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MULTIRESIDUE ANALYSIS OF 79 PESTICIDES IN STRAWBERRY, GREEN BEAN PODS, GRAPES AND PEACH FRUITS BY SOLID-PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY

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ABSTRACT

Five solvents (n-pentane, ethyl acetate, dichloromethane, ethanol and iso propanol) were tested for extraction of six pesticides (lufenuron, chlorfenapyr, penconazole, diniconazole, difenoconazole and azoxystrobin) from strawberry, green bean pods, grapes and peach. Pentane gave the cleanest extracts in comparison with the used solvents, thus it was used in the extraction of tested pesticides from the samples. Clean up using C_{18} cartridge resulted in higher recovery than using silica gel and florisil cartridges.

A fast and easy multiresidue analytical method is presented for identifying and inspecting 79 pesticide residues, including organochlorine, organophosphate, synthetic pyrethroids and other pesticides in fruits and vegetables. Pesticide residues were extracted from samples with pentane followed by solid phase extraction. C_{18} cartridge was chosen for further clean-up of the extract and elution with pentane and ethyl acetate. Sixty-two and 17 pesticides were determined, by gas chromatography with an electron capture detector (GC-ECD) and a flame photometric detector (GC-FPD), respectively. The recovery rates for most pesticides in various fruits and vegetables were 80-109% with relative standard deviations < 9%.

INTRODUCTION

Strawberry and green bean pods, in addition to grapes and peach are important vegetable and fruit crops in Egypt. The commercial cultivation of which, receives frequent application of a large number of pesticides throughout the cropping season to control a variety of pests and diseases.

Multiresidues method development is difficult, due to the fact that compounds of different polarity, solubility and volatility have to be extracted and analyzed using the same procedure. Based on the classes of pesticides, several methods using gas chromatography for separation of individual compounds, followed by detection with selective and sensitive detection methods such as electron capture detection (Ismail *et al.* 1993) and flame photometric detection (Bolles *et al.* 1999) have been proposed.

However, the above mentioned detection methods cover a limited range of pesticide analysis in addition to occurrence of false positive and inaccurate quantitation caused by the interferences of unknown compounds that are co-eluting in the same retention time with analytes. Many of the published methods (Albero *et al.* 2005; Gelsomino *et al.* 1997; Hernando *et al.* 2001 and Štajnbahaer and Zupančič-Kralj, 2003) for the pesticide determination in food commodities seem to be complicated while consuming

a large volume of solvent and are very time costly. Therefore, new methods in sample preparation and measurement should be studied and developed.

Recently, the QuEChERS sample preparation method has been introduced (Anastassiades *et al.* 2003; Lehotay *et al.* 2005; Lehotay *et al* 2005 and Nguyen *et al.* 2007). This method has many advantages such as high recovery for wide polarity and volatility range of pesticides; high sample throughput; the use of smaller amounts of organic solvents and the use of no chlorinated solvents, very little laboratory ware used and more safety for laboratory workers.

A large number of organic solvents are being used for the extraction of pesticides from crops. The use of acetonitrile (Nguyen *et al.* 2008 and Nguyen *et al.* 2010), ethyl acetate (Frenich *et al.* 2004; Ahire *et al.* 2008 and Dasgupta *et al.* 2010), dichloromethane (Martínez-Vidal *et al.* 2002 and Arrebola *et al.* 2003), acetone (Khummueng *et al.* 2006; Fenoll *et al.* 2007; Štajnbaher and Zupančič-Kralj 2008 and Tuan *et al.* 2009) and n-pentane (Munch and Hautman 1995 and Ridal *et al.* 1997) have been reported.

Solid phase extraction (SPE) is being increasingly used in food analysis, mainly for sample clean up. Solid phase extraction columns containing a normal (polar)-phase or reversed (non-polar)-phase support not only offer the potential of simplifying the purification of the initial extract but also reducing the amount of solvent consumed (Štajnbahar and Zupančič-Kralj, 2003). With SPE, many of the problems associated with liquid/liquid extraction can be prevented, such as incomplete phase separations, less-than-quantitative recoveries, use of expensive, breakable specialty glassware, and disposal of large quantities of organic solvents. SPE is more efficient than liquid/liquid extraction, yields quantitative extractions that are easy to perform, rapid and can be automated. SPE is used most often to prepare liquid samples and extract semi volatile or nonvolatile analytes, but also can be used with solids that are pre-extracted into solvents. They are available in a wide variety of chemistries, adsorbents, and sizes. Selecting the most suitable product for each application and sample is important.

This work aims to 1) compare between the efficiencies of five different solvents as well as three packed SPE cartridge with different sorbent in recovering six pesticides from strawberry, green bean pods, grape and peach. 2) establish a simple and effective multiresidue method based on the application of GC-ECD/FPD combined with modified QuEChERS sample preparation procedure for rapid determination of 79 pesticides belonging to several classes from strawberry, green bean pods, grapes and peach.

MATERIALS AND METHODS

Pesticide Standards

Table 1 lists the pesticides tested in this study. In total, 79 pesticides were divided into 8 groups according to the analytical conditions of instruments and retention time determined by GC. Pesticide standards of 97.4-99.7% purity were purchased from Riedel-de Haen (Seelze, Germany) and Dr. Ehrenstorfer (Augsburg, Germany). Stock solutions of 100 µg/mL for pesticides were prepared individually with acetone, n-hexane and ethyl

acetate according to their polarity and solubility. Working solutions were mixed well and then serially diluted with the appropriate solvent. All standard solutions were stored in the dark at 4ºC.

Reagents and Chemicals

Organic solvents, i.e., acetone, n-pentane, n-hexane, ethyl acetate, dichloromethane, ethanol and iso propanol, all residue analysis chemicals were purchased from S.D.S. (France). The clean up-functional solid-phase extraction cartridge (500 mg / 6 ml) $C_{18,}$ Silica gel and Florisil, were purchased from Supelco (Bellefonte, PA, USA).

Table 1: The targeted 79 pesticides in this study and their grouping for multiresidues determination.

Analytical instrument		Pesticides
GC/ECD	Group 1	Aldrin, Dieldrin, Endosulfan, Endrin, Heptachlor, Hep. Epoxide, Methoxychlor, op-DDT, pp-DDD, pp-DDE, pp-DDT, α- BHC, γ - BHC, Δ –BHC and γ- chlordane
	Group 2	Tetramethrin, Permithrin, Cypermethrin and Deltamethrin
	Group 3	Lufenuron, Triflumizole, Tetraconazole, Penconazole, Chlorfenpyr, Diniconazole, Propiconazole, Epoxiconazole, Promoconazole, Triticonazole, Difenconazole and Azoxystrobin
	Group 4	Thiocyclam, Chlorothalanil, Butrallin, Pendimethalin, Flutolanil, Oxadapazon, Fluazinam, Proquinzid, Bifenazate, Lambda cyhalothrin and Cyfluthrin
	Group 5	Atrazin, Acetochlor, Thiomethoxam, Chlorfluazuron, Cyflufenamide, γ –Cyhalothrin, Es-Fenvalerate and Flucarbazone sodium
	Group 6	Triforine, Diclran, Metrobzin, Dicofol, Bioallethrin Hexythiazox, Myclobutanil Oxyflourfen, Clodinafop, Fluopicolide, Fenarimol and tralomethrin
GC/FPD	Group 7	Azinophos-methyl, Cadusafos, Chlorpyriphos, Chlorpyriphos methyl, Diazinon, Ethion, Pirimiphus-methyl, Propetamiphos, Prothiophos and Quinalphos
	Group 8	Dichlorvos, Dimethoate, Malathion, Phenthoate, Profenophos, Fenamiphos and Triazophos

Sample Preparation

a. Extraction

Different solvents were tested to choose the most efficient one for extraction of lufenuron, penconazole, chlorfenapyr, diniconazole, difenoconazole and azoxystrobin from strawberry, green bean pods, grapes and peach fruits. The tested solvents were n-pentane, ethyl acetate, dichloromethane, ethanol and iso propanol. Their ability to extract the used pesticides successfully was tested by using fortified sample for each pesticide. Fresh fruit and vegetable samples were thoroughly chopped, and a 20 g portion was homogenized with 100 mL of the five tested solvents and 20-50 g anhydrous sodium sulfate for 3 min. The homogenate was filtered through cotton and anhydrous sodium sulfate, evaporated to dryness at 40ºC using a rotary evaporator, and then determined by GC.

From the five tested solvents n-pentane, ethyl acetate and dichloromethane were higher in their recovering efficiency than ethanol and iso-propanol.

Dichloromethane for being a chlorinated hydrocarbon and due to interference of impurities highly extracted by ethyl acetate, both solvents were excluded. Thus, n-pentane was used for the following steps of the study.

b- Solid-phase extraction of pesticides in tested vegetables and fruits:

N-pentane extracts of the six tested pesticides from fruit samples were cleaned using three different clean-up cartridges to choose the convenient clean-up cartridge according to percent recovery. The cartridges were $C_{18,}$ silica gel and florisil, which were eluted by 10 ml n-pentane and 5 ml ethyl acetate.

One ml of the sample extract was loaded onto the three used cartridges, pre-rinsed with 5 ml of methanol, followed by eluting with 10 ml n-pentane and then 5 ml ethyl acetate. The collected eluent was evaporated with nitrogen to dryness and quantified to 0.5 ml n-hexane or ethyl acetate for GC determination.C_{18} cartridge appeared to give highest recovery compared to the other tested cartridge. Thus, it was used for the clean-up of all the tested samples through the study.

QuEChERS method

The preliminary studies of using five different solvents for extraction of six pesticides from strawberry, green bean pods, grapes and peach lead to the choice of n-pentane as a solvent for extraction. In addition to testing three cartridges for clean-up C_{18}, silica gel and florisil resulted in choosing C_{18} as the SPE used in clean-up of the samples. Because of that, the following Quechers method was used for multiresidue analysis of 79 pesticides from strawberry, green bean pods, grapes and peach.

Fresh fruit and vegetable samples were thoroughly chopped, and a 20 g portion was homogenized with 100 ml n-pentane and 20-50 g anhydrous sodium sulfate for 3 min. The homogenate was filtered through anhydrous sodium sulfate. The filtrate was evaporated to dryness at 40ºC using a rotary evaporator. The residue was dissolved in 1 ml n-pentane. For clean-up of fruits and vegetables tested samples the C_{18} cartridge was used as previously mentioned above.

GC-ECD Analysis

The HP6890 gas chromatograph equipped with an HP7673 auto-sampler, an electron-capture detector, and column was employed .A 30 nm x 0.32 mm capillary column coated with a 0.25µm thick film of 5% phenylmethylpolysiloxane (HP-5) from Hewlett and Packard was used in combination with the following oven temperature program : Initial temperature 190 ºC for 5 min, 5 ºC / min up to 220 ºC and held for 5 min, 5 ºC/min up to 240 ºC and held for 5 min, 10 ºC/min up to 260 ºC and held for 5 min, 10 ºC/ min. up to 280 ºC and held for 5 min. The carrier gas (N_2) flow rate was 3 ml/min., splitless injection of a 1µL volume was carried out, detector and injector temperatures were 300 ºC and 280 ºC, respectively.

GC-FPD Analysis

The HP6890 gas chromatograph equipped with a flame photometric detector (FPD), with phosphorus filter with HP7673 auto sampler and 30 m x

0.32 mm capillary column coated with a 0.25 µm thick film of 14% cyanopropilsiloxane (PAS-1701) was used. The oven temperature program was as follows: Initial temperature 160ºC for 2 min.6ºC/min up to 260ºC. and held for 30 min. The carrier gas (N_2) flow rate was 4 ml/min. Splitless injection of a 2 µL volume was carried out at 240 ºC. Hydrogen and air were used at flow rate 75 and 100 ml/min. respectively. Detector temperature was 250 ºC.

Recovery test and limit of detection (LOD)

Mixed pesticide standards were spiked into homogenized green bean pods, strawberry, grape and peach samples separately with the given concentration of the 79 pesticides. Each spiked sample was prepared in triplicate. Fortified samples were blown with pure nitrogen gas for 15 min at room temperature to evaporate solvent residues before extraction, and then were analyzed by GC.

The proposed procedure was validated by recovering pesticides from fortified samples. Average recovery of the tested pesticides from each crop was utilized to calculate mean recovery and inter-replicate repeatability (expressed as the relative standard deviation RSD %). The LOD was set at a signal-to noise ratio (S/N ratio) ≥ 3 by chromatography for individual pesticides in crops (Navarro *et al.* 2000, Chu *et al.* 2005, Tseng *et al.* 2007 and Tuan *et al.* 2009).

RESULTS AND DISCUSSION

Selection of solvent for samples extraction:

Pesticides were extracted from samples spiked at 0.5 mg/kg by various organic solvents with different polarities. Tables (2 and 3) summarize recovery results of 6 pesticides obtained by solvent extraction with n-pentane, ethyl acetate, isopropanol, dichloromethane and ethanol.

Table (2) shows the comparison of recovery rates using five extraction solvents from strawberry and green bean pods. The recovery rates of spiked strawberry samples using n-pentane, ethyl acetate, iso propanol, dichloromethane and ethanol ranged from 79.87 to 90.31%, from 86.05 to 102.54%, from 63.87 to 80.21%, from 77.54 to 97.75% and from 69.33 to 80.11%, respectively. The corresponding values of spiked green bean pods samples ranged from 81.77 to 102.00%, from 80.15 to 95.22%, from 65.57 to 78.95%, from 80.15 to 88.92% and from 60.11 to 77.65%, respectively.

Table (3) shows the comparison of recovery rates by five extraction solvents from two fruits, grapes and peach. The recovery rates of spiked grape samples using n-pentane, ethyl acetate, iso propanol, dichloromethane and ethanol ranged from 81.38 to 100.00%, from 77.54 to 100.10%, from 66.10 to 76.55%, from 79.13 to 98.13% and from 33.29 to 64.89%, respectively. And the recovery rates of spiked peach samples using n-pentane, ethyl acetate, iso propanol, dichloromethane and ethanol ranged from 82.51 to 96.72%, from 79.99 to 97.76%, from 63.12 to 73.42%, from 78.48 to 89.19% and from 60.12 to 72.32%, respectively.

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Ethanol and iso propanol though known as a traditional polar solvent, has the lowest recovery efficiencies among the studied solvents. The results show that the extraction using n-pentane, ethyl acetate and dichloromethane gave the highest pesticides recoveries but dichloromethane as a chlorinated solvent was excluded. N-pentane gave the cleanest extracts in comparison with ethyl acetate, thus it was used in the extraction.

Selection of clean up cartridge:

Data in table (4) show the recovery rates of strawberry samples using $C_{18,}$ silica gel and florisil cartridge which ranged from 85.58 to 100.64% with SD ranging from 0.91 to 2.19%, from 60.55to 97.63% with SD ranging from 0.84 to 2.1% and from 74.69 to 100% with SD ranging from 1.6 to 2.95%, respectively. The corresponding values from green bean pods ranged from 68.65 to 97.67% (SD 1.51-2.07), from 79.22 to 96.86% (SD 1.58-2.16) and from 64.99 to 90.74% (SD 0.98-1.89), respectively.

Data in table (5) show that the recovery rates of grapes samples on using $C_{18,}$ cartridge ranged from 88.25 to 100.12 % (with SD value from 0.79 to 2.00), on using silica gel cartridge ranged from 50.44 to 100% (with SD value from 0.69 to 2.1), and on using florisil cartridge recovery ranged from 43.42 to 92.31% (with SD value from 1.690 to 2.17). The recovery rates of peach samples using $C_{18,}$ silica gel and florisil cartridge eluted with n-pentane and ethyl acetate ranged from 79.93 to 100.96%, from 75.34 to 92.32% and from 69.69 to 97.22%, respectively.

It can be concluded that extraction of tested pesticides from the samples with n-pentane and clean up using C_{18} cartridge, resulted in higher recovery than on using silica gel and florisil cartridges.

Table 4: Recovery percentage of tested pesticides from vegetable samples using three types of columns

Comp.	LOD	C_{18}				Silica gel				Florisil			
		Strawberry		Bean		Strawberry		Bean		Strawberry		Bean	
		R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD
Lufenuron	0.005	85.58	2.05	91.27	2.07	70.58	1.89	91.43	1.81	81.09	1.60	76.93	1.89
Penconazole	0.005	97.23	1.16	97.67	1.66	95.11	2.10	96.86	1.79	92.37	2.60	70.81	1.73
Chlorfenapyr	0.003	91.42	1.46	88.43	1.67	97.63	1.12	82.56	2.15	100	2.52	64.99	1.58
Diniconazole	0.007	93.70	1.89	96.08	1.51	86.62	1.09	91.20	1.58	74.69	2.00	70.68	1.49
Difenconazole	0.002	100.64	0.91	68.65	1.93	60.55	1.21	81.30	1.96	94.53	2.21	69.43	1.40
Azozystrobin	0.006	90.23	2.19	81.45	1.57	79.58	0.84	79.22	2.16	86.23	2.95	90.74	0.98

Table 5: Recovery percentage of tested pesticides from fruit samples using three types of columns

Comp.	LOD	C_{18}				Silica gel				Florisil			
		Grapes		Peach		Grapes		Peach		Grapes		Peach	
		R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD	R (%)	SD
Lufenuron	0.005	92.57	2.00	98.11	1.47	50.44	0.69	90.19	1.92	43.42	1.73	89.73	0.90
Penconazole	0.005	100	0.79	100.72	1.06	80.28	2.10	92.32	1.23	92.31	1.99	97.22	0.76
Chlorfenapyr	0.003	90.31	1.22	98.82	0.98	77.13	1.97	88.12	1.17	89.54	1.66	69.69	1.37
Diniconazole	0.007	100.12	0.81	100.96	0.93	78.68	1.71	79.36	1.33	62.97	2.17	70.42	1.47
Difenconazole	0.002	88.25	1.32	98.61	1.22	100	1.80	79.21	1.17	64.53	1.00	78.93	1.78
Azozystrobin	0.006	92.54	2.00	79.93	1.19	87.91	1.10	75.34	1.10	83.34	1.57	78.06	1.04

Method Development

Pesticides extraction

N-pentane was selected as the solvent for extraction due to its effectiveness to remove chlorophyll as possible in vegetable and fruit samples, low toxicity and cost and being readily evaporated. It is an excellent extractant compared with some solvents popularly used in extraction (Munch and Hautman 1995). The boiling point of pentane was lower than that of other solvents like (acetone, hexane, ethyl acetate and dichloromethane). Therefore, using pentane not only could save analytical time but also could reduce the pesticides volatilization in the step of evaporation. As a clean-up process was necessary prior to GC/ECD determination (Tuan *et al.* 2009), the C_{18} SPE cartridge was applied to effectively eliminate matrix interferences of most crops (Kristenson *et al.* 2001; Gándara 2006 and Silve *et al.* 2008). The final identification and quantification of 79 pesticides was achieved by the conventional gas chromatography. In this study, according to the physico-chemical properties of pesticides, sensitive and selective detectors were used. GC/FPD was employed for detecting organophosphate pesticides and GC/ECD for halogenated pesticides, synthetic pyrethroid and other pesticides.

The results of this study show that the proposed method, to determine residues of pesticides in various vegetables and fruits, is rapid, simple, sensitive and uses small volumes of solvents, reducing the risk for human health and the environment. The extraction efficiency was studied for various organic solvent for that, n-pentane gave the best results and could remove as much chlorophyll as possible in vegetable and fruit samples. Twenty grams of sample homogenized using blender were taken for analysis in order to achieve a representative sample.

Clean-up of the extracts

The concentrated sample extracts may contain a high content of co-extractives, which can damage the capillary GC column. For most fruit and vegetable samples, the final extracts using the proposed SPE method were clean enough for direct GC-ECD analysis. Samples that contain more sugars or pigments needed further clean-up. C_{18} cartridge removes many co-extractives interfering with GC determination of pesticides and is very efficient in lowering the matrix effect. This occurs when an organic solvent extract of a food sample matrix co-extractants are retained on the SPE column while the pesticides are eluted. Co-extractives that accumulate in the injector and at the beginning of the column may change the retention time of certain analytes toward longer retention times.

A typical procedure of solid phase extraction was applied which involves as follow the cartridge is conditioned with an appropriate solvent to solvate functional groups of the sorbent. After the sorbent is further conditioned with the sample matrix solvent, the sample solution is forced through the sorbent by aspiration or positive pressure. The column containing retained analyte is subsequently washed with an appropriate solvent that selectively elutes impurities but leaves the analyte on the column. The purified analyte is finally eluted with a solvent strong enough to displace the analyte from the sorbent (Majewska *et al.* 2008).

(Kristenson *et al.* 2001) developed a miniaturized automated matrix solid phase dispersion (MSPD) method for extracting pesticides from apples, pears and grape with ethyl acetate and the extracts were analyzed by GC-MS without any further purification. In terms of recovery, C_{18}, C_8 and silica were compared for use as dispersants. The best results were obtained by using C_{18}.(Silve *et al*. 2008) proposed a simple and effective extraction method based on MSPD to determine dimethoate, malathion, lufenuron, carbofuran, 3-hydroxycarbofuran, thiabendazole, difenoconazole and trichlorfon in coconut pulp using gas-chromatography mass spectrometry. Different parameters of the method were evaluated, such as type of sorbent (C_{18}, alumina, silica gel and Florisil), the amount of sorbent and eluent (dichloromethane, acetone, ethyl acetate, acetonitrile, n-hexane and n-hexane: ethyl acetate (1:1, v/v). The best results were obtained using C_{18} as dispersant sorbent. SPE utilized to determine residues of pesticides, toxins or antibiotics in food and environment. For such a purpose, octadecyl SPE cartridge can be successfully used as well. Although many sorbents like, macroreticular amberlite XAD resins, C_8 or C_{18} modified silica and graphitized carbon black can be used for this aim, they decided to use an octadecyl cartridge (Gándara 2006). Eight different nitrogen- and phosphorus-containing pesticides such as: alachlor, azinphos-ethyl, chlorfenvinphos, chlorpyriphos, deltamethrin, ethoprophos, fenamiphos and malathion pesticides were retained on the sorbent and then eluted with ethyl acetate which was proved to be the most effective solvent**.** In determination of pyrethroid insecticide residues in vegetable oils a combined column packed with deactivated basic alumina and C_{18} was proved to be the most effective. The use of acetonitrile extract as an elution solvent provided the best results.

(Ridal *et al.* 1997) tested three types of SPE disks, Empore C_{18}, Empore C_8, and SPEC C_{18}, in separate experiments using loading and elution procedures suited to the differing physical properties of the disk substrates. Recoveries were very similar for each disk type (differences generally less than 5%) and ranged from 48 to 82% with relative standard deviations (RSDs) between 2 and 12% $n = 3$. Therefore, the SPEC C_{18} disks were selected for further use since the cost was significantly lower than the PTFE-based disks. In addition, the glass fiber composition of the SPEC disks allowed for greater flow rates than the PTFE-based disks and was found easier to handle. It was found that SPEC disks gave cleaner blank chromatograms in the experiments.

Method validation

Peak Resolution

Table 1 present the groups of the tested pesticides the 79 pesticide samples were divided in to 8 groups, fifteen pesticides in group 1, four pesticides in group 2, twelve pesticides in group3, eleven pesticides in group 4, eight pesticides in group 5, twelve pesticides in group 6, ten pesticides in group 7 and seven pesticides in group 8 depending on analytical conditions of instruments and retention time.

Linearity and Limit of Detection (LOD)

Standard solutions in terms of micro-liters, at variable concentrations and containing all pesticides, were divided into individual amounts, with the interval 0.05-2.00 mg/kg for injected solutions. Tests were repeated for three times at each concentration, proving favorable linear relationship of the pesticides. Correlation coefficients ranged from 0.97 to 0.99.

Table 6, show the LOD for pesticides in extracts of vegetables and fruits which was determined by applying the strawberry, green bean pods, grapes and peach samples with pesticides at a concentration range from 0.004 to 6.4 µg/g.

Out of total tested compounds (79), thirteen pesticides were used at the concentration 0.16 µg/g, sixteen pesticides at 0.64 µg/g and two pesticides (azinophos-methyl and fenamiphos) were employed at 6.4 µg/g.

The limit of detection (LOD) ranged between 0.002-0.01 µg/g for GC-ECD and 0.002-0.005 µg/g for GC-FPD. Forty-seven pesticides had LODs less than 0.005 µg/g, while twenty pesticides had LODs equal to 0.005 µg/g and eleven pesticides had LODs equal to or less than 0.007 µg/g. The high LOD, value was found with the tested pesticide fluopicolide (0.01 µg/g)

Performance of the proposed method was assessed by evaluating quality parameters, such as recovery, repeatability, matrix interference and LOD. Experimental data demonstrate that the recovery and repeatability for this multiresidue method were satisfactory.

Over 80% of the pesticides were well recovered by the proposed method from the spiked samples of green bean podes, strawberry, grapes and peach , with relative standard deviations for the recoveries in the crops generally < 9%.

Recovery

Data in Table (6) show average recovery and relative standard deviations (RSD %) from vegetables and fruits materials fortified with 79 pesticides at various concentrations, and limits of detection in addition to maximum residue limits (MRL).

Satisfactory recoveries were obtained for all pesticides ranging from 65.2 % to 104% for green bean bodes, 71.8% to 111% for strawberry, 75.8% to 104% for grapes and 70.8% to 108.5% for peach. Only one pesticide, dichlorvos, 60-70% was recovered for green bean pods fruits. Ten pesticides for strawberry, thirteen for green bean pods, eleven for grape and eleven for peach 70-80 % were recovered. The recoveries were (80-120%)of 69, 65, 68 and 68 pesticides from strawberry, green bean pods, grapes and peach, respectively (table 6).

According to Residues Analysis Quality Control Guide (RAQCG 2002), a typical recovery range is recommended to be 70-110% and a typical coefficient of variation is recommended to be less than 21 at 0.01 mg/kg peak level. Results have proved that the recoveries and precisions of most of the pesticides meet the requirement in guide.

The high recoveries and low RSDs were especially satisfactory for some crops which are of regulatory importance, including green bean pods, strawberry, grapes and peach (Table 6). The majority of recoveries obtained by GC/ECD and GC/FPD were 70.8-108.5% and 65.2-104%, respectively.

The low recoveries of a few pesticides, such as dichlorvos, tetraconazole, triforine, Δ-BHC, pp-DDT, malathion, chlorothalonil and azoxystrobin, may result from the loss during the additional C_{18} clean-up procedure. Generally, the stability and polarity of pesticides are two critical factors affecting recovery. The challenge lies in achieving satisfactory recovery of very polar pesticides (commonly with log K_{ow}<0), taking into consideration of previous reports (Štajnbaher and Zupančič -Kralj 2003; Hiemstra and de Kok 2007and Tseng *et al.,* 2007) that the recoveries of these very polar pesticides generally ranged from 30-60%. On the other hand, (Tuan *et al.* 2009) reported that the method in their study appears to be superior for a wide range of pesticides, and the recoveries of acephate (log K_{ow}= -0.89), methamidophos (log K_{ow}= -0.80), monocrotophos (log K_{ow}= -0.22), and omethoate (log K_{ow}= -0.74) were between 60 and 95%. The method in this study appears to be superior for a wide range of pesticides, and the recoveries of flucarbazone sodium (log K_{ow}= -0.89), thiamethoxam (log K_{ow}= -0.13) and thiocyclam (log K_{ow}= -0.07) were between 76 and 104% (Table 6).

Table 6: Average recovery, relative standard deviations (RSD %) and maximum residue limits (MRL) from vegetables and fruits materials fortified with 79 pesticides at various concentrations, and limits of detection

Detector	Pesticides	Spike level (µg/g)	LOD (µg/g)	Beans			Strawberry			Grapes			Peach		
				MRL (ppm)	R (%)	RSD (%)	MRL (ppm)	R (%)	RSD (%)	MRL (ppm)	R (%)	RSD (%)	MRL (ppm)	R (%)	RSD (%)
ECD	Acetochlor	0.040	0.002	0.01	99.7	4.7	0.02	97.8	3.9	0.02	91.6	3.1	0.02	95.8	3.2
	Aldrin	0.100	0.003	0.01	90.1	3.5	0.01	99.7	4.7	0.01	99.7	4.6	0.01	98.7	4.2
	Atrazine	0.144	0.004	0.05	99.4	7.6	0.05	81.5	4.8	0.05	86.0	3.0	0.05	83.5	2.6
	Azoxystrobin	0.160	0.006	3.00	76.4	5.8	10.0	71.8	4.3	2.00	92.1	2.0	2.00	77.8	4.2
	Bifenazate	0.980	0.005	0.01	81.1	4.7	2.00	79.7	5.4	0.01	96.7	4.5	0.70	79.7	5.0
	Bioallethrin	1.920	0.003	0.01	98.5	4.0	0.01	100.0	4.8	0.01	92.7	5.1	0.01	100.6	2.7
	Bromuconazole	0.160	0.002	0.05	93.2	2.9	0.05	101.0	5.5	0.50	98.0	3.9	0.10	108.5	7.6
	Butralin	0.005	0.002	0.02	86.7	3.8	0.02	99.9	4.7	0.02	80.0	4.4	0.02	99.9	7.8
	Chlorfenapyr	0.160	0.003	0.05	100	3.7	0.05	92.8	3.9	0.05	80.9	3.2	0.05	91.8	4.3
	Chlorfluazuron	0.013	0.002	1.00	95.8	4.5	2.00	80.2	5.2	2.00	83.6	7.7	2.00	80.2	8.4
	Chlorothalonil	0.030	0.002	5.00	77.7	3.4	3.00	73.5	5.1	1.00	77.4	4.0	1.00	75.5	5.0
	Clodinafop-propargyl	1.600	0.002	0.02	90.7	4.7	0.02	100.0	5.0	0.02	96.0	5.0	0.02	101	6.4
	Cyflufenamid	0.013	0.002	0.02	100	4.7	0.02	88.0	4.0	0.02	90.2	6.9	0.02	88.0	6.3
	Cyfluthrin	0.020	0.002	0.10	93.5	4.8	0.02	90.3	3.7	0.30	88.6	7.6	0.30	90.8	3.1
	Cypermethrin	0.640	0.006	0.70	81.7	2.6	0.07	98.3	5.3	0.50	90.2	6.8	2.00	98.7	3.2
	Deltamethrin	0.640	0.005	0.20	82.0	4.6	0.20	99.0	6.4	0.20	94.4	4.3	0.10	99.0	5.5
	Dicloran	1.340	0.004	2.00	79.6	5.6	0.30	83.1	4.2	0.10	89.8	6.9	0.10	82.1	8.9
	Dicofol	1.200	0.003	0.02	90.4	4.9	0.02	81.1	4.9	2.00	88.6	3.5	0.02	81.6	6.6
	Dieldrin	0.180	0.002	0.01	88.7	2.5	0.01	90.7	2.4	0.01	90.8	5.8	0.01	94.8	4.4
	Difenoconazole	0.160	0.002	1.00	95.6	5.7	0.10	100	4.7	0.50	89.7	4.6	0.50	90.5	5.0
	Diniconazole	0.160	0.007	0.05	96.9	4.4	0.05	99.0	4.9	0.20	99.9	4.6	0.20	99.5	4.5
	Endosulfan	0.13	0.006	0.05	95.4	3.3	0.05	99.0	5.0	0.05	78.7	4.9	0.05	90.4	4.9
	Endrin	0.130	0.003	0.01	80.2	4.9	0.01	80.9	5.2	0.01	80.0	4.8	0.01	83.9	2.8
	Epoxiconazole	0.160	0.002	0.05	79.9	5.6	0.05	99.0	6.4	0.05	77.7	4.8	0.05	99.3	6.4
	Esfenvalerate	0.050	0.004	0.02	87.6	3.8	0.02	97.7	2.9	0.02	90.9	4.7	0.02	97.7	5.0
	Fenarimol	0.160	0.006	0.02	98.9	5.8	0.3	78.6	4.3	0.30	89.5	5.8	0.50	78.6	2.8

	Fluazinam	0.004	0.007	0.05	88.8	5.4	0.05	80.7	5.7	0.05	76.6	7.4	0.05	82.3	4.6
	Flucarbazone sodium	0.050	0.002	0.01	99.8	4.9	0.01	76.9	6.9	0.01	104	6.8	0.01	89.4	3.2
	Fluopicolide	0.160	0.010	0.01	96.4	5.3	0.01	80.1	4.5	2.00	96.1	4.5	0.01	98.8	5.1
	Flutolanil	0.025	0.005	0.05	79.7	5.3	0.05	90.9	3.5	0.05	87.9	3.7	0.05	77.8	3.5
	Hep. Epoxide	0.130	0.003	0.01	90.8	3.5	0.01	97.6	5.3	0.01	99.8	3.6	0.01	94.5	3.5
	Heptachlor	0.130	0.003	0.01	87.8	4.0	0.01	99.1	4.1	0.01	79.8	4.2	0.01	83.3	5.0
	Hexythiazox	1.600	0.006	0.50	90.8	3.2	0.50	78.9	4.1	1.00	87.7	5.8	1.00	75.3	4.1
	Lambda-cyhalothrin	0.010	0.002	0.20	100	4.6	0.50	100	4.5	0.20	85.3	7.1	0.20	96.7	4.8
	Lufenuron	0.160	0.005	0.02	96.0	5.9	1.00	86.7	5.1	1.00	94.6	6.4	1.00	96.8	5.5
	Methoxychlor	0.700	0.007	0.01	100	5.8	0.01	78.6	5.3	0.01	93.7	3.2	0.01	100	6.7
	Metribuzin	0.320	0.006	0.10	87.7	5.7	0.10	90.1	4.7	0.10	97.8	3.3	0.10	91.0	4.4
	Myclobutanyl	0.320	0.005	0.30	78.7	5.7	1.00	93.6	6.7	1.00	89.8	4.2	0.50	93.4	2.8
	op-DDT	0.700	0.003	0.05	99.3	4.4	0.05	80.3	5.1	0.05	82.3	2.5	0.05	97.6	6.7
	Oxadiazon	0.005	0.005	0.05	87.8	5.5	0.05	83.0	5.6	0.05	88.0	4.7	0.05	99.4	7.4
	Oxyfluorfen	0.08	0.005	0.05	85.3	6.0	0.05	90.1	5.2	0.10	91.1	3.3	0.10	97.8	6.9
	Penconazole	0.16	0.005	0.05	93.5	4.0	0.50	99.9	5.1	0.20	98.9	5.6	0.10	79.8	4.7
	Pendimethalin	0.004	0.002	0.20	76.3	5.0	0.05	91.8	5.6	0.05	93.8	4.9	0.05	105.6	7.6
	Permethrin	0.64	0.003	0.05	92.7	4.0	0.05	98.0	6.9	0.05	98.8	4.1	0.05	99.0	7.7
	pp-DDD	0.64	0.003	0.05	100	5.0	0.05	90.1	4.3	0.05	91.1	2.7	0.05	95.2	2.8
	pp-DDE	0.06	0.003	0.05	91.4	3.1	0.05	91.7	2.7	0.05	94.7	2.6	0.05	99.1	2.5
	pp-DDT	0.70	0.004	0.05	99.4	3.7	0.05	92.4	3.9	0.05	92.3	3.9	0.05	75.8	4.6
	Propiconazole	0.16	0.003	0.05	92.5	3.3	0.05	96.1	2.8	0.05	97.6	4.2	0.20	94.8	3.2
	Proquinazid	0.005	0.003	0.02	77.7	5.0	0.02	87.6	4.0	0.02	77.7	4.9	0.02	87.6	4.1
	Tetraconazole	0.16	0.003	0.02	89.4	6.7	0.20	100	3.4	0.50	77.6	3.7	0.10	70.8	5.7
	Tetramethrin	0.64	0.005	0.01	88.3	5.9	0.01	99.0	6.9	0.01	99.6	8.0	0.01	80.7	6.8
	Thiamethoxam	0.04	0.005	0.05	101	5.5	0.05	96.4	4.1	0.05	101	3.2	0.05	96.4	2.2
	Thiocyclam	0.005	0.003	3.00	99.2	3.2	3.00	97.7	3.5	3.00	99.1	4.4	3.00	97.7	3.6
	Tralomethrin	0.72	0.003	0.50	78.8	3.5	0.50	100	3.5	0.50	88.6	5.9	0.50	81.6	7.0
	Triflumizole	2.4	0.005	0.10	88.9	4.5	0.20	98.7	6.6	3.00	90.0	3.2	0.10	94.0	5.3
	Triforine	1.6	0.006	0.01	74.9	5.3	0.01	80.5	2.3	0.01	75.8	4.5	0.01	91.0	4.8
	Triticonazole	2.4	0.003	0.01	95.9	4.3	0.01	89.7	2.9	0.01	91.8	4.0	0.01	90.1	3.4
	α- BHC	0.10	0.005	0.20	91.5	3.6	0.20	100	3.1	0.20	88.9	4.6	0.20	92.6	5.0
	γ - BHC	0.13	0.004	0.20	91.8	3.0	0.20	105	6.6	0.20	99.0	7.7	0.20	77.0	5.3
	γ – Cyhalothrin	0.019	0.006	0.20	98.5	4.3	0.20	90.0	2.8	0.20	88.9	5.8	0.20	86.8	7.0
	γ- Chlordane	0.10	0.003	0.01	86.4	5.6	0.01	111	7.3	0.01	93.4	3.6	0.01	91.3	3.3
	Δ -BHC	0.06	0.004	0.20	71.3	6.4	0.20	88.7	4.8	0.20	89.3	5.0	0.20	81.5	4.8
FPD	Azinphos-methyl	6.4	0.005	0.05	100	4.8	0.05	89.6	6.7	0.05	85.7	7.1	0.05	89.7	6.7
	Cadusafos	0.64	0.004	0.01	77.8	3.2	0.05	90.3	4.1	0.05	77.6	3.9	0.05	91.5	3.8
	Chlorpyrifos	0.64	0.005	0.05	95.8	4.3	0.20	99.3	4.2	0.50	98.7	4.1	0.20	99.8	4.7
	Chlorpyrifos-methyl	0.64	0.003	0.05	81.3	4.6	0.50	91.9	4.7	0.20	90.5	5.1	0.50	94.9	4.4
	Diazinon	0.64	0.003	0.01	86.9	6.5	0.01	97.8	3.2	0.01	99.0	3.9	0.01	97.8	3.3
	Dichlorvos	0.64	0.003	0.01	65.2	5.6	0.01	90.1	5.6	0.01	100	5.9	0.01	93.4	5.0
	Dimethoate	0.64	0.005	0.02	97.5	7.8	0.02	88.7	6.2	0.02	90.0	6.2	0.02	88.7	6.2
	Ethion	0.64	0.004	0.01	90.6	6.2	0.01	80.5	7.5	0.01	88.7	6.1	0.01	87.3	6.1
	Fenamiphos	6.4	0.005	0.02	78.6	5.7	0.02	78.4	5.9	0.02	80.0	5.0	0.02	79.2	5.7
	Malathion	0.64	0.002	0.02	89.9	3.1	0.02	80.3	4.4	0.02	76.3	4.2	0.02	89.8	6.3
	Phenthoate	1.28	0.003	0.05	96.8	4.8	0.10	85.0	5.0	0.10	85.0	5.0	0.10	85.4	5.0
	Pirimiphos-methyl	0.64	0.005	0.05	89.9	3.7	0.05	89.7	2.8	0.05	89.7	2.8	0.05	89.3	3.1
	Profenofos	0.64	0.004	0.05	96.8	3.2	0.05	99.2	3.6	0.05	99.0	3.6	0.05	94.4	3.4
	Propetamphos	0.64	0.005	0.01	99.0	4.3	0.01	86.7	4.9	0.01	86.7	4.9	0.01	88.9	4.6
	Prothiofos	2.56	0.005	0.05	101	4.8	0.30	79.3	4.9	2.00	99.8	8.1	0.50	83.5	4.0

	Quinalphos	1.92	0.005	0.05	104	5.5	0.05	101	6.9	0.05	92.8	3.5	0.05	81.6	6.1
	Triazophos	1.92	0.004	0.01	91.8	3.8	0.01	79.6	5.9	0.01	99.1	2.5	0.01	90.6	4.3

The proposed method not only allowed the simultaneous determination and confirmation of a large number of pesticides which was acceptable in terms of recovery and detection limit but also showed to be useful in routine analysis due to its being fast and easy to carry out

Conclusion

A simple and rapid method was developed to determine the residues of 79 pesticides in two vegetables, strawberry and green bean pods and two fruits, grapes and peach. This method, using n-pentane for extraction and C18 cartridge for clean up and GC/ECD and FPD analysis, showed a high sensitivity for the determination of pesticide residues at the levels required in MRLs for the vegetables and fruits.

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تحليل لمتبقيات المتعدده ل ٧٩ مبيداً فى ثمار الفرواله و قرون الفاصوليا الخضراء و العنب و الخوخ باستخدام و الغاز كروماتوجرافىSPE

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*** قسم الحشرات الاقتصاديه و المبيدات - كليه الزراعه- جامعه القاهره**

**** المعمل المركزى للمبيدات- مركز البحوث الزراعيه- الدقى –جيزه**

اختبرت خمسه مذيبات (بنتان-ايثايل اسيتيت- داى كلوروميثان- كحول ايزوبروبايل) لاستخلاص سته مبيدات وهى (lufenuron, chlorfenapyr, penconazole, diniconazole, difenoconazole and azoxystrobin) من ثمار الفراوله- قرون الفاصوليا الخضراء - العنب - الخوخ. وقد اوضحت النتائج ان الاستخلاص باستخدام البنتان و الايثايل اسيتيت و الداى كلوروميثان اعطى اعلى نسبه معدل استرجاع عن استخدام كحول الايثانول او الايزوبروبايل. كما اعطى الاستخلاص بمذيب البنتان اقل نسبه شوائب و اعلى معدل استرجاع و ذلك عند استخدام عمود C_{18} فى التنقيه عن استخدام عمود السليكا جل أو الفلوروسيل .

وقد استخدمت طريقه تحليل سريعه و سهله فى تعريف وتقدير متبقيات ٧٩ مبيد ، تشمل مركبات قسفوريه و كلورينيه ومركبات بيروثرويد و غيرها من المبيدات فى ثمار الفاكهة (العنب و الخوخ) و الخضروات (الفراوله- قرون الفاصوليا الخضراء). هذا وقد تم استخلاص متبقيات المبيدات من العينات باستخدام البنتان يتبعه التنقيه باستخدام عمود C_{18} و استخدام كل من البنتان و الايثايل اسيتيت فى ازاحه المركبات من العمود.

و تم تقدير ٦٢ مبيد باستخدام الغاز الكروماتوجرافى المزود بكاشف ECD و ١٧ مبيد باستخدام كاشف FPD . وتراوحت معدلات الاسترجاع لمعظم المبيدات فى ثمار الفاكهه والخضر ما بين ٨٠-١٠٩% مع انحراف معيارى أقل من ٩ %.

قام بتحكيم البحث

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Table 2: Recovery percentage of tested pesticides extraction from vegetable samples using different solvents

Compound	LOD	n-Pentane				Ethyl acetate				Iso-Propanole				Dichloromethane				Ethanol			
		Strawberry		Bean		Strawberry		Bean		Strawberry		Bean		Strawberry		Bean		Strawberry		Bean	
		R(%)	SD	R(%)	SD	R (%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD
Lufenuron	0.005	88.72	2.04	91.9	2.10	92.50	1.44	90.71	1.00	80.21	2.24	71.93	1.18	96.35	1.06	87.34	1.50	75.47	1.50	69.65	1.67
Chlorfenapyr	0.003	88.77	1.50	86.30	1.10	88.04	1.16	80.15	3.12	70.75	2.05	69.91	1.96	97.75	1.03	80.15	2.57	75.44	1.42	69.37	0.97
Penconazole	0.005	90.31	2.09	102	1.65	93.76	1.00	90.89	1.41	69.01	1.40	65.57	1.58	92.00	0.65	85.90	1.51	67.37	7.13	70.09	1.09
Diniconazole	0.007	87.57	1.57	89.01	1.39	102.54	0.83	95.22	2.44	63.87	1.41	69.43	1.85	90.83	1.49	88.92	0.82	71.34	1.45	70.15	0.53
Difenconazole	0.002	79.87	0.84	81.77	1.49	90.88	1.94	88.31	1.01	70.49	1.01	78.95	1.47	80.12	1.72	81.81	1.64	80.11	2.33	77.65	0.35
Azozystrobin	0.006	84.53	1.54	83.32	1.97	86.05	0.94	80.56	1.65	79.91	1.36	70.13	2.23	77.54	1.13	82.90	2.61	69.33	1.44	60.11	1.11

Table 3: Recovery percentage of tested pesticides extraction from grapes and peach fruit samples using different solvents

Compound	LOD	n-Pentane				Ethyl acetate				Iso-Propanole				Dichloromethane				Ethanol			
		Grapes		Peach		Grapes		peach		Grapes		Peach		Grapes		Peach		Grapes		peach	
		R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD	R(%)	SD
Lufenuron	0.005	100	0.38	95.28	2.60	100.1	2.14	95.14	2.44	66.10	1.61	68.34	1.95	90.62	2.17	89.19	2.22	59.31	1.14	60.12	2.27
Chlorfenapyr	0.003	88.02	1.83	83.12	2.30	97.75	1.94	82.50	2.64	72.91	2.67	65.32	1.39	98.13	1.12	85.41	1.80	63.29	1.02	67.01	1.57
Penconazole	0.005	99.71	1.59	96.72	2.01	92.00	1.67	96.42	2.15	66.55	1.99	63.12	1.16	91.06	2.56	83.18	2.00	64.89	0.99	69.97	2.06
Diniconazole	0.007	99.11	0.54	90.11	1.89	90.83	2.11	97.76	1.48	71.72	1.53	70.69	1.12	89.55	1.50	86.99	2.08	33.29	0.48	65.52	0.79
Difenconazole	0.002	90.51	2.21	87.43	1.91	80.12	2.30	85.45	0.97	76.55	1.61	73.42	0.94	79.13	0.98	78.48	2.00	59.96	0.89	72.32	2.12
Azozystrobin	0.006	81.38	1.63	82.51	2.66	77.54	1.89	79.99	2.00	73.14	3.12	69.79	1.04	80.22	2.31	85.64	3.05	55.01	1.17	61.23	2.08