

Solid-phase Extraction Cleanup Method for the Determination of Organophosphorus Pesticides in Vegetables

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Abstract: A simple solid-phase extraction (SPE) cleanup method has been developed for the determination of organophosphorus (OP) pesticides in vegetables. Pesticide residues are extracted with acetone and dichloromethane. Extracts are cleaned up by an octadecyl, C₁₈ SPE column. The pesticides are determined by gas chromatography (GC) using a flame photometric detector (FPD). The recoveries for 10 OP pesticides in three vegetables; carrot, cucumber and green mustard were in the range of 71.0 % to 107.7 %. Low recovery was obtained for polar pesticide, methamidophos. The results were compared to the method currently used in the laboratory, which does not require any cleanup.

Abstrak: Satu kaedah pembersihan turus pengekstrakan pepejal telah dihasilkan untuk menentukan racun perosak jenis organofosforus dalam sayur-sayuran. Racun perosak diekstrak dengan aseton dan dwiklorometana. Ekstrak dibersihkan dengan turus oktadesil, C₁₈. Racun perosak ditentukan dengan kromatografi gas yang dilengkapi dengan pengesan fotometrik nyala. Pengembalian untuk 10 jenis racun perosak dalam tiga jenis sayur-sayuran iaitu lobak merah, timun dan sawi hijau adalah di antara 71.0 % dan 107.7 %. Pengembalian yang rendah diperolehi untuk racun perosak yang polar iaitu methamidophos. Keputusan ini dibandingkan dengan kaedah yang digunakan di makmal pada masa ini iaitu tanpa menggunakan pembersihan.

Key words : solid-phase extraction, silica gel cleanup, organophosphorus pesticides

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Introduction

Organophosphorus (OP) pesticides are widely used for pest control in vegetable cultivation today. They have replaced the organochlorine (OC) pesticides as the most commonly used insecticides, as concern about the OC persistence and polluting effect on the environment. However, as they are less persistent than OC pesticides, a greater number of applications to a crop may be necessary during the course of the growing season. These pesticides are widely used by vegetable farmers in Sarawak and contributing to 86 % of the total pesticide residue violation in vegetables [1]

The major concern of the pesticide residue laboratory today is the use of large quantity of organic solvents. These solvents are not only expensive but they also incurred high cost of disposal. Solid phase extraction (SPE) technology has great potential for use in pesticide residue analysis, since it often eliminates the need for expensive and environmentally sensitive solvents. It also has the following advantages: batch sample processing capabilities, small size, automation and low cost. The current method used by the Agriculture Research Centre's laboratory to monitor the OP pesticide residues in vegetables and fruits does not require cleanup step. As a result, contamination often occurs at the GC injector inlet and column. Thus, cleaning of

injector port, replacement of glass wool and cutting of GC column need to be carried out regularly.

Several methods have been developed for the analysis of OP pesticides using the SPE cartridge. Pihlstrom & Osterdahl [2] reported a SPE cleanup method for the determination of some OP pesticides in fruit and vegetable. Extraction was carried out using ethyl acetate and cleanup on a polystyrene-divinylbenzene cartridge. Recovery obtained was above 70 %. Lee *et al.* [3] demonstrated the use of acetonitrile for the extraction of 7 OP pesticides in potato, tomato and orange. The extract was passed through a reverse phase SPE column. No solvent was used for elution. The OP pesticides were determined by gas chromatograph (GC) equipped with flame photometric detector (FPD). No matrix interference was reported. The recovery was reported to be in the range of 70.7 to 153.2 %. Sasaki *et al.* [4] reported a simple and efficient cleanup method for the determination of 23 OP pesticides in crops including onion on GC-FPD. The sample was extracted with acetone and benzene. For onion, cleanup was performed on silica cartridge. Recoveries for OP pesticides exceeded 80 %, but the water-soluble pesticides gave poor recoveries in all crops. Some non-polar pesticides were not recovered quantitatively. Some pesticides were also not recovered from onion because of adsorption to the

silica cartridges. Fillion *et al.* [5] developed a method for the determination of OP pesticides in fruits and vegetables using octadecyl C₁₈, carbon and aminopropyl cartridges. No solvent was used for elution using the C₁₈ cartridge. Recovery for pears, carrots and bananas ranged from 67 % to 99 %. Analysis was performed by GC-MSD in selective-ion monitoring mode. Cook *et al.* [6] used gravity-fed C₁₈ SPE as cleanup for detection of OP pesticides in spinach, oranges, tomatoes and peaches. Extraction was carried out with acetonitrile and passed through C₁₈ cartridge. No solvent was used for the elution of C₁₈ cartridge. The recoveries ranged from 76 % to 112 %. Yamazaki & Ninomiya [7] described a method using SPE cleanup of OP pesticides in orange. Samples were extracted with anhydrous sodium acetate with ethyl acetate. The ethyl acetate extract was concentrated and cleaned up by passing through tandem anion-exchange and amine bonded silica columns. The recoveries ranged from 90.4 to 97.0 %.

The objective of this study was to develop a simple and rapid cleanup method to determine the OP pesticides in vegetables. SPE method was chosen because less solvent is used and shorter analysis time. This paper reports the findings on the determination of OP pesticides in vegetables using GC-FPD. Residues are extracted with acetone and dichloromethane. Extracts are passed through C₁₈ SPE column and eluted with hexane and acetone. The results obtained were compared to the method currently used in the laboratory, which does not require cleanup.

Experimental

Chemicals and Reagents

All the chemicals and reagents used were of analytical grade. Pesticide standards were obtained from Ehrenstorfer Company. SPE tubes, Isolute C₁₈ (1 g sorbent in 6 ml tube) were purchased from International Sorbent Technology.

Instrumentation

An Agilent 6890 Gas Chromatograph (GC) equipped with Flame Photometric Detector (FPD) was used for the determination of the OP pesticides. The GC conditions were : Injector temperature, 260°C; detector 250°C; carrier flow (nitrogen) 4 ml/min; oven temperature, 120°C (1.0 min), rate 30°C/min to 150°C, rate 5°C/min to 270°C (10 min); air flow: 80 ml/min; hydrogen flow : 67 ml/min. The OP pesticides were analysed on a HP 5, 15 m x 0.53 mm x 1.5 µm column.

Procedures

Three types of vegetables, namely carrot (*Daucus carota*), cucumber (*Cucumis sativa*), and

green mustard (*Brassica chinensis*) representing the root, cucurbits and brassica families were selected for this study. Each sample was fortified with 0.5 and 0.1 ppm of eleven OP pesticide standards, namely methamidophos, dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl. Three replicate fortifications for each vegetable were prepared.

Extraction was carried out based on procedures described by Steinwandter [8]. 10 g of sample was homogenised in a blender containing 100 ml acetone, 75 ml dichloromethane and 15 g sodium chloride for three minutes. The homogenised mixture was allowed to separate into its organic and aqueous layers. The organic phase was transferred to a beaker and 3 g of sodium sulphate was added to remove the remaining water. This extract was divided into two; one injected directly into GC-FPD for OP determination and the other one for SPE cleanup. For the SPE cleanup, the C₁₈ column was first conditioned with 10 ml hexane. Then, 2 ml of extract was transferred to the tube. Finally, the tube was eluted with 10 ml hexane and followed by 10 ml acetone. The OP pesticides were determined on GC-FPD.

Results and Discussion

Development of SPE Conditions

The selection of the solvent system for the SPE was based on several criteria. Solvents that are hazardous or expensive to dispose off were not evaluated. A volatile solvent system must be used, as rapid evaporation of a large volume of solvent would be required in the sample preparation without causing loss of volatile pesticides. The solvent system must be sufficiently polar to extract most polar pesticides. The final extract should have only minimum of matrix co-extractives. In order to obtain good recoveries for the OP pesticides, various solvent systems with different polarity were evaluated and optimised.

Solvents mixtures or single solvent system consisting of any four solvents, namely hexane, petroleum ether, acetone and methanol, were used in this study. Their polarity indices (p') are 0.06, 0.1, 5.4 and 6.6 respectively [9]. The solubility of the OP pesticides used in this study ranges from 0.05 mg/l to 200,000 mg/l [10]. High polarity solvents such as methanol did not sufficiently remove all the pesticides from the SPE column. Reducing the solvent polarity improved the recovery significantly. It was found that 10 ml of hexane followed by 10 ml of acetone resulted in good recoveries for all the pesticides studied except methamidophos. The first fraction comprised mainly the non-polar OP pesticides such as diazinon, tolcophos-methyl,

fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl. The second fraction consisted the polar pesticides such as methamidophos and dimethoate. However, the composition in both fractions varied from batch to batch. Therefore, the two fractions were combined into one for the GC determination. Attempt was made to use solvent mixtures such as hexane : petroleum ether (1 : 1 v/v), petroleum ether : acetone (1 : 1 v/v), hexane : acetone (1 : 1 v/v and 2 : 1 v/v) did not produce good recoveries for most of the pesticides studied. The critical factor to be observed was that the SPE tube should not be left dry after eluting the samples since low recoveries may result. A flow rate of 1 ml/min was sufficient to elute the analytes. The optimum conditions for the OP pesticides were found to be as follows: (a) solvent: hexane and acetone, (b) volume of eluting solvent : 10 ml of each solvent, (c) flow rate for elution : 1 ml/min.

Recovery Studies and Method Validation

Eleven OP pesticides, namely methamidophos, dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl were selected for this study. Except for tolcophos-methyl, which is a fungicide, the rest are insecticides. The recoveries for the OP pesticides fortified at 0.5 ppm are given in Table 1. The recoveries obtained for all the pesticides tested except methamidophos were in the acceptable range of 70% to 120% [11]. Their recoveries ranged from 80.7 % to 106.0 % with CV of 2.1 % to 11.7 %. A low recovery of 39.3 % was obtained for polar pesticide; methamidophos. The low recovery of methamidophos may due to the possibility of it being leached out during the elution of the 2 ml extract into the SPE tube. This portion was discarded in the experiment. The solubility of methamidophos is 200,000 mg/l in water. The other OP pesticides are less polar than methamidophos. The solubility for dimethoate is 25,000 mg/l in water, while the solubility for other OP pesticides range from 0.6 mg/l to 40 mg/l.

Three types of vegetables, namely carrot, cucumber and green mustard representing root, cucurbits and brassica families, respectively, were selected for this study to illustrate the efficiency of the cleanup procedure for different matrices. As each type of vegetable may contain different co-extractives, these co-extractives may co-elute with the OP pesticides. This may interfere with the GC analysis of sample extracts. The vegetables used in this study were previously analyzed to ensure that they contained no pesticides, thereby providing a true blank for spiking and recovery.

Table 1 : Recovery of OP pesticides (n = 3)

Pesticide	% Recovery \pm CV
Methamidophos	39.3 \pm 19.0
Dimethoate	88.7 \pm 2.3
Diazinon	80.7 \pm 8.3
Tolcofos-methyl	81.3 \pm 9.0
Fenitrothion	97.3 \pm 4.0
Chlorpyrifos	82.0 \pm 11.7
Phenthoate	105.0 \pm 2.7
Prothiofos	106.0 \pm 10.6
Triazofos	83.7 \pm 2.9
Cyanofenfos	96.3 \pm 4.2
Azinphos-ethyl	80.7 \pm 2.1

CV = coefficient of variation

(a) Carrot

The recoveries of the OP pesticides from fortified carrot samples at 0.5 ppm and 0.1 ppm with and without the C₁₈ cleanup are given in Table 2. At 0.5 ppm fortification level, the recoveries obtained using the C₁₈ cleanup for the 10 OP pesticides studied, namely dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl, were in the range of 80.0 % to 107.7 % with CV of 1.0 % to 5.9 %. A low recovery of 6.7 % was obtained for methamidophos. Good recoveries were obtained for all the 11 OP pesticides using the method without cleanup and were within the acceptable range. Their recoveries ranged from 76.0 % to 108.3 % with CV of 5.0 % to 11.0 %. At 0.1 ppm fortification level, good recoveries were obtained for the C₁₈ cleanup for all the OP pesticides tested except methamidophos. The recoveries for dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl were in the range of 85.3 % to 99.7 % with CV of 2.0 % to 8.7 %. A low recovery of 40.7 % was obtained for methamidophos. These results are consistent with those obtained at 0.5 ppm level. For the method without cleanup, good

Table 2 : Recovery of OP pesticides from carrot samples with and without C₁₈ cleanup (n =3)

Pesticide	0.5 ppm		0.1 ppm	
	C ₁₈	No cleanup	C ₁₈	No cleanup
	% Rec ± CV	% Rec ± CV	% Rec ± CV	% Rec ± CV
Methamidophos	6.7* ± 2.5	76.0 ± 5.0	40.7* ± 5.9	108.3 ± 10.5
Dimethoate	107.7 ± 2.3	108.3 ± 6.0	99.7 ± 8.7	118.0 ± 3.5
Diazinon	92.7 ± 3.2	89.3 ± 9.3	93.7 ± 3.1	97.3 ± 4.2
Tolcofos-methyl	92.0 ± 1.7	98.7 ± 10.7	93.3 ± 6.7	97.0 ± 2.7
Fenitrothion	91.7 ± 1.5	102.0 ± 6.1	97.0 ± 4.6	110.7 ± 1.2
Chlorpyrifos	84.7 ± 5.9	99.3 ± 11.0	97.0 ± 2.0	96.0 ± 2.0
Phenthoate	92.3 ± 2.1	97.0 ± 8.9	91.0 ± 2.7	94.0 ± 1.7
Prothiofos	80.0 ± 1.0	103.7 ± 10.0	85.3 ± 2.5	94.0 ± 1.0
Triazofos	102.0 ± 2.0	95.7 ± 8.1	92.7 ± 5.7	124.0 ± 1.0
Cyanofenfos	88.0 ± 1.7	99.7 ± 7.2	96.0 ± 4.4	99.7 ± 0.6
Azinphos-ethyl	102.3 ± 5.0	97.3 ± 9.2	92.0 ± 6.6	112.0 ± 1.0
AV	93.3	99.1	93.8	104.2
SD	8.5	5.1	4.0	11.0

AV = average mean excluding*

SD = standard deviation excluding *

CV = coefficient of variation

Rec = recovery

recoveries were obtained for all the 11 OP pesticides tested. Their recoveries obtained were also higher and ranged from 94.0 % to 118.0 % with CV of 0.6 % to 10.5 %.

The chromatograms for the OP pesticides with and without the C₁₈ cleanup are shown in Figure 1. Both chromatograms showed no interfering peaks between 2 min to 25 min regions where the OP pesticides were eluted. The colour of the extracts was yellow before C₁₈ cleanup and no obvious colour change was observed after the cleanup. However, the colour of the SPE tube was yellowish indicating some colour compounds were absorbed and retained by the tube. It was noted that the polar solvent, namely acetone used as the second eluent leached out the coloured polar matrix co-extractives retained in

the SPE tube. This was because the C₁₈ sorbent lacked the selectivity in retaining them. The use of polar solvent as the second eluant was necessary in order to elute the polar pesticides such as methamidofos and dimethoate from the SPE tube. Thus, it is proposed that smaller amount of extract is used for the cleanup. The Limit of Detection (LOD) obtained for the OP pesticides using the SPE C₁₈ cleanup was 0.02 mg/kg. Similar LOD was also obtained using the silica gel cleanup.

(b) *Cucumber*

Recoveries of the OP pesticides fortified in cucumber samples at 0.5 ppm and 0.1 ppm with and without the C₁₈ cleanup are given in Table 3. At 0.5 ppm fortification level, the recoveries obtained using

the C_{18} cleanup for 10 OP pesticides, namely dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl, were in the range of 76.3 % to 104.0 %. The CV ranged from 1.5 % to 7.9 %. A low recovery of 8 % was obtained for methamidophos. Good recoveries were obtained for methamidophos without cleanup. Their recoveries ranged from 69.3 % to 111.0 % with CV of 1.2 % to 6.2 %. At 0.1 ppm fortification level, the recoveries obtained using the C_{18} cleanup for 10 OP pesticides, namely

dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl were in the range of 82.7 % to 111.0 % with CV of 1.2 % to 9.5 %. A low recovery of 30.7 % was obtained for methamidophos. For the method without cleanup, the recoveries obtained for all the 11 OP pesticides tested were within the acceptable range. Their recoveries ranged from 87.0 % to 111.7 % with CV of 1.5 % to 10.7 %.

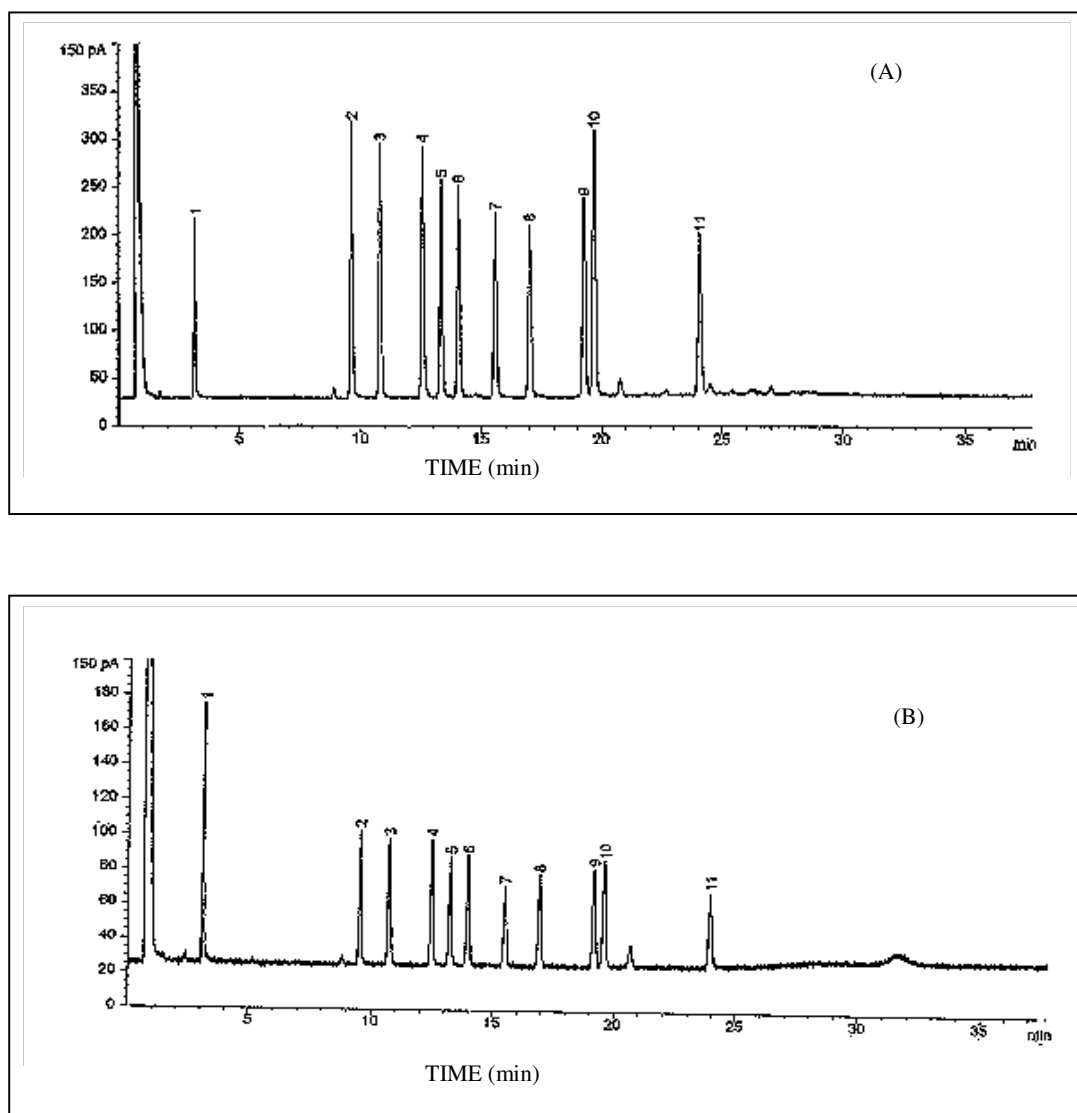


Figure 1 : GC chromatogram of carrot extract after SPE C_{18} cleanup (A) and without cleanup (B). Peaks : 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcophos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazofos; 10, cyanofenfos; 11, azinphos-ethyl

Table 3 : Recovery of OP pesticides from cucumber samples with and without C₁₈ cleanup (n = 3)

Pesticide	0.5 ppm		0.1 ppm	
	C ₁₈	No cleanup	C ₁₈	No cleanup
	% Rec ± CV	% Rec ± CV	% Rec ± CV	% Rec ± CV
Methamidophos	8.0* ± 4.4	69.3 ± 1.5	30.7* ± 1.5	92.0 ± 2.7
Dimethoate	104.0 ± 6.2	111.0 ± 6.2	111.0 ± 9.5	100.3 ± 10.7
Diazinon	82.7 ± 3.2	96.3 ± 4.0	86.7 ± 7.1	98.7 ± 1.5
Tolcofos-methyl	76.3 ± 1.5	94.3 ± 3.1	94.3 ± 8.1	94.0 ± 2.7
Fenitrothion	79.7 ± 2.1	98.3 ± 1.5	95.7 ± 8.7	101.0 ± 2.7
Chlorpyrifos	87.0 ± 7.2	91.7 ± 4.2	88.7 ± 7.0	94.3 ± 1.5
Phenthoate	92.3 ± 7.0	97.3 ± 1.2	103.0 ± 6.0	87.0 ± 7.9
Prothiofos	92.3 ± 3.2	92.3 ± 4.0	82.7 ± 1.2	93.7 ± 7.1
Triazofos	98.3 ± 7.9	97.0 ± 2.0	104.3 ± 1.2	99.3 ± 7.1
Cyanofenfos	86.7 ± 7.4	89.3 ± 1.5	95.7 ± 7.5	91.0 ± 1.7
Azinphos-ethyl	96.3 ± 6.7	101.0 ± 4.0	89.0 ± 7.9	111.7 ± 2.1
AV	89.6	96.9	95.1	97.1
SD	8.7	6.1	8.8	6.7

AV = average mean excluding*

CV = coefficient of variation

SD = standard deviation excluding* Rec = recovery

The chromatograms obtained for cucumber samples with and without the C₁₈ cleanup are shown in Figure 2. No interfering peaks were observed in both chromatograms between 2 min to 25 min regions where the OP pesticides were eluted. However, a large peak was found at 20.5 min in the chromatogram for the method without cleanup and it may co-elute with the OP pesticides if higher temperature programming is used. However, this peak was not found in the chromatogram obtained using the C₁₈ method. This showed that the C₁₈ cleanup has retained this compound from the cucumber samples. It was observed that this peak was

not found in the carrot samples. As less coloured compound was present in cucumber samples, the colour of the extract before cleanup was light green. As the polar solvent, namely acetone that was used as second eluent leached out the coloured compounds from the SPE tube, no obvious colour change was observed in the extract after the cleanup. This is because these compounds were mainly polar and the C₁₈ lacked the selectivity in retaining them. However, the colour of the SPE tube was light yellowish indicating some colour compounds were retained by the tube. The LOD obtained using the SPE C₁₈ and the silica gel cleanup was 0.02 mg/kg.

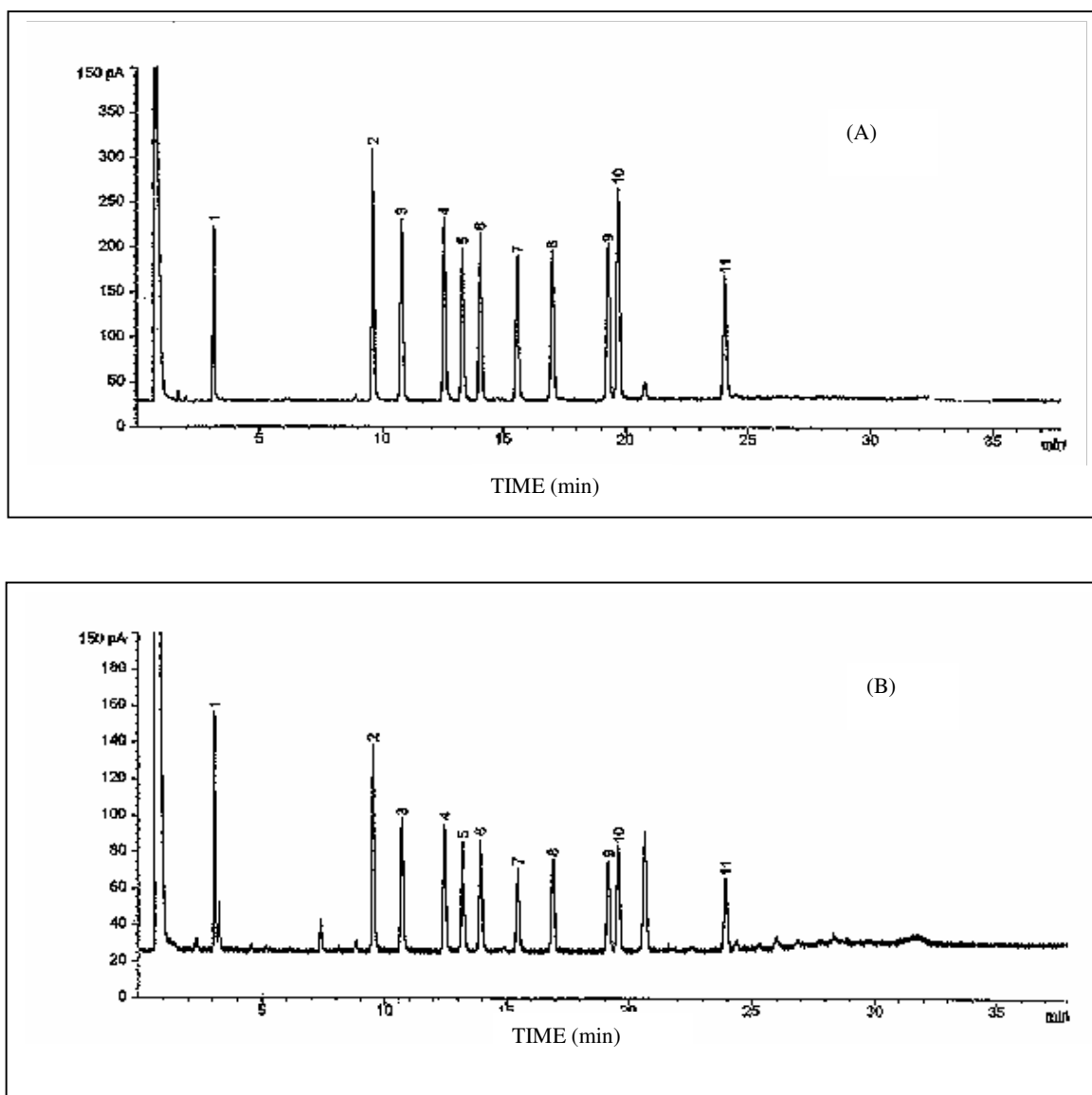


Figure 2 : GC chromatogram of cucumber extract after SPE C_{18} cleanup (A) and without cleanup (B). Peaks : 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcophos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazofos; 10, cyanofenfos; 11, azinphos-ethyl

(c) Green mustard

Recoveries of the OP pesticides fortified in green mustard samples with and without the C_{18} cleanup at 0.5 ppm and 0.1 ppm are given in Table 4. At 0.5 ppm fortification level, the recoveries obtained using the C_{18} cleanup for the 10 OP pesticides, namely dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl were in the range of 71.0 % to 97.3 % with CV of 2.0 % to 8.3 %. A low recovery of 38.0 % was obtained for methamidophos. For the method without cleanup, good recoveries were obtained for

all the 11 OP pesticides tested. Their recoveries ranged from 74.3 % to 118.3 % with CV of 0.6 % to 6.1 %. At 0.1 ppm fortification level, the recoveries obtained using the C_{18} cleanup for 10 OP pesticides, namely dimethoate, diazinon, tolcophos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl were within the acceptable range. Their recoveries ranged from 83.7 % to 106.3 % with CV of 1.7 % to 8.7 %. A low recovery of 37.0 % was obtained for methamidophos. Good recoveries of 86.3 % to 114.7 % were obtained for method without the cleanup. Their CV ranged from 2.5 % to 10.4 %.

Table 4 : Recovery of OP pesticides from green mustard samples with and without C₁₈ cleanup (n = 3)

Pesticide	0.5 ppm		0.1 ppm	
	C ₁₈	No cleanup	C ₁₈	No cleanup
	% Rec ± CV	% Rec ± CV	% Rec ± CV	% Rec ± CV
Methamidophos	38.0* ± 27.8	74.3 ± 1.5	37.0* ± 10.2	93.3 ± 10.4
Dimethoate	97.3 ± 8.3	118.3 ± 6.1	96.7 ± 8.7	99.0 ± 7.6
Diazinon	84.0 ± 2.0	92.3 ± 1.5	94.7 ± 3.8	91.3 ± 2.5
Tolcofos-methyl	80.0 ± 2.0	89.7 ± 1.5	104.3 ± 2.3	89.0 ± 4.0
Fenitrothion	80.0 ± 7.6	93.3 ± 5.9	96.3 ± 3.8	100.3 ± 6.8
Chlorpyrifos	71.0 ± 7.9	96.7 ± 2.1	83.7 ± 3.1	90.3 ± 3.2
Phenthoate	85.7 ± 7.6	93.3 ± 3.2	99.3 ± 6.0	86.3 ± 4.9
Prothiofos	71.0 ± 3.6	97.3 ± 0.6	84.0 ± 5.0	91.3 ± 6.7
Triazofos	77.5 ± 7.9	89.7 ± 4.0	105.7 ± 4.0	96.3 ± 6.7
Cyanofenos	80.7 ± 5.5	91.3 ± 3.2	88.0 ± 1.7	88.3 ± 4.0
Azinphos-ethyl	83.0 ± 3.6	92.3 ± 6.1	106.3 ± 6.7	114.7 ± 8.1
AV	81.0	95.4	95.9	94.7
SD	7.6	8.4	8.4	8.4

AV = average mean excluding* SD = standard deviation excluding*

CV = coefficient of variation Rec = recovery

The chromatograms with and without SPE C₁₈ cleanup are shown in Figure 3. Both chromatograms showed no interference peaks between 2 min and 25 min where the OP pesticides were eluted. As encountered in the cucumber sample, a large peak was observed at 20.5 min in the chromatogram obtained from the method without cleanup. This peak may co-elute with the OP pesticides if high temperature programming is used. However, this peak was not found in the C₁₈ method. Therefore, the C₁₈ cleanup has retained this compound in the SPE tube. The colour of the extracts before the C₁₈ cleanup was dark green, and no obvious colour change was observed after

going through the cleanup process. However, the colour of the SPE tube was slight greenish in colour indicating some of the coloured compounds were retained. It was observed that the polar solvent, acetone, which was used as a second eluant, leached out the coloured matrix co-extractives from the SPE tube. This is because most of these compounds present in the green mustard were polar and the C₁₈ lacks the selectivity to retain these compounds. Thus, it is proposed that smaller amount of extract to be used for cleanup. The LOD for the OP pesticides using the SPE C₁₈ and silica gel cleanups was 0.02 mg/kg.

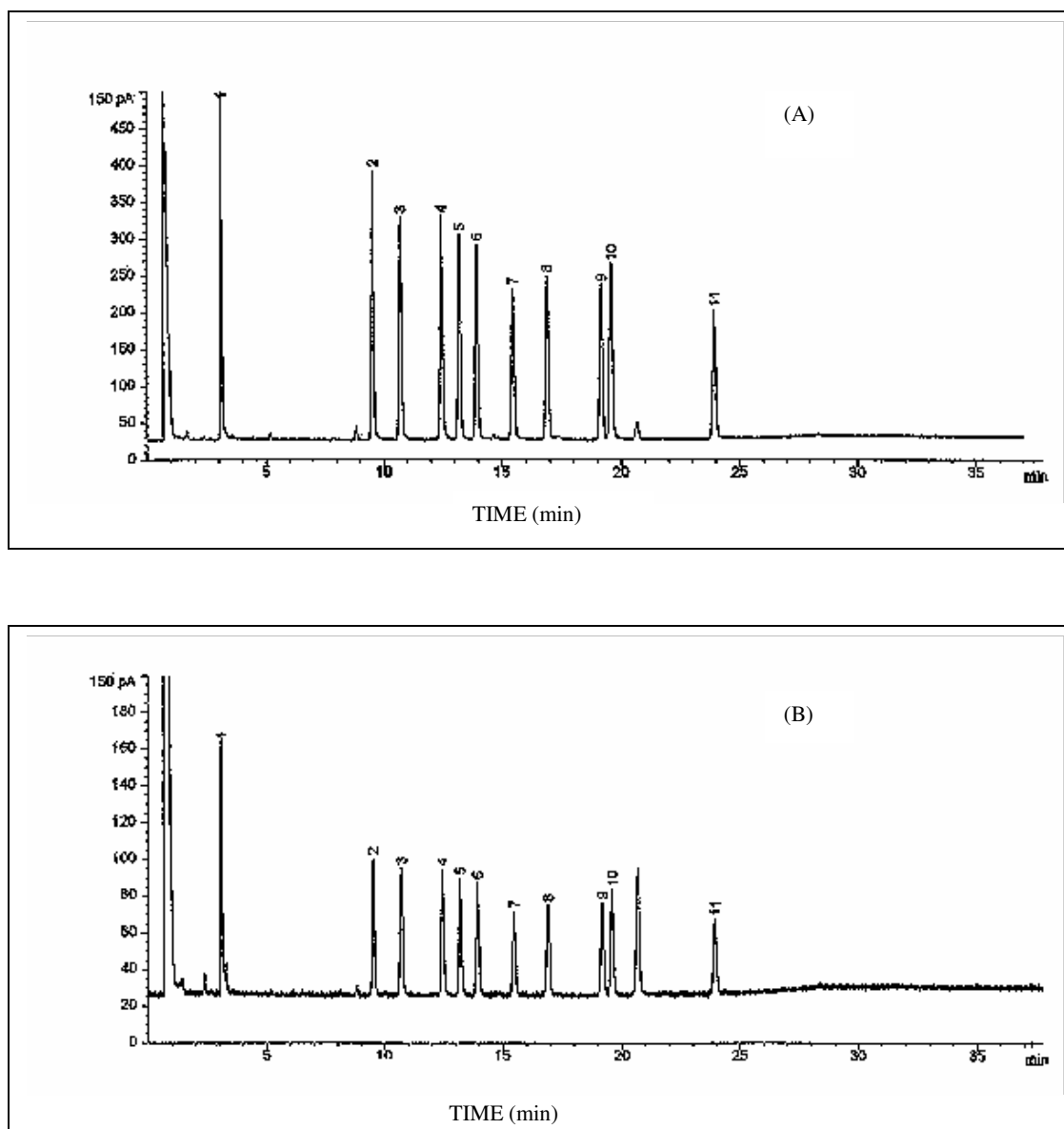


Figure 3 : GC chromatogram of green mustard extract after SPE C₁₈ cleanup (A) and without cleanup (B) Peaks : 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolfos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiophos; 9, triazofos; 10, cyanofenfos; 11, azinphos-ethyl

Conclusion

The crops selected for this study represented divergent chemical problems with regard to the cleanup. While some crops may be high in sugars, while others high in chlorophyll or fats or waxes. The results from this study showed that the C₁₈ has the potential to be used as cleanup for the determination of OP pesticides in vegetables. The recoveries obtained for the OP pesticides except methamidophos in three crops tested, namely carrot,

cucumber and green mustard were within the acceptable range. It was noted that the C₁₈ is not suitable for polar pesticides such as methamidophos as some were leached out together with the coloured extracts before the actual SPE solvent elution. Other solvent systems that do not fall into the criteria of this study may be used to improve the recoveries. Even though the SPE was able to retain some of the coloured compounds or co-extractives, there is no obvious change of colour of the extracts. This is due

to the leaching out of the retained co-extractives from the C₁₈ by the second polar eluent (acetone) used in the study. Therefore, it is proposed that smaller amount of extract to be used for the cleanup especially for more intense coloured vegetables such as carrot and green mustard. In spite of the limited range of this study, it can be predicted that the C₁₈ cleanup can be successfully extrapolated to other less polar pesticides, fruits and vegetables.

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