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RESEARCH ARTICLE

SPECTROPHOTOMETRIC DETERMINATION OF THE DELTAMETHRIN

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ABSTRACT

In the province of Corrientes is found highest production of indoor plants from all Argentina, specially in the northeast of this province. This is because the low frequency orthelack of frosts, allowing a lower cost in the production, since heating is not needed. In this type of cultive is commonly used the deltamethrin, as the result of this, the validation of a simple method comparable with the gas chromatography for the determination of this Pesticide on both, irrigation and consumption water, was studied. In this work, a spectrophotometric method is proposed for the determination of deltamethrin in irrigation water from the area of flower crops located in the Department of Concepción in the province of Corrientes. Deltamethrin solutions in a range from 0,025 to 1 mg/L on irrigation water were prepared. The absorbance spectrum was scanned between 200 and 400 nm. The maximum absorbance was found at 220 nm. A calibration curve in the range from 0.025 to 1 mg/L, responded to A = (0.3246 ± 0.0224) C + (0.0096 ± 0.0068) with R^2 = 0.998. The % RSD was 0.961 indicating good repeatability for the analytical procedure. The accuracy in the recovery experience was 99.0 - 109.6%. The statistical comparison using the t-test and the F-test indicates that there are no significant differences between GC and spectrophotometric methods, with a confidence level of 95%. The specificity and intermediate accuracy tests were satisfactory.

INTRODUCTION

The use of agrochemicals has extended to all regions of the world wherever there are important and high quality harvests. Chemical synthetic products are sprayed on the ground on greenhouses with flower crops. At southeast from the Corrientes capital and towards to the center of the province there is the department of Concepción, where flower crops are cut but mainly in the town of Santa Rosa at 160 km away from Corrientes Capital. Different methods are used for pest control in flower crops, including chemical control based on pyrethroids, which may be causing damage to the health of agricultural workers, as these insecticides are neurotoxic.The analyzes of chemical contaminants in water is often less prioritary than microbiological analyzes, because the adverse effects of chemicals occur in a long-term (http://www.who.int/water_sanitation_health/dwq/dwchem_safety/en/index.html.; http://www.epa.gov/safewater/agua/estandares.html).

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Contamination of water by pesticides occurs when water is drawn from crop fields to the rivers and lagoons where it is introduced into the food chain. Agrochemicals accumulated in water endanger the life of plants and aquatic animals. It can also remain in the tissues of some fish that affect the health of the people who consume them regularly. Because of this, there are regulations that establish the maximum concentrations allowed for some pesticides in the water known as the Maximum Residue Limit for Pesticides (MRLs).To monitor these limits of pesticide residues, representative samples should be obtained and the analyzes performed in laboratories specially dedicated to this task, with capacitated analysts and using methodologies developed and validated under a quality management system. The quality of the results obtained by the laboratory depends on many factors: human, facilities, equipment, trial methods, traceability, calibration and validation of methods, sampling, manipulation and sample management. In order to ensure the quality of the results emitted by the laboratory, it is necessary to validate the methods used, in a way that the recipients feel satisfied and confident by the results provided. Validation is the confirmation, through examination and the provision of objective evidence, that the particular requirements for an

intended specific use are fulfilled[5]. The same is reached by obtaining work parameters, through experimentation and documentation of results, to finally detail and / or correct the procedure. The validation is perfomed by means of recovery tests of fortified samples at different concentrations according to the action levels for each analyte established by the competent authority. This allows determining the efficiency of the method. For routine analysis, it is desirable that the technique be simple, rapid and sensible. The proposed method, which is UV spectrophotometry, meets the previous characteristics. This study proposes and validates an analytical methodology that uses UV spectrophotometry to detect the deltamethrin agrochemical in irrigation water and consumption. The parameters evaluated were: specificity, linearity, precision, accuracy, and limits of detection and quantification (Guía para validación de métodos de ensayo, 2008; Quality control Procedures for Pesticide Residues Analysis, 2004).

MATERIALS AND METHODS

Reagents and samples

Was used a formulation of deltamethrin. The stock solution was prepared in concentration the 50 mg / L in methanol and stored in amber flasks at -20°C. The standard solutions of deltamethrin were prepared by successive dilutions from the stock solution to obtain solutions of 0.025; 0.25; 0.50; 0.75; 1.0 and 2.0 mg L^{-1}, dissolved in irrigation water. Also these solutions were stored in amber flask at -20 ° C. The solvents methanol used in this study were HPLC grade. For the extraction tests, were used Agilent solid phase extraction cartridges.

Equipment

SpectrophotometerS26, UV-Visible brand Boecorange 190-900 nm

Extraction of pyrethroid insecticides in water

The methodology used for the extraction process of pyrethroid insecticides was the solid phase extraction (SPE). It was performed using the following procedure: 30 mL of water was passed through C-18 cartridges. Once the sample was passed it was eluted with 1 mL of methanol (J.T. Baker, HPLC grade). The eluate was read at 220 nm on Spectrophotometer S26, UV-Visible.

RESULTS AND DISCUSSION

Validation of analitical methodology

The specificity of the methodology was evaluated by comparing matrix blank and fortified matrix blank; In addition, to evaluate the accuracy and precision, samples of irrigation water were fortified at four different equivalent concentrations of the calibration curve. To evaluate the intermediate precision, fortified samples were analyzed at the four concentrations, at different time periods.

Matrix effect

In the analysis of agrochemicals, the matrix effect's defined as the variation of the spectrophotometric response induced by the matrix compounds (Hadi, 2006). The matrix effect was evaluated by comparing calibration curves performed in solvent and blank matrix. The results of these tests are evaluated by calculating the percentage of matrix effect and the analysis of covariance[10]. In the evaluation it was observed that deltamethrin has a matrix effect percentage lower than 73%.

Specificity

The comparison between the obtained matrix blank and the fortified blank (lowest concentration of the calibration curve) showed that it was in accordance with the parameters established on the validation of analytical methods of the European Union (SANCO, 2009).

Linearity

According to the results of matrix effect obtained, the linearity of the methodology was evaluated by the preparation of the matrix calibration curves. Table 1 and Figure 1 show the concentration ranges evaluated and the regression parameters (slope, intercept and correlation coefficient)

Table 1. Concentration range and regression parameters obtained

Pesticide	Concentration range mg L^{-1}	Slope	Intercept	R^2
Deltamethrin	0.25-1.00	0.3237±0.0224	0.0096±0.0068	0.998

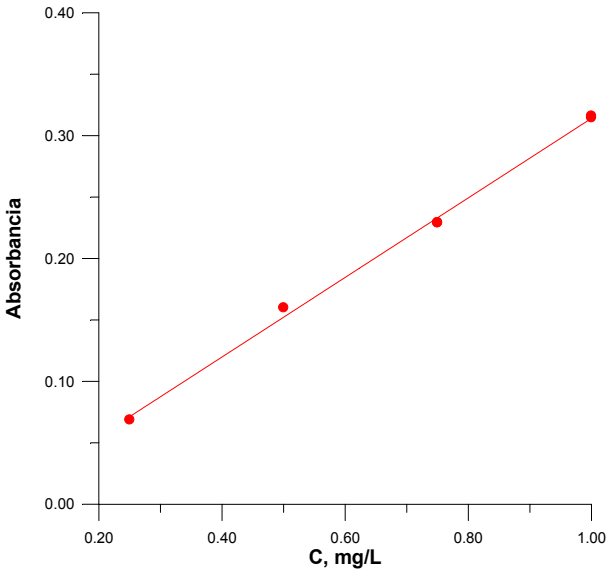

Figure 1. Curve of Calibration of Standards in blank Matrix for Deltamethrin

The first aspect that was evaluated for linearity was the significance of linear regression. By means of a variance analysis, the validity of the model y = mx + b was established with a = 0.05; consequently, the calibration curves are effectively fitted to the proposed model. Once the significance of the model was established, we determined whether the parameters m and b are statistically equal to zero, using a t-test. It was found that, the slope is statistically different from zero (a = 0.05); and that the intercept is statistically different from zero (a = 0.05), which implies that it is indispensable to use the intercept at the time of quantification. Another aspect evaluated corresponds to the correlation between the variables X and Y, (concentration and response of the spectroscopy).

For this evaluation a t-test was applied, which indicated that the correlation coefficient is statistically equal to 1 (a = 0.05).Likewise, a non-linearity adjustment or diversion test was performed to evaluate the concentration ranges in which the curve was drawn and to determine if deviations occur at high or low concentrations as a function of concentration.

Precision

The precision of the methodology was evaluated studying the repeatability and intermediate precision and applying the determination of the coefficient of variation (% CV). Table 2 presents the% CV, we obtained CV% less than 4%, indicating that the dispersion is quite low. As for the values obtained for the intermediate precision, a small increase of the dispersion was observed. With this we can say that there are no perturbations in the spectrophotometric responses and we can conclude that the precision of the methodology does not vary according to the concentration.

Table 2. Parameters corresponding to repeatability for deltamethrin

C [mg/L]	Repeatability	Intermediate Precision
	%CV	%CV
0.025		2.9
0.25	3.1	
0.5	3.7	
0.75	3.4	
1.0	3.2	
2.0		4.3

Accuracy

This validation parameter was evaluated by determining the percent of recovery by fortification of samples at three different concentrations, to which the extraction process were applied. This validation parameter was evaluated by determining the percent of recovery by fortification of samples at three different concentrations, whose the extraction process was applied to. Because of the homogeneity of variances, it is possible to average the percentages of recovery obtained at the different levels of concentration. Figure 2 shows the percentages obtained.

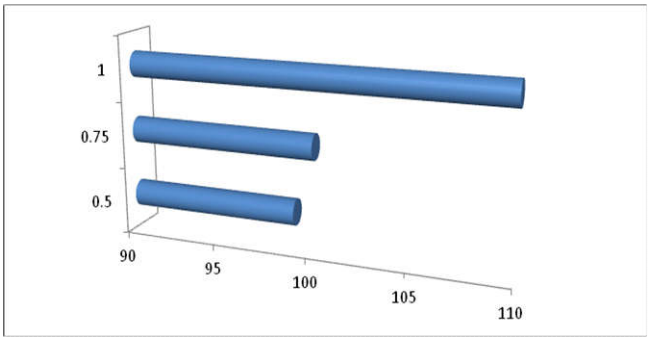

Figure 2. Recovery percentages of deltamethrin

Limits of detection and quantification

The method was linear in the range of the concentrations studied.

The limits of detection (LOD) and limits of quantification (LOQ) reached values of 0.0010 and 2.0 mg L^{-1} respectively. They were calculated as follows:

$LOD = y_A + 3.\ s_A$Ec. 1
$LOQ = y_A + 10.\ s_A$Ec. 2

Where: y_A: intercept; s_A: Deviation of the intercept.

Conclusion

The results of the validation performed showed that the accuracy of the method developed for the analysis of deltamethrin in water irrigation was adequate, expressed as percentage of recovery between 99 and 109.9%.In the evaluation of the precision considering the repeatability, it presented coefficients of variation less than 5% recommended. In the evaluation of the matrix effect, the presence of this effect was evidenced positively during the analysis of the linearity, determining that it was adequate in all the concentration ranges evaluated.

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