

AN IMPROVED METHOD FOR THE DETERMINATION OF CHLORPYRIFOS IN PALM OIL MATRICES USING GAS CHROMATOGRAPHY

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ABSTRACT

The objective of this study was to improve the method for determining chlorpyrifos, an organophosphorus insecticide, in various palm oil matrices. Chlorpyrifos was separated from the oil matrices using acetonitrile extraction and then subjected to the solid phase extraction (SPE) clean-up process. A silica-based SPE was used for the clean-up process. Quantification of the extracted chlorpyrifos was carried out using a gas chromatograph (GC) equipped with an electron capture detector (ECD). The GC detector response was tested using standard solutions containing 0.005 to 0.12 mg ml⁻¹ of chlorpyrifos. The retention time for chlorpyrifos was 4.8 min with the minimum detection limit at 0.005 mg ml⁻¹. The average recoveries of chlorpyrifos from crude palm oil (CPO) spiked with 0.02, 0.04, 0.06, 0.08 and 0.1 mg ml⁻¹ chlorpyrifos were 94 ± 2.3%, 93 ± 1.4%, 99 ± 1.6%, 97 ± 2.9% and 95 ± 0.7%, respectively. In the case of crude palm kernel oil (CPKO) and refined, bleached, deodorised palm olein (RBDPOo), the recovery of chlorpyrifos from the spiked oil samples containing 0.02 to 0.1 mg ml⁻¹ of chlorpyrifos ranged from 100% to 101% and from 93% to 99%, with the coefficient of variation ranging from 1.3% to 3.0% and from 0.7% to 2.9%, respectively. The method developed was used to determine the chlorpyrifos content in samples of CPO, CPKO and RBDPOo from mills and a refinery in Selangor, Malaysia. No chlorpyrifos residue was detected in any of the CPO, CPKO and RBDPOo samples collected.

Keywords: chlorpyrifos, solid phase extraction, palm oil, palm olein, crude palm kernel oil.

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INTRODUCTION

In oil palm plantations, organophosphorus (OP) insecticides such as chlorpyrifos are used widely to control insect pests through direct application onto the palms and fruit bunches. Chlorpyrifos is the common name for o,o-diethyl 1-o(3,5,6-trichloro-2-pyridyl) phosphorothioate. It is available in a

variety of formulations under the trade names of Dursbon® and Lorsbon®, and is recommended for the control of a broad spectrum of agricultural and other insect pests (Kidd and James, 1991; Mauldin *et al.*, 2006).

Most methods of pesticide residue determination require two steps, namely the extraction of the analyte from the matrix, followed by a clean-up step to eliminate the interfering substances before analysis using gas chromatography (GC) (Walters, 1990; Li *et al.*, 2007). The clean-up step is required because certain products in the oil matrix can interfere with the identification and quantification of the analyte (Badrul Hisyam *et al.*, 2009).

There are numerous extraction techniques for separating out pesticides in fatty samples, and these include liquid-liquid partitioning (Claborn *et al.*,

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1968) and supercritical fluid extraction (Sterzenbach *et al.*, 1997; Hopper, 1999; Aini and Smith, 2000). For example, the use of liquid-liquid partitioning with acetonitrile and hexane, followed by adsorption on a silica column for the determination of OP in mollusks, was reported by Hernandez *et al.* (1996). However, Gillespie *et al.* (1995) proposed the use of multicolumn commercial SPE cartridges in the clean-up process for the determination of OP residues in vegetable oils and butter fat. An automated supercritical fluid extraction and in-line clean-up system has been developed by Hopper (1999) for determining organochlorine (OC) and OP residues in fats. This procedure utilises supercritical carbon dioxide modified with 3% acetonitrile at 27.58 MPa and 60°C to extract and separate out the pesticide residues from the fat on a C₁ bonded phase preparative column at 95°C. Niessner *et al.* (1999) reported a new approach in the multiresidue screening methods for determining pesticides in samples with low and high fat content. To separate the pesticides from polar lipids, a combination of the matrix solid-phase dispersion (MSPD) and florisil clean-up processes was used. For the above method, fatty samples are usually blended with silica particles and then placed over a layer of poly(styrene-divinylbenzene) particles in an SPE cartridge, eluted with acetonitrile saturated with *n*-hexane, and cleaned up with florisil before injection into GC. However, the extraction procedure in the present study utilised petroleum ether-saturated acetonitrile, followed by the SPE clean-up process.

Gillespie and Walters (1991) used the multiple extraction procedure for extracting OP mixtures from oil matrices. The extraction was done five times with 2 ml of light petroleum ether-saturated acetonitrile. In the clean-up step, a C₁₈ cartridge was used, and elution of the OP mixture from the C₁₈ cartridge was undertaken using acetonitrile (Gillespie and Walters 1991). Three types of C₁₈ were used in the clean-up process, namely, Sep-Pak C₁₈ (400 mg) connected to eight cartridges; Bakerbond C₁₈ (1 g) connected to six cartridges, and Mega Bond Elut C₁₈ (5 g) with one cartridge per sample. In the current method, a silica cartridge (1 g) was used, and chlorpyrifos was eluted from the cartridge five times with 4 ml of 5% ethyl acetate in *n*-hexane.

Halimah *et al.* (1999) reported a method for the determination of chlorpyrifos residues in refined, bleached, deodorised palm olein (RBDPOo) but not for crude palm oil (CPO) and crude palm kernel oil (CPKO) which are also important products of the palm oil industry. The technique involves the use of liquid-liquid partitioning with acetonitrile and hexane, followed by adsorption on an acidified silica column (Halimah, 2000). It is known that most of the OP pesticides like chlorpyrifos are slightly soluble in lipid because their partition

coefficient value, log K_{ow} is 4.7 (Kidd and James 1991). However, the above method is considered tedious, with an additional disadvantage of using a large volume of solvent.

Ferrer *et al.* (2005) developed and evaluated a method for the quantitative analysis of the pesticides dimethoate, simazine, atrazine, diuron, terbuthylazine, methyl-parathion, methyl-pirimiphos, endosulfan I, endosulfan II, endosulfan sulphate, cypermethrin and deltamethrin in olive oil and olives. Their proposed methodology is based on matrix solid-phase dispersion (MSPD), (after a preliminary liquid-liquid extraction in olive oil samples) using aminopropyl as the sorbent material, with a clean-up performed in the elution step with florisil. This was followed by mass spectrometric identification and quantification of the selected pesticides using both gas chromatography-mass spectrometry (GC-MS) in a selected ion monitoring (SIM) mode, and liquid chromatography tandem mass spectrometry (LC-MS-MS) in a positive ionization mode. The pesticide recoveries had mean values between 85% and 115%, with relative standard deviation (RSD) values below 10% in most cases (Ferrer *et al.*, 2005).

A method for analysing pesticide residues in olive oil by GC-MS and high performance liquid chromatography with mass spectrometry (HPLC-MS) was developed by Barrek *et al.* (2003). Pesticides were separated from the oil matrix by size-exclusion chromatography. After extraction, 20 pesticides were separated and analysed by GC-MS and 11 others by HPLC-MS in an electrospray mode. This method enabled the identification and quantification of the pesticides of interest in olive oil.

The objective of the present study was to determine the amount of chlorpyrifos residue in three types of palm oil, namely RBDPOo, CPO and CPKO, using a modified version of the Gillespie and Walters method (1991). The validity of the modified method was determined by comparing the results from different operators carrying out the analyses while using the method. These operators who are involved in residue analysis in four organisations were invited to analyse for chlorpyrifos in CPO, CPKO and RBDPOo at Pesticide Laboratory, Malaysian Palm Oil Board, Bandar Baru Bangi, Selangor.

Materials and Methods

Chemicals and equipment. Standard chlorpyrifos (98.7% purity) was obtained from Dr Ehrenstorfer, GmbH Co., Germany. SPE was purchased from Supelco™ LC-Si (1 g). A Hewlett-Packard GC (Model 5890) equipped with an electron capture detector (ECD) was used. The column was non-polar, coated with 5% diphenyl (HP 5 MS),

30 m in length, had 0.25 mm i.d. and 0.25 μm film thickness. Operating conditions for the GC-ECD were as follows: carrier gas (nitrogen) 2.7 ml min⁻¹, auxiliary gas (nitrogen) 27 ml min⁻¹, split 50 ml min⁻¹, and anode purge for ECD 5 ml min⁻¹. The injector temperature was set at 250°C on the splitless mode. The oven temperature was programmed from 170°C to 220°C with a gradual increase by 5°C min⁻¹ till it reached the final temperature which was held for 4 min.

Method of sampling from the blank samples. Blank oil samples were obtained from five fresh fruit bunches (FFB) collected from the Malaysian Palm Oil Board (MPOB)/Universiti Kebangsaan Malaysia (UKM) Research Station. These FFB were free of chlorpyrifos residues as no insecticide spraying had been done in that area. Random sampling was done on the FFB to obtain a bulked 3-kg sample of loose fruits.

The sample was placed in a plastic bag and taken to the Pesticide Laboratory of MPOB in Bandar Baru Bangi, Selangor, immediately after harvest. The harvested fruits were subjected to the normal extraction procedure to obtain oil from both the mesocarp and kernel for analysis. The RBDPOo samples were obtained from a refinery in Selangor, Malaysia. The blank oil samples were spiked with known amounts of chlorpyrifos, and then the percentage recovery was determined.

Sample processing and extraction of CPO and CPKO. Loose fruits (3 kg) were placed into autoclave-safe plastic bags to avoid contamination and then sterilised in an autoclave (Sakura Neoclave ASV-302) at 120°C and 1.2 kg cm⁻² for 40 min. The sterilised fruits were manually stripped from the spikelets and placed in a mini hydraulic hand press to extract the oil. A centrifuge set at 3000 rpm for 20 min was used to separate the extracted CPO from the fibre and other solid materials. CPO was then decanted, and filtered through Whatman No. 4 filter paper containing anhydrous sodium sulphate to remove moisture. The CPO sample obtained was kept in a freezer at 0°C prior to extraction for chlorpyrifos residue.

After the extraction of CPO, the remaining fibre and nuts were kept at 0°C in the freezer before extraction for CPKO. Prior to extracting CPKO, mesocarp fibre from the pressed sterilised fruits was peeled off from the nut with a knife. The nuts were then cracked using a hammer to obtain the kernels which were then broken into smaller pieces using a mortar and pestle. The broken kernels were further ground in a blender to obtain a homogenous mixture. Ten grammes of the ground kernel were weighed into an extraction thimble which was then plugged with a wad of cotton wool. Ten thimbles with 10 g each of ground kernel

were solvent-extracted with 150 ml of *n*-hexane for 6 hr to extract CPKO for analysis. The solvent was evaporated off using a rotavapor (N-Evap Model 1111; Organomation Assoc. Inc. USA). After removal of the solvent, nitrogen was passed through the oil mixture to remove any remaining solvent. The CPKO sample were then stored in brown bottles and kept in a freezer at -20°C prior to extraction for chlorpyrifos residue.

Preparation of standard chlorpyrifos solution. A standard solution of chlorpyrifos was prepared by dissolving 5 mg of chlorpyrifos in 50 ml of *n*-hexane in a 50-ml volumetric flask. Working standard solutions ranging from 0.008-0.12 $\mu\text{g ml}^{-1}$ were prepared by diluting the standard solution with appropriate amounts of *n*-hexane. To determine the reproducibility of the injection technique and linearity of the ECD response, each concentration of the standard chlorpyrifos solution was injected thrice into the GC (*i.e.* analysed in three replicates).

Spiking of the blank CPO and CPKO samples with chlorpyrifos. The frozen CPO and CPKO samples were melted at 60°C and well homogenised. Three grammes of the oil were weighed into each of 20-ml centrifuge tubes. The appropriate amount of standard chlorpyrifos solution was added to the oil to obtain five levels of spiked samples containing chlorpyrifos ranging from 0.02-0.1 $\mu\text{g g}^{-1}$. The extraction and clean-up steps were carried out as described below prior to GC analysis.

Extraction. For extraction of chlorpyrifos, a sample of 3 ± 0.001 g of oil was first weighed into a 20-ml centrifuge tube, 0.5 ml of petroleum ether was added and the contents mixed for 15 s on a vortex mixer. Four millilitres of analytical grade petroleum ether-saturated acetonitrile (Merck) were then added and the whole were vortex-mixed for 30 s. The tube containing the mixture was then centrifuged (in a Hettich centrifuge) at 3000 rpm for 2 min. The top acetonitrile layer which contained the pesticide residue was removed using a Pasteur pipette. The extraction of chlorpyrifos from the petroleum-ether layer (lower layer) was repeated four times. Then, the acetonitrile extracts were pooled and concentrated to 1 ml prior to the SPE clean-up. Each concentration of the spiked RBDPOo, CPO and CPKO samples was replicated five times.

SPE clean-up process. The silica (1 g) cartridges (Supelco) were connected to a vacuum manifold to assist in the elution of the solvent through the cartridges. The silica cartridges were pre-washed with 2 ml of *n*-hexane and the washings discarded. The combined and concentrated sample from the above extraction step was transferred onto the

column and washed down with 1 ml of *n*-hexane and the washings were discarded. The column was then eluted with 4 ml of 5% ethyl acetate in *N*-hexane under gravity flow, and the eluate was collected in a vial. This eluate was dried under a stream of nitrogen and the remaining residue was redissolved in 10 ml of *n*-hexane. Three microlitres of the solution were injected into GC. The quantification of chlorpyrifos in the samples was done by comparing to the chromatographic peaks of the chlorpyrifos standard solutions.

Analysis for chlorpyrifos residues in oil samples from local mills and a local refinery. Samples of CPO and CPKO were obtained from mills while the RBDPOo sample was obtained from a local refinery in Bangi, Selangor. In order to determine the amount of chlorpyrifos residue, the same extraction procedure and clean-up process were used for the samples as described above prior to injection into GC.

Method evaluation. In order to confirm its robustness in terms of efficiency and precision of the results, the method was validated by inviting participants from other organisations to test it out using the same equipment in the Pesticide Laboratory of MPOB. The samples were spiked with a chlorpyrifos standard solution to obtain $1 \mu\text{g g}^{-1}$ of chlorpyrifos in CPO, CPKO and RBDPOo. The spiked samples were put in three different bottles and labelled with different code numbers. The analyses were carried out in three replicates according to the procedure described earlier.

The participants involved in performing the reproducibility test were from Universiti Kebangsaan Malaysia (A), Universiti Putra Malaysia

(B), the Malaysian Institute for Nuclear Technology (C) and the Ministry of Health, Malaysia (D).

RESULTS AND DISCUSSION

The reproducibility of the injection technique and linearity of the ECD response was observed over a series of standard chlorpyrifos solutions injected into GC. The calibration data of the various concentrations of standard chlorpyrifos against the GC peak area are shown in *Figure 1*. The coefficient of variation for each of the series of standard solutions ranging from 0.008 to $0.12 \mu\text{g chlorpyrifos ml}^{-1}$ was 2% or less. The linear equation derived from the above data was $y = 86238x + 107.61$, where y was the gas chromatographic area of the standard chlorpyrifos solution and x the concentration in $\mu\text{g ml}^{-1}$. The r^2 value for the equation was 0.9987 at 99.9% confidence level.

Table 1 shows the elution profile of 3 g oil and the percentage of fat removed at each solvent extraction, followed by the clean-up step. In the solvent extraction step, 88.5% of the lipids was removed from the samples, and subsequently the SPE clean-up with the commercial silica cartridge

TABLE 1. AMOUNT OF LIPID BREAKTHROUGH AFTER EXTRACTION AND COLUMN CLEAN-UP

Step/process	Percentage oil removed	Total percentage oil removed
Extraction with petroleum ether-saturated acetonitrile	88.5	98.3
Clean-up step using silica cartridge (1 g)	9.8	-

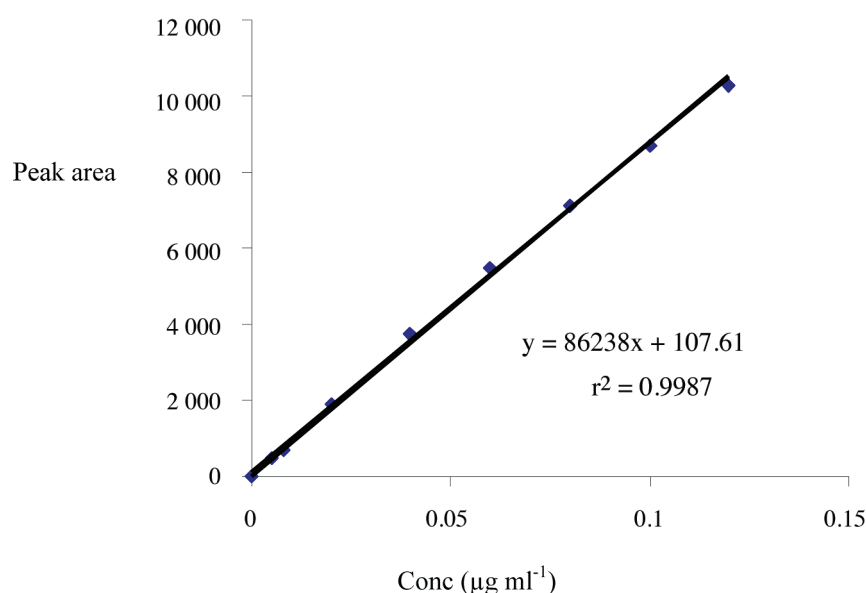


Figure 1. Calibration curve of standard chlorpyrifos against peak area.

removed another 9.8% of the lipid. Therefore, solvent extraction together with the SPE clean-up removed a total of 98.3% of the lipid. Gillespie and Walters (1991) reported that in the initial extraction, 5%-20% of the 3 g lipid sample was extracted into the acetonitrile layer, indicating that the amount of lipid breakthrough from the commercial cartridge varied, depending on the type of sample and the quantity of the packing material in the cartridges. It was also reported that the total amount of lipid removed after the extraction and clean-up steps using 5 g of C₁₈ SPE was 99.9%, 99.8%, 99.8%, 99.5%, 99.4% and 99.1% for sunflower oil, corn oil, safflower oil, soyabean oil, olive oil and butter fat, respectively (Gillespie and Walters, 1991). The present study shows that 98.3% of the lipid was removed by using the acetonitrile extraction followed by a silica-based SPE (1 g) clean-up step. The above fat removal process ensured that a tolerable level of lipid remained in the sample for GC analysis. This indicates that by using significantly less silica in the cartridge, an alternative rapid and inexpensive method had been developed for effective extraction of chlorpyrifos from palm oil and palm oil products.

Data on the recovery from chlorpyrifos-free samples of RBDPOo, CPO and CPKO spiked with 0.02 to 0.1 $\mu\text{g ml}^{-1}$ chlorpyrifos are shown in Table 2. It should be noted that no chlorpyrifos residue was detected in the control samples of RBDPOo from the refinery, or in the control samples of CPO and CPKO from the Universiti Kebangsaan Malaysia research plots. The results show that the average recovery of chlorpyrifos from the spiked RBDPOo samples ranged from 93% to 99%, with a coefficient of variation ranging from 0.7% to 2.9%. The recovery of chlorpyrifos extracted from spiked CPO samples ranged from 92% to 101% with a relative standard deviation of 0.7%-1.2%, and for spiked CPKO samples the recovery ranged from 100%-101% with a standard deviation of 0.2%-0.3%. These results for each set of samples were analysed to show linearity, thus satisfying one component of the method validation process.

Halimah *et al.* (1999) investigated the GC method for the determination and quantification of chlorpyrifos in refined palm olein (RBDPOo) using GC equipped with FPD and ECD. The recovery of chlorpyrifos in spiked RBDPOo using GC-FPD at levels from 0.04-0.1 $\mu\text{g g}^{-1}$ ranged from 89% to 100% with the coefficient of variation from 2.9% to 10.8%. Meanwhile, the recovery of chlorpyrifos using GC-ECD ranged from 97% to 105%. The coefficient of variation for samples with 0.02 to 0.1 $\mu\text{g g}^{-1}$ of chlorpyrifos ranged from 0.5% to 2%. In the extraction step, 97.6% of the lipid was removed from the samples, while in the clean-up step with a commercial silica cartridge, another 1.8% of the lipid was removed (Halimah, 2000). The method was based on liquid-liquid extraction using 200 ml of acetone, followed by a clean-up step using an acidified silica column. The amount of solvent used to subsequently extract chlorpyrifos was 180 ml of 7.5% v/v dichloromethane in hexane. In comparison, the present method which is also based on liquid-liquid extraction used only 4 ml of petroleum ether-saturated acetonitrile (Merck), followed by a clean-up step using a silica SPE cartridge instead of an acidified silica column. The amount of solvent used to elute chlorpyrifos was 4 ml of 5% ethyl acetate in *n*-hexane which is very much less than the 180 ml of eluting solvent required in the previous method. Therefore, this modified method shows a significant improvement of the earlier method (Halimah *et al.*, 1999) in terms of the amount and type of solvent used.

Figure 2 shows the chromatograms of spiked and blank samples of RBDPOo, CPKO and CPO. The minimum detection limit for chlorpyrifos was 0.005 $\mu\text{g ml}^{-1}$, and the retention time of chlorpyrifos was 4.8 min. Figure 3 shows the chromatograms obtained using GC-ECD for a standard chlorpyrifos solution of 0.1 $\mu\text{g ml}^{-1}$, a commercial sample of RBDPOo obtained from a local refinery, and CPKO and CPO samples obtained from local mills.

As mentioned earlier, the extraction method used in the current experiment for the determination of chlorpyrifos in palm oil and its products is a

TABLE 2. RECOVERY (%) OF CHLORPYRIFOS FROM SPIKED SAMPLES OF CRUDE PALM OIL (CPO), REFINED BLEACHED DEODORISED PALM OLEIN (RBDPOo) AND CRUDE PALM KERNEL OIL (CPKO)

		Spiking level ($\mu\text{g g}^{-1}$)				
		0.02	0.04	0.06	0.08	0.1
Amount recovered	CPO	0.0197	0.0496	0.0737	0.1006	0.0950
	RBDPOo	0.0188	0.0372	0.0594	0.0776	0.0950
	CPKO	0.0202	0.0400	0.0600	0.0800	0.1010
Recovery (%)	CPO	100	99.6	92	101	95
	RBDPOo	94	93	99	97	95
	CPKO	101	100	100	100	101
Relative standard deviation	CPO	1.23	0.90	1.20	0.90	0.70
	RBDPOo	2.30	1.40	1.60	2.90	0.70
	CPKO	0.30	0.18	0.27	0.28	0.21

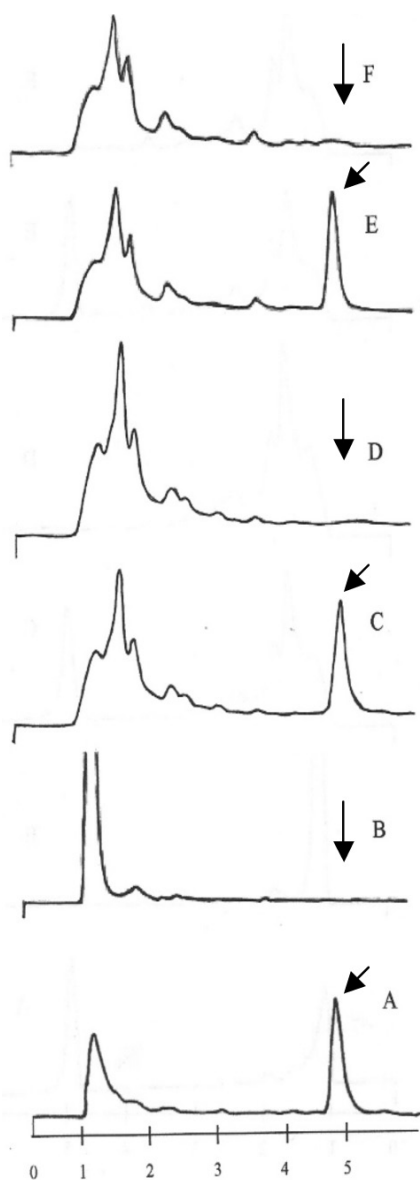


Figure 2. Chromatograms obtained using GC-ECD for: A) spiked sample of refined bleached deodorised palm olein (RBDPOo) at a fortification level of $0.1 \mu\text{g ml}^{-1}$, B) blank sample of RBDPOo, C) spiked sample of crude palm kernel oil (CPKO) at a fortification level of $0.1 \mu\text{g ml}^{-1}$, D) blank sample of CPKO, E) spiked sample of crude palm oil (CPO) at a fortification level of $0.1 \mu\text{g ml}^{-1}$, and F) blank sample of CPO.

modification of the method by Gillespie and Walters (1991) which required 10 ml petroleum ether-saturated acetonitrile to extract the OP pesticides from 3 g of oil. In the present experiment, 20 ml of the same solvent mixture were needed for complete extraction. For extracting OP from C_{18} SPE in the clean-up step, 35 ml of methanol were used by Gillespie and Walters (1991) whilst in the current method 4 ml of 5% ethyl acetate in hexane were used for extracting chlorpyrifos from the silica SPE. Gillespie and Walters (1991) used 5-g commercial C_{18} reverse phase cartridges for the clean-up *vis-à-vis* the 1 g normal phase silica cartridges used in this method. The results of this study show that 98.3% of the lipid was removed with only

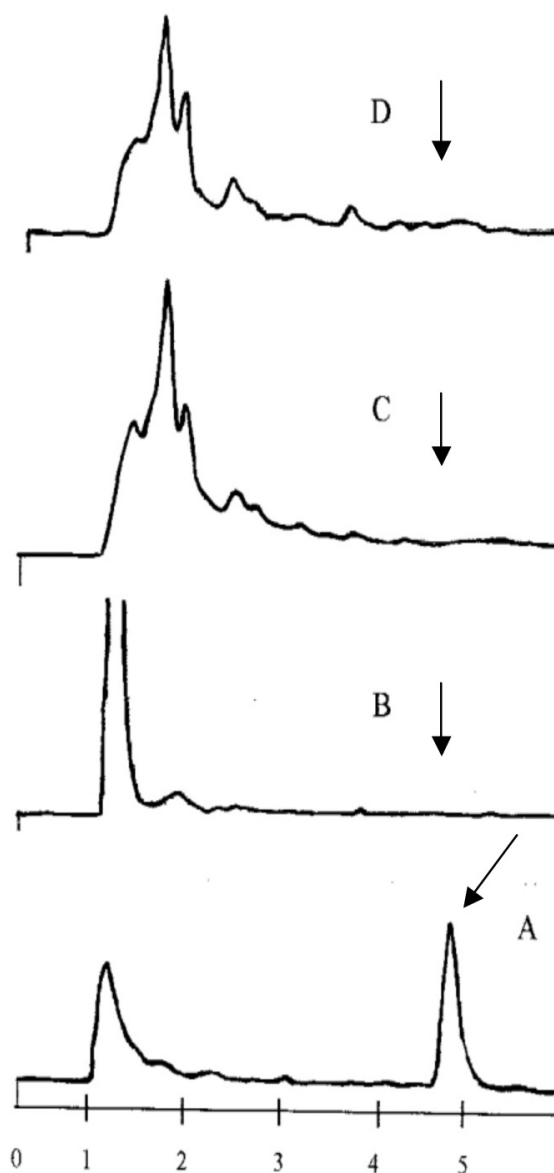


Figure 3. Chromatograms obtained using gas chromatography-electron capture detector for: A) chlorpyrifos standard solution $0.1 \mu\text{g ml}^{-1}$, B) commercial sample of refined bleached deodorised palm olein, C) commercial sample of crude palm kernel oil, and D) commercial sample of crude palm oil.

1 g of silica, whereas in the method of Gillespie and Walters (1991) 5 g of C_{18} were used to remove 99.1% of the lipid from butter fat and 99.9% from sunflower oil. Therefore, the results suggest that the silica cartridge is more efficient than C_{18} in removing fat from oil matrices. The reduction in packing material resulted in less eluting solvents being required. Silica is also cheaper than C_{18} , besides showing no significant difference in lipid breakthrough.

Table 3 shows the recovery of chlorpyrifos in tests carried out by the participants from different organisations in the reproducibility test. Based on the results of the reproducibility study, the average recoveries of chlorpyrifos from CPO, CPKO, and

TABLE 3. RECOVERY OF CHLORPYRIFOS IN SPIKED SAMPLES FROM THE VALIDITY STUDY

Spiking level ($\mu\text{g g}^{-1}$)	Organisation	Recovery (%) n=3		
		CPO n = 3	CPKO n = 3	RBDPOo n = 3
1	A	98	98	101
1	B	93	95	100
1	C	94	99	98
1	D	96	94	100
	Average	95	97	100
	Relative standard deviation (%)	2.3	2.5	1.3

Note: A = Universiti Kebangsaan Malaysia.
 B = Universiti Putra Malaysia.
 C = Malaysian Institute for Nuclear Technology.
 D = Ministry of Health, Malaysia.
 The reproducibility test was performed at MPOB, Bandar Baru Bangi, Selangor, Malaysia.
 CPO – crude palm oil. CPKO - crude palm kernel oil.
 RBDPOo - refined bleached deodorised palm olein.

RBDPOo were $95 \pm 2.3\%$, $97 \pm 2.5\%$, and $100 \pm 1.3\%$, respectively. Chlorpyrifos residues were not found in the CPO, CPKO and RBDPOo samples obtained from the local palm oil mills and refinery.

CONCLUSION

The data presented in this article show that acetonitrile extraction followed by silica SPE clean-up and GC analysis can be used to determine the presence of chlorpyrifos residue in palm oil products. The method gives a high recovery with low coefficient of variation as well as good repeatability, and is therefore suitable for monitoring the presence of chlorpyrifos residue in palm oil and its products.

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