Development of Multi-residues Method for Pesticide Residues Analysis in Essential Oils Using Chromatographic Technique

Thesis Submitted By

Mahmoud Samir Mohamed El Saied

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Chemistry Department - Faculty of Science Ain Shams University

Under Supervision of

Prof. Dr. Mohamed Mahmoud Mohamed Abo-Aly

Chemistry Department, Faculty of Science, Ain Shams University.

Prof. Dr. Mona Abd El Aziz Khorshed

Chief Researcher and Technical Manager - Central Lab of Residue Analysis of Pesticides and Heavy Metals in Food - Agriculture Research Center

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ABSTRACT

Orange oil is considered as the largest produced essential oil worldwide due to its unique properties. Pesticide residues in orange oil are expected to be much higher than the original fruit due to orange peel's cold-pressing during orange oil production. These residues may cause various health problems if consumed. The purpose of our study was to develop, optimize and compare four multi-residues extraction methods (dilution, QuEChERS, ethyl acetate, and mini-Luke) for analysis of 387 pesticides in orange oil using LC-MS/MS and GC-MS/MS. To our knowledge, this is the first report on the use of ethyl acetate and the mini-Luke method for the analysis of orange oil. The comparison was based on recoveries, matrix effect, and the amount of co-extract matrix. The optimum mean recoveries were obtained by the ethyl acetate method, which successfully analyzes 371 out of 387 pesticides with acceptable recovery (70-120%). It also showed a narrow recovery distribution in the range of 90-110% for 69% of all studied pesticides. Regarding the matrix effect, the QuEChERS method gave the highest number of pesticides with an insignificant matrix effect (80-120%) for both LC and GC amenable pesticides. The least amount of co-extract matrix components according to GC-MS/MS scan and gravimetric analysis has been achieved by the QuEChERS method.

In conclusion, the Ethyl acetate method gives acceptable recovery for a wide range of pesticides with a narrow recovery distribution and a moderate amount of co-extract matrix. While the QuEChERS method provides better selectivity and cleaner extract but with a narrow scope and less precision.

A monitoring program has been conducted to analyze the pesticide residues content in the orange oil sample that has been produced in Egypt using the ethyl acetate method. Thirty five orange oil samples have been analyzed and found to contain several pesticides (at least 15 pesticides) in each sample with various classes. The risk assessment to these pesticide levels couldn't be evaluated due to the absence of MRL. The risk of this pesticide depends mainly on the manufacture dilution factor in each application.

Keywords: multi-residue extraction methods; Orange oil; Liquid chromatography; Gas chromatography; Tandem mass spectrometry, Pesticide residues.

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LIST OF ABBREVIATIONS

Abbreviations	Synonyms
ACN	Acetonitrile
amu	atomic mass unit
API	Atmospheric Pressure Ionization
CAD	collision gas
CE	Collision Energy
CI	Chemical ionization
CUR	Curtain Gas
CXP	Cell Exit Potential
DC	direct-current
DP	Declustering Potential
DW	Deionized water
E	Extreme
EI	Electron ionization
EO	Essential oil
EP	Entrance Potential
ESI	Electrospray ionization
EU	Europe union
FAB	Fast atom bombardment
GC-MS/MS	Gas Chromatography Coupled with Triple Quadrupole Mass Spectrometry
HPLC	High-pressure liquid chromatography
IS	Ion spray
ISO	International Organization for Standardization
K_{ow}	Octane-water partion coefficient
LC-MS/MS	Liquid Chromatography Coupled with Triple Quadrupole Mass Spectrometry
	Medium
M	mass-to-charge ratio
m/z	Matrix-assisted laser desorption/ ionization

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Abbreviations	Synonyms
MRL	maximum residue limit
MRM	Multiple Reaction Monitoring
ppb	part per billion
ppm	part per million
PSA	Primary secondary amine bonded phase silica
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, And Sa
RF	Radiofrequency
RSD	Relative Standard Deviation
SRM	Selected Reaction Monitoring
TEM	source temperature
TOF	Time-of-flight