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# Validation of a solid-phase microextraction method for the determination of organophosphorus pesticides in fruits and fruit juice

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**Abstract**

A method for the determination of organophosphorus pesticides (diazinon, fenitrothion, fenthion, quinalphos, triazophos, phosalon and pyrazophos) in fruit (pears) and fruit juice samples was developed and validated. The samples were diluted with water, extracted by solid-phase microextraction (SPME) and analysed by gas chromatography (GC) using a flame photometric detector in phosphorous mode. Limits of detection of the method for fruit and fruit juice matrices were below 2 μg/kg for all pesticides. Relative standard deviations for triplicate analyses of samples fortified at 25 μg/kg of each pesticide were not higher than 8.7%. Recovery tests were performed for concentrations between 25 and 250 μg/kg. Mean recoveries for each pesticide were all above 75.9% and below 102.6% for juice, and between 70 and 99% for fruit except for pyrazophos in the fruit sample (with mean recovery of 53%). Therefore, the proposed method is applicable in the analysis of pesticides in fruit matrices and the use of the method in routine analysis of pesticide residues is discussed. 

*Keywords:* Fruits; Fruit juices; Sample handling; Food analysis; Pesticides; Organophosphorus compounds

## 1. Introduction

Routine methods used in pesticide residue analysis are often time and solvent consuming due to steps of sample preparation before the chromatographic analysis.

The analytical control of a large number of agricultural and agroindustrial samples is likely to continue, although most samples will present concentrations below the maximum residue limit (MRL) allowed for pesticides. On the other hand, there will be many samples with pesticide residues below the limits of quantification (or even detection) by the methods of analysis currently available.

Solid-phase microextraction (SPME) was introduced in 1990 by Arthur and Pawlizyn [1]: a silica capillary coated with a polymeric compound is dipped in the solution to be analysed. This fiber is then transferred to the gas chromatograph. The compounds are desorbed at the high temperature of the injector and analysed by gas chromatography (GC). It is a rapid and simple procedure of extraction with a great capacity of concentration without need of any organic solvent.

Since 1990 the use of SPME has been increasing

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for the extraction of organic compounds from several matrices.

In agricultural and agroindustrial samples the technique has been applied mainly to the characterisation of commodities such as tobacco [2], alcoholic beverages [3,4], juices [5], herbs and spices [6,7].

In water samples, SPME has been used for the analysis of pollutants such as polycyclic aromatic hydrocarbons [9], BTX [8,9], fatty acids [10] and phenols [11,12]. SPME has been extensively used also for extraction and concentration of pesticides from simple aqueous samples [11,13]. However, SPME has not been used in the analysis of pesticide residues in agricultural commodities: the complex matrices of such products may cause interference in the extraction procedure.

In this work we describe a method, proposed for analysis of pesticide residues in fruit and fruit juices, using a sample preparation step by SPME.

## 2. Experimental

### 2.1. Materials

Pesticides Pestanal grade from Riedel-de Haën (Seelze, Germany) were used without further purification (degrees of purity were >95% for all pesticides except for triazophos which had a degree of purity of 70%). For the preparation of standard stock solutions, acetone Pestanal from Riedel-de Haën was used. Working solutions of pesticides were prepared daily with water obtained from a Milli-Q water purification system from Millipore (Bedford, MA, USA).

Apple pectin (galacturonic acid content >77.5%), Pectinase and sodium dodecyl sulphate (95% purity) from Sigma (Madrid, Spain) were used.

One hundred percent pear/apple juice, apple and peach nectar and pears commercially available were used.

### 2.2. Apparatus

A SPME fiber holder for manual use and fibers of PDMS (polydimethylsiloxane, 100 μm), CW–DVB (Carbowax–divinylbenzene, 65 μm), PDMS–DVB (polydimethylsiloxane–divinylbenzene 65 μm) and PA (polyacrylate, 85 μm) from Supelco (Bellefonte, PA, USA) were used.

A magnetic stirrer AM3003 from Bioblock Scientific (Strasbourg, France) was used for stirring the samples during extraction.

A blender from Waring (New Hartford, CO, USA) and an Ultraturrax T25 from IKA (Staufen, Germany) were used to comminute and homogenise the fruit samples.

A Beckman (Glenrothes, UK) J2-21M/E centrifuge was used to separate suspended matter from samples.

Gas chromatographic analyses were carried out in a Fisons (Rodano, Italy) GC 8000 series gas chromatograph equipped with a split-splitless injector, a flame photometric detector in phosphorous mode and the data acquisition system Chrom-Card also from Fisons.

### 2.3. Conditions

The column used was a DB-1 (15 m×0.32 mm I.D., 0.25 μm) from J&W (Folsom, CA, USA). The temperature program was 100°C to 230°C at 20°C/min, 1 min at 230°C. The injector was at 250°C, the base of the detector was at 250°C and the body of the detector was at 150°C. Carrier gas was hydrogen with an inlet pressure of 90 kPa.

SPME conditions used for method validation were as follows: 20 min of immersion of the PDMS fiber in the stirred solution (3 ml, 1250 rpm) at room temperature and 2 min in the GC injector for thermal desorption.

### 2.4. Preparation of standard solutions

Individual solutions of about 1 g/l of each pesticide (diazinon, fenitrothion, fenthion, quinalphos, triazophos, phosalon and pyrazophos) were prepared in acetone. A stock standard solution of 10 mg/l of each pesticide was prepared in acetone.

Working solutions with concentrations of 0.050, 0.250, 1, 5, 10, 25, 100 and 500 μg/l of each pesticide were prepared in water. For method development solutions of 10 and 100 μg/l were used. For method validation, solutions of 0.050, 0.250, 1, 5, 25, 100 and 500 μg/l were used.

### 2.5. Sample preparation

Samples of 20 g of juice were spiked at 25, 50, 100 and 250 μg/kg and samples of 20 g of fruit were fortified at 25, 100 and 250 μg/kg with the stock solution containing 10 mg/l of each pesticide.

For validation purposes, fortified juice samples were analysed after 1/100 dilution with water. Fortified fruit samples were comminuted and homogenised with 60 ml of water. Homogenate (4 ml) was further diluted to 100 ml.

## 3. Results and discussion

### 3.1. Method development

Conditions for SPME were tested using standard solutions of 10 and 100 μg/l and the following parameters were adjusted to optimise extraction: the type of fiber, the speed of stirring and the immersion time.

Several procedures were tried in order to improve the accuracy of the method: filtration, centrifugation, addition of pectinase and dilution.

#### 3.1.1. Analysis of standard solutions

##### 3.1.1.1. Comparison of fiber coatings

. As there are different coating materials used for SPME, it was necessary to compare the performance of different fibers in extracting pesticides from the aqueous solution. For comparison of fiber coatings, a standard solution of 100 μg/l of each pesticide in water was analysed with the different fibers.

For each fiber, the areas measured in the chromatogram for each pesticide were compared with the corresponding peak areas obtained in the analysis by direct injection of 1 μl of a solution with the same concentration: these comparisons of areas are convenient in order to account for the different response factors of the GC detector for each pesticide. The ratios between the peak areas obtained by SPME and the peak areas obtained by direct injection were used as a measure of the performance of the fiber to extract pesticides from the solution: these ratios are presented in Table 1 showing that PDMS–DVB fiber was the most effective in concentrating pesticides.

Table 1
For each pesticide, the values represent the ratio of the areas of the peaks obtained with different fiber coatings (analysis after 20 min immersion in 3 ml of a stirred standard solution of 100 μg/l in water) and the areas of the corresponding peak obtained for direct injections of 1 μl of a standard solution (100 μg/l in acetone)

| | PDMS | PA | CW–DVB | PDMS–DVB |
|---|---|---|---|---|
| Diazinon | 262 | 117 | 179 | 312 |
| Fenitrothion | 165 | 183 | 247 | 385 |
| Fenthion | 302 | 248 | 310 | 341 |
| Quinalphos | 202 | 178 | 241 | 305 |
| Triazophos | 92 | 180 | 283 | 312 |
| Phosalon | 277 | 275 | 272 | 438 |
| Pyrazophos | 229 | 228 | 264 | 414 |

Nevertheless, PDMS fiber was preferred for subsequent analyses in this work due to its robustness (over 100 injections) and because it allowed a larger range of concentrations to be analysed in the same detector range.

##### 3.1.1.2. Speed of stirring

. The efficiency of extraction may be increased by stirring of the aqueous solution and it is important to maintain a constant stirring speed in order to obtain reproducible results. As it is not possible to reach equilibrium conditions in a short time, as shown in the following section, PDMS fiber was exposed to a standard solution (10 μg/l) for 10 min at different stirring speeds. Glass magnetic stirring followers were preferred over PTFE because it was found that PTFE adsorbed the analytes.

Fig. 1 shows that, at all stirring speeds, the signal does not reach a maximum. Nevertheless, the slopes of the curves were lower at speeds >500 rpm than at lower speeds and therefore the maximum speed (1250 rpm), where larger areas were achieved, was chosen for the subsequent analyses.

##### 3.1.1.3. Immersion time

. The time of contact should be sufficient to allow the fiber to sorb a significant quantity of analyte.

The influence of immersion time was evaluated using a standard solution (10 μg/l) in water stirred at 1250 rpm. After 80 min equilibrium had not yet been reached, as shown in Fig. 2, which suggests that it will not be practical to try the use of the full capacity of the fiber: immersion times shorter than equilibration times will be used in analyses by

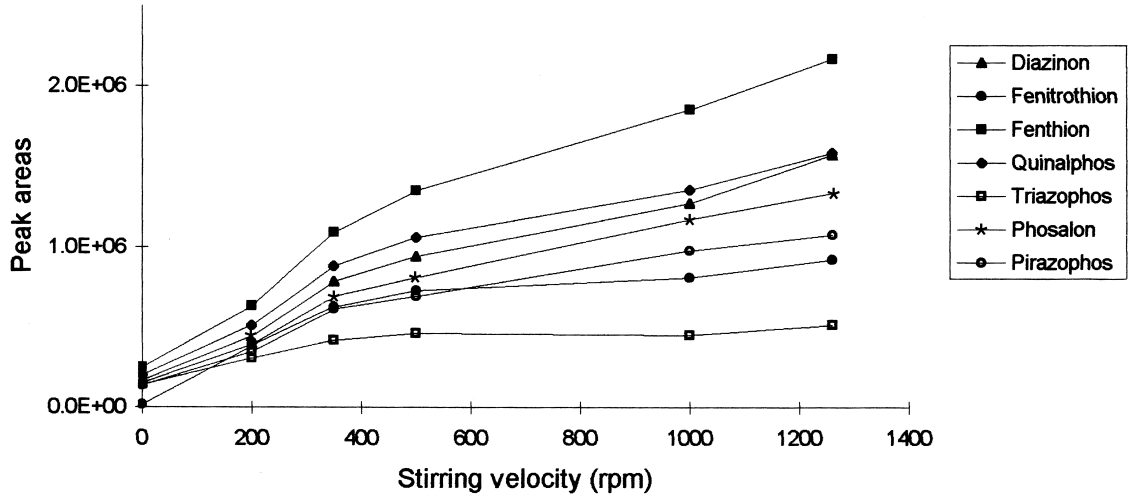


Fig. 1. Variation of peak areas with stirring (standard solution of 10 μg/l analysed with the PDMS fiber after 10 min of immersion).

SPME, but both time of immersion and stirring speeds have to be carefully controlled.

*3.1.2. Analysis of spiked samples*

In order to study the accuracy of the method, samples of fruit nectars and juices were fortified and analysed under the same conditions as standard solutions. Low recoveries (percentage of expected area by comparison with standard solution) in analyses of spiked samples usually correspond to low

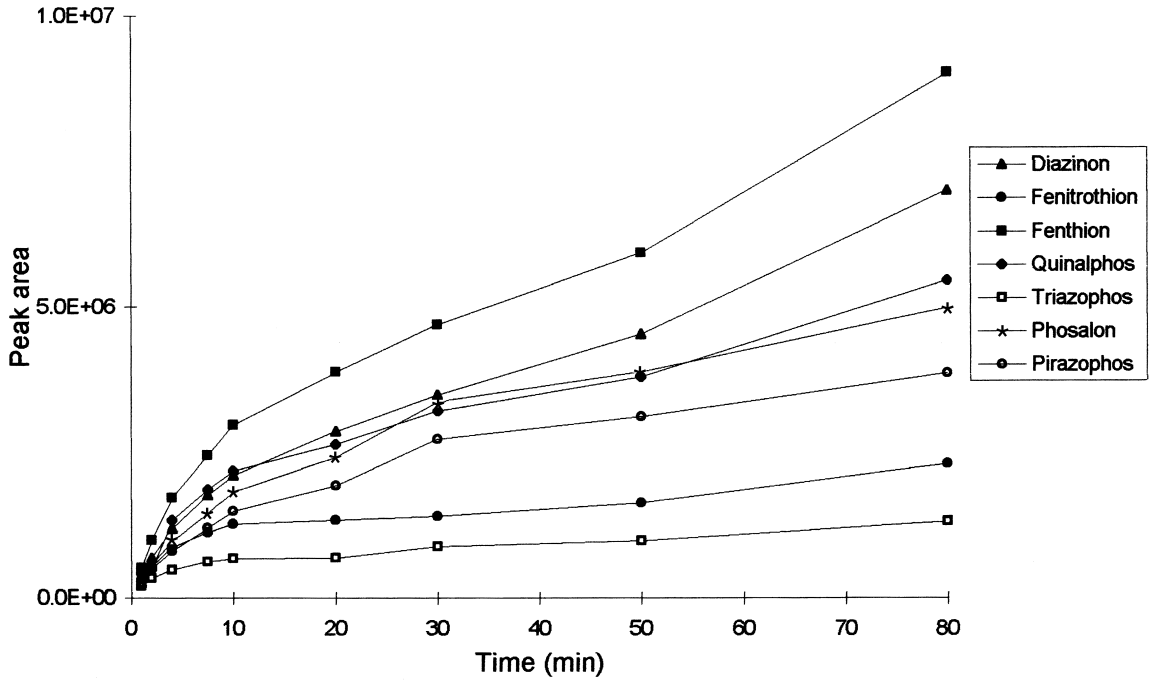


Fig. 2. Variation of peak areas with time of immersion (10 μg/l standard solution stirred at 1250 rpm analysed with the PDMS fiber).

accuracy. The use of internal standards and surrogates may be used to correct such deviations but, in order to assure the accuracy of the analytical method, it is preferable to set up experimental conditions in order to have similar areas for samples and standards of the same concentration.

*3.1.2.1. Identification of the origin of the interference*

. Small recoveries (usually <10%) were found in the analysis of nectars fortified with several pesticides at 100 μg/kg. In clarified apple juice the recoveries were all >70% [14] leading to the conclusion that suspended matter could interfere with the analysis.

Some tests were performed on standard solutions and spiked samples in order to identify the origin of the interference:

1. On centrifuging the sample at 21 000 rpm before SPME analysis, the recoveries increase to about 10–30%. When samples were fortified *after* the centrifugation, all recoveries became >40%, confirming that suspended matter is causing interference in the extraction by SPME.
2. Sodium dodecyl sulfate (SDS) was used as a model to test the effect of the possible existence of emulsion in the samples. SDS was added (3 mg/ml) to a standard solution of pesticides (100 μg/l) so that a concentration above the critical micelle concentration (2.8 mg/ml) was achieved. A reduction in the area of the peaks of between 60 and 75% was observed.
3. The possible interference by pectin (3 mg/ml) was tested by adding pectin to a standard solution of pesticides. The peak areas were reduced between 10 and 50%, but the addition of pectinase (1 mg/ml, 1 h reaction) to degrade pectin causes the peak areas to return to values near those measured before adding pectin to the solution.
4. Addition of pectinase to a fortified juice increases recoveries to nearly 50%. This was not considered sufficient for an accurate method of analysis and therefore this procedure was not used further.

These observations confirm that suspended matter as well as dissolved compounds may be responsible for interference on sample extraction by SPME, either by adsorbing analytes, forming micelles and/or making it difficult for analytes to reach the fiber (interfering with diffusion).

*3.1.2.2. Effect of dilution on sample extraction*

. The results of recovery tests were much improved by diluting samples: with a dilution of 1/10 of the fortified juice, the recoveries became four times higher than the recoveries from the undiluted samples, but acceptable values (>70% recovery) are achieved only with dilutions greater than 1/50, as shown in Fig. 3.

This observation may be explained if we consider the pesticide (P) and interfering compounds represented by Int (which may be pectin, for example) in equilibrium with a certain amount of the hypothetical compound PInt:

$$\mathrm{P} + \mathrm{Int} \rightleftarrows \mathrm{PInt} \tag{1}$$

The concentrations [P], [Int] and [PInt] are related to the equilibrium constant $K$:

$$K = \frac{[\mathrm{PInt}]}{[\mathrm{P}][\mathrm{Int}]} \tag{2}$$

The total concentration of pesticide in dilute solution $[\mathrm{P}]_t$ is equal to the sum of the concentrations of free pesticide [P] and the concentration of pesticide bonded to interferent [PInt]:

$$[\mathrm{P}]_t = [\mathrm{P}] + [\mathrm{PInt}] \tag{3}$$

Combining Eqs. (2) and (3), Eq. (4) is obtained, where $[\mathrm{P}]_t/[\mathrm{P}]$ represents 1/recovery

$$\frac{[\mathrm{P}]_t}{[\mathrm{P}]} = 1 + K[\mathrm{Int}] \tag{4}$$

The concentration [Int] decreases on diluting the solution:

$$[\mathrm{Int}] = [\mathrm{Int}]_0 \frac{V_0}{V} \tag{5}$$

where $[\mathrm{Int}]_0$ is the initial interference concentration and $V_0$ and $V$ are the initial and final volumes of solution, respectively.

When applied to data presented in Fig. 3, linear relationships (Eq. (6)) between 1/recovery and $V_0/V$ were confirmed.

$$\frac{[\mathrm{P}]_t}{[\mathrm{P}]} = 1 + K[\mathrm{Int}]_0 \frac{V_0}{V} \tag{6}$$

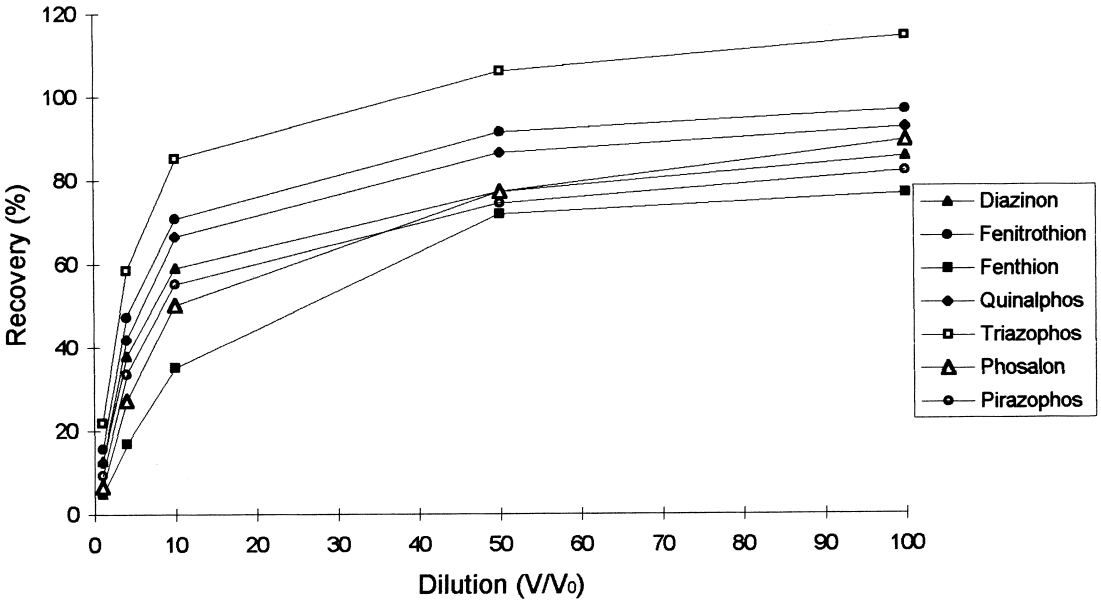


Fig. 3. Effect of dilution of juices on recovery (juice fortified at 100 μg/l, stirred at 1250 rpm and analysed after extraction with the PDMS fiber dipped in the solution for 20 min).

Using these linear plots, it was found that, in order to have recoveries >70% ($[P]_t/[P]<1.42$) for all pesticides, it is necessary to dilute samples at least 50 times ($V_0/V=0.02$).

### 3.2. Validation of the analytical method

Based on the method development described above, the following conditions were chosen for the analytical method: 20 min of immersion of the PDMS fiber in 3 ml of the solution being analysed with stirring at 1250 rpm; 1 to 100 dilution of samples.

#### 3.2.1. Repeatability

To evaluate the precision of the measurements, analysis of standard solutions with concentrations of 0.050, 0.250, 1, 5, 25, 100 and 500 μg/l were performed in triplicate. The analyses led to RSDs of the peak areas from 0.4 to 7.3%. Results for the 5 μg/l standard solution are presented in Table 2.

Spiked samples were analysed in triplicate to evaluate the precision of the method: RSDs are

Table 2
Analysis of standard solutions: limits of detection and quantification, precision of measurement with standard solution (5 μg/l, $n=3$) and coefficients of correlation in the range 0–25 and 0–100 μg/l

| Pesticide | Limit of detection (μg/l) | Limit of quantification (μg/l) | RSD (%) at 5 μg/l | $r^2$, 0–25 μg/l | $r^2$, 0–100 μg/l |
|---|---|---|---|---|---|
| Diazinon | 0.004 | 0.020 | 3.4 | 0.9997 | 0.998 |
| Fenitrothion | 0.011 | 0.056 | 0.8 | 0.99997 | 0.998 |
| Fenthion | 0.003 | 0.016 | 1.5 | 0.999999 | 0.997 |
| Quinalphos | 0.004 | 0.020 | 1.3 | 0.9999 | 0.995 |
| Triazophos | 0.014 | 0.070 | 1.1 | 0.998 | 0.992 |
| Phosalon | 0.012 | 0.052 | 1.7 | 0.99997 | 0.999 |
| Pyrazophos | 0.014 | 0.055 | 2.1 | 0.99993 | 0.997 |

indicated in Tables 4 and 5 for juice and fruit samples and are similar to those reported for conventional methods of pesticide residue analysis.

*3.2.2. Linearity*

Analyses of the same standard solutions were used to test linearity.

Peak areas for 500 μg/l were significantly smaller than expected probably due to fiber saturation and for this reason this concentration was not used for regression. For the 100 μg/l solution, areas were also smaller than expected which led to smaller correlation coefficients than when this concentration was not considered (Table 2). Deviations from linearity for the regression in the 0–25 μg/l range are presented in Table 3. Since residues for the less concentrated standard solution (0.050 μg/l) are quite high, the range from 0.250 to 25 μg/l was chosen as a practical range for calibration.

*3.2.3. Limits of detection and quantification*

Theoretical limits of detection and quantification were determined taking into account the usual definitions: the concentration that originated, for each pesticide, a signal equal to three times the noise signal was considered the limit of detection. The concentration that originated, for each pesticide, a signal equal to 10 times the noise level was considered the limit of quantification.

Limits of detection and quantification (listed in Table 2) were evaluated for each pesticide as follows:

1. Retention times were determined running the chromatogram of a standard solution containing 0.050 μg/l of each pesticide.
2. The fiber was dipped in water and a blank was run. From this chromatogram, average noise levels were measured in windows of 20 times the peak widths at half height centered at the retention times.
3. The concentrations that led to signals three or 10 times the noise level were evaluated using the average of the peak areas obtained in three injections of the standard solution and taking into account the values of the noise level.

Since samples are diluted 100 times before analysis, the limits of detection and quantification for juices and fruits are about 100 times higher than those listed in Table 2.

*3.2.4. Accuracy*

Recovery tests were performed in order to study accuracy. These tests were based on the addition of known amounts of pesticides to samples. The areas of the peaks obtained when these samples were analysed were compared with the areas of the peaks obtained when analysing standard solutions with the same concentration by the same procedure.

Mean recoveries obtained in the analysis of fortified juice and fruit are listed in Tables 4 and 5, respectively.

For fortified juice the recoveries were all >70%, which may be considered adequate for a routine analytical method. For fruit samples, the recoveries were, in general, lower than for fortified juice but, with the exception of pyrazophos (mean recovery 53%), they had values >70%.

## 4. Conclusions

The complexity of the fruit matrix makes it difficult to obtain a quantitative extraction of pesticides, but the decrease in concentration of the

Table 3
Residuals from regression presented as the difference between calculated and measured peak areas divided by calculated peak areas

| Concentration (μg/l) | Diazinon | Fenitrothion | Fenthion | Quinalphos | Triazophos | Phosalon | Pyrazophos |
|---|---|---|---|---|---|---|---|
| 0.05 | −58.6 | −46.1 | −5.1 | −56.1 | −72.1 | −1.2 | −45.8 |
| 0.25 | −14.5 | −5.5 | 6.0 | −9.6 | −32.8 | 23.7 | −4.2 |
| 1 | 2.9 | 2.3 | −0.4 | 2.2 | 1.0 | 0.3 | 4.6 |
| 5 | 6.6 | 2.1 | −0.2 | 3.7 | 15.5 | −1.6 | 2.8 |
| 25 | −0.3 | −0.1 | 0.0 | −0.2 | −0.6 | 0.1 | −0.1 |

Table 4
Recoveries over fortified pear/apple juice

| Spike (μg/kg) | Recovery (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Diazinon | | Fenitrothion | | Fenthion | | Quinalphos | | Triazophos | | Phosalon | | Pyrazophos | |
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD |
| 25 | 82.0 | 1.7 | 102.6 | 5.8 | 96.7 | 5.9 | 94.2 | 5.5 | 94.2 | 7.2 | 83.5 | 2.8 | 75.9 | 8.6 |
| 50 | 94.7 | 6.9 | 91.7 | 3.3 | 85.8 | 5.6 | 91.8 | 5 | 99.8 | 4.8 | 90.2 | 9.8 | 87.6 | 7.7 |
| 100 | 84.3 | 6.1 | 99.1 | 3.9 | 93.6 | 3.3 | 94.5 | 1.9 | 99.4 | 4.7 | 88.8 | 6.9 | 81.3 | 6.8 |
| 250 | 88.0 | 3.6 | 97.4 | 3.4 | 99.0 | 6.3 | 99.2 | 4.1 | 98.2 | 1.6 | 100.5 | 5.3 | 99.6 | 2.8 |

Table 5
Recoveries over fortified pears

| Spike (μg/kg) | Recovery (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Diazinon | | Fenitrothion | | Fenthion | | Quinalphos | | Triazophos | | Phosalon | | Pyrazophos | |
| | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD | Mean | RSD |
| 25 | 89.6 | 8.7 | 91.5 | 1.8 | 73.7 | 8.3 | 89.8 | 4.0 | 85.3 | 6.1 | 74.4 | 2.5 | 50.5 | 5.8 |
| 100 | 90.2 | 7.8 | 81.1 | 1.4 | 70.0 | 7.4 | 80.4 | 4.4 | 93.3 | 2.4 | 80.5 | 7.7 | 53.1 | 10.4 |
| 250 | 89.5 | 13.0 | 94.7 | 1.8 | 95.8 | 11.2 | 92.0 | 8.9 | 99.5 | 2.5 | 95.4 | 10.5 | 54.6 | 10.8 |

interfering components by a simple dilution of the sample makes possible the quantification of pesticides.

The method was validated in a range below the MRLs (European regulations) for the pesticides studied. Since improved results are obtained when samples are diluted, it is also possible to quantify pesticides at higher levels simply by diluting the sample to bring concentrations to the validated range: 25–250 μg/kg.

Although dilution of samples may seem inconvenient for a trace analysis, the proposed analytical method is adequate to determine levels of pesticides below the MRLs (all $>200$ μg/kg for the compounds and fruits analysed) because of the low limits of detection of the method.

Due to the limitation of the selective detector used, the method is applicable only to organophosphorus pesticides. Nevertheless, it is possible to analyse other classes of pesticides making use of a mass spectrometer as detector [15].

The method described is suitable for the detection (screening tests) and quantification of organophosphorus pesticides in fruit matrices.

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