



# **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**

**2017**

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**Determination of Pesticide Residues**  
**in Cotton Matrix Using LC-MS\MS and**  
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# *Acknowledgment*

*Firstly thanks for my God.*

*I would like to express my gratitude to **Prof. Dr. Mohamed Mahmoud Mohamed Abo-Aly** Professor of Inorganic and Analytical Chemistry, Faculty of Science, Ain Shams University For his supervision, guidance, useful criticism and his efforts to fulfill this work.*

*I am particularly grateful to **Prof. Dr. Emad Ramadan Mohamed Attallah** Chief Researcher and Quality Manager, in Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food (QCAP), Agricultural Research Center (ARC) not only for supporting my desired topic but also for his continuous advice and valuable criticism during this work.*

*I would like to express my sincere thanks to **Dr. Moustapha N. Mohammed** and **Dr. Mohamed E. Amer** for taking their time to answer my questions and bearing my optimism.*

*I would like to express my sincere thanks to **Dr. Sherif M. Taha** for assisting in GC/MS/MS and **Dr. Osama El-sayed Hussein** for assisting in LC/MS/MS in the experimental part of this work.*

*I would like to thank All my colleges in the laboratory for their help and encouragement.*

*Last but not least I would like to give my special thanks to my beloved family for all their help and for giving me the chance to realize my dreams.*

## *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  $0.01 \text{ mg kg}^{-1}$  for all pesticides except for 3 GC-compounds and 19 LC-compounds which have LOQ of  $0.05 \text{ mg kg}^{-1}$ . 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  $0.416 \text{ mg kg}^{-1}$  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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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 <sub>e</sub> | Expected concentration of the standard added to the bank matrix.  |
| Cm             | Centimeter.   |
| C <sub>m</sub> | 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”.                                       |
| r <sup>2</sup>  | The regression coefficients.   |
| RMG             | Ready-Made Garments.   |
| rpm             | Round per minute.  |
| RSD %           | Relative standard deviation.   |
| RT              | Retention Time.  |
| SANTE           | (Sant  et Consommateurs), Directorate General Health and Consumers; European Commission. |
| SD              | Standard deviation.  |
| SOX             | Soxhlet Extraction.  |
| SP <sub>e</sub> | Expected concentration of the Spiked blank sample.                                       |
| SP <sub>m</sub> | 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

➔Print ISSN: 0040-5000 Online ISSN: 1754-2340

➔2017

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

➔Middle East Journal of Applied Sciences (MEJAS) in current research web publisher

➔ISSN 2077-4613

➔2017

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