MINIATURIZED AUTOMATED MATRIX SOLID PHASE DISPERSION EXTRACTION FOR THE PREPARATION OF SMALL AMOUNTS OF SOLID SAMPLES

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INTRODUCTION

Matrix solid-phase dispersion (MSPD) is an analytical technique for the preparation and extraction of solid and viscous samples. The sample is homogenized together with an adsorbent. During the preparation step, the sample structure is completely disrupted and dispersed over the surface of the adsorbent. The interactions between the matrix components and the adsorbent, and the nature of the elution solvent determine the selectivity of the extraction process.

The main objective of this study was to develop and evaluate a simple and fast miniaturized automated MSPD method for the sample preparation and quantitative extraction of pesticides in fruit. The method was optimised for orange, by testing different extraction solvents and adsorbents, using a selection of organophosphorous pesticides and a pyrethroid, at concentration levels below the maximum residue levels (0.02-2 mg/kg) allowed by the European Union. Further, sample size, clean-up step and feasibility for other samples were evaluated as a preparation for the analysis of samples where only a small amount is available. Finally the method was used for extraction of pesticides from individual insects.

PROCEDURE

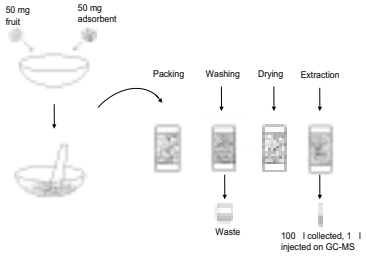

Figure 1.
8 min washing with water at 1 ml/min
30 min drying under N_2
Extraction with ethyl acetate at 100 µl/min

SET-UP

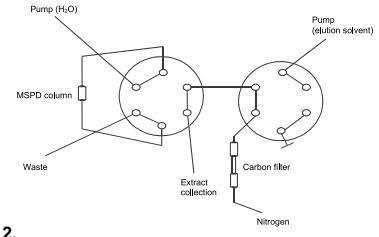

Figure 2.
All extracts were analysed on a GC-MS (HP 6890 Series, Hewlett-Packard, Palo Alto, CA, USA) with an Optic2-200 injector (Ai Cambridge, Cambridge, UK) in the cold splitless mode on a HP-5 MS column (30 m x 0.25 mm I.D., d_f = 0.25).

Table I.
The molecular mass (M_r), ions (m/z) used for SIM and Log $P_{o\ w}$ of the target compounds.

	Pesticides	M_r	*m/z*	Log P_{ow}
1	Diazion	304.4	304, 199, 179, 137	3.11 – 3.81
2	Parathion-methyl	263.2	263, 125, 109	1.80 – 3.04
3	Fenitrothion	277.2	277, 259, 125, 109	3.30 – 3.47
4	Malathion	330.4	173, 158, 125, 93	2.84 – 2.94
5	Fenthion	278.3	278, 169, 109, 125	4.09 – 4.17
6	Chlorpyriphos	350.6	314, 258, 197	4.96 – 5.27
7	Bromophos-methyl	366.0	331,125	4.88 – 5.21
8	Methidathion	302.3	145, 85	2.42
9	Azinfos-methyl	317.3	160, 132, 77	2.69
10/11	Permethrin (cis/trans)	391.3	183, 163	5.84 – 6.60
IS	Trifluralin	335.3	306, 335, 264	3.97
	Cyfluthrin	434.3	163, 206, 226, 434	5.95

RESULTS AND DISCUSSION

Support material

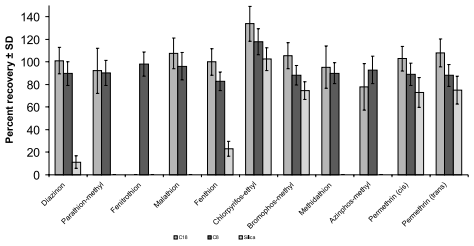

Figure 3.
Percent recoveries ± SD (n=4) of the analytes, obtained for oranges, using different sorbents, spiking level: 0.5 ng/mg.

- ➞ Loss of polar analytes when using silica.
- ➞ Lower background with C8 then with C18.
- ➞ Chlorpyriphos and fenitrothion are badly separated from interfering compounds when using C18.
- ➞ C8 was used for the following experiments.

Clean-up

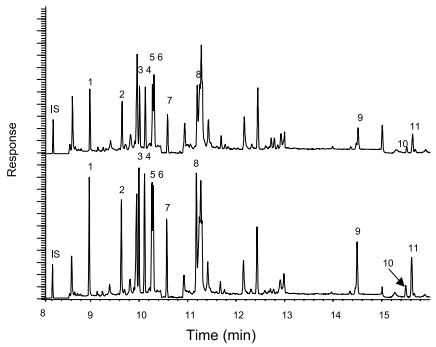

Figure 4.
GC-MS chromatograms (SIM) of orange extracts using C8 for MSPD without (top) and with(bottom) clean-up step. See Table I for peak identification.

- ➞ No clean-up necessary
- ➞ Faster sample preparation

Sample size

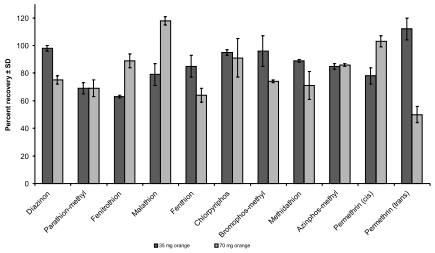

Figure 5.
Percent recoveries ± SD (n=4) of the analytes, obtained for oranges, using MSPD columns of two different sizes, spiking level: 0.5 ng/mg.

- ➞ The smaller column gave the best overall recoveries

Performance

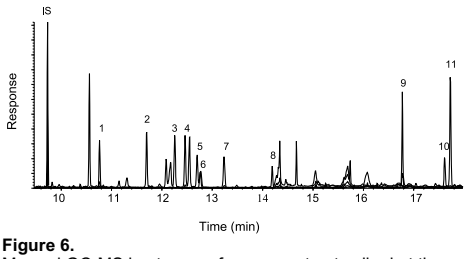

Figure 6.
Merged GC-MS ion traces of orange extract spiked at the 0.2 ng/µl level: the concentration of the IS was 0.2 ng/µl. See Table I for peak identification.

Table II.
Percent recovery (RSD; n=4) of the selected pesticides in orange, pear, grape and apple, spiked at 0.5 ng/mg

Pesticides	Orange	Pear	Grape	Apple	
				Clean-up	No clean-up
Diazinon	90 (12)	73 (8)	51 (4)	22 (15)	80 (4)
Parathion-methyl	90 (12)	72 (4)	47 (5)	22 (21)	94 (8)
Fenitrothion	98 (11)	78 (8)	52 (7)	23 (18)	88 (6)
Malathion	96 (13)	79 (4)	51 (6)	23 (21)	82 (2)
Fenthion	83 (10)	43 (2)	31 (32)	9 (16)	76 (3)
Chlorpyrifos-ethyl	118 (10)	76 (4)	51 (6)	22 (18)	78 (3)
Bromophos-methyl	88 (10)	75 (3)	62 (5)	21 (21)	90 (3)
Methidathion	90 (10)	79 (11)	47 (3)	22 (24)	97 (4)
Azinphos-methyl	93 (13)	79 (2)	48 (3)	27 (22)	74 (7)
Permethrin (cis)	89 (11)	80 (3)	54 (2)	20 (28)	87 (8)
Permethrin (trans)	88 (11)	80 (1)	53 (5)	21 (25)	89 (8)

- ➞ Good recoveries for most compounds.

Table III.
LODs (pg/mg = g/kg) of the analytes in fruits.

Pesticides	Orange	Pear	Grape	Apple
Diazinon	40	50	30	25
Parathion-methyl	10	10	4	6
Fenitrothion	50	40	50	8
Malathion	40	40	10	4
Fenthion	10	20	6	60
Chlorpyrifos-ethyl	10	7	7	25
Bromophos-methyl	10	80	4	90
Methidathion	10	10	20	8
Azinphos-methyl	30	30	40	30
Permethrin (cis)	30	50	30	155
Permethrin (trans)	10	20	10	20

- ➞ Possible to analyse pesticides at levels far below the maximum residue levels set by the EU

Feasibility study on insects

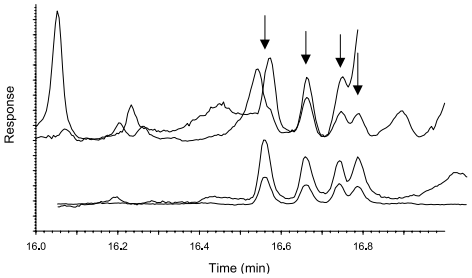

Figure 7.
Ion traces showing the 20 l injections of a caterpillar extract spiked at 20 ng/caterpillar (top) and a standard of 1 ng/ l (bottom),the arrows indicate the isomer peaks of cyfluthrin.

CONCLUSIONS

- ✓ The miniaturized automated MSPD method is a viable approach.
- ✓ Accurate quantification of pesticides at low levels in small amounts of samples.
- ✓ Method provides excellent means to analyse small samples, e.g. insects.