Determination of Pesticide Residues in Cotton Matrix Using LC-MS\MS and GC-MS\MS

Thesis Submitted BY

Mahmoud Hamdy Ahmed Abd El-Wahed

B.Sc. in Applied Chemistry, Faculty of Science,
Ain Shams University, 2011

In the Partial Fulfillment for the Requirement for the Degree in Master of Science (M.Sc.) In Chemistry

Chemistry Department, Faculty of Science
Ain Shams University

Under Supervision of

Faculty of Science, Ain Shams University

EGYPT

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Under Supervision of
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Prof. Dr. Emad Ramadan Mohamed Attallah

Chief Researcher and Quality Manager, Central Lab of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center (ARC)

APPROVAL SHEET

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Acknowledgment

Firstly thanks for my God.

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Thank you!

Mahmoud Hamdy Ahmed Abd El-Wahed

DEDICATION

I dedicate this work to my father, mother, wife, children and brothers for all the support they lovely offered during my post-graduate studies.

Abstract

Name: Mahmoud Hamdy Ahmed Abd El-Wahed

Title of the thesis: Determination of Pesticide Residues in Cotton Matrix Using LC-MS\MS and GC-MS\MS

Position: Chemist

Degree: M.Sc., Faculty of science, Ain Shams University

Public worldwide application of pesticides in crops and environment have been increased for the past several decades. The new global concept is to care about textiles and clothes safety to improve the protection of the human health and the environment from the harmful pesticide residues. Very few articles have been published for determination of several pesticide classes in cotton fibers in one multi-residue method. A simple, efficient, sensitive, accurate and reliable multi-residue method was developed for the determination of 412 residual pesticides in cotton fibers by using modified QuEChERS method with Liquid and Gas Chromatography coupled to Triple Quadrupole Mass Spectrometer (LC-MS/MS & GC-MS/MS) for qualitative and quantitative analysis according to the international standards concepts. The developed method covered several pesticide classes, including 43 carbamates, 16 pyrethroids, 27 organochlorines (OCs), 54 organophosphorus (Ops), 31 urea derivatives, 7 Polychlorinated biphenyl (PCBs), 6 Neonicotinoid and 228 other pesticides. Most of the target pesticides were listed in Oeko-Tex Standards, the EU Ecolabel for textile products, and the Egyptian recommendations of the Agricultural Pesticide Committee (APC-Egypt). The method optimization and validation were carried out according to the EU guidelines. The results were shown to be reliable where the corresponding average recoveries within the acceptable range of 70-120%; the relative standard deviations were less than 20%. The limit of quantitation (LOQ) of this method is 0.01 mg kg^{-1} for all pesticides except for 3 GC-compounds and 19 LC-compounds which have LOQ of 0.05 mg kg-1. the local markets in Egypt need to be monitored to evaluate the risk of these contaminants in scientific terms. Pesticide residues were determined in some cotton products that were collected from different local markets in Egypt during 2017. Among the collected cotton product samples, 14 different pesticides were detected in 20 samples in the concentration range from 0.01 to 0.416 mg kg^{-1} for the detected pesticides. The obtained

results reflected that chlorpyrifos, malathion, profenofos and cypermethrin were the most frequently detected pesticide residues in the cotton product samples. Only one raw cotton sample has exceeded the summation of detected pesticide residues.

Keywords: Cotton; Pesticide Residues; Oeko-Tex; QuEChERS; GC-MS/MS; LC-MS/MS.

Supervisors' approval:

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Prof. Dr. Ibrahim Hosseini Ali Badr

Head of Chemistry Department

Aim of Study

The present study aimed to introduce a sensitive and simple method for determination of 412 pesticide residues of different chemical classes in a cotton matrix using liquid and gas chromatography coupled with a tandem mass spectrometer (LC-MS\MS and GC-MS\MS) in one multi-residue method that can be used for the routine work.

Method validation and optimization were carried out according to the EU guidelines. Monitoring of pesticide residues in some cotton products such as medical cotton, raw cotton, medical gauze, cotton surgical face masks, tissues paper, and diapers that were collected from different local markets in Egypt to evaluate the risk of these products in scientific terms.

List of abbreviations

Abbreviations	Synonyms
AA	Acetic Acid.
ACN	Acetonitrile.
AGA	Algae Growth Analyzer.
APC	Agricultural Pesticide Committee.
ASE	Accelerated Solvent Extraction.
BTA	Biosensor Toxicity Analyzer.
CAC	Codex Alimentarius Commission.
CAS	Chemical Abstracts Service Number.
CE	Collision Energy.
C_e	Expected concentration of the standard added to the bank matrix.
Cm	Centimeter.
C_m	Measured concentration of the standard added to the blank matrix.
CXP	Collision Cell Exit Potential.
DIW	Deionized Water.
DOE	Design Of Experiments.
DP	Declustering Potential.
d-SPE	dispersive-Solid Phase Extraction.
EC	European Communities.
ECD	Electron Capture Detector.
EI	Electron Impact.
EICD	Electrolytic Conductivity Detector.
EP	Entrance Potential.
EPA	Environmental Protection Agency.
ESI	Electrospray Ionization.
EU	European Union.
Exp.	Experiment.
FAO	Food and Agriculture Organization.
FDA	Food and drug administration
GC	Gas Chromatography.
GM	Genetic Modified.
GOEIC	General Organization of Export and Import Control.
GPC	Gel permeation chromatography.
HF-LPME	Hollow Fiber Liquid-Phase Micro Extraction.
HPLC	High Performance Liquid Chromatography.
ISO	International Organization for Standardization.
IUPAC	International Union of Pure and Applied Chemistry nomenclature.

Abbreviations	Synonyms
JECFA	Joint FAO/WHO Expert Committee on Food Additives.
Kg	Kilo-gram, 10^3 g.
LC	Liquid Chromatography.
LOD	Limit of detection.
LOQ	Limit of quantification.
ME	Matrix Effect.
Mg	Milli-gram, 10^{-3}g.
mm	Millimeter
MRLs	Maximum Residue Limits.
MRM	Multiple Reaction Monitoring.
MS	Mass Spectrometry.
MS/MS	Triple Quadrupole Mass Spectrometer.
MSD	Mass Selective detector.
n	Number of replicates.
OCs	Organochlorines.
Oeko-Tex	the international association for research and testing in the field of textile ecology.
Ops	Organophosphorus.
PCBs	Polychlorinated Biphenyl.
PSA	Primary Secondary Amin Bonded Phase Silica.
PTFE	Polytetrafluoroethylene.
QuEChERS	"Quick, Easy, Cheap, Effective, Rugged, and Safe".
r2	The regression coefficients.
RMG	Ready-Made Garments.
rpm	Round per minute.
RSD %	Relative standard deviation.
RT	Retention Time.
SANTE	(Santé et Consommateurs), Directorate General Health and Consumers; European Commission.
SD	Standard deviation.
SOX	Soxhlet Extraction.
SP_e	Expected concentration of the Spiked blank sample.
SP_m	Measured concentration of the spiked blank sample.
T-Bt	Transgenic Bacillus thuringiensis.
UAE	Ultrasound Assisted Extraction.
WHO	World Health Organization.

List of Publications

1- Development and Validation of Multi-residue Method for Determination of 412 Pesticide Residues in Cotton Fiber Using GC-MS/MS and LC-MS/MS

➔The Journal of The Textile Institute (TJTI) in Taylor & Francis publisher

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2- Monitoring of Pesticide Residues in some Cotton Products in Egypt using GC-MS/MS and LC-MS/MS

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