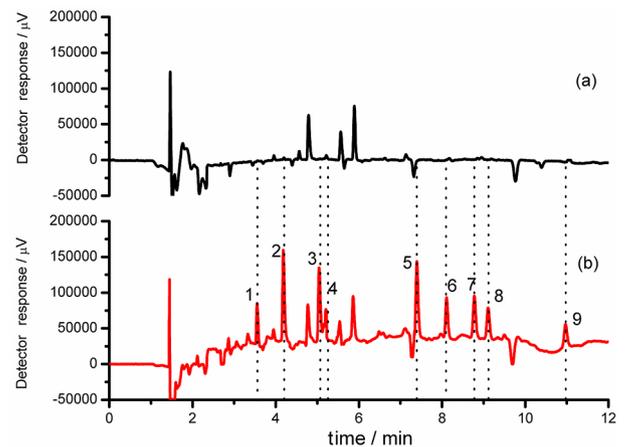


Figure 5. Chromatograms of water samples (a) free sample contamination pesticides (b) sample fortified with pesticides at concentrations equal to $20 \mu\text{g L}^{-1}$: trifluraline (1); alachlor (2); lindane (3); methyl parathion (4); alpha-endosulfan (5) endrin (6); dieldrin (7); beta-endosulfan (8) and 4,4'-DDT (9).

measured for extracts obtained from water sample containing low analyte concentrations with that of the blank. This procedure is valid for analytical procedures that exhibit a baseline, and signal/noise ratios of 3:1 and 10:1

Table 3. Main figures of merit for the validation of SDME method in water

Pesticide	Linearity		LOD / (ng L ⁻¹)	LOQ / (ng L ⁻¹)	Coefficient of variation / %		Recovery / %			EF ^a
	Linear working range / (ng L ⁻¹)	r			Repeatability	Intermediate precision (three non-consecutive days)	LOQ	6 LOQ	12 LOQ	
Trifluraline	60 to 720	0.992	17.8	58.8	22.9	19.8	92.5	104.1	101.7	48
Alachlor	40 to 480	0.994	11.5	37.8	20.6	22.7	103.1	107.4	93.5	17
Lindane	20 to 240	0.993	5.9	19.5	20.1	22.9	95.7	106.1	96.2	448
Alpha-endosulfan	80 to 960	0.993	24.0	79.5	22.8	21.6	122.7	98.5	90.7	22
Methyl parathion	105 to 1269	0.994	32.0	105.6	17.9	21.8	105.7	98.6	90.5	54
Endrin	40 to 720	0.990	12.4	40.8	17.3	21.1	99.4	98.4	96.7	53
Dieldrin	35 to 420	0.985	10.1	33.2	15.3	22.0	97.2	95.1	89.5	64
Beta-endosulfan	80 to 960	0.993	58.9	194.3	20.5	19.7	115.3	93.7	90.4	51
4,4'-DDT	100 to 1200	0.986	30.4	100.0	21.6	22.4	96.5	94.3	92.3	42

^aEnrichment factor.

are accepted as estimates of the detection and quantification limits, respectively. The values found for the detection and quantification limits ranged from 5.9 to 58.9 ng L⁻¹ and from 19.5 to 194.3 ng L⁻¹, respectively (Table 3).

Higher quantification limits were found by Carlos *et al.*,¹³ for the compounds endrin (50 ng L⁻¹) and lindane (30 ng L⁻¹) in water. The value for dieldrin obtained in the present work was higher than that found for the method proposed by Carlos (10 ng L⁻¹),¹³ and lower than that reported by Cortada *et al.* (74 ng L⁻¹) for dieldrin in water.²² For methyl parathion in water, the lowest value (3 µg L⁻¹) was reported by Pinheiro *et al.*²⁹ For the compounds alpha-endosulfan, beta-endosulfan, 4,4'-DDT, and endrin, the quantification limits found in the present study were lower than the values of 213, 237, 337, and 227 ng L⁻¹, respectively, reported by Cortada *et al.*²³

Accuracy and precision

The accuracy of the method was investigated using recovery assays at three concentration levels (LOQ, 6×LOQ, and 12×LOQ). The percentage recoveries varied between 89.5 and 122.7% (Table 3).

The precision of the analytical method was evaluated in terms of repeatability and intermediate precision. The repeatability of the SDME method for the pesticides in water samples was estimated by calculating the coefficient of variation of seven repetitions of the optimized methodology. This involved the preparation, injection, and analysis (on the same day) of seven extracts of reagent water fortified with the pesticides at concentrations equal to six times the limit of quantification of each compound (Table 3).

The intermediate precision of the method was established using the peak areas obtained for the analytes and the

corresponding coefficients of variation obtained from the preparation and analysis of extracts of reagent water fortified with pesticides at concentrations equal to six times the limit of quantification. These analyses were performed using the optimized extraction technique on three different days (1st, 3rd, and 7th day), with seven replicates (Table 3).

Even with a manual method, deviations obtained are always lower than 23%, which is the acceptable limit by Ministério da Agricultura, Pecuária e Abastecimento (MAPA)³⁰ for this concentration range.

Enrichment factor

The enrichment factors were determined by constructing calibration curves using the concentrations of the pesticides in the solvent drop and the concentrations calculated for the water samples. The enrichment factors were mostly between 42 and 64 (Table 3), with the lowest values for alachlor (17) and methyl parathion (22), and a very high value for lindane (448), indicative of its very low affinity for the aqueous phase. The behavior of lindane can be explained by its low molecular weight and lack of oxygen atoms or other species able to promote solvation by water; these species are more prevalent in the polar groups of the other analyte.

Kinetics of transfer of the pesticides from the aqueous phase to the organic phase

The first order, second order, intraparticle diffusion, and Noyes-Whitney diffusion models were applied in order to identify the model that best explained the transfer of the analytes from the aqueous sample to the n-hexane microdrop. An example is provided for lindane (Table 4).

Table 4. Equations, coefficients of determination, standard deviation of the residue and k values for the models studied for the pesticide lindane

Model	Equation	R ²	s _{res} / (ng L ⁻¹)	k / (min ⁻¹)
first order	Y= 43.9(1 - e ^{-kt})	0.97834	1.18	0.03734
second order	Y= 69.485t/(0.0144k ⁻¹ + t)	0.98072	1.11	0.000357
intraparticle diffusion	Y= 5.071 t ^{0.5}	0.92801	2.41	–
Noyes-Whitney	Y= 75.977 - (72.517) e ^{-kt}	0.9846	0.86	0.01528

The model fits were assessed using the coefficients of determination, the residual standard deviations (S_{res}), and the residual plots generated for each kinetic model and each pesticide. The data obtained for lindane are illustrated in Figure 5. It was found that the Noyes-Whitney model gave the best fits for all the compounds, with higher values of R² and lower values of the standard deviations of the residuals. Graphical residual analysis showed that use of this model resulted in the lowest dispersion, compared to the other models. Nonetheless, the data obtained for alachlor, 4,4'-DDT, and dieldrin could not be explained by any of the models evaluated.

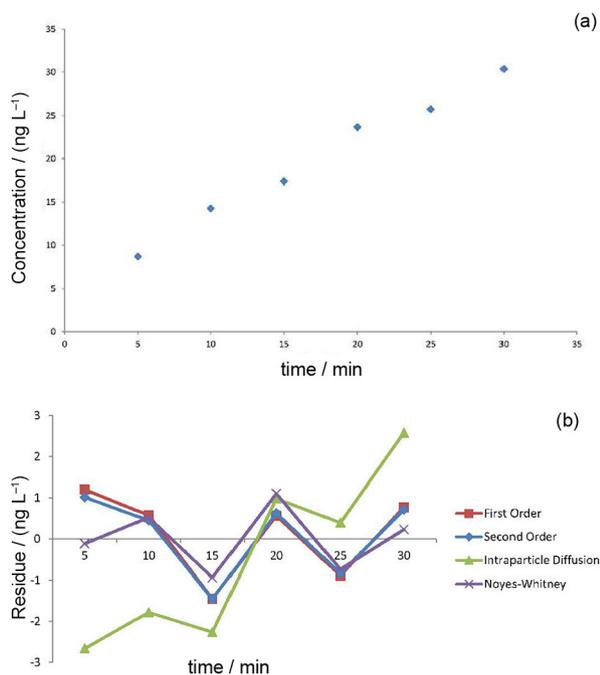
**Figure 6.** Concentration of the pesticide lindane in the organic phase as a function of exposure time in the aqueous phase of the single drop (a) and the graph of residues of the kinetic model adjustments (b).

Table 5 shows the results for the kinetic constants (k), with the highest value for methyl parathion indicating that the transfer rate was fastest for this compound. There was an inverse relationship between the rate constant and the saturation concentration in the microdrop. The saturation concentration is the estimated concentration in

the microdrop when the time approaches infinity according to the equation provided by the fit of the kinetic model of diffusion Noyes-Whitney. The rate constant obtained for endrin was much lower, compared to the other compounds, and its equilibrium concentration was much higher.

Table 5. Kinetic parameters obtained transfer material by the Noyes-Whitney model for pesticides in SDME

Pesticide	Saturation concentration / (ng L ⁻¹)	k / (min ⁻¹)	R ²
trifluraline	69.71	0.0161	0.9897
lindane	75.98	0.0153	0.9846
alpha-endosulfan	23.04	0.0321	0.9531
methyl parathion	39.98	0.0418	0.9624
endrin	22125.83	1.99 × 10 ⁻⁵	0.9457
beta-endosulfan	253.52	0.00716	0.9853

Application of the analytical method using water samples

The procedure was applied for the analysis of three water samples collected in the city of Viçosa. The results showed that the samples were not contaminated by the pesticides. The possible existence of matrix effects during the extraction of the pesticides was investigated by fortifying the samples at levels equal to 1 and 3 times the limit of quantification of each pesticide.

For most analytes, the extraction recoveries ranged from 67.9 to 115.2% (Table 6), showing that the method is suitable for determination of pesticides in water samples. Exceptions were beta-endosulfan and dieldrin, which showed recoveries between 52.5 and 147.6% (for water samples 1 and 3). Differences between the values obtained in these experiments and those found in the validation procedure resulted from the use of concentrations that were closer to the LOQ of the method. These results are similar those obtained by Lambropoulou *et al.*,³¹ which have higher coefficients of variation possibly attributed to the presence of organic matter and suspended solids in water samples. The small matrix effect observed for some compounds in the results can also be attributed to the

Table 6. Percentage of recovery for spiked water samples

Pesticide	Spiked / (ng L ⁻¹)	Water 1 / (% rec. ^a ± RSD ^b)	Water 2 / (% rec. ± RSD)	Water 3 / (% rec. ± RSD)
trifluraline	60	88.7 ± 4.0	86.2 ± 2.3	86.5 ± 9.4
	180	87.0 ± 9.1	85.8 ± 0.8	116.5 ± 3.8
alachlor	40	100.0 ± 6.0	85.0 ± 1.0	98.1 ± 1.3
	120	105.1 ± 1.5	111.4 ± 0.1	112.5 ± 1.5
lindane	20	91.0 ± 7.5	100.8 ± 16.2	105.4 ± 6.1
	60	81.1 ± 3.7	67.9 ± 10.6	98.8 ± 13.0
methyl parathion	105	101.6 ± 12.3	107.4 ± 14.2	104.9 ± 1.8
	315	88.1 ± 10.6	84.5 ± 5.2	107.8 ± 4.8
alpha-endosulfan	80	80.1 ± 13.8	92.2 ± 16.6	115.2 ± 0.1
	240	70.2 ± 4.3	72.9 ± 4.8	77.1 ± 10.4
dieldrin	35	147.6 ± 15.8	108.1 ± 12.1	103.0 ± 11.2
	105	103.3 ± 12.6	99.8 ± 5.8	148.3 ± 12.1
endrin	40	88.7 ± 4.2	89.1 ± 6.3	98.2 ± 2.3
	120	106.1 ± 1.7	76.8 ± 7.1	93.4 ± 19.6
beta-endosulfan	80	81.1 ± 10.6	82.3 ± 2.8	57.5 ± 9.6
	240	52.5 ± 9.3	84.2 ± 3.2	57.3 ± 13.9
4,4-DDT	100	93.3 ± 0.8	72.0 ± 0.5	85.6 ± 1.7
	300	85.7 ± 4.2	83.3 ± 13.1	96.2 ± 5.9

^aPercentage of recovery relative (% rec.); ^brelative standard deviation (RSD).

presence of organic matter and suspended solids present in the water samples.

Conclusions

A method based on single drop microextraction and gas chromatography was developed for the multiresidue analysis of pesticides in water. The technique offers low cost, reduced solvent volumes, and a small number of sample manipulation steps. The method was shown to be linear, selective, precise, and accurate, with a high enrichment factor and low limits of detection and quantification.

No evidence was found for the presence of the pesticides in samples of river water collected in Viçosa.

The kinetic model that best fit was broadcast Noyes-Whitney and kinetic constants for transfer of the analytes to the organic phase were inversely proportional to the saturation concentrations, and among the compounds investigated, methyl parathion showed the highest rate of transfer from the sample (aqueous phase) to the microdrop (organic phase), as well as the lowest saturation concentration.

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