



## Analytical Methods

# Analyses of selected non-authorized insecticides in peppers by gas chromatography/mass spectrometry and gas chromatography/tandem mass spectrometry

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## ABSTRACT

Two methods based on gas chromatography coupled with mass spectrometry and tandem mass spectrometry analyzers are described for the identification, confirmation and quantitation of two EU-banned insecticides: isocarbophos and isofenphos-methyl, detected in recent monitoring programmes in pepper samples. The proposed methodologies involved a liquid–liquid extraction with acetonitrile followed by a cleanup step by dispersive solid-phase extraction using primary–secondary amine as sorbent material. Recovery studies performed on peppers spiked at different fortification levels (10 and 50  $\mu\text{g kg}^{-1}$ ) yielded average recoveries in the range 85–98% with RSD values below 8%. Identification, confirmation and quantitation were carried out by gas chromatography/mass spectrometry (GC–MS) in selected ion monitoring mode and gas chromatography/tandem mass spectrometry (GC–MS/MS) using an ion trap operating in the multiple reaction monitoring (MRM) mode. The obtained limits of detection (LODs) were in the range 0.1–0.3  $\mu\text{g kg}^{-1}$ , depending on the technique. The proposed methods were successfully applied to the analysis of suspected pepper samples.

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## 1. Introduction

International trade of fresh fruits and vegetables is an important issue in the European Union frame. In this sense, the use of a large number of well known and frequently applied pesticides has been banned in the European Union as a consequence of the Directive 91/414/EEC Council Directive, 1991; Regulation (EC), 2005. Recent alerts reported by European countries have pointed out a serious problem related with the presence of illegal or misused pesticides in various crops, particularly in peppers. For instance, residues of the insecticide isofenphos-methyl (which is not authorized in the EU) were detected in peppers from Spain in 2006 and 2007 (<http://www.cvuas.de> and <http://www.untersuchungsamter-bw.de>).

The presence of non-authorized pesticides in the European Union can be explained by a lack of authorized insecticides to avoid some persistent pests that have become resistant against common insecticides. In fact, to a greater or lesser extent, all chemical insecticides exert a selective evolutionary pressure upon the insect pests they are intended to control. Therefore, over a period of time, resistant strains of insects are certain to emerge. Consequently, pests develop resistance to the insecticides which are used to con-

trol them. Another key issue is that greenhouse crops seem to accelerate resistance with species – intensively sprayed – such as pepper. In particular, pest management of pepper is a task that is difficult to tackle, which drives the alternate use of different active substances, some of them might be non-authorized ones or banned for pepper, which would imply an infringement to EU regulations.

Isocarbophos is a broad-spectrum organophosphate (OP) insecticide, effective against a wide range of insect pests. Isofenphos-methyl is also a high-effective, broad-spectrum OP insecticide used to control soil pests, such as grub, mole cricket, and click beetles, etc. on wheat, peanut, bean, corn, sugarcane, beet, tobacco and cotton, as well as to control some ground pests. However, it has never been approved in any EU member state. A plant protection product containing isofenphos-methyl is not authorized in any EU Member State, because it is not included in Annex 1 of the Council Directive 91/414/EEC, and no appraisal for an authorization is currently scheduled. To the best of our knowledge, isofenphos-methyl is most likely produced in Asian countries and has been imported and applied illegally in Spain, without any toxicological risk evaluation.

Scarcely any literature is available on the development of analytical methodology for the analysis of these key compounds in pepper (Tang et al., 2005; Zhao, Han, Jiang, Wang, & Zhou, 2006). Therefore, there is a need to develop and describe in detail such methods. In the case of volatile and thermally stable

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pesticides, the most frequently used technique in routine laboratories for the determination of pesticides is GC–MS, since a large number of pesticides are volatile and thermally stable (Aguëra & de Kok, 2005; Alder, Greulich, Kempe, & Vieth, 2006; Careri, Bianchi, & Corradini, 2002; Fernandez-Alba, 2005; Geerdink, Niessen, & Brinkman, 2002; Lehotay & Hajslova, 2002; Rissato, Galhiane, de Almeida, Gerenutti, & Apon, 2007; Stan, 2005). In this work, we describe for the first time the application of various analytical methodologies to facilitate an appropriate selection of them in the combined determination of these two important substances in pepper at concentrations in the low  $\mu\text{g kg}^{-1}$  range. The proposed methods consist of a sample treatment step based on QuE-ChERS extraction method (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003; Lambropoulou & Albanis, 2007; Lehotay, Mastovska, & Lightfield, 2005; Hercegova, Dömötörövá, Kruzlicová, & Matisova, 2006; Paya et al., 2007) followed by quantitative analyses by GC–MS and GC–MS/MS. The sensitivity, linearity, repeatability and LODs obtained with the different techniques studied have been evaluated. Finally, the proposed method has been successfully applied to the determination of these insecticides in pepper samples.

## 2. Experimental

### 2.1. Reagents and materials

Pesticide analytical standards were purchased from Dr. Ehrenstorfer (Ausburg, Germany) and from Riedel de Haën, Pestanal® quality (Seelze, Germany). Individual pesticide stock solution of isocarbophos and isofenphos-methyl ( $1000 \mu\text{g ml}^{-1}$ ) was prepared in toluene and stored at  $-20^\circ\text{C}$ . HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). PSA (primary–secondary amine) Bond Elut was obtained from Varian, Inc. (Palo Alto, CA, USA). Acetic acid was from Panreac (Barcelona, Spain). Anhydrous magnesium sulfate and sodium acetate were from Sigma–Aldrich (Madrid, Spain).

### 2.2. Sample treatment

Pepper samples were obtained from different plantations. The employed procedure (the so-called “QuEChERS”, acronym of “Quick, Easy, Cheap, Effective, Rugged and Safe”) described elsewhere (Anastassiades et al., 2003; Lehotay et al., 2005; Hercegova et al., 2006) comprised the following steps: a representative 15 g portion of previously homogenised sample was weighed in a 200 ml PTFE centrifuge tube. Then 15 ml of acetonitrile was added, and the tube was vigorously shaken for 1 min. After that, 1.5 g of NaCl and 4 g of  $\text{MgSO}_4$  were added and the shaking process was repeated for 1 min. Then the extract was centrifuged (3700 rpm) for 1 min. Five millilitre of the supernatant (acetonitrile phase) was then taken in a pipette and transferred to a 15-ml graduated centrifuge tube containing 250 mg of PSA and

**Table 2**

Recovery studies of the insecticides assayed in peppers using the GC–MS method

Pesticide	Amount added			
	10 $\mu\text{g kg}^{-1}$		50 $\mu\text{g kg}^{-1}$	
	Rec (%)	RSD (%) <sup>a</sup>	Rec (%)	RSD (%) <sup>a</sup>
Isocarbophos	89.1	5.7	98.2	7.6
Isofenphos-methyl	84.9	7.1	87.1	6.8

<sup>a</sup>  $n = 6$ .

**Table 3**

Analytical parameters for the analysis of selected insecticides in pepper by GC–MS/MS(IT) and GC–MS(SIM)(Q)

Compound	Concentration range ( $\mu\text{g kg}^{-1}$ )	Linearity ( $R^2$ )	LOD ( $\mu\text{g kg}^{-1}$ )	RSD (%) $n = 6$	
				Intra-day	Inter-day
<i>GC–MS (SIM) (Q)</i>					
Isocarbophos	0.1–100	0.9955	0.3	4.6	7.0
Isofenphos-methyl	0.1–100	0.9969	0.2	2.0	9.0
<i>GC–MS/MS (IT)</i>					
Isocarbophos	0.1–100	0.9732	0.3	6.0	10.0
Isofenphos-methyl	0.1–100	0.9822	0.1	7.5	10.5

750 mg of  $\text{MgSO}_4$ , that was energetically shaken for 20 s. The extract was centrifuged again (3700 rpm) for 1 min. Finally, an extract containing the equivalent of 1 g of sample per ml in nearly 100% acetonitrile was obtained. Two millilitre of this extract was then evaporated to near dryness, and reconstituted with ethyl acetate/hexane (1:1). Prior to GC–MS analysis the extract was filtered through a  $0.45 \mu\text{m}$  PTFE filter (Millex FG, Millipore, Milford, MA, USA).

### 2.3. Spiking procedure

For recovery studies, the samples were spiked with the studied insecticides before the corresponding extraction procedure. A representative 200 g portion of an homogenized pepper sample was weighed and transferred to a glass mortar, where it was fortified homogeneously with 0.2 ml (0.2 ml of standard + 0.8 ml of methanol) and 1 ml of a  $10 \mu\text{g ml}^{-1}$  standard solution in methanol to reach  $10 \mu\text{g kg}^{-1}$  and  $50 \mu\text{g kg}^{-1}$  of the studied insecticides, respectively. The mixture was then gently blended in the mortar for 1 h, to assess the homogeneity of the sample. Then the sample was allowed to stand at room temperature for 2 h, before it was kept at  $-18^\circ\text{C}$ , until analysis. Then, six extractions of 15 g portions from the spiked pepper were made, and were processed using the procedure described in Section 2.2.

**Table 1**

Identification of isocarbophos and isofenphos-methyl by GC–MS-SIM (Q) and GC–MS/MS (IT)

	GC–MS-SIM (Q)		GC–MS/MS (IT)		
	Retention time (min)	Selected ions $m/z$ (relative abundance) <sup>a</sup>	Retention time (min)	Precursor ion $m/z$	Fragments ions $m/z$ (relative abundance) <sup>a</sup>
Isofenphos-methyl	16.4	121 (70), <b>199</b> (100), 241 (44), 231 (33)	20.9	199	167 (40), <b>121</b> (100), 199 (37)
Isocarbophos	15.5	121 (80), <b>136</b> (100), 230 (40), 289 (40)	20.4	230	136 (50), <b>155</b> (100), 198 (70), 212 (50)

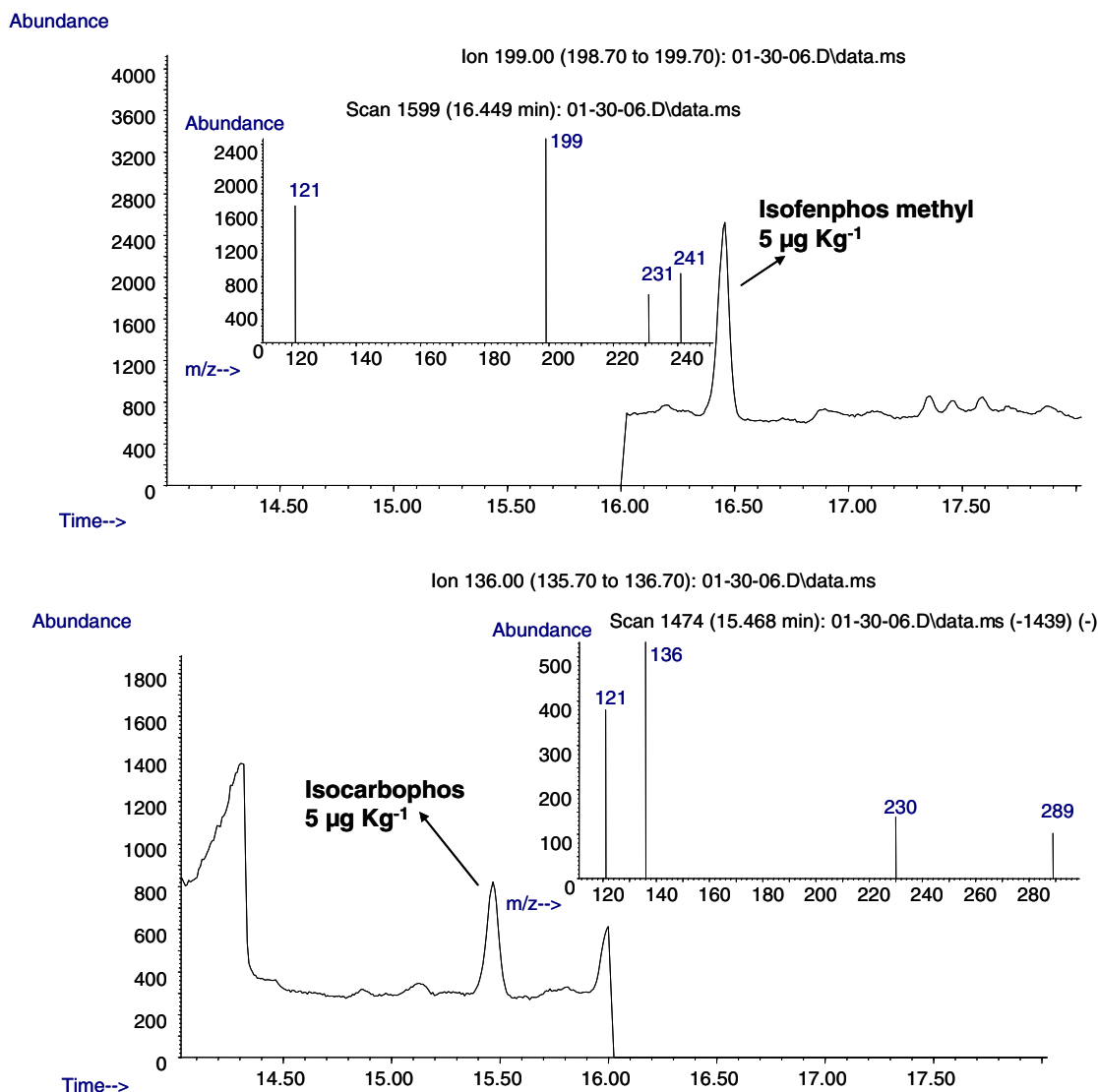
<sup>a</sup> Quantitation ions in bold letters.

## 2.4. Gas chromatography quadrupole mass spectrometry (GC-Q-MS)

Gas chromatography–mass spectrometry (GC–MS) analyses were run on a HP 6890 series gas chromatograph (Hewlett-Packard, Palo Alto, CA) interfaced to a HP 5973 mass-selective detector. Data acquisition, processing, and instrumental control were performed by the HP MSD Chem-Station software. Analytes were separated in a Hewlett-Packard HP-5MS capillary column (5% biphenyl/95% dimethylsiloxane), 30 m × 0.25 mm i.d., 0.25 μm film thickness. A split/splitless injector was used in the pulse splitless mode. An empty liner was filled with 0.5 cm Carbofrit (Restek, Bellefonte, CA) placed 3.6 cm from the upper part of the liner. The injector operating conditions were as follows: injection volume 10 μL; injector temperature 250 °C; initial pulse pressure 30 psi (1.5 min). The helium carrier gas flow was maintained at 1 ml/min. The oven temperature programme was 70 °C for 3.50 min, programmed to 180 °C at 30 °C min<sup>-1</sup> (10 min), then to 300 °C at 8 °C min<sup>-1</sup> (5 min). Electron impact (EI) mass spectra in full scan mode were obtained at 70 eV, the monitorization was from *m/z* 50 to 400. The ion source and quadrupole analyzer temperatures were fixed at 230 °C and 106 °C, respectively.

## 2.5. Gas chromatography tandem mass spectrometry (GC-IT-MS)

Analyses were performed using a Varian 4000 GC–MS/MS system (Varian, Walnut Creek, CA, USA) equipped with a CP-8400 auto-sampler. Data acquisition and processing were performed using the Varian Star Workstation software 6.42 version. The system worked under internal configuration, using electron impact (EI) as the ionization mode. A fused silica tubing 2 m × 0.25 mm i.d. from Supelco (Bellefonte, PA, USA) was used as guard column connected to a J&W Scientific capillary column HP-5MS (5% diphenyl 95% dimethylsiloxane), 30 m × 0.25 mm i.d., 0.25 μm film thickness. Sample injections were performed in a 1079 PTV septum-equipped programmable temperature injector (Varian, Walnut Creek, CA, USA) (SPI) operating in the large-volume injection technique, through an empty liner, filled with 0.5 cm Carbofrit (Restek, Bellefonte, USA) placed at 3.6 cm from the upper part of the liner. Injector operating conditions were as follows: injection volume, 10 μL; vent time, 50 s; split ratio, 50, and injection speed, 5 μL s<sup>-1</sup>. The injector temperature was held at 70 °C during the solvent evaporation stage and then ramped to 180 °C at 80 °C min<sup>-1</sup>. This temperature was held for 10 min. Helium carrier gas flow was



**Fig. 1.** Selected ion monitoring traces obtained in the analysis of a pepper extract spiked with 0.005 mg kg<sup>-1</sup> of isofenphos-methyl and isocarbophos; (inset) corresponding mass spectra obtained for each compound.

maintained at 1 ml/min. The GC temperature program was 70 °C for 3.50 min, programmed to 180 °C at 30 °C min<sup>-1</sup> (10 min), then to 300 °C at 8 °C min<sup>-1</sup> (5 min).

### 3. Results and discussion

#### 3.1. Mass spectrometric conditions

##### 3.1.1. GC–Q–MS

Four ions were selected for each compound from the full scan spectra obtained at 70 eV, once the ions selected, all the analyses were performed in selected ion monitoring (SIM) mode. The base peak was the choice as a quantification ion,  $m/z$  199 for isofenphos-methyl, and  $m/z$  136 for isocarbophos, which correspond with the ions  $[C_8O_4H_8]^+$  and  $[C_7O_3H_6]^+$ , respectively.

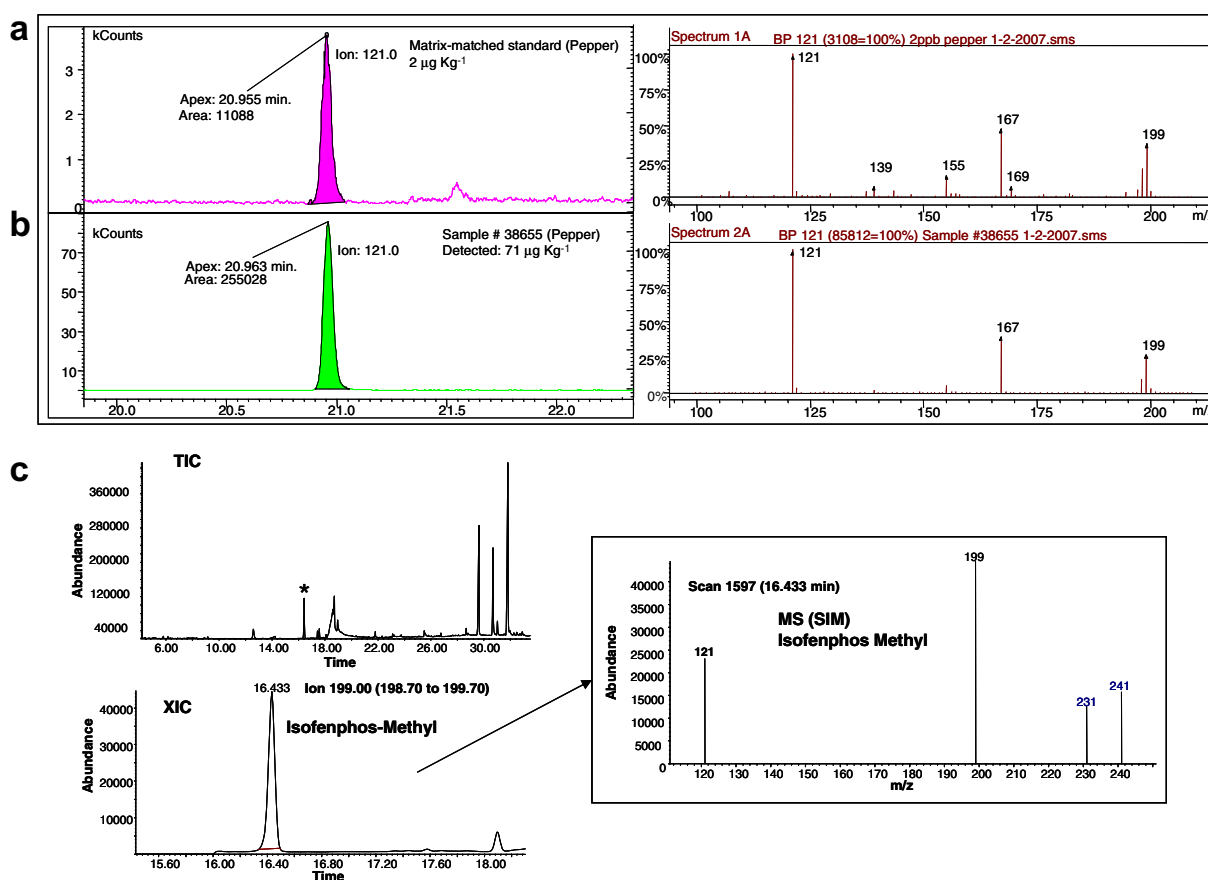
##### 3.1.2. GC–MS/MS

Typical MS/MS parameters were optimized for each compound as follows. The precursor ion chosen to be isolated in the trap was the base peak on the *full scan* mass spectrum for each compound. A narrow isolation window of 3 ( $\pm 1.5$  mass units wide) was selected. Fragmentation of the precursor ions was performed by collision-induced dissociation (CID) in the non-resonant (inter molecular) excitation mode for all the compounds. The excitation storage level, which is the lowest mass stored during CID, was calculated by using the “*q* calculator” tool included in the software, which sets, setting the precursor mass by the operator, limits to the exci-

tation storage level. The parameter *q* was set to an optimum value of 0.4. The excitation amplitude was determined experimentally running several analyses with different values of this parameter using the automated method development (AMD) tool. The value at which the precursor ion remained with a relative abundance of around 30% and at which at least two fragment ions were achieved with appreciable abundance was chosen. Once the MS/MS conditions were optimized, the base peak in the product ion spectrum of each compound was selected as the quantification mass. Table 1 shows the precursor and fragments ions obtained under the optimized values of, excitation storage level,  $m/z$  101 and  $m/z$  87.7 for isofenphos-methyl and isocarbophos, respectively, and excitation amplitude, 89 v and 68 v for isofenphos-methyl and isocarbophos, respectively. The confirmation of the analytes was carried out with their retention times and the presence of two fragment ions for each compound. Both, retention time and relative abundance of the diagnostic ions must be within the established range. The precursor ions selected for each compound were  $m/z$  199  $[C_8O_4H_8]^+$  and  $m/z$  230  $[C_8O_4PH_7]^+$  for isofenphos-methyl and isocarbophos, respectively.

#### 3.2. Evaluation of sample treatment procedure

To evaluate the effectiveness of the extraction method, different recovery studies were carried out. Several portions of pepper were spiked at two different concentration levels (10 and 50  $\mu\text{g kg}^{-1}$ ) with the working standard solution. Then, the spiked samples were extracted with the method described. The obtained extracts were



**Fig. 2.** Chromatograms obtained for the analysis of a positive pepper sample (#38655) analyzed by GC–MS and GC–MS/MS; (a) chromatogram and corresponding mass spectrum obtained by GC–MS/MS analysis of a spiked pepper extract containing 0.002 mg kg<sup>-1</sup> of isofenphos-methyl; (b) chromatogram and corresponding mass spectrum obtained by GC–MS/MS analysis of pepper sample (#38655) containing 0.071 mg kg<sup>-1</sup> of isofenphos-methyl and; (c) total ion chromatogram (TIC), extracted ion chromatogram (XIC) and corresponding mass spectrum (MS (SIM)) obtained by GC–MS analysis of the same positive pepper sample.

analyzed by both techniques obtaining recoveries between 80% and 100%, with RSD values ( $n = 6$ ) below 8% in the case of the GC–MS method, as can be seen in Table 2. These results show the feasibility of the studied extraction method for the extraction of these insecticides in vegetable samples.

### 3.3. Analytical features

The analytical performance of the proposed methods was studied in order to evaluate its usefulness for quantitative analyses in the studied matrix. Matrix-matched standards were used for both methods in order to circumvent quantitation errors, related to signal enhancement due to the matrix. Linearity was evaluated by analyzing these matrix matched standards solutions, prepared at different concentration levels in the range 0.001–0.1 mg kg<sup>-1</sup> depending on each method/technique. As can be observed, the linearity of the analytical response within the studied range was suitable, with correlation coefficients better than 0.99 in most cases as shown in Table 3, where these values are summarized together with the limits of detection and intra- and inter-day RSD (%). The relative standard deviation (RSD) ( $n = 6$ ) values for run-to-run studies were in the range 2.0–7.5% and inter-day RSD ( $n = 6$ ) values were between 7.0% and 10.5% for all the different methods developed. These results demonstrate the precision of the developed method and the potential of the proposed approach for quantitative purposes. As an example, a typical chromatogram obtained by GC–MS of a 0.005 mg kg<sup>-1</sup> matrix-matched standard pepper is shown in Fig. 1.

The limits of detection (LODs) obtained were estimated from the injection of matrix-matched standard solutions at concentration levels corresponding to a signal-to-noise ratio ( $S/N$ ) of 3. The results obtained for each insecticide are shown in Table 3.

### 3.4. Application to real samples: GC–MS analyses of insecticides in pepper samples from Andalusian Food Safety Authority

The proposed method was applied to the analysis of over 50 pepper samples. Some of the samples tested contained at least one of the studied insecticides. As an example, Fig. 2 shows the analysis of a pepper sample (which contained isofenphos-methyl) by GC–MS and GC–MS/MS.

The positive findings of the detected insecticides were confirmed by using one of the following criteria: 4 ions (and their relative abundances) by GC–MS (in SIM mode) and the presence of precursor ion together with at least two product ion (within the maximum permitted tolerances for the relative ion intensities) by GC–MS/MS.

## 4. Concluding remarks

Two analytical methods based on gas chromatography coupled with various mass spectrometric analyzers (GC–MS and GC–MS/MS) were described for the identification, confirmation and quantitation of two EU-non-authorized insecticides (isocarbophos and isofenphos-methyl) in pepper samples. No significant differences on the performance of both methods were noticed in terms of sensitivity and limit of detection, although the unambiguous confirmation capabilities provided by MS/MS cannot be achieved with a single quadrupole analyzer. It is clear that the information provided by the ion trap MS/MS method, that is a second generation full scan mass spectrum, exceeds that provided by a SIM single quadrupole method.

The potential of the proposed methods was demonstrated by analyzing real samples with excellent selectivity and sensitivity, thus enabling the unambiguous identification of trace levels of these insecticides in pepper samples. From the sample treatment validation data and analytical parameters obtained with the

different techniques employed, it can be concluded that any of the proposed methods enables the unambiguous confirmation and accurate quantitation of these non-authorized substances in complex vegetable samples such as pepper. Besides, from the data provided in this work, these compounds can be easily incorporated in any GC–MS or GC–MS/MS pesticide multi-residue method based on QuEChERS sample treatment in any vegetable matrix.

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