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Contributed Paper

Gas Chromatographic- Flame Photometric Detection of Organophosphate Pesticide Residues and Its Application in Real Vegetable and Fruit Samples from Chiang Mai City, Thailand

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ABSTRACT

Analysis of pesticide residues is usually limited by expensive analytical apparatus and trained laboratory scientist. We developed a method for detecting 20 organophosphate (OP) pesticide residues in vegetable and fruit matrices using gas chromatographic- flame photometric detection. OP pesticide residues were extracted from well-homogenized vegetable or fruit samples using acetonitrile and clean-up with graphite carbon black solid phase extraction. The clean OP residues' extract was finally dissolved in ethyl acetate and analyzed by GC-FPD. Mean recovery (±SD) of 20 OP pesticides was 92.9 (±10.8) % and individual mean ranged from 76.8 % (methamidophos) to 114 % (triazophos). Limits of detection of 20 OP pesticides ranged from 0.0003 mg/kg (diazinon) to 0.015 mg/kg (azinphos-methyl) which are well below the Codex maximum residue limits (MRLs). In addition, determination of 20 OP pesticides in the present method has proven to be suitable for detecting OP residues in Thailand food safety policy since major imported active OP pesticides were already covered.

Keywords: organophosphate pesticides, gas chromatographic-flame photometric detection, vegetables, fruits, Thailand

1. INTRODUCTION

In Thailand, organophosphate (OP) pesticides are imported more than a million kilogram a year for agricultural purpose [1]. This implies heavily used of these pesticides in this country as confirmed by their residues contaminated in vegetables in Thailand and Asian countries and the environment [2-6] and human exposure in many regions [7-9] which posed risk to human health [10].

Some studies reported that OP pesticides were also detected in both domestic and exported products [11-12]. These evidence indicate a problem of capacity for controlling pesticide residues in agricultural products in Thailand. Meanwhile, the contamination data of pesticide residues among agricultural developing countries including Thailand is often scarce by the limitation of analytical apparatus, trained laboratory scientist, and well set-up method in place [13]. In Thailand,

there are 12 laboratories performing official pesticide residue analysis and only some of them were qualified on analytical techniques [14]. Therefore, analytical methods which are efficient and suitable for Thailand's laboratories are needed for detecting pesticide residues including OP pesticides in agricultural crops.

Although many methods for detecting OP pesticides in agricultural crops have been reported, most of them employed various techniques in sample preparation and chemical analysis using advance analytical techniques such as tandem mass spectrometry [15-17]. These methods used advance instruments that may not available in common pesticide laboratories in Thailand as well as some other developing countries.

According to these limitation, GC-FPD, a selective detector for phosphorus-containing compounds, is a good choice for detecting OP residues. This will help to build capacity of Thailand's laboratories to analyse OP residues in both domestic and exported agricultural commodities. Here, we proposed to use a method modified from a published method [15] and using GC-FPD for detecting 20 OP pesticides in vegetable and fruit samples in Thailand.

2. MATERIALS AND METHODS

2.1 Standard OP Pesticides

Twenty organophosphate pesticides to be assayed include azinphos-ethyl, azinphos-methyl, chlorpyrifos, diazinon, dicrotophos, dimethoate, EPN, ethion, fenitrothion, malathion, methamidophos, methidathion, mevinphos, monocrotophos, parathion-methyl, pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, and triazophos. All OP were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Triphenylphosphate was purchased from Fluka (Buchs, Germany). Purity of all OP standards was >98%.

2.2 Chemicals and Organic Solvents

All organic solvents were analytical grade: acetone, acetonitrile, ethyl acetate and toluene were purchased from J.T. Baker (PA, USA). Sodium chloride, sodium sulfate, potassium dihydrogen phosphate, and dipotassium hydrogen phosphate were purchased from Merck (Darmstadt, Germany). The graphite carbon black (GCB) 500 mg 6 mL tube SampliQ was purchased from Agilent Technologies (USA). The filter papers no.1, 55 mm, was purchased from Whatman (Maidstone, England).

2.3 Preparation of Stock Standard and Calibration Solutions

Stock solution (500 µg/mL) of each standard OP pesticides was prepared in acetone. Mixed-standard solution prepared in ethyl acetate for calibration solutions (7 levels) and spiking into mixed vegetables for the range of 5-500 ng/mL. Triphenylphosphate (TPP) was used as a surrogate internal standard, and its solution was prepared in acetone, giving the concentration of 1000 µg/mL. All stock and mixed standard solutions were dispensed into screw cap tube and stored at -20 °C until used.

2.4 Preparation of Calibration Curve

A pool of vegetable matrices was prepared from representative local-grown vegetables including water morning glory, yard long bean, and cucumber as representative matrices and used for spiked calibration curve preparation. A seven-point calibration curve was prepared by spiking 250 µL of mixed standard solution and 250 µL of internal standard (TPP) solution into 5 g of mixed vegetables prior to extraction.

The range of the calibration curve was shown in Table 1. The calibration curves were plotted using peak area ratios of analyte to surrogate TPP internal standard versus the analyte concentrations.

Table 1. Concentrations of 20 OP pesticides in calibration curve.

OP pesticides	Concentrations (mg/kg)						
	1	2	3*	4	5	6	7
Azinphos-ethyl	0.005	0.010	0.015	0.020	0.050	0.075	-
Azinphos-methyl	0.020	0.025	0.030	0.05	00.075	0.10	-
Chlopyrifos	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Diazinon	0.001	0.001	0.002	0.005	0.010	0.025	0.05
Dicrotophos	0.002	0.004	0.010	0.015	0.020	0.050	0.075
Dimethoate	0.001	0.002	0.005	0.010	0.025	0.050	0.075
EPN	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Ethion	0.001	0.001	0.002	0.005	0.010	0.020	0.050
Fenitrothion	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Malathion	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Methamidophos	0.005	0.010	0.015	0.020	0.050	0.075	-
Methidathion	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Mevinphos	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Monocrotophos	0.002	0.004	0.010	0.015	0.020	0.050	0.075
Parathion-methyl	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Pirimiphos-ethyl	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Pirimiphos-methyl	0.001	0.002	0.005	0.010	0.025	0.050	0.075
Profenofos	0.006	0.010	0.015	0.020	0.025	0.050	0.075
Prothiofos	0.005	0.008	0.010	0.015	0.020	0.050	0.075
Triazophos	0.001	0.002	0.005	0.010	0.025	0.050	0.075
* Concentration was used as QC samples in sample analysis.							

2.5 Preparation of Vegetables and Fruits Samples

Ten vegetables including baby corn, broccoli, cabbage, cauliflower, Chinese cabbage, cucumber, kale, sweet pea, water morning glory, and yard long bean and five fruits including apple, dragon fruit, guava, tangerine and watermelon were purchased (about 2 kg each) from 10 retail markets in Chiang Mai City. The processing procedure was performed according to Codex protocol [18].

Briefly, for sampling vegetables and fruits from markets, each type of vegetable and fruit was purchased from 4 retail shops (4 units) in each market and composited into one sample Unpeeled and unwashed samples were chopped and homogenized. Since tangerine, dragon fruit and watermelon are sometime served in slice with skin to hold, unpeeled and unwashed samples were also processed the same procedure. The processed samples were kept into zip lock plastic bag and frozen at -20 °C until analyzing at Toxicology Laboratory, Environment and Health Research Unit, Research Institute for Health Sciences, Chiang Mai University, Chiang Mai.

2.6 Sample Extraction and Clean-up

All vegetable and fruit samples were extracted and cleaned up using the modified procedure from Fillion's method [15]. Five grams of homogenized sample in a 50-mL centrifuge tube were spiked with 25 µL of internal standard. Then, 15 mL of acetonitrile were added and the mixture was shaken for 5 min. The mixture was filtered through Whatman No.1 filter paper and additionally rinsed with 5 mL of acetonitrile. The solution was transferred into a new 25-mL centrifuge tube followed by a salting-out step with 3 g of sodium chloride and 10 mL of 0.5 M phosphate buffer (pH 7.00). After shaking for 3 min, the mixture was left to separate layers for 10 min. The upper layer solution was pipetted into a cylinder tube and added 2 g of anhydrous sodium sulfate and 5 mL of toluene. The mixture was filtered through filter paper containing 2 g of anhydrous sodium sulfate into 25-mL evaporating flask. The solution was concentrated to less than 1 mL using a rotary evaporator in water bath at 40 °C. The residue was dissolved in 2 mL of acetonitrile:toluene (3:1) mixture. The extracted sample was cleaned up using SampliQ GCB cartridge 500 mg (Agilent Tech., USA) which was preconditioned with 5mL of acetonitrile:toluene mixture. After loading the extract, the analytes were additionally eluted with 30 ml of acetonitrile:toluene mixture. The eluate was evaporated using rotary evaporator at 40°C. The residue was concentrated to less than 0.3 mL and redissolved with 0.5 mL of ethyl acetate. Then, 1 µL of the cleaned-up sample was injected into the GC-FPD system.

2.7 GC-FPD Condition

Sample extracts are injected into the GC-FPD (HP 6890 Series, USA) under the following conditions: column HP-5 (0.25 mm I.D. × 30 m length × 0.25 µm film thickness); splitless injection mode; injection volume, 1 mL; injector temperature 220°C; detector temperature 100°C; and carrier gas, helium. The gas chromatograph is operated in constant flow mode at 2.5 mL/min. GC temperature program: hold 0 min at 100°C, 100° to 180°C at 15°C/min hold 5 min, 180° to 245°C at 5°C/min hold 1 min, post run at 280°C, 2 min. The total run time was 26.33 min.

2.8 Method Validation and Quality Control

Limit of detection (LOD) was defined as the lowest amount of an analyte in a sample that can be detected but not necessarily quantified as an exact value (AOAC, Gaithersburg, 2002). Limit of quantification (LOQ) was defined as the lowest concentration tested at which an acceptable mean recovery with an acceptable relative standard deviation (RSD) is obtained. For example, sample with spiked 0.0009 mg/kg chlorpyrifos gave the signal different from blank sample and 10 replicates of samples with spiked 0.0012 mg/kg chlorpyrifos gave an acceptable mean recovery (86.9±9.7%) with an acceptable RSD (9.61%). Therefore, LOD and LOQ of chlorpyrifos in the present study were 0.0009 and 0.0012 mg/kg, respectively.

The linearity of the method was determined by analysing calibration standard samples spiked at 7 concentrations (Table 1). The calibration standard samples were prepared as described above. The equation of the curve was calculated by linear regression and the correlation coefficient (r) was used as a measure of the fit of the curve (Table 2).

Table 2. Retention times, ranges, LODs, LOQs, MRLs and correlation coefficients of spiked calibration curve of 20 OP pesticides.

OP pesticides	RT (min)	Linear range (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)	Codex MRL (mg/kg)	correlation coefficient of calibration curve
Azinphos-ethyl	23.63	0.0050-0.0750	0.0035	0.0050	0.05-1	0.9963
Azinphos-methyl	22.30	0.0200-0.1000	0.0150	0.0200	0.5-1**	0.9868
Chlopyrifos	12.14	0.0012-0.0750	0.0009	0.0012	0.01-2	0.9997
Diazinon	8.21	0.0005-0.0500	0.0003	0.0005	0.05-0.5	0.9990
Dicrotophos	6.56	0.0020-0.0750	0.0015	0.0020	0.5***	0.9977
Dimethoate	7.24	0.0012-0.0075	0.0010	0.0012	0.05-1	0.9988
EPN	21.08	0.0012-0.0075	0.0009	0.0012	0.02-0.1*	0.9905
Ethion	18.02	0.0006-0.0500	0.0004	0.0006	0.1-2**	0.9944
Fenitrothion	11.17	0.0012-0.0075	0.0009	0.0012	0.5	0.9984
Malathion	11.75	0.0012-0.0075	0.0009	0.0012	0.2-8	0.9958
Methamidophos	3.02	0.0050-0.0075	0.0035	0.0050	0.01-0.3*	0.9937
Methidathion	14.53	0.0014-0.0075	0.0011	0.0014	0.05-1	0.9996
Mevinphos	4.53	0.0008-0.0075	0.0006	0.0008	0.05-0.5*	0.9993
Monocrotophos	6.56	0.0020-0.0075	0.0015	0.0020	0.05-1*	0.9885
Parathion-methyl	9.93	0.0012-0.0075	0.0009	0.0012	0.05-0.5	0.9973
Pirimiphos-ethyl	13.25	0.0012-0.0075	0.0009	0.0012	NA	0.9998
Pirimiphos-methyl	11.35	0.0012-0.0075	0.0009	0.0012	0.05-5*	0.9998
Profenofos	15.91	0.0060-0.0075	0.0040	0.0060	0.05-0.2*	0.9953
Prothiophos	15.77	0.0050-0.0075	0.0040	0.0050	0.2-2*	0.9588
Triazophos	18.52	0.0012-0.0075	0.0009	0.0012	0.1	0.9988

LOD = Limit of detection, LOQ = Limit of quantification, RT = Retention time, * Japan MRL, ** EU MRL, *** Taiwan MRL, NA not available

Note : All MRLs of each compounds were from 15 kinds of vegetables and fruits (baby corn, broccoli, cabbage, cauliflower, Chinese cabbage, cucumber, kale, sweet pea, water morning glory, and yard long bean, apple, dragon fruit, guava, tangerine and watermelon).

Due to juicy nature of fruits, internal quality control (QC) samples were prepared by mixing several kinds of vegetables as pooled matrices and aliquoted 5 g in 50-mL centrifuge tube, kept at -20 °C prior used. An aliquot (5 g) was thawed at RT and spiked with 20 OP pesticides at level-3 concentrations for precision and recovery testing and internal control. The replicates of spiked QC samples were processed for determining intra-batch (n=10) and inter-batch (n=3) precisions. Accuracy (n=10) was shown as %recovery. The precision was calculated as RSD of repeated measurements. Each sample batch contained a maximum of 20 samples was controlled for analysis' quality by using two QC samples before and after batch.

3. RESULTS AND DISCUSSION

This method was developed for the purpose of detecting OP pesticides in

vegetable and fruit samples in Thailand as well as other agricultural developing countries. Twenty OP pesticides were selected from the mostly used pesticides in Thailand. This method can be used for determining residues for compliance with MRLs applicable for monitoring according to food safety policy.

3.1 Sample Preparation

Sample preparation step in this study was modified from Fillion's method. For cleaning-up samples, only GCB cartridge was used in this study while C18 and amino propyl cartridges were used in the previous study. However, the chromatogram of unspiked or blank matrix showed no matrix interference (Figure 1). There was no peak of contaminated compound at the same retention times of interesting analytes in blank matrix which prepared from representative local-grown vegetables including water morning glory, yard long bean, and cucumber. This suggested good selectivity of this method.

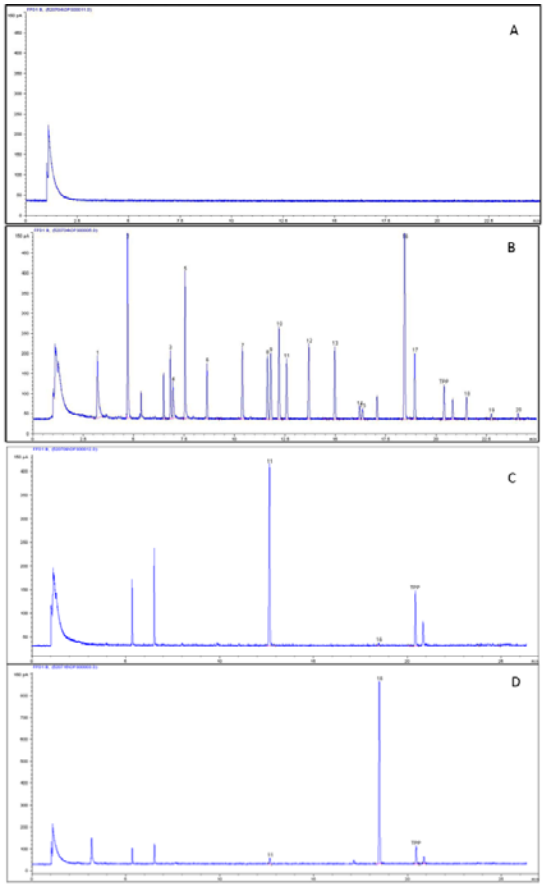

Figure 1. Typical chromatograms of (A) blank reagent, (B) QC sample spiked with 20 OP pesticides, (C) Chinese kale sample and (D) guava sample
1=methamidophos, 2=mevinphos, 3=dicrotophos, 4=monocrotophos, 5=dimethoate, 6=diazinon, 7=parathion-methyl, 8=fenitrothion, 9=pirimiphos-methyl, 10=malathion, 11=chlorpyrifos, 12=pirimiphos-ethyl, 13=methidathion, 14=prothiophos, 15=profenofos, 16=ethion, 17=triazophos, 18=EPN, 19=azinphos-methyl, 20=azinphos-ethyl and TPP= triphenylphosphate (internal standard).

3.2 Method Validation and Quality Control

The linearity of response was examined from calibration curves of 20 OP pesticides (Table 2). The correlation coefficients of linear curves were 0.959-0.999.

LODs and LOQs of 20 OP pesticides were in the range of 0.0003 (diazinon) -0.0150 (azinophos-methyl) and 0.0005-0.0200mg/kg, respectively. All LODs and LOQs were lower than the MRLs (Table 2). This method, therefore, allowed the detection of OP pesticides in vegetable and fruit samples.

The relative standard deviations (RSD) were calculated intra-batch (n=10) and inter-batch (n=3) precisions of 20 OP pesticides. Intra-batch RSDs were 1.90-19.4 % which were in the acceptable range at below 20%. However, most OP pesticides had inter-batch RSDs higher than 20% (Table 3). Since the spiked concentrations of 20 OP pesticide in QC samples in the present study were very low (0.003-0.030 mg/kg) comparing to other studies (0.1-5 mg/kg) [15, 19], this led to high RSDs which produced low reproducibility. The accuracy was represented by %recovery. All compounds had good recovery which ranged 76.8-114 % (Table 3).

Table 3. Precision and recovery data of 20 OP pesticides.

OP pesticides	Precision: %RSD		%Recovery
	Intrabatch (n=10)	Interbatch (n=3)	Mean±SD (n=10)
Azinphos-ethyl	3.98	21.4	111±4.40
Azinphos-methyl	16.4	31.2	81.9±13.4
Chlopyrifos	5.35	28.4	97.3±5.20
Diazinon	7.64	32.6	81.6±6.20
Dicrotophos	4.85	37.4	81.3±3.90
Dimethoate	6.67	18.9	85.5±5.70
EPN	1.90	24.2	95.8±1.80
Ethion	24.1	15.1	78.6±14.3
Fenitrothion	12.2	16.6	102±12.5
Malathion	13.8	24.6	86.2±11.9
Methamidophos	13.6	41.7	76.8±10.4
Methidathion	7.59	18.7	98.3±7.50
Mevinphos	6.39	21.7	86.7±5.50
Monocrotophos	3.98	26.9	82.2±3.30
Parathion-methyl	10.4	13.9	95.1±9.90
Pirimiphos-ethyl	9.96	43.7	98.8±9.80
Pirimiphos-methyl	6.90	27.2	100±6.90
Profenofos	19.4	22.1	80.3±15.6
Prothiofos	9.13	28.4	105.7±9.70
Triazophos	4.87	24.7	114.0±5.60

3.3 Comparison of Different Methods

Some OP pesticides-detecting methods have been used many techniques, including SPE [20], liquid-liquid microextraction (LLE) followed by SPE [15], dispersive liquid-liquid microextraction (DLLME) [21-22], QuEChERS [23-27], ultrasonic solvent extraction (USE)[22] and microwave-assisted extraction (MAE) [28] followed by various detectors were compared with the present method for OP pesticide extraction in vegetable and fruit samples, and the results are shown in Table 4. LODs and LOQs were broadly different because of the difference in preparation techniques and detectors. However, the recoveries obtained by those methods were similar.

Table 4. Comparison with some reported chromatographic methods for detecting OP pesticides in vegetable and fruit samples.

Method's references	Sample preparation techniques	Analytical techniques	LODs[a]/LOQs[b]	%recovery
The present developed method	LLE followed by SPE	GC-FPD	0.0003-0.0150 mg/kg[a] /0.0005-0.0200 mg/kg[b]	78.6-114%
Cervera et al., 2014[27]	QuEChERS	GC-(APCI)-QTOF MS	0.01 mg/kg[a]	Not available
Fillion et al, 2000[15]	LLE followed by SPE	GC-MS	0.02-1.0 mg/kg[a]	70-120% for 90% of pesticides
Guan et al., 2010[23]	QuEChERS	GC-MS	0.0004-0.0059 mg/kg[b]	72 -116%
Hanot et al., 2015[32]	Ultra-Turrax homogenization with a	LC-MS/MS	0.010 mg/kg[b]	within 70-120%
Ho et al., 2013[21]	dispersive liquid-liquid microextraction (DLLME)	GC-MS	0.00012-0.00492 mg/kg	70-119%
Li et al., 2014[30]	QuEChERS with Fe_3O_4 magnetic nanoparticles	GC-MS/MS	0.03-2.17 ug/kg[a]	71.5 -111.7%
Lopez et al., 2014[26]	QuEChERS	UPLC-QTOF-MS	0.01-0.05 mg/kg[a]	Not available
Lozowicka et al., 2012[20]	SPE	GC-ECD/NPD	0.001-0.010 mg/kg[a]	70.1- 119%
Lu et al., 2012[24]	QuEChERS	on-line gel permeation chromatography-GC-MS	5 ug/kg[b]	68-118%
Marchis et al., 2012[25]	QuEChERS	GC-MS	0.0002-0.0060 mg/kg[a]	52-105%
Pirsaheb et al., 2013[22]	ultrasound-assisted solvent extraction followed by DLLME	HPLC-UV	1-4 µg/kg[a]	88-106%
Sivaperumal et al., 2015[31]	SPE	UHPLC-TOF-MS	0.8- 11.8 ug/kg[b]	74%-111%
Wu et al., 2015[28]	dynamic microwave-assisted extraction (DMAE) and solvent elution (MASE),	GC-MS	0.09-0.26 ug/kg[a]	71.5-101.6%

LOD = limit of detection; LOQ = limit of quantification; LLE = liquid-liquid extraction; SPE = solid phase extraction; GC-FPD = gas chromatography - flame photometric detection; GC-MS = gas chromatography-mass spectrometry; GC-MS/MS = gas chromatography-tandem mass spectrometry; GC-ECD/NPD = gas chromatography - electron capture detection/nitrogen phosphorous detection; GC-(APCI)-QTOF MS= gas chromatography-atmospheric pressure chemical ionization- quadrupole-time of flight mass spectrometry; HPLC-UV = high performance liquid chromatography-UV detection; LC-MS/MS = liquid chromatography-tandem mass spectrometry; UPLC-QTOF-MS = ultra performance liquid chromatography- quadrupole-time of flight mass spectrometry; UHPLC-TOF-MS = ultra high performance liquid chromatography/time-of-flight mass spectrometry.

Due to limitation of supplies and apparatus, this developed method was modified from Fillion's method [15] by changing from two SPE tubes (C18 and amino propyl coupled with carbon) to single SPE tube (GCB) and changing detecting technique from GC-MS to GC-FPD. This method was employed to analyse real vegetable and fruit samples that contained a wide range of colours and found that the use of single SPE (GCB) provided effective clean-up capacity and good recovery. Furthermore, the similarity of recoveries in this method and Fillion's method revealed that the use of SPE tubes from this two study did not provide the different yields. Since real vegetable and fruit samples analysed in the present study were containing different colours, C18 and amino propyl sorbents found not to be necessary confirmed by the similar recoveries of single GCB and C18 and amino propyl coupled with GCB. Using FPD, a phosphorous-specific detector, provided less vulnerable to matrix interfering compounds. Although these two methods used the same weights of samples, LODs and LOQs in the present developed method were lower those in Fillion's method. This revealed that the FPD detector is suitable to use and provide sufficient sensitivity and selectivity for detecting OP pesticides in real vegetable and fruit samples.

3.4 Application of the Developed Method

The developed method was employed to analyse a total of 150 real samples including100 vegetable and 50 fruit samples collected from local markets in Chiang Mai City. Out of all 150 samples, 45% were detected with 13 OP pesticides including chlopyrifos, diazinon, dicrotophos, dimethoate, fenitrothion, malathion, methamidophos, mevinphos, pirimiphos-ethyl, pirimiphos-methyl, prothiophos, profenophos and triazophos. The most frequently detected OP pesticide in all samples was chlorpyrifos (mean 0.054 mg/kg; range 0.005-0.649 mg/kg; MRL 0.05 mg/kg). It was detected in 30 % of all samples (45 samples in 150 samples). Among these 150 real samples, there were 35 vegetable and fruit samples (23%) were contaminated with OP residues exceeded the MRLs. The detection of OP contamination in vegetable and fruit samples in central Thailand showed the same trend of detection by using GC-MS/MS [2-4, 29]. The present method of 20 OP pesticides determination showed to be sufficient for detecting OP residues in vegetables and fruits in Thailand.

4. CONCLUSIONS

We have developed a method for detecting 20 organophosphate (OP) pesticide residues in vegetable and fruit matrices using GC-FPD which is commonly available in pesticide laboratory especially in developing countries. This method has been successfully applied in the detection of OP pesticide residues below the Codex MRLs. The developed method was tested to analyse real vegetable and fruit samples and found no matrix interferences.

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