Determination of fenthion in environmental water samples by dispersive liquid–liquid microextraction coupled with spectrofluorimetric and chemometrics methods

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A B S T R A C T

In the present study, a simple, rapid and efficient dispersive liquid–liquid microextraction (DLLME) coupled with spectrofluorimetry (SFM) and chemometrics methods have been proposed for the preconcentration and determination of fenthion in water samples. Box–Behnken design was applied for multivariate optimization of the extraction conditions (sample pH, the volume of dispersive solvent and volume of extraction solvent). Analysis of variance was performed to study the statistical significance of the variables, their interactions and the model. Under the optimum conditions, the calibration graph was linear in the range of 5.0–110 ng mL^{-1} with the detection limit of 1.23 ng mL^{-1} ($3S_b/m$). Parallel factor analysis (PARAFAC) and partial least square (PLS) modelling were applied for the multivariate calibration of the spectrofluorimetric data. The orthogonal signal correction (OSC) was applied for preprocessing of data matrices and the prediction results of model, and the analysis results were statistically compared. The accuracy of the methods, evaluated by the root mean square error of prediction (RMSEP) for fenthion by OSC-PARAFAC and OSC-PLS models were 0.37 and 0.78, respectively. The proposed procedure could be successfully applied for the determination of fenthion in water samples.

1. Introduction

The organophosphorous pesticides (OPPs) have been widely used in agriculture for crop production and fruit tree treatment, but many of them are identified as highly toxic compounds [1–3]. They are released into the environment from manufacturing, transportation and agriculture applications. OPPs have been found in ground waters, surface waters, lagoons and drinking water. Fenthion (O,O-Dimethyl   O-[3-methyl-4-(methylsulfanyl)phenyl]

phosphorothioate) is a contact and stomach organophosphorous pesticide widely used in the control of many sucking, biting pests, especially fruit flies, stem borers and mosquitoes on crops such as alfalfa, rice, sugar, vegetables and forests. Fenthion is toxic for the human and animal health [4–6]. The toxicological effect of fenthion, is almost entirely due to the inhibition of acetylcholinesterase in the nervous system, resulting in respiratory, myocardial and neuromuscular transmission impairment [5, 7]. Due to the low concentration of the analytes and the complex matrix of the samples, a preliminary sample preconcentration and a separation

technique are required. Thus, different extraction processes have been used for separation and pre-concentration of trace pesticide residues, such as solid phase extraction method (SPE) [8–11], solid phase microextraction (SPME) [12], [13], single drop microextraction (SDME) [14] and dispersive liquid–liquid microextraction (DLLME) [15–17]. In the last decades, liquid–phase microextraction (LPME), based on the miniaturization of traditional LLE technique by greatly reducing the use of organic solvent has been reported as an alternative for sample preparations. One of the most popular LPME techniques is dispersive liquid-liquid microextraction (DLLME) which is widely used as a preconcentration method [18-21]. DLLME was developed by Assadi and co-workers [16]. By consisting of the formation of a cloudy solution promoted by the fast addition in the aqueous sample of a mixture of extractor and dispersive solvents. The tiny droplets formed and dispersed among the aqueous sample solution are further joined and sedimented in the bottom of a conical test tube by centrifugation. This method provides many advantages including rapidity, simplicity of operation, high recovery and enrichment factor. After sample preparation, the determination of OPPs in different sample matrices was carried out by using gas chromatography mass spectrometry (GC-MS) [9, 22], gas chromatography (GC) [23–25] and high-performance liquid chromatography (HPLC) [26,27]. Fluorescence spectrometry is a sensitive, selective and relatively low cost method for the quantitative analysis of pesticides and other pollutants [28–30]. Different experimental variables can affect the extraction yield in the DLLME procedure; therefore, a multivariate approach has been widely used for their optimization. Statistical methods are useful to determine the effects of variables on the extraction procedure. The response surface methodology (RSM) based on statistical design of experiments (DOEs) has been extensively used for modelling and optimization in various analytical procedures [31–36]. Response surface methodology (RSM) is powerful multivariate technique that used for building empirical model via collection of mathe-

matical and statistical method. The main advantage of RSM is that it reduces the number of experiment because several factors can be varied simultaneously for optimization and as a result saves time, energy, and chemicals [16,37,38]. Box–Behnken design is the most common and efficient design used in RSM. Box–Behnken design is a second order multivariate technique based on three level partial factorial designs. Box–Behnken is a spherical, rotatable or nearly rotatable that consists of a central point and with the midpoints of the edges of the variable space [15–17], [33, 34]. Two dimensional excitation emission (EEM) fluorescence data can be obtained by measuring the emission spectra at various excitation wavelengths. In recent years, application of multi-way data analysis techniques has increased significantly in the analytical chemistry. There are several multivariate calibration procedures that can be used for the treatment of EEM fluorescence data, in order to quantify the compounds, present in a mixture [39]. In fluorescence analysis, parallel factor analysis (PARAFAC) [28], [40–44] and partial least-squares regression (PLS) [34, 43], [45–47] has been mostly applied for the analyses of three-way data obtained as series of emission spectra measured for different excitations. PLS is a factor analysis method that has been used in multi-component quantitative analysis from several spectral data, such as IR, UV-visible or fluorescence [47]. Partial Least Squares (PLS) regression is a method to predict the response variable based on predictor variables and to describe their common structure. The main advantage of PLS calibration procedures is that they can model a system even in the presence of interfering signals, provided that they are included in the calibration step. PARAFAC is a multi-way decomposition method that has investigated to be useful for the analysis of second-order calibration. The main advantages of the PARAFAC model are the uniqueness, simplicity of its solutions and quantification of an analyte, even in the presence of unknown interferences (the second-order advantage) [40, 44].The orthogonal signal correction (OSC) is a useful pre-processing step that improves the chemometrics model

by filtering systematic variation in the spectra not associated with the concentration [40].

The aim of this paper is to develop a fast, sensitive and inexpensive spectrofluorimetric method coupled with PARAFAC modelling for the determination and preconcentration of fenthion in environmental water samples using DLLME procedure. Also, the effects of various experimental variables, including sample pH, the volume of extraction solvent and volume of dispersive solvent were investigated and optimized using Box–Behnken design.

2. Experimental

2.1. Chemicals and reagents

All chemicals and solvents, such as methanol, ethanol, acetonitrile, chloroform, carbon tetrachloride, chlorobenzene, and dichloromethane were purchased from Sigma–Aldrich and Merck. fenthion standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). All of the reagents used in this work were of analytical grade. Chloroform, carbon tetrachloride, chlorobenzene and dichloromethane purchased from Sigma, Germany. A buffer solution was prepared using universal buffer solution. Universal buffer solutions were prepared by mixing phosphoric, acetic, and boric acid. A stock solution of Fenthion ($C_{10}H_5O_3PS_2$, 1000 mg L^{-1}) was prepared by dissolving appropriate amounts of analyte in methanol, stored under dark conditions in refrigerator (Schema 1) and synthesized by condensation of 4-methylmercapto-m-cresol and dimethyl phosphorochloridothionate. Working standard solutions were obtained daily by appropriately diluting this stock solution with ultrapure water.
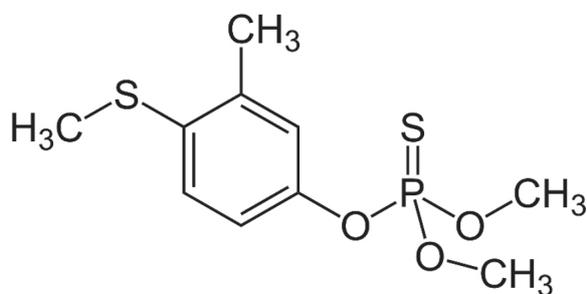
Schema1: Picture of Fenthion as an organothiophosphate insecticide

2.2. Apparatus and software

The pH was determined with a model 780 Metrohm pH-meter with combined glass–calomel electrode. A centrifuge (Sigma) was used to accelerate the phase separation process. A PerkinElmer, LS 45 Spectrofluorimeter enhanced by 150 W Xe lamp was coupled with a computer and equipped with a 300 µL quartz microcell which was used for recording the spectra using Windows 7 operating system. All the measurements were done at the exciting wavelength of 200-300 nm for every 10 nm, and at the emission wavelength in the 300-500 nm range for every 1 nm. Box–Behnken design and statistical analysis were performed with Minitab Version 16. The programs for PLS, PARAFAC, and OSC calculation were written in MATLAB 2018 and run on a personal computer (CPU 3.0 GHz and RAM 4 GB) equipped with the Windows 7 operating system. The applied OSC version is based on the Wold et al. algorithm.

2.3. Experimental procedure

10 mL of sample solution containing 5.0–110.0 ng mL^{-1} of Fenthion, and 1.0 mL of buffer solution (pH was adjusted to 10.0) was poured into a test tube with a conical bottom. Then an appropriate mixture of disperser solvent (methanol, 600 µL) and extraction solvent (chlorobenzene, 220 µL) was rapidly injected into the sample tube. In this step, a cloudy solution was immediately formed in the test tube and then, it was centrifuged for 1 min at 3000 rpm to separate the phases. Finally, the upper aqueous solution was removed by syringe, and the sediment phase was used for subsequent measurement by spectrofluorimetric which was shown in Fig.1.

3. Result and discussion

3.1. Selection of extraction and dispersive solvent

The selection of an appropriate extraction solvent is very important for a DLLME procedure. It must have some properties, such as higher density than water, good extraction efficiency of the analytes, and low solubility in water. Chloroform, carbon
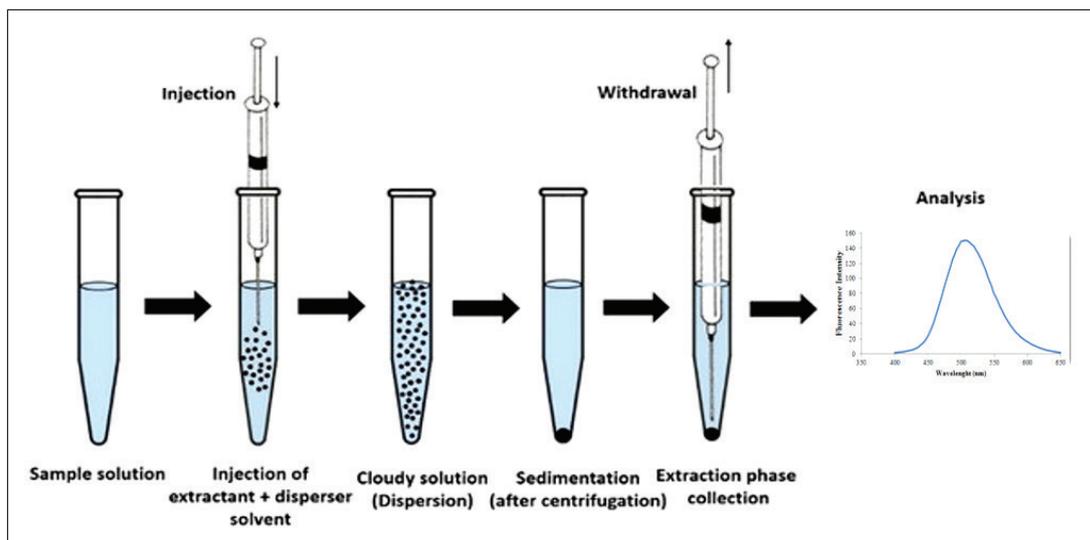
Fig.1. Dispersive liquid–liquid microextraction (DLLME) procedure.

tetrachloride, chlorobenzene and dichloromethane were studied as extraction solvents. The results showed that among the solvents tested, chlorobenzene has the highest recovery in comparison with the other tested solvents. Therefore, chlorobenzene was chosen for further experiments. The dispersive solvent should be miscible with the organic extraction solvent and the aqueous phase. Suitable dispersive solvent can increase the surface area for transferring the analyte from sample to extraction solvent. Thereby, ethanol, methanol, acetonitrile and acetone are selected for this purpose. The results indicated that the best recovery was obtained by using methanol. Thus in this study methanol was selected as suitable disperser solvent.

3.2. Effect of pH and salt addition

The extraction efficiency for analyte can be affected by adjusting the pH of the aqueous solution. The effect of pH variation on extraction efficiency was investigated in the range of 1-12 and the optimal pH was found to be 10 (Fig. 2). The influence of salt addition is also an important factor for extraction. Salt addition can improve extraction yield in DLLME, especially for those analytes with a lower solubility, as a result of a salting out effect. Therefore, NaCl in the concentration range of 1–15% (w/v) was studied as a salting agent and no significant effect on the extraction efficiency was observed. Considering the obtained results, no addition of salt was chosen in the further analysis.
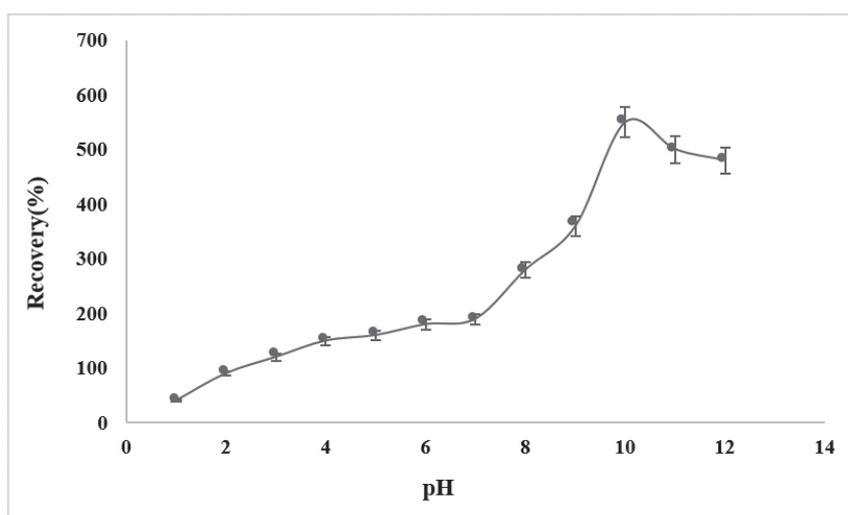
Fig. 2. The effect of pH variation on extraction efficiency

3.3. Effect of extraction and centrifugation time

In DLLME, extraction time is defined as the interval time between injection of the extraction mixture into the aqueous sample and starting to centrifuge. The effect of the extraction time was studied in the range of 1–10 min. The experimental results showed that time has no impact on extraction efficiency. This means that the transfer of the analyte from aqueous phase to the extraction solvent was fast, which was the advantage of DLLME procedure. Therefore, 1 min was defined as extraction time. Centrifugation is a critical step in the DLLME technique, in order to achieve the phase separation of extraction phase from the aqueous phase. So, the effect of centrifugation time was also examined in the ranges of 1–5 min. It was observed that by increasing the centrifugation time, the response remained constant. Therefore, the time and rate of centrifugation had no significant effect on the extraction efficiency. According to this result, 1 min was selected as the optimum centrifuge time, in the following study.

3.4. Box–Behnken analysis

Box–Behnken experimental design was used to optimize and evaluate the main effects and interaction effects of the process variables on the recovery. The sample pH (X_1), the volume of extraction solvent (X_2) and volume of dispersive solvent (X_3) were selected as the three independent variables as showed in Table 1. The number of experiments (N) required for the development of Box– Behnken design was defined as $N = 2k(k-1)+C_0$, (where k was the number of factors and C_0 is the number of central points). Thus, a total of 15 runs were carried out for optimizing these three variables at three levels (low, medium and high). The Box–Behnken design matrix and the recovery are presented in Table 2. According to Box–Behnken matrix, a total of 15 tests containing 3 replicates at the center point were performed in random order. An empirical relationship between the response and the variables can be presented by the flowing equation (Eq.1):

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_i X_i^2 + \sum \beta_j X_i X_j + \varepsilon$$

(Eq. 1)

Where Y is the predicted response and X_i represented the effect of the independent variables. Thus, X_i^2 and $X_i X_j$ represented the quadratic, and interaction terms respectively[7]. β_i, β_{ii} and $\beta_{ij\ (i\neq j)}$ were the coefficient of linear, quadratic and interaction, respectively. β_0 and ε represented the constant and the random error, respectively.

Experimental data were fitted to a second-order polynomial mathematical equation. Analysis of variance (ANOVA) was applied to the analysis of experimental data at 95% confidence interval so that the significance of each term was evaluated by their corresponding *p*-values which are presented in Table 3.

According to Table 3, it was concluded that all the linear (X_1, X_2, X_3 and X_4) and quadratic terms (X_1^2, X_2^2, X_3^2 and X_4^2), were significant at 5% probability level. As shown in Table 3, the interaction between sample pH and volume of extraction solvent (X_1X_2) and the volume of extraction solvent and dispersive solvent (X_2X_3) were significant. The polynomial model is represented in Equation 2:

"Y"=-2068·95+311·71X_1+1·2X_2+1·56X_3-14·98X_1^2-0·01X_2^2-0·03X_3^2+0·04X_1X_2+0·01X_2X_3

(Eq.2)

The 3D response surface graphs of the effect between each factor were shown in Figure 3. The plot in Figure 3 displayed that the recovery increased with the increase of initial solution pH ranging from 9 to 10. However, pH values higher than 10 reduced the recovery. Also, the response first increased with extraction solvent volume approximately 220 µL, and thereafter decreased. The optimum values of the tested variables were obtained as follows: X_1= 10.0, X_2= 220.0 µL and X_3= 600.0 µL.

Table 1. Variables and their levels in Box-Behnken design.

Factors	Symbol	Level		
		Low (-1)	Medium (0)	High (+1)
pH	X_1	9	10	11
V_{ext} (µL)	X_2	100.0	200.0	300.0
V_{disp} (µL)	X_3	500.0	600.0	700.0

Table 2. Box-Behnken design matrix with obtained result.

Run No.	Actual level of factors			Recovery (%)
	X_1	X_2	X_3	
1	10.0	100.0	500.0	59.2
2	10.0	300.0	700.0	78.4
3	10.0	200.0	600.0	97.1
4	9.0	300.0	600.0	77.6
5	11.0	300.0	600.0	69.5
6	11.0	200.0	700.0	73.2
7	10.0	100.0	700.0	71.2
8	9.0	100.0	600.0	60.4
9	10.0	200.0	600.0	95.7
10	11.0	200.0	500.0	68.5
11	11.0	100.0	600.0	70.1
12	10.0	300.0	500.0	81.3
13	10.0	200.0	600.0	96.5
14	9.0	200.0	500.0	65.2
15	9.0	200.0	700.0	71.5

Table 3. Analysis of variance evaluation of linear, quadratic, and interaction terms for each response variable.

Variables	DF[a]	SS[b]	MS[c]	F-values	p-value
Model	9	2092.19	232.465	50.44	0.000
X_1	1	820.22	820.222	177.97	0.000
X_2	1	379.47	379.466	82.33	0.000
X_3	1	374.70	374.700	81.30	0.000
X_1^2	1	828.46	828.463	179.76	0.000
X_2^2	1	536.50	536.503	116.41	0.000
X_3^2	1	518.85	518.848	112.58	0.000
X_1X_2	1	79.21	79.210	17.19	0.009
X_1X_3	1	0.64	0.640	0.14	0.725
X_2X_3	1	55.50	55.502	12.04	0.018
Residual	5	23.04	4.609	-----	-----
Lack-of-Fit	3	22.06	7.352	14.90	0.064
Pure Error	2	0.99	0.493	-----	-----
Total	14				

$R^2 = 98.91$; Adjusted $R^2 = 96.95$.
[a] DF: degree of freedom.
[b] SS: sum of squares.
[c] MS: mean square.
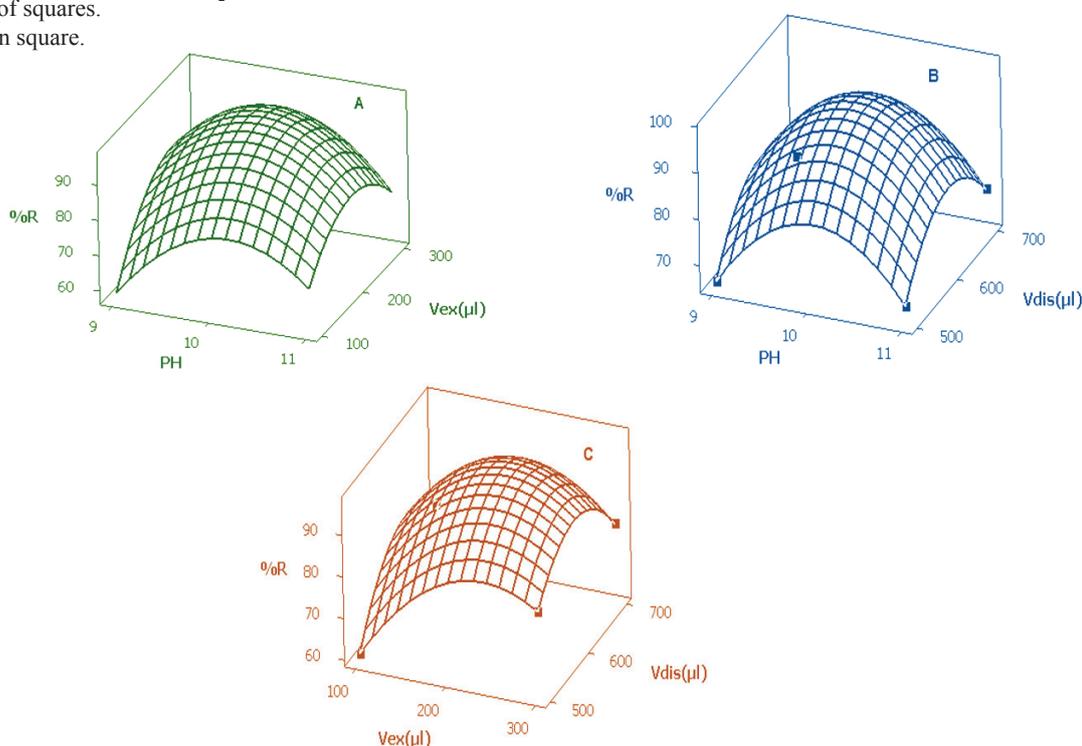
Fig.3. Three dimensional response surface plots representing the effect of process variable on recovery (A): (A) pH–volume of extraction solvent (V_{ext}); (B) pH–volume of dispersive solvent (V_{dis}); (C) volume of extraction solvent–volume of dispersive solvent.

3.5. Statistical analysis

The suitability of the model was analyzed by ANO-VA and the results shown in Table 3. The analysis of variance of regression model demonstrated that the model was highly significant at probability level (p-value is below 0.05). Also, the quality of the fitted model was studied by the coefficients of determination and adjusted the determination coefficient. The coefficient of determination R^2 and adjusted R^2 values were 0.9891 and 0.9695, respectively. In other words, the model could explain 98.91% of the variability in the response. The validation of the goodness of fit was evaluated by the lack of fit test. The lack of fit p-value of 0.064 implies the lack of fit is not significant and it means that the quadratic polynomial model fit the data well.

3.6. Analytical figures of merit

The linear range, repeatability, reproducibility and limit of detections (LODs) for fenthion were investigated under the optimized conditions to evaluate the proposed procedure performance. The Linearity was obtained over the range of 5.0–110.0 ng mL^{-1} with a calibration curve (I=0.024+0.3745C) and with a correlation coefficient (r^2) of 0.9870. The limit of detection which is defined as $3S_b/m$ (where S_b is the standard deviation of the blank signals for ten replicate, and m is the slope of the calibration curve after extraction) was calculated to be 1.23 ng mL^{-1}. Precision, accuracy and stability were evaluated by repeatability (intra-day) and reproducibility (inter-day) analyses. The precision of the method was determined by analysing 5 samples on the same day (intra-day) or 5 samples on consecutive days (inter-day), and represented as RSD%. The intra-day precision was 2.74 % and the inter–day precision was 3.82 %. Finally, the enrichment factor (EF) (calculated from the ratio of the slopes of the calibration curves obtained with and without pre-concentration) of 80.12 for Fenthion were determined.

3.7. Partial least squares analysis

PLS model was prepared and recorded for an excitation wavelength in the 200-300 nm range for each 10 nm, while emission wavelength was in the range of 300-500 nm for every nm. 15 samples were used for calibration set and five samples not used for building the PLS calibration model were selected as a validation test. Using the PLS and OSC-PLS methods, the concentration of fenthion in the validation set were calculated. The predicted concentrations of analyte with these methods are shown in Table 4. In the PLS model, the number of factors was determined by the cross-validation (leave-one-out) method components and the predicted residual error sum of squares (PRESS) was calculated. As shown in Table 4, the optimum number of factors of PLS for fenthion (N.F. = 5) was larger than the theoretically expected value of 1.

OSC is a preprocessing technique that improves the calibration model by removing the information from the spectrofluorimetric data that unrelated to target variables based on constrained principal component analysis. Therefore, the spectral data were preprocessed by OSC method. The results (Table 4) showed that OSC preprocessing has reduced the number of factors (N.F. = 3).

3.8. Parallel factor analysis

The data was then arranged in a 10 × 11 × 251 three-dimensional array consisting of 11 solutions with different fenthion concentrations in the rows (5.0-110.0 ng mL^{-1}), 200 emission wavelengths in the columns, and 10 excitation wavelengths in the slices. For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) were also applied. The obtained results were summarized in Table 4. The RMSEP and RSEP values with OSC-PARAFAC were 0.37, 0.45% for fenthion, respectively. These results confirmed that the OSC-PARAFAC method provided high prediction ability with low RMSEP values with respect to PLS method. Statistical parameters of the linear relationship between the proportion loadings calculated by PARAFAC and OSC-PARAFAC are shown in Table 5.

Table 4. Added and obtained results of the prediction set of fenthion using different methods (ng mL^{-1}).

Added fenthion (ng mL^{-1})	Founded fenthion (ng mL^{-1})			
	PLS	OSC-PLS	PARAFAC	OSC-PARAFAC
15.0	15.7	15.4	14.7	15.1
35.0	36.2	35.8	34.6	35.5
55.0	56.3	56.1	55.8	55.3
75.0	74.2	74.5	75.8	75.5
95.0	92.2	93.6	94.5	95.4
Number of factor	5	3	2	1
PRESS	2.81	1.23	-	-
RMSEP	0.92	0.78	0.64	0.37
RSEP	1.46	1.21	0.74	0.45

Table 5. Statistical parameters of the linear relationship between the proportion loadings calculated by PARAFAC and OSC-PARAFAC.

Parameters	PARAFAC[a]	OSC-PARAFAC[b]
Number of data point	11	11
Intercept	0.0841	0.0103
Standard deviation of intercept	0.4531	0.1381
Slope	0.1241	0.3681
Standard deviation of slope	0.2140	0.0985
Correlation coefficient	0.9412	0.9826

[a] PARAFAC: parallel factor analysis;
[b] OSC-PARAFAC: orthogonal signal correction parallel factor analysis.

3.9. Application of the method in synthesis and real matrix samples

In order to investigate the applicability of the optimized methods for real samples, it was used to the preconcentration and determination of the fenthion in spiked water sample and real samples including three water samples (tap, river and waste water). The concentrations of fenthion were determined by the OSC-PLS, and OSC-PARAFAC and the results are summarized in Table 6. Moreover, the OSC-PARAFAC model was better than OSC-PLS model in terms of the determination of fenthion in complex matrices, without considerable error. The results demonstrated that satisfactory recovery for fenthion could be obtained using the proposed procedures. Hence, the OSC-PARAFAC model was able to predict the concentrations of fenthion in the real matrix samples.

Table 6. Application of the proposed method for the determination of fenthion in real samples.

Sample	Added	Found (ng mL^{-1})			
		OSC-PLS	Recovery (%)	OSC-PARAFAC	Recovery (%)
Tap water	-	N.D.[a]	-	N.D.	-
	50.0	52.3	104.6	50.6	101.2
River water	-	N.D.	-	N.D.	-
	50.0	48.7	97.4	49.3	98.6
Waste water	-	N.D.	-	N.D.	-
	50.0	51.7	103.4	48.6	97.2

[a] N.D.: Not Detected.

4. Conclusions

A simple and efficient DLLME coupled with spectrofluorimetry was developed for the extraction and determination of fenthion in water samples. The proposed method has numerous advantages such as, simplicity and rapidity of extraction and analysis that reduced the organic solvent consumption within a short time. In this study, the RSM based on the BBD was successfully used for optimization of variable the DLLME method that led to a saving of experimental time and materials. PLS and PARAFAC multivariate calibration models, with and without OSC pre-processing, were used for Modelling second-order fluorescence signals and quantification of fenthion. The predicted values obtained by application of OSC-PARAFAC model showed the high predictive ability compared with OSC-PLS method, which explained that the tolerance limit of three-way calibration methods for the matrix effect was better than that of the two-way methods. Therefore, the proposed procedure can be successfully applied for analysis and monitoring of fenthion in water samples.

5. Acknowledgment

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