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Determination of Organophosphorus Pesticides in Vegetables by Solid-Phase Extraction Cleanup and Gas Chromatography

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ABSTRAK

Satu kaedah yang ringkas dan cepat telah dihasilkan untuk menentukan racun perosak jenis organofosforus di dalam sayur-sayuran dengan kromatografi gas. Sisa baki racun perosak diekstrak dengan aseton dan diklorometana. Ekstrak dibersihkan dengan turus ekstraksi fasa pepejal mod bercampur iaitu amina kuaterner dan aminopropil. Racun perosak ditentukan dengan kromatografi gas yang dilengkapkan dengan pengesan fotometrik nyala. Pengembalian 9 racun perosak untuk tiga jenis sayur-sayuran iaitu lobak merah, timun dan sawi hijau pada aras 0.5 mg/kg adalah di antara 80.3% dan 115.0%. Pengembalian yang rendah telah diperoleh untuk methamidophos dan dimethoate. Keputusan ini dibandingkan dengan kaedah yang digunakan pada masa ini iaitu tanpa menggunakan pembersihan.

ABSTRACT

A simple and rapid gas chromatography method has been developed for simultaneous determination of organophosphorus pesticides in vegetables. Residues are extracted with acetone and dichloromethane. Extracts are cleaned up by a mixed-mode solid-phase extraction column, quaternary amine and aminopropyl silane. The pesticides are determined by gas chromatography using a flame photometric detector. The recoveries for 9 pesticides in three vegetables: carrot, cucumber and green mustard, fortified at 0.5 mg/kg were in the range of 80.3% to 115.0%. Lower recoveries were obtained for methamidophos and dimethoate. The results were compared to the method currently used in the laboratory which does not include any cleanup.

Keywords: Solid phase extraction, organophosphorus pesticides, gas chromatography

INTRODUCTION

Organophosphorus pesticides (OP) are commonly used on vegetables in Malaysia. Many pesticides are classified under this group. Among the most commonly detected OP pesticides in vegetables are acephate, diazinon, dichlorvos, dimethoate, fenitrothion, malathion, methamidophos, phenthoate, prothiophos, triazophos and tolcofos-methyl. In a 1997 residue survey carried out by the Department of Agriculture Sarawak, organophosphate pesticides accounted for 95% of the total residue violation (Chai 1997).

Numerous methods have been developed for the analysis of organophosphorus pesticides. Lee *et al.* (1991) demonstrated the use of acetonitrile for the extraction of 7 OP pesticides in vegetables and fruits and cleaned up on reverse phase solid phase extraction (SPE). Final determination was carried out by gas chromatography (GC) using a flame photometric detector (FPD). Sasaki *et al.* (1987) reported a simple and efficient cleanup method for GC determination of 23 OP pesticides in crops including onion using GC-FPD. The sample was extracted with acetone and benzene. A multiresidue method for the quantitative determination of OP pesticides in both fatty and non-fatty foods was developed by Blaha *et al.* (1985). The sample was extracted with acetone, methylene chloride-hexane (1:9) and methylene chloride-acetone (3:1). Fatty food extracts are cleaned up on gel permeation chromatography (GPC). Leoni *et al.* (1992) reported a method for the determination of 28 OP pesticides in fatty and non-fatty foods. Extraction was carried out using acetone, acetone-water and cleanup on carbon-celite. Holstege *et al.* (1991) described a multiresidue method for the determination of 43 OP insecticides in plant and animal tissues. The OP insecticides were extracted with methanol-dichloromethane (1:9) and cleaned up using automated GPC and silica gel mini columns.

The present method used in the laboratory for the analysis of OP pesticides does not include cleanup procedures prior to GC-FPD determination. As a result, contamination often occurs in the GC inlet and GC column. In order to address this problem, a simple and rapid cleanup method needs to be developed for routine analysis. The SPE method was chosen because less solvent is used, sample clean up time can be reduced and cross-contamination can be eliminated.

Several SPE methods for OP pesticides cleanup in different matrixes have been reported. Bennett *et al.* (1997) described a method using octadecyl (C18) and aminopropyl (NH_2) silica cartridges for the determination of 19 OP pesticides in liquid whole milk. Fillion *et al.* (2000) developed a method for the determination of OP pesticides in fruits and vegetables using octadecyl C18, carbon and aminopropyl cartridges. Cook *et al.* (1999) used C18 SPE as cleanup for the detection of pesticides in spinach, oranges, tomatoes and peaches. A method using silica gel SPE cleanup for OP nematicides determination was described by Cooper *et al.* (1994). Jansson (2000) reported good recoveries for OP pesticides, parathion, trichlorfon and dimethoate in honey using Isolute ENV+. Sheridan *et al.* (1999) used quaternary amine (SAX), PSA and Envi-carb for OP pesticides cleanup prior to gas chromatograph-mass spectrometry (GC/MS) determination. A method using C18 and LC-amino for cleanup of soil extract and GC/MS determination was reported by Mogadati *et al.* (1999). Yamazaki *et al.* (1999) described a method using SAX and PSA for cleanup of chlorpyrifos and methyl parathion in oranges. Gillespie *et al.* (1995) used C18 and alumina cleanup method for OP in vegetable oils and butter fat. An SPE C18 method for cleanup of methyl parathion and methyl paraoxon in milk was reported by Baynes *et al.* (1995).

This paper reports the determination of OP pesticides in vegetables using GC-FPD. Residues were extracted with acetone and dichloromethane. Extracts were cleaned up on solid-phase extraction, SAX/NH_2. The results obtained were compared to the method currently used in the laboratory.

PROCEDURE/METHOD

Chemicals and Reagents

All the chemicals and reagents were of analytical grade. Pesticide standards were obtained from Dr. Ehrenstorter™ , Germany. SPE tubes, Isolute SAX/NH_2 (1 g sorbent in 6 mL tube) were purchased from International Sorbent Technology.

Instrumentation

A Hewlett-Packard Gas Chromatograph 5890 Series II equipped with Flame Photometric Detector was used. GC conditions were : Injector temperature, 260°C; detector (FPD) 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. OP pesticides were analysed on a HP5, 15 m x 0.53 mm x 1.5 mm column.

Procedures

Three types of vegetables: carrot (*Daucus carota*), cucumber (*Cucumis sativa*), and green mustard (*Brassica chinensis*) which represent root, cucurbits and brassica families respectively were selected for this study. Each sample was fortified with eleven pesticide standards at 0.5 ppm. Three replicate fortifications for each matrix type were prepared.

Extraction was carried out based on procedures described by Steinwandter (1985). Fifty g of the sample was homogenised with 100 mL acetone, 75 mL dichloromethane and 15 g sodium chloride in a blender for 3 min. The organic phase was transferred to a beaker and 3 g of sodium sulphate was added. For the routine method, the extract was injected directly into the GC for OP determination without cleanup. For the SPE method, the SAX/NH_2 sorbent was used for cleanup of the OP extract.

The SAX/NH_2 was conditioned with 10 mL of acetone : petroleum ether (1:2). 2 mL of extract was transferred to the SPE tube. The SPE tube was eluted with 10 mL of conditioning solvent at a flow rate of 1 mL/min. The eluate was analysed for OP pesticides using GC-FPD.

Statistical Analysis

A t-test was used to determine the significance of the difference between the current method and the SPE method in terms of recovery. They were considered significantly different when values of t(calculated) > t(critical) at 95% confidence level.

RESULTS AND DISCUSSION

Optimisation of SPE Conditions

The SPE conditions were optimised to obtain good recoveries for OP pesticides. Among the parameters studied were flow rate and solvent polarity. The studies showed that a flow rate of 1 mL/min for the elution was sufficient to recover most of the OP pesticides. The flow rate can be increased to 3 – 4 mL/min without affecting the results.

Development of the solvent system was based on several criteria. Solvents which were hazardous or expensive to dispose of were not evaluated. A volatile solvent system must be used as rapid evaporation of a large solvent volume would be required in sample preparation without causing loss of volatile pesticides. The solvent system must be sufficiently polar to extract most polar pesticides. The final sample extract should have minimum matrix co-extractives.

Mixtures of three solvents were used in this study: acetone, hexane and petroleum ether. A low polarity solvent mixture such as acetone:hexane (5:95) did not sufficiently remove all the OP pesticides. Increase of the solvent mixture polarity improved recovery. It was found that acetone : petroleum ether (1:2) resulted in good recoveries for most of the OP pesticides studied except methamidophos. However, increasing the composition of polar solvent further resulted in low recoveries for some of the pesticides studied. The critical factor observed was that the SPE tube should not be left dry after eluting the samples, since low recoveries may result. Ten mL of eluting solvent was sufficient to condition the SPE tube and to elute the analytes. Increasing the amount of solvent for elution did not improve recovery. The optimal conditions for OP pesticides were found to be as follows : (a) solvent mixture:acetone: petroleum ether (1:2); (b) volume of eluting solvent:10 mL; (c) flow rate of elution:1 mL/min.

Recovery Studies

Eleven OP pesticides were selected for this study. They were methamidophos, dimethoate, diazinon, tolcofos-methyl, fenitrothion, chlorpyrifos, phenthoate, prothiofos, triazofos, cyanofenfos and azinphos-ethyl. Except for tolcofos-methyl which is a fungicide, the rest are insecticides. These pesticides are frequently used by vegetable farmers and commonly detected in residue surveys. The pesticides were fortified at 0.5 ppm level and the results are given in Table 1. The recoveries for ten OP pesticides were within the acceptable range of 70 - 120% (Parker 1991). The recovery for these pesticides ranged from 94.3 % - 108.7% with coefficient of variation (CV) of 3.1% to 8.1%. A low recovery of 17.3% was obtained for the polar pesticide, methamidophos. This is due to strong retention of this pesticide by the polar SPE anion exchange sorbent, SAX/NH_2. Methamidophos is a polar pesticide with solubility of 200,000 mg/L in water. Dimethoate is less polar with solubility of 25,000 mg/L while solubility for other OP pesticides tested is in the range of 0.05 mg/L to 40 mg/L.

TABLE 1
Recovery of organophosphorus pesticides

Pesticide	Recovery[(a)] %	CV %
Methamidophos	17.3	4.2
Dimethoate	108.7	5.9
Diazinon	104.3	5.5
Tolcofos-methyl	103.3	8.1
Fenitrothion	95.0	4.6
Chlorpyrifos	102.3	4.6
Phenthoate	105.7	4.9
Prothiofos	102.7	4.9
Triazofos	103.7	4.0
Cyanofenfos	101.7	3.2
Azinphos-ethyl	94.3	3.1

(a) : n = 3
CV : coefficient of variation

Method Validation

Three types of vegetables: carrot, cucumber and green mustard which represent root, cucurbits and brassica families respectively were selected for this study. Each group contains different chemical compounds which may co-elute with the pesticide. This may interfere with the GC analysis of sample extracts.

a. Carrot

Recoveries of OP pesticides from fortified carrot samples using SAX/NH_2 cleanup and without cleanup are shown in Table 2. For the method without cleanup, the recoveries for eleven pesticides were within the acceptable range. The recoveries for these pesticides were from 76% to 108.3% with CV of 5.0 - 11.0%. Comparable results were obtained for SPE SAX/NH_2 cleanup method for nine OP pesticides. The recoveries ranged from 92.0% to 115.0% with CV of 4.0 - 7.2%. Low recoveries were observed for methamidophos and dimethoate. This is due to strong retention by polar anion exchange sorbents, SAX/NH_2 as these pesticides are more polar compared to the other OP pesticides. Statistical analysis showed that the t-value for nine pesticides was 7.13 which was higher than the critical value. Therefore, there was a significant difference between the SPE method and the current method without cleanup. The SPE cleanup method results in improvement in the recoveries.

The chromatograms for carrot samples using SAX/NH_2 cleanup and without cleanup are shown in *Figs. 1* and *2*. Both chromatograms showed no interference peaks co-eluted with OP pesticides because FPD in phosphorus mode is selective and specific responding to phosphorus compounds. The colour of the extract without cleanup was red while after the cleanup it was yellow. The glass wool in the liner and the head of the GC column were cleaner after several injections compared to the method without cleanup. This effect is more prominent and is reflected in the chromatogram when a less specific detector

TABLE 2
Recovery of organophosphorus pesticides from spiked carrot samples with and without SAX/NH_2 cleanup

Pesticide	SAX/NH_2 Recovery[(a)] %	SAX/NH_2 CV %	No cleanup Recovery[(a)] %	No cleanup CV %
Methamidophos*	0	0	76.0	5.0
Dimethoate*	30.3	17.0	108.3	6.0
Diazinon	92.0	6.1	89.3	9.3
Tolcofos-methyl	113.3	5.8	98.7	10.7
Fenitrothion	108.7	5.7	102.0	6.1
Chlorpyrifos	112.3	5.8	99.3	11.0
Phenthoate	109.7	5.7	97.0	8.9
Prothiofos	115.0	7.2	103.7	10.0
Triazofos	105.3	4.0	95.7	8.1
Cyanofenfos	112.7	4.0	99.7	7.2
Azinphos-ethyl	102.3	6.8	97.3	9.2
AV	107.9		98.1	
SD	7.2		4.1	

AV : Average mean excluding *
SD : Standard deviation excluding *
CV : Coefficient of variation
(a) : n = 3

such as electron capture detector is used. The advantage of the SPE method over the current method without cleanup is that the former removed a substantial amount of co-extractives from the samples. This can reduce the cost of GC maintenance especially for the GC inlet and column. Without the SPE cleanup, the glass wool insert in the liner needs to be replaced very often and the liner needs to be cleaned regularly. Contaminants significantly reduce the performance and lifetime of chromatography columns. The other advantage of SPE is that less solvent is used compared to conventional cleanup methods such as gel permeation chromatography (GPC) which requires large amounts of solvent and is time consuming. Also, cross-contamination can be eliminated as the SAX/NH_2 tube is discarded after use.

b. Cucumber

Recoveries of OP pesticides from fortified cucumber samples using SAX/NH_2 and without cleanup are given in Table 3. The recoveries for 9 OP pesticides using cleanup were within the acceptable range. They ranged from 80.3% to 95.3% with CV of 2.5% to 7.1%. A lower recovery was obtained for dimethoate while all the methamidophos was lost during the cleanup. This is due to strong retention of these pesticides by the polar anion exchange sorbent, SAX/NH_2 as they are more polar compared to other OP pesticides. As a result, they were not eluted by the polar solvent. The recoveries for the method without cleanup ranged from 69.3% to 111.0% with CV of 1.2% to 6.2%. Statistical analysis

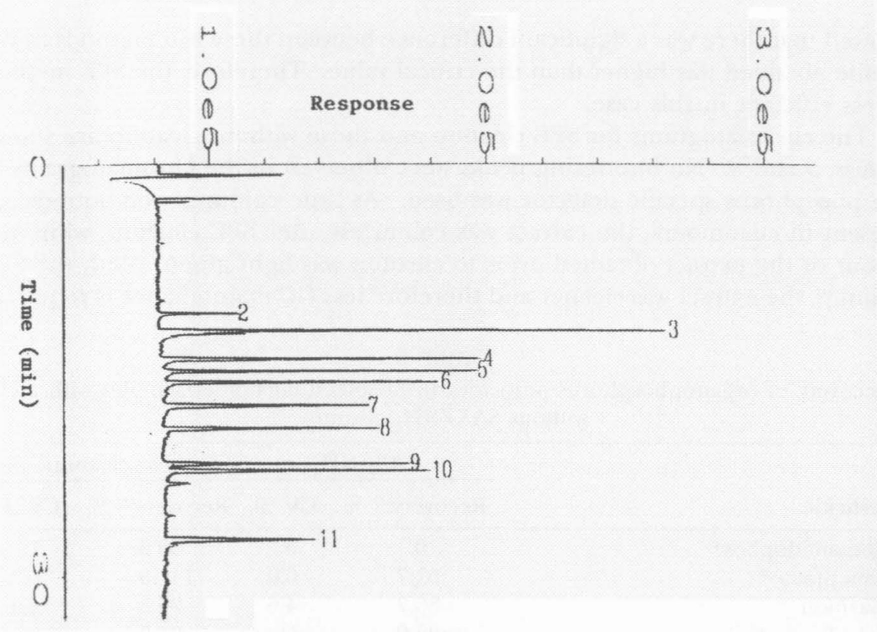

Fig. 1: GC chromatogram of carrot extract after SPE cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; 10, cyanofenfos, 11, azinphos-methyl

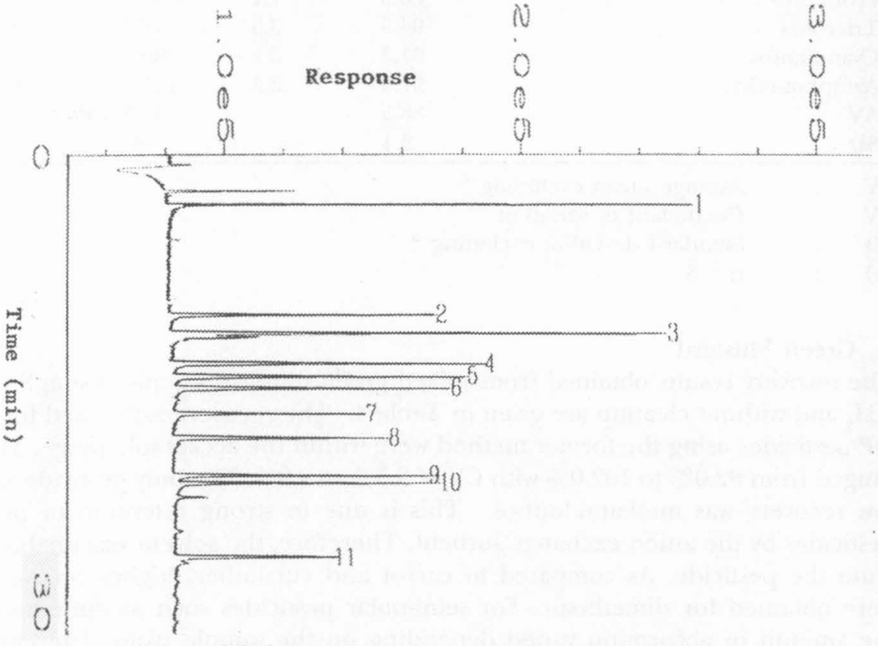

Fig. 2: GC chromatogram of carrot extract without cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; cyanofenfos, 11, azinphos-methyl

showed that there was a significant difference between these two methods as the t-value obtained was higher than the critical value. Therefore, the SPE method is less efficient in this case.

The chromatograms for SPE cleanup and those without cleanup are shown in *Figs. 3* and *4*. No interfering peaks were observed in the chromatograms as the phosphoros specific detector was used. As little coloured compounds are present in cucumbers, the extract was colourless after SPE cleanup, while the colour of the extract obtained prior to cleanup was light green. With the SPE cleanup, the extract was cleaner and therefore less GC maintenance is required.

TABLE 3

Recovery of organophosphorus pesticides from spiked cucumber samples with and without SAX/NH_2 cleanup

	SAX/NH_2		No cleanup	
Pesticide	Recovery$^{(a)}$ %	CV %	Recovery$^{(a)}$ %	CV %
Methamidophos*	0	0	69.3	1.5
Dimethoate*	51.7	6.0	111.0	6.2
Diazinon	86.7	4.6	96.3	4.0
Tolcofos-methyl	87.0	5.3	94.3	3.1
Fenitrothion	89.0	6.1	98.3	1.5
Chlorpyrifos	82.0	7.0	91.7	4.2
Phenthoate	95.3	5.9	97.3	1.2
Prothiofos	80.3	7.1	92.3	4.0
Triazofos	94.0	3.5	97.0	2.0
Cyanofenfos	91.3	6.1	89.3	1.5
Azinphos-ethyl	91.3	2.5	101.0	4.0
AV	88.5		95.3	
SD	5.1		3.7	

AV : Average mean excluding *
CV : Coefficient of variation
SD : Standard deviation excluding *
(a) : n = 3

c. Green Mustard

The recovery results obtained from spiked green mustard samples using SAX/ NH_2 and without cleanup are given in Table 4. The recoveries obtained for 10 OP pesticides using the former method were within the acceptable range. They ranged from 82.0% to 102.0% with CV of 2.7% to 9.9%. The only pesticide with low recovery was methamidophos. This is due to strong retention of polar pesticides by the anion exchange sorbent. Therefore, the solvent was unable to elute the pesticide. As compared to carrot and cucumber, higher recoveries were obtained for dimethoate. For semi-polar pesticides such as dimethoate, the amount of absorption varied depending on the sample types. Therefore, there was wide variation among the three types of vegetables tested. The recoveries obtained for the method without cleanup were between 74.3% to

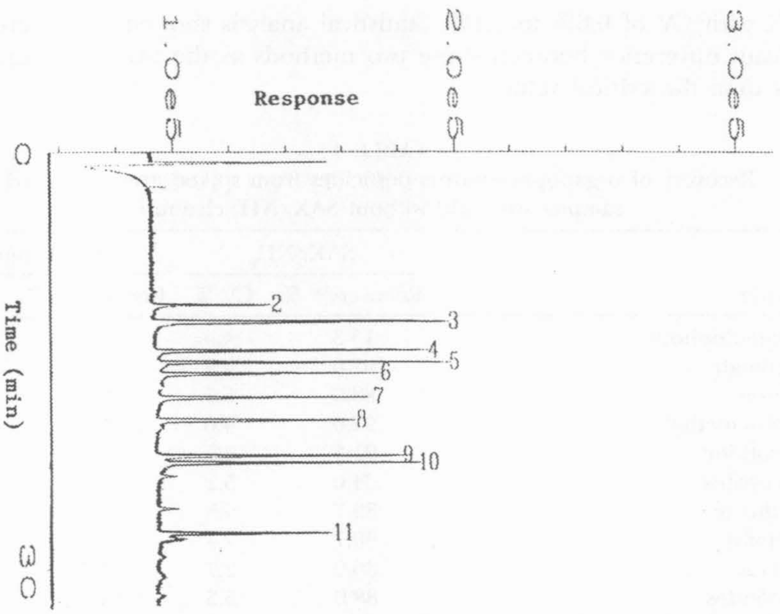

Fig. 3: GC chromatogram of cucumber extract after SPE cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; 10, cyanofenfos, 11, azinphos-methyl

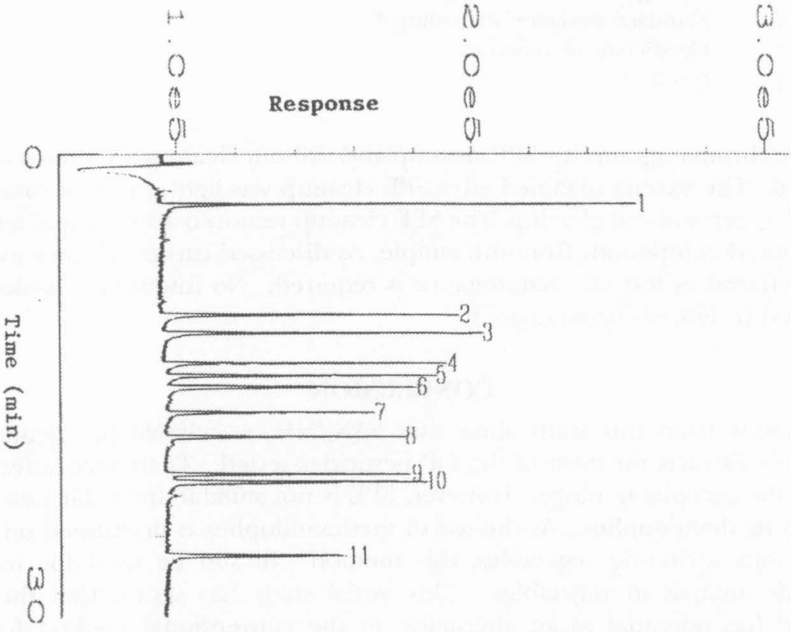

Fig. 4: GC chromatogram of cucumber extract without cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; 10, cyanofenfos, 11, azinphos-methyl

118.3% with CV of 0.6% to 6.1%. Statistical analysis showed that there was a significant difference between these two methods as the t-value obtained was higher than the critical value.

TABLE 4
Recovery of organophosphorus pesticides from spiked green mustard samples with and without SAX/NH_2 cleanup

	SAX/NH_2		No cleanup	
Pesticide	Recovery[(a)] %	CV %	Recovery[(a)] %	CV %
Methamidophos*	15.3	4.5	74.3	1.5
Dimethoate	102.0	9.9	118.3	6.1
Diazinon	88.3	6.5	92.3	1.5
Tolcofos-methyl	92.0	4.6	89.7	1.5
Fenitrothion	91.3	4.7	93.3	5.9
Chlorpyrifos	94.0	5.2	96.7	2.1
Phenthoate	89.7	4.5	93.3	3.2
Prothiofos	90.7	7.4	97.3	0.6
Triazofos	86.0	2.7	89.7	4.0
Cyanofenfos	88.0	5.3	91.3	3.2
Azinphos-ethyl	82.0	4.6	92.3	6.1
AV	90.4		95.5	
SD	5.3		8.4	

AV : Average mean excluding *
SD : Standard deviation excluding *
CV : Coefficient of variation
(a) : n = 3

The chromatograms for SPE cleanup and without cleanup are shown in *Figs. 5* and *6*. The extract obtained after SPE cleanup was light green as compared to dark green without cleanup. The SPE cleanup removed a substantial amount of coloured compounds from the sample. As discussed earlier, cleaner extracts are preferred as less GC maintenance is required. No interfering peaks were observed in either chromatogram.

CONCLUSION

The results from this study show that SAX/NH_2 is suitable for cleanup of vegetable extracts for most of the OP pesticides tested. Their recoveries were within the acceptable range. However, SPE is not suitable for polar pesticides such as methamidophos. As the use of methamidophos is prohibited on most food crops including vegetables, this method can still be used for routine pesticide analysis in vegetables. This initial study has shown that the SPE method has potential as an alternative to the conventional method for OP pesticide analysis in vegetable and fruit crops. The SPE method affords a cleaner extract and as such it reduces GC maintenance, especially on capillary columns and the injector inlet. This clean extract may also be suitable for ECD

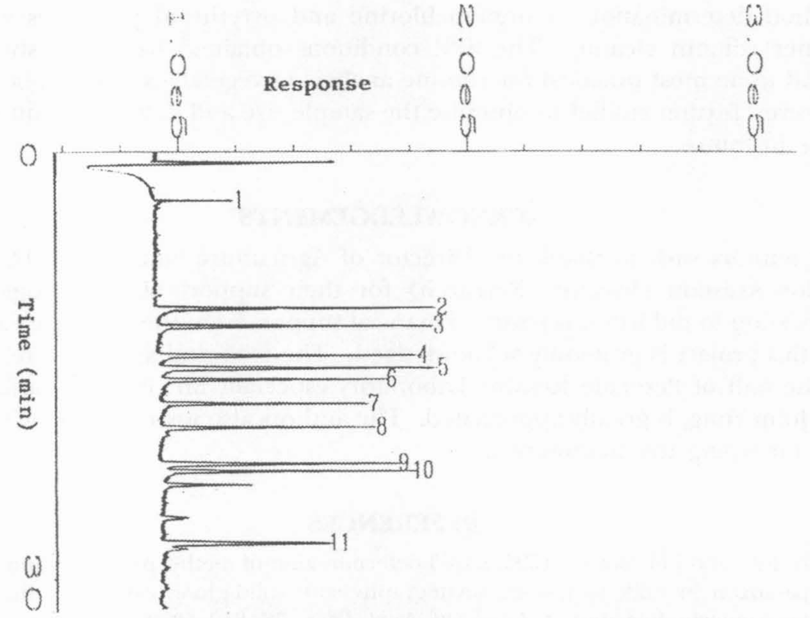

Fig. 5: GC chromatogram of green mustard extract after SPE cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; 10, cyanofenfos, 11, azinphos-methyl

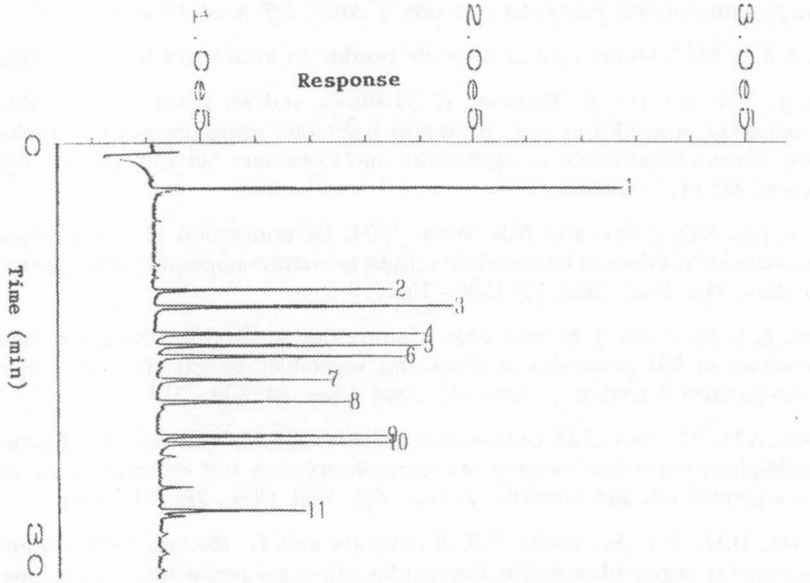

Fig. 6: GC chromatogram of green mustard extract without cleanup.
Peak: 1, methamidophos; 2, dimethoate; 3, diazinon; 4, tolcofos-methyl; 5, fenitrothion; 6, chlorpyrifos; 7, phenthoate; 8, prothiofos; 9, triazophos; 10, cyanofenfos, 11, azinphos-methyl

method determination of organochlorine and pyrethroid pesticides without further column cleanup. The SPE conditions obtained from this study are found to be most practical for routine analysis of vegetables in our laboratory. However, further studies to optimise the sample size and detection limit will be done in future.

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