

**MULTIRESIDUE DETERMINATION OF PESTICIDES IN
OLIVE AND PALM OIL BY LC-QTOF-MS**

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**THESIS SUBMITTED IN FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY**

**FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2011

UNIVERSITI MALAYA
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Registration/Matric No: **SHC090069**

Name of Degree: **DOCTOR OF PHILOSOPHY**

Title of thesis:

Multiresidue determination of pesticides in olive and palm oil by LC-QTOF-MS

Field of Study: **ENVIRONMENTAL ANALYTICAL CHEMISTRY**

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ABSTRACT

In this study a comprehensive evaluation of two efficient sample treatment methods based on LLE/freezing-out coupled with matrix solid-phase dispersion-sonication (UA-MSPD) and precipitation at low temperature followed by dispersive solid-phase extraction (d-SPE) has been performed for determination of dimethoate, malathion, carbaryl, simazine, terbuthylazine, atrazine and diuron in both olive and palm oil using liquid chromatography time-of-flight mass spectrometry (LC-QTOF-MS) and electrospray as the ionization source. Identification and confirmation of the compounds were based on retention time matching along with the accurate mass measurements of the protonated molecules ($[M+H]^+$) and their main fragment ions. Typical electrospray ionization parameters such as nebulizer and drying nitrogen flow rates, drying gas temperature and capillary voltage as well as fragmentor voltage which affecting the performance of LC-TOF-MS were carefully studied. Optimization approaches were studied in terms of LLE/LTP to select efficiency of type and volume of extracting solvent with and without LTP to obtain the highest recovery yield of pesticides and the lowest co-extract fat residues in the final extract, UA-MSPD clean-up conditions to select type and amount of both dispersant and clean-up sorbent as well as to evaluate the extraction condition from the point of with or without sonication, finally d-SPE cleanup to choose nature and value of clean-up sorbent. The optimal conditions for UA-MSPD were obtained using 5 g of palm oil, 750 mg of PSA as dispersing sorbent, 250 mg of florisil as clean up sorbent and 15 mL of acetonitrile as eluting solvent under conditions of 15 min ultrasonic bath at room temperature. However, when d-SPE was used as the clean-up procedure, high recoveries and good sensitivity were obtained with 150 mg PSA and 50 mg GCB (PSA: GCB (3:1 w/w)).

Method validation was performed in order to study sensitivity, linearity, precision, and accuracy for both sample treatment methods. The mean recoveries obtained at three concentration levels (25, 50 and 100 ng g⁻¹) for both palm and olive oil using UA-MSPD procedure ranged from 68.5% to 109.4% and 71.8% to 112.4% with the relative standard deviations (RSDs) from 5.4-14.2% and 6.2-13.3% respectively. Linearity for all compounds was determined blank oil samples fortified at concentration levels ranging from 5 to 1000 ng g⁻¹. Linear regression coefficient for all pesticides using both analytical methods was above 0.9985. Detection and quantification limits were ranged from 1 to 5 ng g⁻¹ and from 2.5 - 9 ng g⁻¹ for palm oil and 0.6 - 5.4 ng g⁻¹ and 2.1 - 14.2 ng g⁻¹ for olive oil respectively.

Average recoveries at three concentration levels (25, 50 and 100 ng g⁻¹) using d-SPE procedure ranged between 75.6 and 107.4% for olive oil and between 76.4% and 107.2% for palm oil with relative standard deviations of 6.2-13.1% and 5.4-14.2% respectively. Detection and quantification limits ranged from 0.6-5.6 ng g⁻¹ and 1.9-17.8 ng g⁻¹ for olive oil and from 0.8-2.7 ng g⁻¹ and 2.1-8.2 ng g⁻¹ for palm oil respectively. Both analytical methods were applied to two different brands of virgin olive oil and palm oil coming from market. No pesticide residues were found at concentrations above the detection limit and the permitted MRLs.

ABSTRAK

Dalam kajian ini satu penilaian yang komprehensif yang melibatkan dua kaedah rawatan sampel yang berkesan seperti pengekstrakan cecair-cecair / pembekuan yang keluar ditambah pula dengan matriks serakan pepejal fasa sonication(UA-MSPD) serta pemendakan pada suhu yang rendah diikuti dengan pengekstrakan serakan fasa pepejal (d-SPE) telah dilaksanakan untuk menentukan dimethoate, malathion, carbaryl, simazine, terbuthylazine, atrazine dan diuron dalam minyak zaitun dan sawit dengan menggunakan kaedah kromatografi cecair masa penerbangan spektrometri jisim (LC-QTOF-MS) dan electrospray sebagai sumber pengionan.

Pengenalpastian dan pengesahan sebatian dilakukan berdasarkan masa tahanan yang hampir sama dengan ukuran tepat jisim molekul protonated ($[M + H]^+$) dan serpihan ion utama. Parameter pengionan electrospray yang tipikal seperti nebulizer dan pengeringan kadar aliran nitrogen, gas pengeringan suhu dan voltan rerambut serta voltan fragmentor yang memberi kesan kepada prestasi LC-TOF-MS telah dikaji dengan teliti. Pendekatan pengoptimuman telah dari pengekstrakan cecair-cecair/ pemendakan suhu rendah (LLE / LTP) untuk memilih kecekapan jenis dan jumlah untuk mengekstrak pelarut dengan dan tanpa LTP untuk mendapatkan hasil pemulihan tertinggi racun perosak dan yang paling rendah bersama ekstrak sisa-sisa lemak dalam cabutan terakhir, UA-MSPD bersih-syarat untuk memilih jenis dan jumlah dispersant kedua-duanya dan bersih sorbent serta untuk menilai keadaan perahan dari titik-dengan atau tanpa sonication, akhirnya d-SPE pembersihan untuk memilih sifat dan nilai kebersihan sorbent.

Syarat-syarat yang optimum untuk UA-MSPD diperolehi dengan menggunakan 5 g minyak kelapa sawit, 750 mg PSA sebagai sorbent bersurai, 250 mg florisil untuk membersihkan sorbent dan 15 mL asetonitril sebagai pelarut eluting di bawah syarat-

syarat 15 minit mandian ultrasonik pada suhu bilik. Walau bagaimanapun, apabila d-SPE telah digunakan sebagai kaedah pembersihan, pemulihan dan kepekaan yang tinggi dan baik diperolehi dengan 150 mg PSA dan 50 mg GCB (PSA: GCB (3:1 w / w)).

Pengesahan kaedah dilakukan untuk mengkaji sensitiviti, kelinearan, ketepatan, dan ketepatan untuk kedua-dua kaedah rawatan sampel. Pemulihan min yang diperolehi daripada tiga tahap kepekatan (25, 50 dan 100 ng g⁻¹) untuk kedua-dua sawit dan minyak zaitun menggunakan prosedur UA-MSPD berjulat dari 68.5% hingga 109.4% dan 71.8% hingga 112.4% dengan sisihan piawai relatif (RSDs) dari 5.4-14.2% dan 6.2-13.3%, masing-masing. Kelinearan bagi semua sebatian adalah ditentukan dengan menggunakan sampel minyak kosong yang diperkaya pada tahap kepekatan dari 5 hingga 1000 ng g⁻¹. Pekali regresi linear untuk semua racun perosak diperolehi dengan menggunakan kedua-dua kaedah analisis di atas adalah 0.9985. Had pengesanan dan kuantifikasi berkisar dari 1 hingga 5 ng g⁻¹ dan dari 2.5 - 9 ng g⁻¹ bagi minyak sawit dan 0.6 – 5.4 ng g⁻¹ dan 2.1 – 14.2 ng g⁻¹ bagi minyak zaitun µg, masing-masing. Kedua-dua kaedah analisis digunakan untuk dua jenama yang berbeza iaitu minyak zaitun dara dan minyak kelapa sawit yang diperolehi dari pasaran di sekitar Kuala Lumpur. Tiada sisa-sisa racun perosak telah dijumpai pada kepekatan melebihi had pengesanan dan MRLs yang dibenarkan.

ACKNOWLEDGEMENT

First and foremost, I would like to express my deep and sincere gratitude to my supervisors, Prof. Mhd. Radzi Bin Abas and Dr. Nor Kartini Abu Bakar for their kind support, valuable guidance and extensive discussions during the course of this research project. I am especially grateful to them for encouraging and showing great patience through this work.

It's a pleasure to thank Head of the Department of Chemistry for her important support through this study. I am indebted to my colleagues in the Lab, staff and all those who have helped me with my work in the Faculty of science and Department of Chemistry at University of Malaya.

I wish to extend my warmest thanks due to my parent for their loving support. I also owe my loving thanks to my husband Keivan. Without his encouragement and understanding it would have been impossible for me to finish this work. My sons Armia and Ilia, they were patient and gracious to let me spend extra hours in the Lab due to my research abroad. Thank you all to let me own a happy family in Malaysia.

Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the project. The financial support of the University of Malaya is gratefully acknowledged.

Elham Sobhanzadeh

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LIST OF ABBREVIATIONS:

GAP	- Good Agricultural Practices
OC	- Organochlorine
OP	- Organophosphate
IPM	- Integrated Pest Management
ETU	- Ethylenethiourea
GC	- Gas chromatography
LC	- Liquid chromatography
LD ₅₀	- lethal dose 50
LC ₅₀	- lethal concentration 50
MRL	- Maximum Residue Limit
FAO	- Food and Agriculture of the United Nations
WHO	- World Health Organization
FDA	- Food and Drug Agency
CFIA	- Canadian Food Inspection Agency
NGOs	- Non-Governmental Organizations
EU	- European Union
ATP	- Adenosine Triphosphate
QuEchERS	- quick, easy, cheap, effective, rugged, and safe
LLE	- liquid-liquid extraction
PLE	- Pressurized liquid extraction
MAE	- Microwave assisted extraction
USE	- Ultrasonic extraction

SFE	- Supercritical fluid extraction
SPE	- Solid-phase extraction
SPME	- Solid-phase microextraction
SBSE	- Stir-bar-sorptive extraction
MSPD	- Matrix solid-phase dispersion
SE	- Solvent extraction
LLP	- Liquid-liquid partition
SEC	- Size exclusion chromatography
MeCN	- Acetonitrile
EtAc	- Ethyl acetate
DCM	- Dichloromethane
DEE	- Diethyl ether
MeOH	- Methanol
DP	- Diphenyl
OCLLE	- On-column liquid-liquid extraction method
d-SPE	- dispersive solid-phase extraction
GPC	- Gel-permeation chromatography
PSA	- Primary-secondary amine
OPPs	- Organophosphoro pesticides
GC- MS	- Gas chromatography-mass spectrometry
LC- MS	- Liquid chromatography-mass spectrometry
SIM	- Selected ion monitoring
SRM	- Single reaction monitoring

MRM	- Multi-residue method
IT	- Ion trap
LOD	- Limit of detection
LOQ	- Limit of quantification
PAHs	- Polycyclic aromatic hydrocarbons
ASE	- Accelerated solvent extraction
PCBs	- Polychlorinated biphenyls
RSD	- Relative standard deviation
FMAE	- Focused microwave-assisted extraction
CRM	- Certified reference material
PMAE	- Pressurized microwave-assisted extraction
AMAE	- Atmospheric pressure microwave assisted extraction
GC-ECD	- Gas chromatography-electron capture detector
GC-NPD	- Gas chromatography- nitrogen phosphorus detector
GC-FID	- Gas chromatography- flame ionization detector
GCB	- Graphitized carbon black
SWCNTs	- Single-walled carbonnanotubes
MWCNTs	- Multi-walled carbonnanotubes
HPLC-DAD	- High performance liquid chromatography- diode array
HPLC-UV	- High performance liquid chromatography- Ultraviolet detector
RP-C ₁₈	- Reversed-phase octadecyl silica
PDMS	- Polydimethylsiloxane
DVB	- Divinylbenzene

DI	- Direct immersion
HS	- Head-space
SDME	- Single-drop microextraction
HFM	- Hollow fiber membrane
DLLME	- Dispersive liquid-liquid microextraction
MEKC	- Micellar electrokinetic chromatography
REPSM	- Reversed-electrode polarity stacking mode
LVI	- Large-volume injection
WCOT	- Wall-coated open tubular
PTV	- Programmed-temperature vaporization
QTOF	- Quadrupole Time of Flight
TLC	- Thin layer chromatography
PB	- Particle beam
API	- Atmospheric pressure ionization
ISP	- Ionspray
ESI	- Electrospray ionization
APCI	- Atmospheric pressure chemical ionization
TSP	- Thermospray
APPI	- Atmospheric pressure photo-ionization
CID	- Collision-induced dissociation
PIS	- Product-ion scan
MPOC	- Malaysian Palm Oil Council
FIA	- Flow injection analysis

LTP	- Low temperature precipitation
XIC	- Extracted ion chromatogram
TIC	- Total ion chromatogram
UA	- Ultrasonic assisted
ME	- Matrix effect