DETERMINATION OF SEVEN PROBLEMATIC PESTICIDES IN OLIVE OIL

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INTRODUCTION

Recoveries of seven problematic pesticides in olive oil, including six base sensitive compounds (chlorothalonil, dicofol, dichlofluanid, tolylfluanid, folpet and captan), and one acid sensitive compound (pymetrozine) were determined by a modified QuEChERS procedure using GC/MS in SIM mode. Different percentages of acetic acid in acetonitrile were evaluated. Extracting with 0.5% acetic acid in acetonitrile resulted in better recoveries than the traditional 1% acetic acid in acetonitrile. Comparisons of different clean-up methods including dSPE, endcapped C_{18} SPE cartridges, and PSA/C_{18} dual layer SPE cartridges were also evaluated. PSA/C_{18} dual layer SPE cartridges provided the best extract clean-up. GC injection ports were fouled by the olive oil extract and were cleaned when folpet and captan showed a decreased response.

EXPERIMENTAL

Materials:

50 mL QuEChERS extraction tube with 6000 mg anhydrous magnesium sulfate and 1500 mg anhydrous sodium acetate (UCT: ECMSSA50CT)

15 mL dSPE tube with 1200 mg anhydrous magnesium sulfate, 400 mg PSA and 400 mg endcapped C_{18} (UCT: CUMPSC1815CT2)

C_{18} SPE cartridge: 500 mg endcapped C_{18} in a 6 mL cartridge (UCT: EEC18156)

PSA/C_{18} dual layer SPE cartridge: 500 mg of PSA and 500 mg of endcapped C_{18} in a 6 mL cartridge for high lipid clean-up (UCT: ECPSAC1856)

QuEChERS Multi-Packs
Part Number: ECMSSA50CT

Vacuum Manifold System
16 Position System
Part Number: VMF016GL

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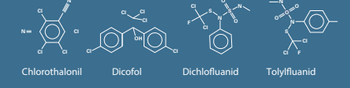
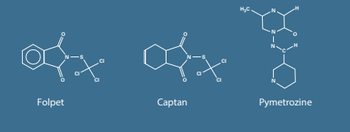
PROCEDURES

Chemical Structures:





Procedures:

Extraction
Weigh 1 g olive oil into 50 mL QuEChERS tube, spike, wait for 15 min for solvent to evaporate, Add 10 mL MeCN (with 0.5 or 1% acetic acid), 9 mL DI H_2O, shake vigorously for 1 min or vortex for 20 sec. Centrifuge at 4000 rpm for 10 min.
Clean-up (dSPE, endcapped C_{18} SPE cartridge, PSA/C_{18} dual layer SPE cartridge)

1. With dSPE:
Transfer 7.5 mL extract into 15 mL dSPE tube, shake vigorously for 1 min or vortex for 20 sec. Centrifuge at 4000 rpm for 10 min. Transfer 5 mL into 6 mL test tube, concentrate by N_2 at 35 °C to dryness, reconstitute with 0.5 mL toluene.

2. With SPE cartridge:
Attach cartridges to the vacuum manifold ensuring that the bulkhead fittings are clean and dry Pour approx 1 g muffled Na_2SO_4 into the cartridge, load extract, collect 5 mL eluent (Gravity elution for endcapped C_{18} cartridge; 5" Hg vacuum for PSA/C_{18} dual layer cartridge). Concentrate by N_2 at 35 °C to dryness, reconstitute with 0.5 mL toluene.

Instrumental:

GC/MS: Agilent 6890N GC coupled with 5975C MSD, equipped with 7683 auto sampler. Chemstation™ software for data acquisition and analysis.
Injector: 1 µL splitless injection at 250 °C, with a split delay of 1 minute.
Liner: 4 mm splitless gooseneck, 4mmID*6.5mmOD*78.5mm (UCT#: GCLGN4MM)
Glass wool for liner: Restek® Deactivated Wool
GC capillary column: Rtx-1701 column, 30m*0.25mm*0.25 µm
GC guard column: Restek® Siltek Guard Column, 10m*0.25mm
Column connector: Sigma Aldrich® Capillary Column Butt Connector
Oven temperature program: Initial oven temperature of 70 °C, hold for 1 min, ramp at 20 °C/min to 300 °C, hold for 2.5 min. Total run time is 15 min.
Carrier gas: Helium at a constant pressure of 17 psi.
MSD condition: Aux temperature: 280 °C, MS Source: 230 °C, MS Quad: 150 °C
Tune file: atune.u
Simultaneous Scan/SIM
Scan range: 45-500

RESULTS

Method development:

Percentage of acetic acid in Acetonitrile (MeCN):
0.5% acetic acid in MeCN yielded higher recoveries than 1% acetic acid in MeCN for all three clean-up techniques (dSPE, endcapped C_{18} cartridges and PSA/C_{18} cartridges), indicating that 0.5% acetic acid had enough acidic capacity for these base sensitive pesticides. It was determined that excessive acetic acid did not increase recoveries, and may adversely affect gas chromatography. Thus 0.5% acetic acid in MeCN was selected as the extraction solvent.

Clean-up methods:
Noisy background was observed with dSPE clean-up.
Slightly higher recoveries were obtained with endcapped C_{18} SPE cartridges.
Good recoveries and the cleanest chromatographic background were obtained with PSA/C_{18} dual layer.
SPE cartridges.

GC column:
The Rtx®-1701 column was selected for this study as Dicofol demonstrated a very low response on Rxi®-5Sil MS column.

Solvents:
MeCl2, n-hexane, toluene and 0.5% acetic acid in MeCN were tested n-hexane demonstrated a very low Pymetrozine response MeCl2, toluene and 0.5% acetic acid in MeCN all worked well. 0.5% acetic acid in MeCN yielded the best Pymetrozine response. These seven problematic pesticides are thermal stable at an injector temperature of 250 °C, so solvent exchange into toluene is not necessary.
Note: The injector was easily contaminated by the olive oil extract and should be cleaned when Folpet and Captan show a decreased response.

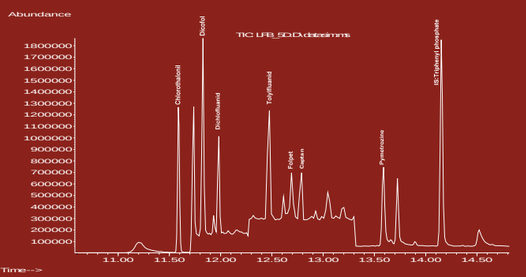
Optimized procedures:
Extraction: Weigh 1 g of olive oil into the 50 mL QuEChERS tube, spike, wait 15 min for the solvent to evaporate. Add 10 mL MeCN with 0.5 % acetic acid, 9 mL DI H2O and shake vigorously for 1 min or vortex for 20 sec. Centrifuge at 4000 rpm for 10 min.
Clean-up: Attach PSA/C18 dual layer SPE cartridges to the vacuum manifold ensuring that the bulkhead fittings are clean and dry. Pour approx. 1 g muffled Na2SO4 into the cartridges, load extract, apply approx. 5" Hg vacuum. Collect 5 mL of extract; concentrate to 0.5 mL by N2 at 35 °C.
GC/MS: Add 5 µL 250 ppm Triphenyl phosphate (IS), Inject 1 µL

Method Performance Data

Name	Fortified at 100ng/mL[a,*]		Fortified at 250ng/mL[b,*]		Fortified at 25ng/mL[c,*]	
	Recovery%	RSD% (n=4)	Recovery%	RSD% (n=4)	MDL (ng/mL)	RSD% (n=7)
Chlorothalonil	123	3.8	111	8.0	8.2	22
Dicofol	68	3.7	66	1.4	0.8	4.7
Dichlofluanid	86	6.1	86	2.6	2.6	9.6
Tolylfluanid	84	3.4	79	3.4	3.4	3.4
Folpet	89	1.3	90	13	4.9	21
Captan	88	6.1	104	8.0	3.6	15
Pymetrozine	78	5.2	78	1.7	2.0	8.0

a: Except for Tolylfluanid at 500 ng/mL
b: Except for Tolylfluanid at 1250 ng/mL
c: Except for Tolylfluanid at 125 ng/mL
*: Concentration in the 10 mL extract

Chromatogram of olive oil spiked at 250 ng/mL a,*



a: except for Tolylfluanid at 1250 ng/mL.

*: Concentration in the 10 mL extract.

CONCLUSION

An optimized QuEChERS procedure was successfully developed, using UCT's QuEChERS product (ECMSSA50CT) and PSA/C_{18} dual layer SPE cartridge (ECPSAC1856) for the determination of seven problematic pesticides in olive oil. Dicofol does not chromatograph well on the Rxi®-5Sil MS, a widely used GC column, but responds well on the Rtx®-1701 column, which was selected for this study. Using the optimized rocedure, acceptable recoveries (66-123%) and precision (RSD <13%, n=4) were achieved for all of the seven problematic pesticides. This procedure can be also used for the determination of problematic pesticides in other fatty matrices.