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

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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 kebarsihan 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.

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LIST OF CONTENTS:

CHAPTER I: INTRODUCTION

CHAPTER II: OVEREVIEW OF ANALYTICAL METHODS AND PESTICIDE FORMULATIONS FOR PESTICIDES ANALYSIS IN FOOD MATRICES BY CHROMATOGRAPHY-BASED TECHNIQUES

CHAPTER III: METHODOLOGY

CHAPTER IV: RESULTS AND DISCUSSION

CHAPTER V: CONCLUSION

CHAPTER VI: BIBLIOGRAPHY

LIST OF FIGURES:

LIST OF TABLES:

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 dertector

GC-NPD - Gas chromatography- nitrogen phosphorus detector

GC-FID - Gas chromatography- flame ionization detector

GCB - Graphitized carbon black

SWCNTs - Single-walled carbonanotubes

MWCNTs - Multi-walled carbonanotubes

HPLC-DAD - High performance liqiud chromatography- diode array

HPLC-UV - High performance liqiud 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