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Supercritical fluid extraction and quantitative determination of organophosphorus pesticide residues in wheat and maize using gas chromatography with flame photometric and mass spectrometric detection

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Abstract

An automated method using supercritical CO_2 and clean-up by solid-phase extraction (SPE) using graphitized carbon black, has been developed for the quantitative determination of organophosphorus pesticide (OPP) residues in wheat and maize. Recoveries were as good as, or better than, those obtained using liquid extraction (LE) and gel permeation chromatography (GPC) for 10 OPP's spiked at levels equivalent to 0.05 and 0.50 μg/g. Lower limits of detection were possible using supercritical fluid extraction (SFE). Incurred residues were found in wheat and maize samples, and good agreement was obtained using SFE+SPE and LE+GPC. The SFE+SPE method required less analyst time and organic solvent, and hazardous waste was reduced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Current methodologies to determine pesticide residues usually use liquid extraction (LE), often incorporating a partitioning stage, concentration of extract as well as a clean-up stage prior to determination using chromatography. An attractive alternative is to use supercritical fluids which have similar densities to liquids, but lower viscosities and higher diffusion coefficients. This combination of properties results in a fluid which is more penetrative, has a higher solvating power and will extract solutes faster than liquids. Supercritical CO_2 is a suitable fluid for the extraction of pesticide residues and has the additional advantages of being readily available and 'environmentally friendly'. Commercial instrumentation is available which controls supercritical conditions and automatically extracts samples. Once conditions are established, routine extractions are straightforward, and labour costs are reduced compared to conventional liquid extractions.

A number of supercritical fluid extraction (SFE) methods to determine pesticide residues have been published for a variety of foods such as fruits [1,2], vegetables [3,4], meat [5], eggs [6] and oils [7–9]. SFE methods for the determination of pesticides in cereals such as wheat [10–12], rice [13] and wheat flour [14,15] describe a variety of extraction conditions suitable for organophosphorus (OPP),

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organochlorine and synthetic pyrethroid pesticides. However, the SFE methods for wheat describe the recovery of OPPs from spiked samples and only one determination of an incurred residue [11] using gas chromatography (GC) with flame photometric detection (FPD). Similarly the SFE methods for flour recover spiked pesticides from inert material such as sand or filter papers [14], and pesticides from reference materials [14] and certified reference materials [15] using GC–FPD and GC with nitrogen–phosphorus detection (NPD). It is still possible to obtain spurious results using such detection systems, even after a second analysis using a different GC column. Skopec et al. [13] obtained good recoveries of OPP residues from spiked rice using SFE and compared SFE to LE using GC and atomic emission detection (AED). Significant numbers of rice samples containing incurred OPP residues were also analysed giving excellent correlation between extraction methods. Although GC–AED is much more selective than GC with conventional detection it is still desirable to use mass spectrometric (MS) detection, which has the potential for unequivocal identification of OPP residues and is therefore essential to provide reliable quantitative confirmation of positive results.

The purpose of this study was to evaluate an automated SFE and solid-phase extraction (SPE) method for the determination of ten OPPs typically used to treat wheat and maize. Recovery data from spiked wheat and maize using SFE+SPE determined by GC–FPD and GC–MS are presented, and SFE+SPE was compared to an established LE and gel permeation chromatography (GPC) method for the determination of incurred OPP residues in wheat and maize. The performance of GC–MS was compared to GC–FPD for the quantitative determination of OPP residues in SFE+SPE extracts.

2. Experimental

2.1. Chemicals

SFE-grade CO_2 (99.995%) was obtained from Air Products (Crewe, UK). Pesticide standards dichlorvos, methacrifos and fenitrothion were obtained from Promochem (Welwyn Garden City, UK). Chlorpyrifos-methyl, phosphamidon, pirimiphos-methyl and chlorpyrifos were obtained from Greyhound (Birkenhead, UK) and diazinon, etrimfos and malathion were obtained from Qmx (Saffron Walden, UK). All standards were 94% or higher purity except for etrimfos which was 57%. Acetone (Certified for Analysis), acetonitrile, cyclohexane, methylene chloride, ethyl acetate, hexane, methanol and toluene (Certified for HPLC, Fisher, Loughborough, UK). Individual pesticide standard stock solutions of 1000 μg/ml in acetone were prepared and a standard mix containing 40 μg/ml of each of the pesticides was prepared in acetone from the individual standard stocks. The standard mix was suitable for spiking samples and preparing matrix matched standards appropriately diluted.

2.2. Preparation of samples and matrix matched standards

Field samples of wheat and maize were obtained from grain producers, millers and merchants. Whole grains (2 kg) were mixed by sub-dividing with a Glen Creston Retsch sample divider (Stanmore, UK) and recombining fractions from the sample divider. A portion of the recombined fractions (500 g) was milled with a Glen Creston Type 11-500 Laboratory Disc Mill (Stanmore, UK) on setting 10 to a course powder/particles of which 99% passed through a 1 mm screen. Organically grown wheat and maize were used for spiking experiments.

A glass microfibre filter disc, Whatman GF/F 15 mm diameter (Maidstone, UK) was placed in the bottom of an SFE extraction thimble and packed with ground sample (3.1–3.8 g) using a funnel. Any dead volume was filled with sand, BDH GPR 50–100 mesh acid washed (Poole, UK), and topped with a glass microfibre filter disc before sealing with an SFE extraction thimble cap.

Matrix matched standards were prepared from organically grown wheat and maize extracted by SFE and LE, using their associated clean-up procedures given in Sections 2.3 and 2.4 respectively. Known amounts of pesticides were added to clean extracts in acetone using a microlitre syringe. Calibration curves were prepared from the average of two sets of calibrants bracketing samples using four levels.

2.3. Supercritical fluid extraction and clean-up

A Hewlett-Packard 7680T supercritical fluid extractor (Palo Alto, CA, USA) was used for SFE. Samples were extracted with supercritical CO_2 at 24.5 MPa (245 bar) and 70°C (density, 0.73 g/ml) for a 5 min static period, followed by a 35 min dynamic extraction period at a flow-rate of 1.0 ml/min. Analytes were collected following decompression of CO_2 on an octadecylsilane (ODS) trap at 10°C with a nozzle temperature of 50°C. Acetone (1.5 ml) was used to desorb the ODS trap at 30°C with a flow-rate of 2 ml/min into a 2 ml vial sealed with a PTFE faced septum. The trap was then rinsed with acetone (5 ml) at 30°C to waste. SFE extracts were quantitatively transferred to a 2 ml volumetric flask and made to volume with acetone.

Recovery data was obtained by spiking blank commodity (3.1–3.8 g) with 90 μl of acetone containing OPPs (2 μg/ml or 20 μg/ml), corresponding to a residue of approximately 0.05 or 0.5 μg/g, and allowing the solvent to evaporate (10 min). Four replicates of each level were extracted in a sequence. Field samples were extracted in a sequence containing a blank sample spiked at 0.05 μg/g and seven field samples. Matrix matched extracts were prepared in separate extraction sequences as required.

SFE extracts were cleaned up by SPE using an automated Gilson ASPEC XL (Villiers-Le-Bel, France) with 6 ml cartridges containing ENVI-Carb (500 mg) supplied by Supelco (Poole, UK). SPE cartridges were conditioned with 5 ml of elution solvent [acetonitrile–toluene (3:1)] at a flow-rate of 5 ml/min [16]. SFE extract (1 ml) was loaded onto the cartridge (5 ml/min) and eluted with 5 ml of elution solvent (1 ml/min) and collected in a Corning Pyrex disposable borosilicate culture tube, 85 mm×15 mm (New York, USA). The extract was reduced to near dryness (0.2 ml) under nitrogen (45°C) and the residue transferred to a 2 ml volumetric flask using 3 aliquots of acetone (0.5 ml) and made to volume.

2.4. Liquid extraction and clean-up

Milled sub-samples (25 g), were homogenised for 2 min with 100 ml of extraction solvent [acetone–methanol (1:1)], centrifuged at 2500 rpm and the supernatant decanted into a separating funnel as described previously [17]. The filter cake was re-homogenised with extraction solvent (80 ml), re-centrifuged and the supernatant decanted as before. The combined extracts were partitioned between methylene chloride (50 ml) and sodium sulfate solution (2.5%, w/v) three times. The methylene chloride extracts were combined, evaporated to near dryness, and the residue was re-dissolved in 25 ml of GPC solvent [ethyl acetate–cyclohexane (1:1)]. An aliquot (5 ml) was cleaned up by GPC using Bio-Beads SX3 (200–400 mesh, Bio-Rad Labs., Hercules, CA, USA) with a flow-rate of 5 ml/min, the fractions containing the analytes were evaporated to near dryness. The residuum was made up in acetone (5 ml) and was analysed using GC–FPD and GC–MS. Recovery data was obtained by spiking blank commodity (25 g). Milled samples were spiked with acetone containing OPPs corresponding to a residue of approximately 0.05 μg/g and extracted as described above.

2.5. GC analysis

Pesticide residues were determined using a Hewlett-Packard 5890 Series II gas chromatograph (Waldbronn, Germany) fitted with an FPD system operated in the phosphorus mode at 250°C. Samples, equivalent to 1 mg of commodity in SFE+SPE and LE+GPC extracts, were injected (1 μl), using a Hewlett-Packard 7673 autosampler, into a split–splitless injector containing a 4 mm I.D. deactivated single taper liner at 250°C. Helium carrier gas was used with electronic pressure control to maintain a linear velocity of 30 cm/s. The analytical column was a 30 m×0.25 mm DB-5 (J&W Scientific), with a film thickness of 0.25 μm. The column oven temperature was held at 100°C for 1 min, then programmed at 20°C/min to 170°C for 15 min, 2°C/min to 180°C for 2 min and at 30°C/min to 290°C and held for 1.33 min.

Mass spectrometric detection used a Hewlett-Packard 5971a detector (Palo Alto, CA, USA) interfaced with a Hewlett-Packard 5890 Series II gas chromatograph (Waldbronn, Germany). The GC–detector interface was set at 300°C, and the mass spectrometer was operated with electron impact ionisation at

70 eV. Selected ion monitoring acquisition was used to collect from 3 to 6 ions in 8 timed windows. Samples were injected into a split–splitless injection port as detailed above. Helium carrier gas was used with electronic pressure control to maintain a linear velocity of 27.5 cm/s. The analytical column was a 30 m×0.25 mm DB-5 ms (J&W Scientific), with a film thickness of 0.25 μm. The column oven temperature was held at 100°C for 1 min, then programmed at 25°C/min to 180°C for 2.1 min, 1°C/min to 190°C for 2.5 min and at 25°C/min to 310°C and held for 2.4 min.

3. Results and discussion

3.1. Evaluation of SFE conditions

Lopez-Avila and Dodhiwala [18] extracted dichlorvos, diazinon, malathion, chlorpyrifos and 21 other OPPs from spiked sand using supercritical CO_2 at 25.0 MPa (250 bar) and 70°C, trapped in solvent and achieved acceptable recoveries (60–90%) for seventeen of the twenty-five components. Preliminary work for this study using similar SFE conditions [24.5 MPa (245 bar), 70°C] and a solid trap, determined recoveries of dichlorvos, methacrifos, diazinon, etrimfos, phosphamidon, chlorpyrifos-methyl, fenitrothion, pirimiphos-methyl, malathion and chlorpyrifos from spiked glass beads. The supercritical CO_2 flow-rate was optimised at 1.0 ml/min, which extracted pesticides in an acceptable time without unduly compromising the recovery of more volatile pesticides such as dichlorvos and methacrifos following the decompression of CO_2. Pesticide trapping conditions were based on those used by Lehotay and Valverde-García [19], using an octadecylsilane trap maintained at 10°C and desorbed at 30°C with acetone. Good recoveries (90–108%) were obtained which showed the OPPs studied were soluble in supercritical CO_2, were swept out of the extraction thimble, trapped effectively and completely desorbed using acetone.

3.2. SFE+SPE of spiked commodities

Wheat and maize known not to contain OPP residues were spiked with dichlorvos, methacrifos, diazinon, etrimfos, phosphamidon, chlorpyrifos-methyl, fenitrothion, pirimiphos-methyl, malathion and chlorpyrifos (0.05 and 0.50 μg/g) to assess the effect of co-extracted materials on the extraction, trapping, reconstitution and subsequent analysis of the OPPs using GC–FPD and GC–MS. Initial data showed recoveries were good for all pesticides without any interfering co-extractives from either commodity using both detectors. However, detector response decreased by as much as 45% between sets of matrix matched calibrants when using GC–MS, and up to 30% when using GC–FPD, when bracketing 8 samples. Changing the injector liner and cutting the first 30 cm from the front of the analytical column improved the change in detector response, but changes of greater than 20% were still observed, and were not acceptable for quantitative analysis [20]. Further clean-up of the SFE extract was necessary. The volume of SFE extract collected was convenient for GPC or SPE clean-up, the latter was selected for its speed and minimal solvent consumption.

ENVI-Carb cartridges have been reported as being appropriate for a wide range of pesticides including OPPs of varying polarity [16] and were assessed for clean-up of SFE extracts. Figs. 1 and 2 show the recovery of OPPs from 4 replicates of wheat and maize spiked at residue levels equivalent to 0.05 μg/g and 0.50 μg/g determined by GC–FPD and GC–MS following extraction and SPE clean-up. A new injection port liner was installed, and the first 30 cm of analytical column was removed before each analytical sequence which consisted of about 40 injections. A typical chromatogram using GC–FPD is shown in Fig. 3. The detector response of calibrants decreased by less than 20% for both detector systems when bracketing eight samples, which satisfied quality control procedures for quantitative analysis [20]. Recoveries were good and the mean for individual pesticides generally fell within the desired range of 70–110% [21]. Recoveries of wheat were higher than maize spiked at both levels, with excellent agreement between detector systems. Recoveries of dichlorvos were the lowest (45–74%) probably associated with its relatively high vapour pressure (2100 mPa) and subsequent losses sustained during decompression of supercritical CO_2. Such recoveries were similar to those reported by other workers using

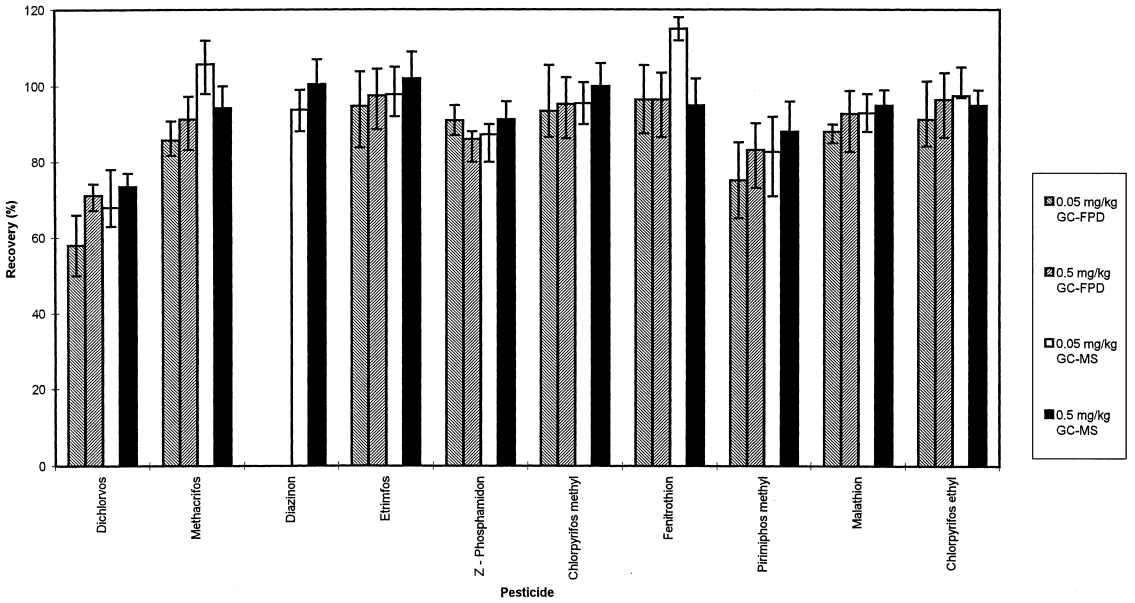

Fig. 1. OPP recoveries from spiked wheat using SFE+SPE (n=4).

SFE [14,19,22]. Recoveries of methacrifos were good even though its vapour pressure (160 mPa) is 10–100 times greater than the other OPPs studied, however, the mean recovery for maize spiked with 0.05 μg/g methacrifos was low at 62%. It was not possible to determine diazinon recoveries using GC–FPD as this compound was not resolved from *E*-phosphamidon. A low mean recovery of *Z*-phos-

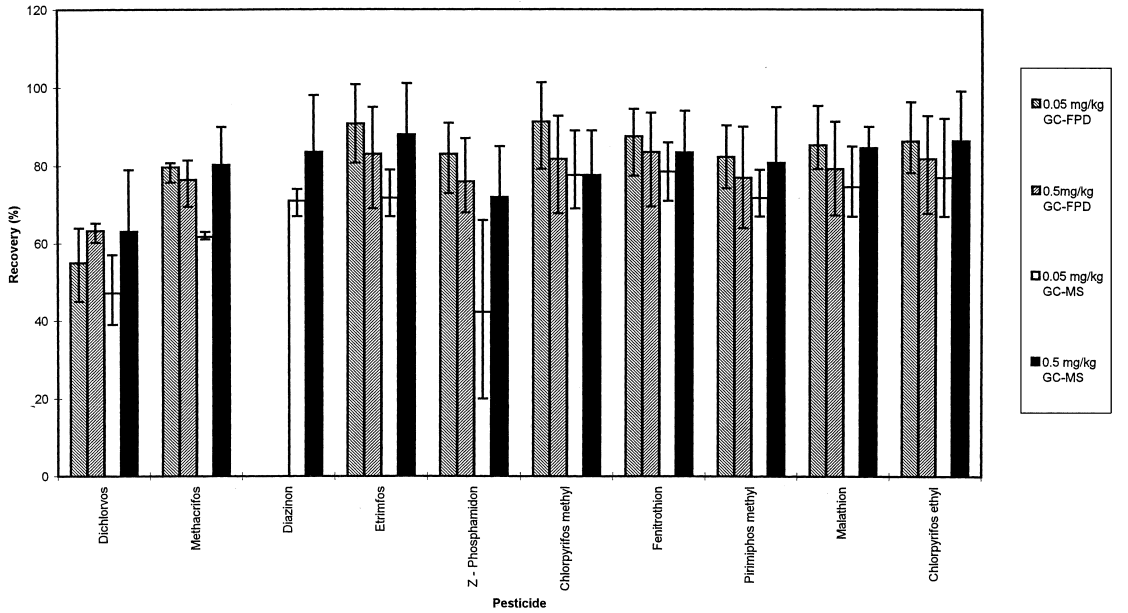

Fig. 2. OPP recoveries from spiked maize using SFE+SPE (n=4).

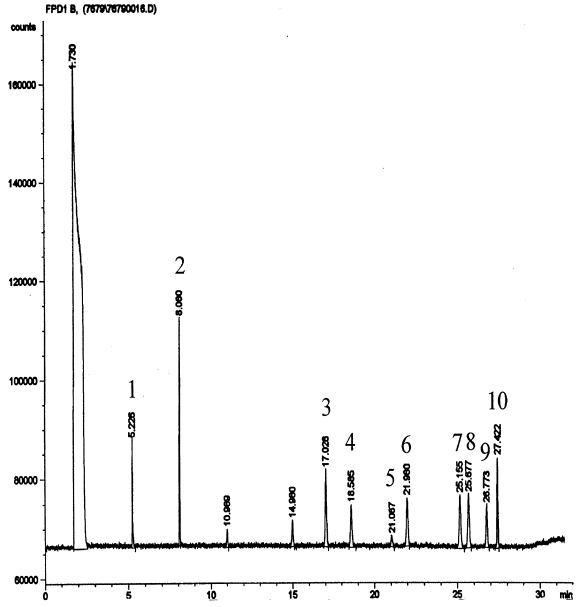

Fig. 3. Gas chromatogram of wheat spiked with OPPs equivalent to a residue level of 0.05 μg/g using GC–FPD. Peaks: 1=dichlorvos, 2=methacrifos, 3=diazinon+*E*-phosphamidon, 4=etrimfos, 5=*Z*-phosphamidon, 6=chlorpyrifos-methyl, 7=fenitrothion, 8=pirimiphos-methyl, 9=malathion and 10=chlorpyrifos.

phamidon (42%) was obtained from spiked maize (0.05 μg/g) determined using GC–MS with a signal-to-noise ratio less than 4. A high fenitrothion recovery (118%) for low level spiked wheat was due to a spurious peak present for *m/z* 277 and *m/z* 125, it was not possible to calculate a recovery at such a low level using *m/z* 109.

Mean recoveries for all spiked pesticides are shown in Table 1. A higher mean recovery of all pesticides was obtained using SFE+SPE compared to LE+GPC for wheat, whilst similar values were obtained for maize using both extraction techniques. The mean recoveries for all pesticides using SFE+SPE were higher at a spike level of 0.50 μg/g than at the lower spike level as would be expected for residues at a level much greater than the limit of detection (LOD). The relative standard deviation (RSD) values shown are the mean for all spiked pesticides and were good (≤10%) for both extractions, although maize spiked at the higher level was the exception with RSDs of 12.8 and 13.5%, i.e. similar using GC–FPD and GC–MS indicating either

Table 1
Mean recoveries and precision for 10 OPP recovered from spiked commodities using SFE+SPE and LE+GPC

Commodity	Spike level (μg/g)	Mean recovery and mean (RSD) (%)		
		SFE+SPE		LE+GPC, FPD[a]
		FPD[a]	MS	
Wheat	0.05	86.1 (7.8)	94.1 (6.4)	79.9 (7.6)
	0.50	90.1 (5.5)	93.5 (6.5)	N/A[b]
Maize	0.05	82.3 (9.1)	67.5 (10.0)	84.8 (6.4)
	0.50	86.2 (12.8)	80.8 (13.5)	N/A[b]

[a] Mean for 9 OPP, i.e. excluding diazinon (n=4).
[b] N/A=not analysed.

analytical system was suitable for SFE+SPE extracts. The higher mean RSD observed for the maize spiked at 0.50 μg/g may be explained because the samples were analysed at the end of a sequence which consisted of 44 injections when column performance may have been impaired by co-extracted material. Recoveries and corresponding mean RSDs for all spiked OPPs were satisfactory for maize using SFE+SPE at the lower spike level determined on each analytical system. However, a higher mean RSD was obtained for spiked maize using SFE+SPE compared to LE+GPC, possibly due to more co-extracted material such as lipids or chromophores present in the final SFE+SPE extract compared to the LE+GPC extract, which benefited from GPC. The mean RSD obtained for spiked wheat using SFE+SPE for the low spike level was similar to that obtained using LE+GPC.

3.3. Limits of detection

LOD was calculated for a signal-to-noise ratio equal to 4 and expressed as an equivalent residue. Table 2 shows the extrapolated LOD value for each analytical system calculated using a 1 μl injection of matrix matched standard containing 0.05 ng of pesticide. Values given are the highest LOD measured in a chromatographic run. It was possible to determine OPP residues at a level of 0.05 μg/g for wheat and maize using either detector. Each commodity had a similar LOD using GC–FPD. LODs for wheat were lower than for maize using GC–MS

Table 2
Limits of detection of OPP in wheat and maize using SFE+SPE

Pesticide	Detector	Limit of detection (μg/g)	
		Wheat	Maize
Dichlorvos	FPD	0.006	0.007
	MS	0.008	0.036
Methacrifos	FPD	0.004	0.007
	MS	0.007	0.013
Diazinon	FPD	N/D[a]	N/D[a]
	MS	0.022	0.013
Etrimfos	FPD	0.023	0.026
	MS	0.004	0.010
Z-Phosphamidon	FPD	0.049	0.053
	MS	0.021	0.050
Chlorpyrifos methyl	FPD	0.024	0.022
	MS	0.004	0.010
Fenitrothion	FPD	0.022	0.021
	MS	0.010	0.027
Pirimiphos methyl	FPD	0.019	0.021
	MS	0.004	0.010
Malathion	FPD	0.026	0.025
	MS	0.010	0.042
Chlorpyrifos ethyl	FPD	0.024	0.013
	MS	0.021	0.046

[a] N/D=not determined.

except for the early eluting compounds dichlorvos and methacrifos. Lower LODs were achieved using GC–FPD with SFE+SPE compared to LE+GPC for wheat by 21% and maize by 14% averaged for all of the OPPs.

3.4. Comparison of incurred residues

Thirteen samples of wheat and thirteen of maize were each extracted in duplicate using SFE+SPE and LE+GPC [23] and analysed using GC–FPD. There was excellent agreement between extraction techniques for both wheat and maize and for all pesticides found. Six samples of wheat and four samples of maize were found not to contain any OPP residues above 0.05 μg/g using both extraction techniques. Five OPPs were found between 0.05 and 0.71 μg/g in sixteen samples and are shown in Fig. 4. The overall agreement between SFE+SPE and LE+GPC was good with a correlation coefficient of 0.978, and a gradient of 1.24 for the regression of SFE+SPE on LE+GPC which was significantly different to 1 (t=3.97 with 19 degrees of freedom

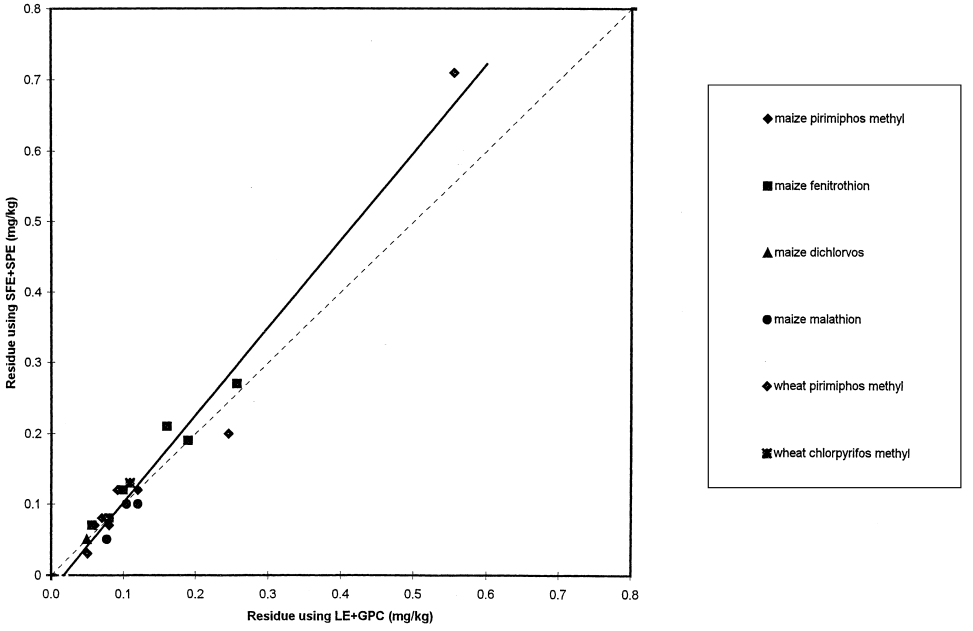

Fig. 4. SFE+SPE and LE+GPC (correlation coefficient=0.978) of incurred residues determined by GC–FPD.

(d.f.), $P=<0.001$), indicating SFE+SPE was more efficient than LE+GPC for the extraction of incurred OPP residues which was also the case for the SFE of OPPs from rice [13]. The consistency of each extraction method was evaluated by comparing the variances between replicates ($n=2$), for the incurred residues. All results were processed together as there was no obvious sign of variability between different pesticides and commodities. The RSD, calculated from the variability between the replicates gives a measure of the variability of each method taking into account the sub-sample size and ignores the magnitude of the pesticide residue. This value was 16.0% for LE+GPC, but was 46.1% for SFE+SPE, calculated for the 21 residues determined. Such an apparent variation in results was strongly influenced by one wheat sample which contained residues of pirimiphos methyl and gave replicate residue levels of 0.36 and 0.03 μg/g. Inspection of the associated chromatograms did not suggest a chromatographic error. However, treating this sample as an outlier gives a RSD of 19.3% for SFE+SPE and 16.9% for LE+GPC, i.e. there was no significant difference between the variance for the SFE+SPE and LE+GPC methods ($F=1.61$ with 20 and 20 d.f., $P>0.1$). Because one sample had a significant effect on the overall variation of the SFE+SPE method it is recommended to extract two sub-samples routinely to identify all samples containing pesticide residues. Further data may show it is only necessary to extract one sub-sample using SFE+SPE to be certain of identifying samples containing OPP residues. It was noteworthy that dichlorvos was detected in a maize sample at a residue level of 0.05 μg/g using both extraction techniques even though much lower recoveries of this compound were obtained using SFE+SPE (wheat 58% and maize 55%) compared to LE+GPC (wheat 78% and maize 81%).

The SFE+SPE extracts were also analysed using GC–MS and gave excellent agreement compared to results obtained using GC–FPD. An example of a gas chromatogram using GC–MS for the analysis of maize containing OPP residues is shown in Fig. 5. There was a correlation coefficient of 0.955 between the detector systems. Regression analysis of GC–MS on GC–FPD gave an intercept close to zero (−0.003) and a formal *t*-test of the slope gave a value which was not significantly different to 1 ($t=0.80$ with 19 d.f., $P=0.435$), showing either analytical system was suitable for determining OPPs using SFE+SPE of wheat or maize containing residues at 0.05 μg/g or above.

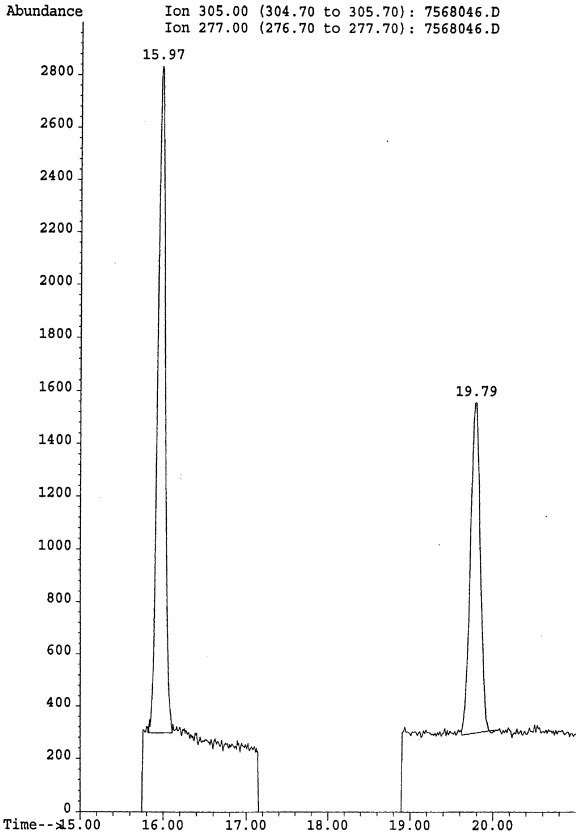

Fig. 5. Gas chromatogram of maize containing 0.12 μg/g pirimiphos methyl (15.97 min, ion *m/z* 305) and 0.18 μg/g fenitrothion (19.79 min, ion *m/z* 277) using GC–MS. Time scale in min.

4. Conclusion

Recoveries of 10 OPPs using SFE+SPE were shown to be as good as or better than LE+GPC from spiked wheat and maize. No co-extractive components interfered with the analyte suite when using GC–FPD or GC–MS and the change in detector response during an analytical sequence complied with EU quality control guidelines [20]. Lower LODs were achieved using SFE+SPE rather than

LE+GPC for wheat and maize. Incurred residues determined using SFE+SPE were shown to be accurate compared to those determined using LE+GPC. It was possible for an analyst to prepare 8 extracts using SFE+SPE and solid-phase clean-up in 2.5 h for GC analysis compared to 9 h using LE and GPC. Solvent consumption was minimal using the SFE+SPE technique.

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