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Article

Determination of Fenitrothion in Commercial Formulations by Square Wave Voltammetry and UV-Vis Spectroscopy

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A voltametria de onda quadrada foi utilizada com o eletrodo de gota suspensa de mercúrio para determinar o conteúdo de Fenitrothin em três diferentes formulações comerciais. Em princípio, as determinações de Fenitrothion foram feitas em uma solução tampão BR (pH 10,5) preparada com água pura. Nestas soluções, os limites de determinação e quantificação encontrados foram $5{,}20 \times 10^{-3}$ μmol L^{-1} (1,44 ppb) e $18{,}80 \times 10^{-3}$ μmol L^{-1} (4,8 ppb), respectivamente. Numa próxima etapa, amostras de Periphos CE, Sumithion UBV e Sumithion 500 CE foram diluídas conforme necessário e os conteúdos de Fenitrothion avaliados com a técnica da adição de padrão. Fatores de recuperação, baseados na composição nominal fornecida pelo fabricante foram 108,9, 106,5 e 97% respectivamente. Uma boa concordância foi observada entre os resultados obtidos por voltametria cíclica e por absorção na região do UV-Vis. A principal vantagem observada para a técnica eletroanalítica foi a sua baixa sensibilidade para os outros componentes da formulação. Como conseqüência, esta técnica se mostrou mais rápida e menos dispendiosa do que aquelas mais tradicionais como, por exemplo, cromatografia líquida de alta eficiência ou determinações colorimétricas, nas quais são necessárias etapas prévias de extração, *clean-up* e pré-concentração.

Square wave voltammetry at a hanging-drop mercury electrode was used as the analytical technique to determine Fenitrothion content in three different commercial formulations. Initially, Fenitrothion determinations were performed in BR buffer (pH 10.5) prepared with pure water. In such solutions, determination and quantification limits of 5.20×10^{-3} μmol L^{-1} (1.44 ppb) and 18.80×10^{-3} μmol L^{-1} (4.8 ppb), respectively, were obtained. In the next step, samples of Periphos CE, Sumithion UBV and Sumithion 500 CE were appropriately diluted and the contents evaluated by the standard addition method. Recovery factors, based on the nominal composition given by the manufacturer, were 108.9, 106.5 and 97.6% respectively. A good agreement between the voltammetric and the UV-Vis results was observed. The main advantage of such electroanalytical methodology is related to the low sensibility to other formulation components. As a consequence, this technique is faster and less expensive than traditional ones, such as high performance liquid chromatography or colorimetric determinations, which require extraction, clean-up and pre-concentration steps.

Keywords: Fenitrothion, square wave voltammetry, electroanalysis, commercial formulation, pesticides

Introduction

Fenitrothion (O,O-dimethyl O-4-nitro-m-tolyl phosphorothionate – IUPAC) is a contact insecticide and selective acaricide from the organophosphate family. It is widely used in the control of penetrating, chewing and sucking insect pests (coffee leafminers, locusts, rice stem borers, wheat bugs, flour beetles, grain beetles, grain weevils) on cereals, cotton, orchard fruits, rice, vegetables and forests. It is also used as fly, mosquito and cockroach residual contact spray for farms and public health programs. It is also effective against household insects and all of the nuisance insects listed by the World Health Organization.[1] It is a non-systemic and non-persistent pesticide. Fenitrothion is far less toxic than parathion with a range of insecticidal activity that is very similar. The difference in chemical precursors might make Fenitrothion somewhat more expensive, but it is heavily used in countries where parathion has been banned, including Japan. Fenitrothion is sold in dust, emulsifiable, concentrate, flowable, fogging concentrate, granules, oil-based liquid spray and wettable powder formulations. It is available as a 95% concentrate, 50% emulsifiable concentrate, 40% and 50% wettable powder and 2%, 2.5%, 3% and 5% dusts.

Fenitrothion presents hazardous effects to human health as it promotes inhibition of cholinesterase. In animals the Fenitrothion molecule is oxidized to

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derivatives that contain P=O groups, which are more powerful inhibitors of cholinesterase than thiophosphate itself.[2]

Fenitrothion levels in technical products and formulations are usually determined by the diazo method, colorimetric methods, or gas-liquid chromatography.[3] The common procedure consists of: (*i*) dissolution or extraction, (*ii*) separation of impurities and (*iii*) determination. Granules should be pulverized before analysis. Table 1 presents the conventional methods for Fenitrothion analysis in formulations and technical products. Quantification of the pesticide in commercial products is a matter of importance for both quality control in the chemical industry and in studies of the interaction between the several components of the formulations used. However, to the best of our knowledge, no applications of electroanalytical techniques for Fenitrothion quantification in formulations are available in the literature.

Electroanalytical techniques present some advantages in relation to traditional methods. For example, it is possible to perform the analysis directly in the formulation, without any extraction, clean-up or pre-concentration steps. However, electroanalytical techniques, with a few exceptions, are rarely applied to the analysis of organophosphate pesticides in technical formulations.[4-11] Among the available electrochemical techniques, square wave voltammetry (SWV) has proven to be a very sensitive pulse technique for the detection of organic molecules.[12-13]

In this light, the aim of this study is to determine the content of Fenitrothion in commercial formulations by square wave voltammetry using a hanging-drop mercury electrode (HDME).

Experimental

Reagents

Fenitrothion (MW 277.25, 96.75% pure) was supplied by Bayer, Brazil. All reagents were Merck P.A. grade and were used without further purification. Agrochemical formulations Sumithion UBV®, Periphos CE® and Sumithion 500CE®, containing 800 g L^{-1}, 950 g L^{-1} and 500 g L^{-1} of Fenitrothion, respectively, were supplied by Sumitomo Chemical Co., Brazil. Electrolytes were prepared with water purified in a Milli-Q Millipore Inc. system (conductivity > 10 MΩ). Stock solutions containing

Table 1. Analytical methods for Fenitrothion in technical products and formulations[2,3]

Sample	Sample preparation	Determination
Diazo method		
TG and EC	dissolution (ether) partition (ether / 1% Na_2CO_3)	reduction (Zn-acetic acid) titration ($NaNO_2$) end-point (potentiometer or iodide-starch paper)
Colorimetric method		
TG and EC	dissolution (methanol)	addition (1% Na_2CO_3), determination (free NMC)
WP and dust	extraction (methanol)	400 nm hydrolysis (5 mol L^{-1} KOH), determination (total NMC)
Granule	pulverization extraction (methanol)	400 nm
TLC-UV method		
TG and EC	dissolution ($CHCl_3$) TLC (benzene/diethyl ether=19/1)	determination: 271 nm
WP	extraction (methanol) TLC (benzene/diethyl ether=19/1)	
Dust	extraction ($CHCl_3$) TLC (benzene/diethyl ether=19/1)	
Granule	pulverization extraction ($CHCl_3$) TLC (benzene/diethyl ether=19/1)	
TLC-phosphorus method		
TG and EC	dissolution ($CHCl_3$) TLC	digestion (H_2SO_4 and HNO_3) coloring (ammonium metavanadate and ammonium molybdate) determination
WP	extraction (methanol) TLC	
Dust	extraction ($CHCl_3$) TLC	420 nm
Granule	pulverization extraction ($CHCl_3$) TLC	
GC method		
TG and EC	dissolution (IS solution)	GC: FID2% DC-QF-1, 170 °C
WP and dust	extraction (IS solution) centrifuge	
Granule	pulverization extraction (IS solution) centrifuge	

TG = technical grade; EC = emulsifiable concentrate; WP = water-dispersible powder; NMC = 3-methyl-4-nitrophenol; IS = internal standard (dibutyl sebacate); GC = gas-liquid chromatography.

$2x10^{-3}$ mol L^{-1} Fenitrothion were freshly prepared every week, by dissolving 5 μL of the compound in 10 mL of water containing 10% (v/v) Merck HPLC grade methanol.

The electrolyte consisted of 0.1 mol L^{-1} Britton-Robinson buffer with the pH adjusted by adding the appropriate amount of 1 mol L^{-1} NaOH.

Apparatus

The electrochemical analyses were carried out in an electrochemical trace analyzer, model 394, from EG&G PARC with a hanging-drop mercury electrode (HMDE), model 303A from EG&G PARC as the working electrode. The reference was the Ag/AgCl system and a platinum wire was used as the counter electrode. The pH measurements were carried out using a pH-meter Methrom Titroprocessor, model 682 with a combined glass-calomel electrode. All analyses were conducted at room temperature (25±3 °C).

Spectrophotometric measurements were performed with a VARIAN (Cary/5G/UV-Vis-NIR) spectrophotometer.

Procedures

The electrochemical response of Fenitrothion at the HMDE was analyzed in 0.1 mol L^{-1} BR buffer with pH varying in the range of 3.5 to 10.5 in a $1.25x10^{-6}$ mol L^{-1} Fenitrothion solution. The optimum pH for the Fenitrothion analysis was selected by the maximum current value obtained.

The analytical curves for Fenitrothion were obtained by standard addition of the pesticide to the electrolyte and the evaluation of peak currents in the SWV experiments, in the linear concentration range of $0.092x10^{-6}$ to $0.89x10^{-6}$ mol L^{-1}.

Formulations assay procedure

Aliquots of 5 mL of each commercial formulations: Sumithion 500CE® and Sumithion UBV® were accurately measured and transferred into a calibrated flask containing 10 mL of HPLC grade methanol. The content was then submitted to ultrasound treatment for 10 min. The samples were then diluted to 25 mL with pure water and used as stock solutions. In the SWV experiments, 50 μL of such solution was added to 10 mL of the BR buffer (pH 10.5) in the electrochemical cell (previously de-aerated for 15 min with humidified, ultra-pure nitrogen) and analyzed in the potential range of -0.3 to -0.8 V, by the standard addition method. The same procedure was employed in the UV-Vis analyses (performed at 271 nm - the maximum absorption signal). In both procedures no extraction or clean-up step was introduced.

Discussion

Optimization of SWV parameters

Fenitrothion is reduced at the HMDE, producing a single, cathodic SWV peak at around -0.63 V *vs*. Ag/AgCl (Figure 1). The effect of pH on the SW response was investigated in BR buffer in the pH range of 3.5 to 10.5. It was observed that the peak potential shifted to more negatives values and that peak current varied as the pH was increased. The largest peak current was obtained at pH 10.5, suggesting that this is the optimal value for the analysis procedure.

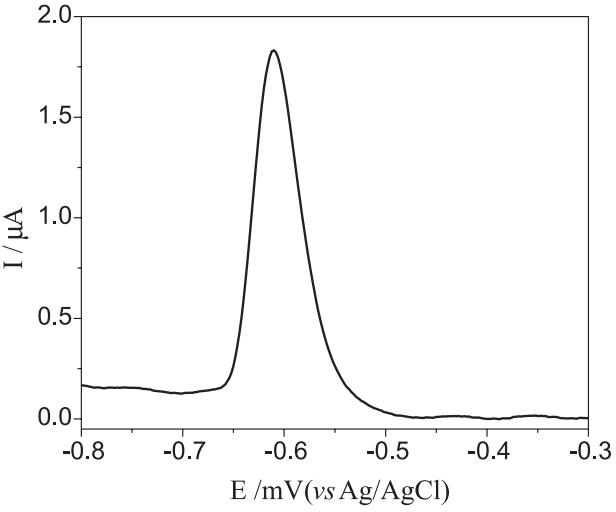

Figure 1. SWV responses for 0.631 μmol L^{-1} Fenitrothion in 0.1 mol L^{-1} BR buffer at pH 10.5, ΔE_s = 2 mV, a = 50 mV, f = 100 s^{-1}.

In order to maximize the analytical signal (peak currents) the SWV parameters were optimized for Fenitrothion reduction in BR buffer with pH 10.5. For that reason, the frequency (f) of application of potential pulses was varied between 10 and 100 s^{-1} for samples containing $5x10^{-6}$ mol L^{-1} Fenitrothion. A constant scan increment (ΔE_s) (the variation of potential in the staircase wave) of 2 mV and pulse amplitude (a) (the variation of the potential of applied pulses in the square wave) of 50 mV, were used. As the frequency increases, the intensity of peak current increases proportionally. The dependence of both parameters generates a straight line with a linear relationship given by $i_p(\mu A) = 0.49 + 0.024f(s^{-1})$, with a correlation coefficient of 0.9998 and n = 3. The linear dependence of peak current and frequency suggests an electrode process controlled by electron transfer to an adsorbed reagent. The peak potential was also displaced towards more negative values as f was increased. The influence of pulse amplitude (a) in the SWV profile was

evaluated under the same conditions, but at a constant frequency of 100 s^{-1}. The pulse amplitude was varied from 10 to 100 mV. A linear increase in the peak current was obtained for *a* values up to 50 mV. After this point the relationship lost its linearity. For that reason, the value of 50 mV was selected for *a*. Finally, the influence of scan increment (ΔE_s) was studied between 1 and 5 mV. The peak current increased with ΔE_s. For ΔE_s values above 2 mV, a widening of the reduction peak occurs thus diminishing the resolution of the square wave technique. Therefore, a value of 2 mV was selected for the analytical determinations.

Analytical curves in pure water electrolyte

The consecutive additions of Fenitrothion to the 0.1 mol L^{-1} BR buffer, pH 10.5, prepared with pure water resulted in the SWV responses displayed in Figure 2. The peak currents obtained from the voltammograms were linearly related to the pesticide concentration between 0.093 and 0.89 μmol L^{-1}, with an analytical equation given by:

$$i_p\ (mA) = (8.6x10^{-3} \pm 0.4x10^{-3}) + (0.29x10^{7} \pm 0.01x10^{7})\ C\ (mol\ L^{-1})$$
$$r = 0.9997,\ n=5 \qquad (1)$$

Detection and quantification limits were obtained from IUPAC[14-16] and are given as LOD = 3s/m, LOQ = 10s/m, where s is the standard deviation for an avergae of 10 blank current values taken at the same potential of the Fenitrothion peak and m is the slope of the linear relationship between peak current and concentration (equation 1). Here, the values obtained for pure electrolyte were $5.20x10^{-3}$ μmol L^{-1} (1.44 ppb) and $18.80x10^{-3}$ μmol L^{-1} (4.80 ppb), respectively.

Determination of Fenitrothion in commercial formulations

The SWV responses in the three formulations under study were obtained by diluting the appropriate amount of each formulation in BR electrolyte, pH 10.5, in order to obtain approximately 0.09 μmol L^{-1} Fenitrothion in solution, following the nominal concentration of the active principle in each formulation. The voltammograms are presented in Figure 3, where lines *e* and *f* represent the responses after addition of 1.01 and 2.02 mmol L^{-1} Fenitrothion from the stock solution. The peak potential observed, at -0.63 V is coincident with that obtained in pure water, Figure 2. A first approach analysis of the peak current values with the analytical curve obtained in pure electrolyte indicates measured concentration values that

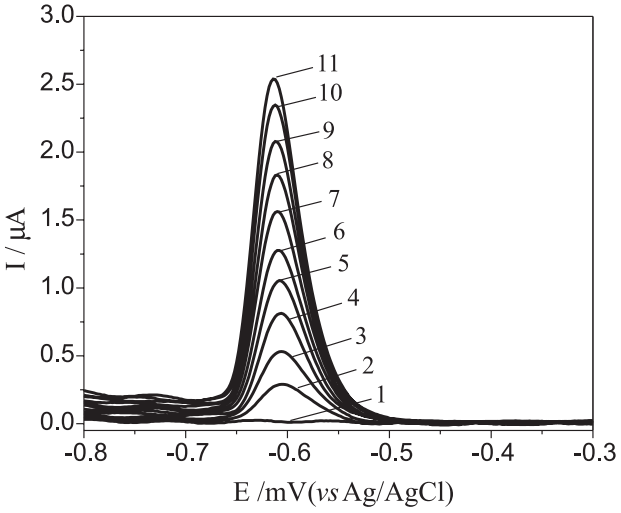

Figure 2. SWV responses for several concentrations of Fenitrothion in 0.1 mol L^{-1} BR buffer at pH 10.5: (1) supporting electrolyte, (2) 0.09, (3) 0.18, (4) 0.28, (5) 0.37, (6) 0.45, (7) 0.54, (8) 0.63, (9) 0.72, (10) 0.80, (11) 0.89 mmol L^{-1}, f = 100 s^{-1}, a = 50 mV and ΔE_s = 2mV.

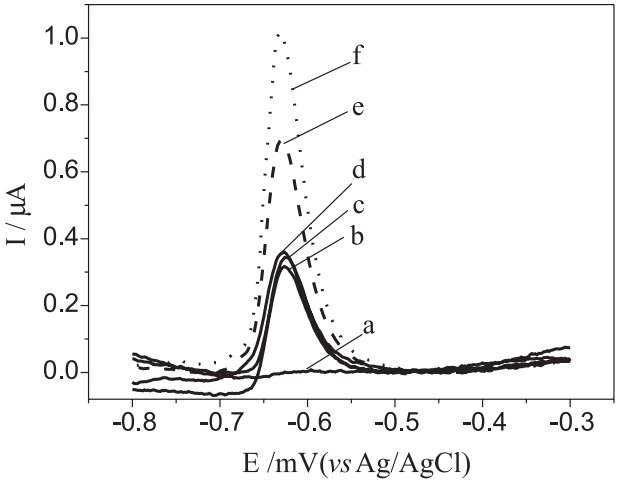

Figure 3. SWV responses for commercial formulation samples (diluted to labeled 0.09 mmol L^{-1} Fenitrothion). (a) 0.1 mol L^{-1} BR buffer (blank); (b) Sumithion 500CE; (c) Sumithion UBV; (d) Periphos CE; (e) after addition of 0.09 mmol L^{-1} Fenitrothion; (f) after addition of 0.18 mol L^{-1} Fenitrothion. f = 100 s^{-1}, a = 50 mV and ΔE_s = 2mV.

vary less than 5% from those specified by the manufacturer. Thus, no significant interference from other formulation components was detected in the peak potential range.

The analyses of pesticide content in formulations were then performed by the standard addition method described in the Experimental section. Four consecutive additions of 1 mmol L^{-1} from standard solution of Fenitrothion were performed and the results are presented in Figure 4. Extrapolation of the straight lines obtained allows the quantification of Fenitrothion in each sample. The results for two initial concentrations of the formulation are

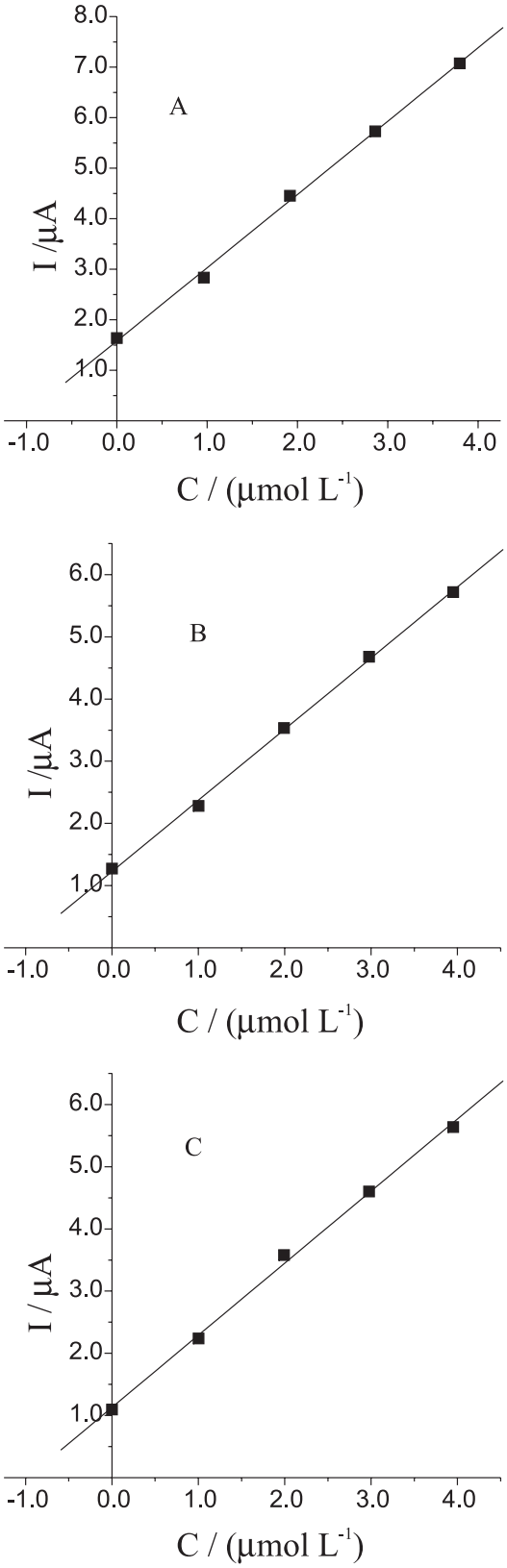

Figure 4. Analytical curves after the standard addition in the commercial formulation samples (diluted to labeled 0.09 mmol L^{-1} Fenitrothion). (a) Periphos CE; (b) Sumithion UBV; (c) Sumithion 500CE. Four consecutive additions of aliquots containing 1.0 mmol L^{-1} Fenitrothion.

presented in Table 2. All experiments were repeated 5 times. For comparison, the same methodology was repeated and the Fenitrothion amounts were obtained by UV-Vis spectroscopy. The spectra are shown in Figure 5 for three formulation samples that were calculated to contain approximately 1.01 μmol L^{-1} Fenitrothion. Again, lines *e* and *f* represent the responses after the addition of 1.01 and 2.02 μmol L^{-1} Fenitrothion to the electrolyte. The standard addition method was used again and the results, which are quite similar to those presented in Figure 4, are presented in Table 3. A comparison of recovery factors obtained with electrochemical and UV-Vis methods demonstrated

Table 2. Data from the recovering experiments with the formulations

Formulations	Labelled (μmol L^{-1})	Recovered (μmol L^{-1})	Average recovery (% ± SD)
Periphos CE	0.090	0.093	103.0 ± 4.1
	1.01	1.100	108.9 ± 3.5
Sumithion UBV	0.090	0.089	99.4 ± 3.9
	1.010	1.076	106.5 ± 2.8
Sumithion 500CE	0.090	0.086	95.0 ± 3.7
	1.01	0.985	97.6 ± 4.1

Each value is the mean average of five determinations.

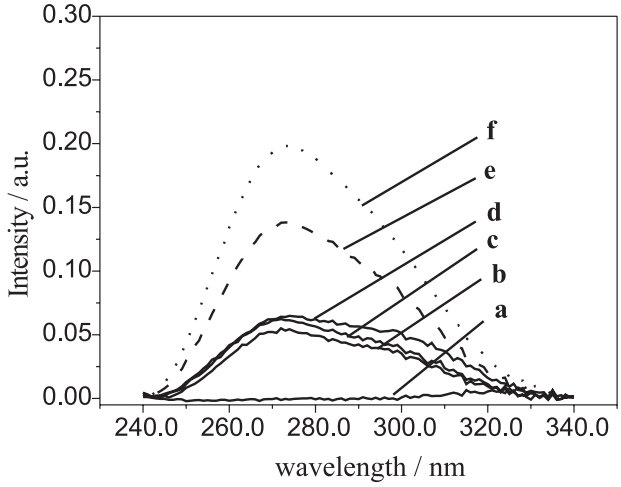

Figure 5. UV-Vis spectrum for the commercial formulation samples (diluted to labeled 1.1 mmol L^{-1} Fenitrothion). (a) 0.1 mol L^{-1} BR buffer (blank); (b) Sumithion 500CE; (c) Periphos CE; (d) Sumithion UBV; (e) after addition of 1.01 mmol L^{-1} Fenitrothion; (f) after addition of 2.02 mmol L^{-1} Fenitrothion.

Table 3. Determination of Fenitrothion by UV-vis spectrophotometry

Sample	Labelled (μmol L^{-1})	UV-Vis (% ± SD)
Periphos CE	1.01	105.5 ±3.1
Sumithion UBV	1.01	105.9 ±3.5
Sumithion 500CE	1.01	96.7 ±3.8

Each value is the mean average of five determinations.

comparable values, thus confirming the suitability of the SWV technique for such determinations.

Conclusions

An electroanalytical procedure involving SWV and HMDE was used to determine Fenitrothion content in commercial formulations. The main advantage of such a procedure is the possibility to determine the concentration of the active component directly from the pesticide formulation, without the need for any prior steps (e.g. isolation, clean-up, pre-concentration), which are indispensable in many other analytical procedures.

For that reason, the analyses performed in the present paper are fast, cheap and do not require the manipulation of organic solvents or other toxic substances.

Moreover, the low values obtained for detection and quantification limits in pure electrolytes suggest that the methodology used is suitable for use in the quality control of drinking water. This would help prevent Fenitrothion contamination in situations where the possibility of pesticide contamination of water sources must be considered (especially in plantations for crops such as strawberry, potato and tomato).

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