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Pesticide Multiresidue Analysis in Fresh and Canned Peaches Using Solid Phase Extraction and Gas Chromatography Techniques

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Insecticides, fungicides and herbicides are agrochemicals designed to combat the attacks of various pests on agricultural crops. However in many cases hazardous residues are left, becoming a permanent danger to the quality of food, environment and consumers health and for that purpose their determination is a priority goal at the preferences of Imathia and Pella (N. Greece).

During the last decades public concern over pesticide residues in fresh fruits and vegetables has led to the development of many analytical methods for monitoring these compounds. These methods include the traditional liquid-liquid extraction (LLE) (Fytianos et al. 1998, Stensvand 2000) as well as the supercritical fluid extraction technique (SFE) (Lehotay 1997).

However from the analyst point of view a large number of analytical problems have arisen like large solvent volume needed, long extraction and procedure times as well as poor recovery for groups of compounds. These problems have led to the development of specialized methods for the groups of pesticides. In recent years new techniques such as solid phase extraction (SPE) (Hela et al. 1995, Torres et al. 1997) and solid phase microextraction (SPME) (Lambropoulou et al. 2000, Kataoka et al. 2000) are utilized for extraction, clean up and preconcentration steps in several sample matrices like environmental waters, soils, biological fluids and fruits.

This work describes the development of a routine multiresidue method for the quantitative determination of organophosphorous, organonitrogen and organochlorine pesticides in fresh and canned peaches.

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The method involves a solid-phase extraction method with nonporous carbon based packing (ENVI^{TM}-Carb), followed by gas chromatography coupled to Flame Thermionic (FTD) and Mass Spectroscopy (MS) detectors. The above detectors have proven to be very sensitive and selective for separation and trace level identification of a wide range of target pesticides (Fillion et al. 1995, Hogenboom et al. 2000). The method has been applied for the determination of pesticides in fresh peaches produced with and without Integrated Crop Management from the area of Imathia and Pella.

MATERIALS AND METHODS

All solvents used, acetonitrile, toluene and acetone were pesticide residue analysis grade. Sodium chloride and sodium sulphate were analysis grade and all purchased from Riedel de Haen (Seelze, Germany). Solid Phase Extraction cartridges ENVI-18 and ENVI^{TM}-Carb were available from SUPELCO (Bellefonte, USA). Analytical standards shown in Table 1 were used without further purification.

Three types of peaches were chosen for recovery and reproducibility studies. Fresh cling peaches were collected from a field near the town of Skydra in the middle of the last harvesting period (5 August 2000) and were of Adross species. Two types of canned halves peaches (one kilo can), in syrup of 14° and 18° Brix respectively, were also used of the past production period (July-September 1999). Previous study has shown that both fresh as well as canned peaches (including their syrup) did not contain detectable residues of the pesticides under consideration. Fresh peaches were chopped and homogenised with their skin while canned peaches were homogenised with their syrup. A portion (50g) of fresh and canned peaches was spiked respectively with a pesticide mixture in acetone in order to give a nominal concentration of 0.5 mg/Kg for each analyte.

The spiked samples (50 g) were homogenised with acetonitrile (100 mL) by mechanical shaker for (5 min). Sodium chloride (10 g) was then added and the mixture was homogenised again for 10 min. An aliquot of the supernatant acetonitrile layer (13 mL) was concentrated to a pre-conditioned (5 mL acetonitrile) ENVI-18 SPE cartridge and eluted to a test tube. The extract was dried with sodium sulphate and concentrated with a gently stream of nitrogen to 0.5 mL. Then the sample was loaded onto a pre-conditioned (5 mL acetonitrile:toluene, 3:1) ENVI-Carb SPE cartridge and eluted with 10 mL mixture of acetonitrile:toluene (3:1). Finally the extract was evaporated almost to dryness and reconstituted to 1 mL acetonitrile and analysed by gas chromatography.

Table 1. Target pesticides, supllier and detection limits in GC-FTD and GC-MS system

Pesticide	Supplier	Limit of detection (µg/Kg)	
		FTD	MS
1 Acephate	Poly Science Corporation	6	12
2 Alachlor	Poly Science Corporation	8	15
3 Atrazine	Poly Science Corporation	4	8
4 Azinphos-methyl	Poly Science Corporation	8	20
5 Captan	Riedel de Haen	20	40
6 Chlorothalonil	Riedel de Haen	10	15
7 Chlorpyriphos	Poly Science Corporation	8	20
8 Chlorpyriphos-Methyl	Riedel de Haen	8	20
9 Coumaphos	Poly Science Corporation	10	20
10 Diazinon	Poly Science Corporation	6	18
11 Dicofol	Riedel de Haen	-[1]	20
12 Dieldrin	Poly Science Corporation	-	15
13 Dimethoate	Poly Science Corporation	6	12
14 Endosulfan	Poly Science Corporation	-	20
15 Ethion	Poly Science Corporation	4	12
16 Fenthion	Poly Science Corporation	6	15
17 Methamidophos	Poly Science Corporation	20	40
18 Methidathion	Riedel de Haen	12	30
19 Omethoate	Riedel de Haen	8	20
20 Phosmet	Riedel de Haen	8	15
21 Parathion	Poly Science Corporation	4	10
22 Parathion-Methyl	Poly Science Corporation	4	10
23 Phosalone	Poly Science Corporation	10	20
24 Simazine	Poly Science Corporation	4	12

[1] not analysed by flame thermionic detector

GC-FTD. Pesticide residues were analysed using a GC-17A Shimadzu gas chromatograph (Kyoto, Japan) equipped with flame thermionic detector (FTD) working at 300° C. Pesticide standards and analytical products were injected (1.5 µL) at a temperature of 220 °C in the splitless mode. Analytes were separated by a MDN-5S fused silica capillary column, 30 m X 0.32 mm i.d. (SUPELCO, Bellefonte, USA) programmed at the following temperatures: from 50 °C to 160 °C (10 min) at 5 °C/min (first step) and from 160 °C to 250 °C (30 min) at 15 °C/min (final step). Nitrogen and Helium were used as the carrier and make-up gases respectively. Their flow rates were regulated according to results given through the simplex optimisation of the analytical variables.

GC-MS. The analysis of pesticides was also performed using a Shimadzu (Kyoto, Japan) QP 5050A gas chromatograph-Mass spectrometer fitted with an MDN-5S fused silica capillary column 30 m X 0.32 mm i.d. (SUPELCO, Bellefonte, USA). Helium was used as carrier gas at a flow rate of 1.5 mL/min. The injection temperature was 220 °C. The column was programmed from 50 °C to 160 °C (10 min) at 5 °C/min (first step) and from 160 °C to 250 °C (20 min) at 15 °C/min (final step). The interface was programmed at 250 °C. The mass range was set from 45 to 400 m/z at a scan speed of 1000 amu/sec. Analyses were performed in the electron impact (EI) mode, at 70 eV potential using full scan mode.

Quantification was performed by external and internal calibration using authentic standards. The recovery test was performed at one concentration level that would be applicable to monitoring maximum residue levels while fairly low levels such as the detection limits might not be sufficiently validated.

RESULTS AND DISCUSSION

Recoveries were measured for three replicate samples at fortified level of 0.5 mg/Kg for each pesticide. The results obtained from fresh and canned peaches in the GC-MS system are summarised in Table 2. A typical chromatogram using GC-MS is shown in Figure 1. Overall, recoveries were between 70% (for methamodophos) and 112% (for parathion) with relative standard deviations (RSDs) ranged from 3% to 7%. Slight differences were observed for the recoveries in fresh and canned peaches, with the recoveries in fresh being always greater. Minor differences have been determined between the two types of canned peaches. The detection limits were found between 4 to 40 μg/Kg for the GC-FTD and GC-MS systems respectively, according to compound response (Table 1).

The above analytical method was applied to peach samples that were produced by Integrated Crop Management (ICM) and samples produced without ICM (Figure 2) for the determination of pesticide residues. The aim of ICM is to secure the product safety, keeping pesticide residues under the maximum Residue Limit (MRL) set by European Union.

The results of two types of fresh fruit samples under ICM and without ICM, are summarised in Table 3. From the fruit samples analysed none was found to exceed the Maximum Residue Limit (MRL) when produced by ICM while 9% and 2% of the fruit samples were found to be contaminated with chlorpyriphos and parathion-methyl respectively when produced without ICM.

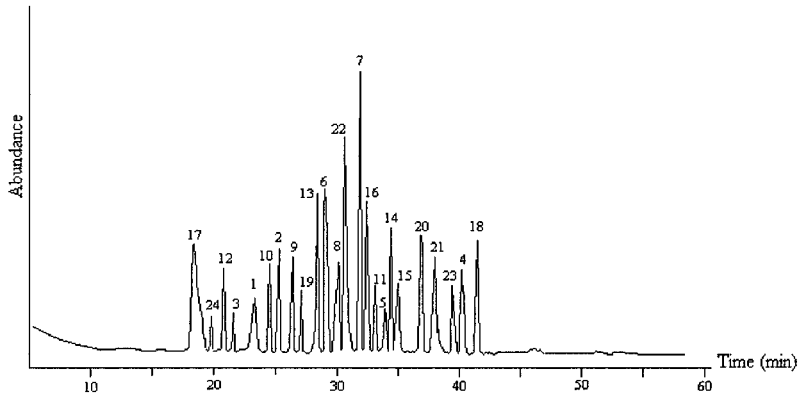

Figure 1. GC-MS chromatogram of fresh canned peach extract spiked with pesticides mixture at a concentration of 0.5 mg/Kg (numbers correspond to pesticides in Table 1)

Table 2. Mean recoveries and Relative Standard Deviations (RSD) of pesticides from fresh and canned peaches in GC-MS with MDN-5S column. Fortified level 0.5 mg/Kg (n=3)

	Fresh Peaches	**Canned Peaches**	
		14° Brix	**18° Brix**
Pesticide	**Recovery ± RSD %**		
Acephate	79 ± 3	75 ± 4	73 ± 3
Alachlor	96 ± 5	95 ± 5	96 ± 5
Atrazine	105 ± 7	95 ± 5	95 ± 4
Azinphos-methyl	105 ± 3	100 ± 4	101 ± 5
Captan	89 ± 4	85 ± 3	84 ± 4
Chlorothalonil	95 ± 5	94 ± 4	94 ± 6
Chlorpyriphos	96 ± 3	93 ± 3	94 ± 5
Chlorpyriphos-Methyl	93 ± 7	89 ± 6	90 ± 7
Coumaphos	104 ± 5	100 ± 7	101 ± 8
Diazinon	95 ± 3	95 ± 4	95 ± 4
Dicofol	110 ± 4	105 ± 5	106 ± 3
Dieldrin	92 ± 7	90 ± 4	89 ± 5
Dimethoate	94 ± 3	92 ± 5	92 ± 7
Endosulfan	97 ± 5	92 ± 5	91 ± 6
Ethion	101 ± 4	98 ± 5	97 ± 5
Fenthion	92 ± 3	85 ± 6	86 ± 5
Methamidophos	74 ± 5	71 ± 7	70 ± 7

(continued)

(**Table 2** continued)

Pesticide	Fresh Peaches	Canned Peaches	
		14° Brix	18° Brix
	Recovery ± RSD %		
Methidathion	105 ± 5	99 ± 5	100 ± 4
Omethoate	96 ± 4	93 ± 7	93 ± 6
Parathion	112 ± 6	104 ± 7	104 ± 7
Parathion-Methyl	100 ± 5	97 ± 6	95 ± 6
Phosalone	90 ± 6	88 ± 7	88 ± 6
Phosmet	93 ± 3	90 ± 7	91 ± 5
Simazine	108 ± 7	100 ± 6	102 ± 7

Table 3. Percent detection of the most common used pesticides in peach cultivation below (<) and above (>) the European Union's Maximum Residue Limit (MRL)

Pesticide	% detection[1]			
	< MRL		> MRL	
	ICM	non ICM	ICM	non ICM
Chlorpyriphos	46	49	n.d[2]	9
Chlorpyriphos-methyl	14	5	n.d.	n.d.
Phosmet	9	11	n.d.	n.d.
Captan	2	4	n.d.	n.d.
Parathion-methyl	11	31	n.d.	2

[1] 210 samples under Integrated Crop Management (ICM) and without Integrated Crop Management (non ICM) by GC-MS system
[2] not detected

Table 4. Concentration Range of the detected pesticides used in peach cultivation bellow (<) European Union's Maximum Residue Limit using GC-MS system

Pesticide	MRL (mg/Kg)		Range (mg/Kg)	
	E.U	U.S.A.	ICM	non ICM
Chlorpyriphos	0.2	0.05	n.d[1] – 0.09	n.d. – 0.19
Chlorpyriphos-methyl	0.5	-	n.d. – 0.06	n.d. – 0.12
Phosmet	10.0	10.0	n.d. – 1.20	n.d. – 5.79
Captan	15.0	50.0	n.d. – 0.18	n.d. – 0.25
Parathion-methyl	1.0	1.0	n.d. – 0.31	n.d. – 2.80

[1] not detected

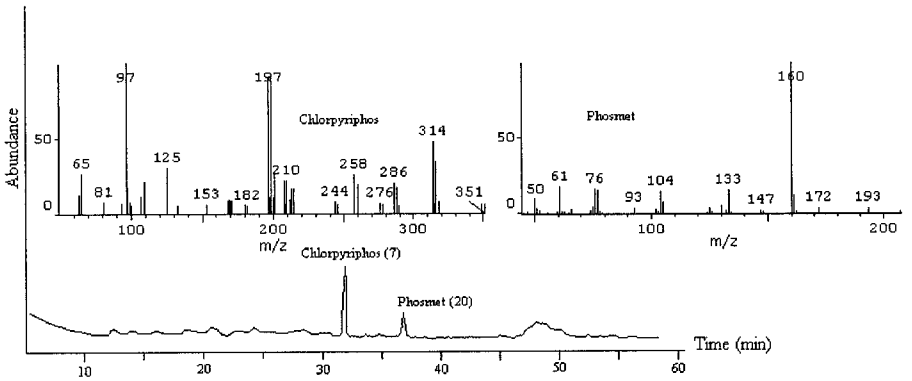

Figure 2. GC-MS chromatogram of an unknown fresh canned peach sample extract without ICM containing chlorpyrifos (22 μg/Kg) and phosmet (16 22 μg/Kg).

For concentration levels below MRL the percentage of pesticide detection was lower for ICM compared to samples produced without ICM. The range of detection was also lower in this case (Table 4) proving that Integrated Crop Management secure product safety keeping pesticide residues below the Maximum Residue Limit.

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