Determination of pesticide residues in food using some recent applications in gas chromatography coupled with tandem mass spectrometry

Thesis Submitted

By

Mostafa Soliman Abd-el-Ghaffar Abd-el-Megid Abd-ellah
M.Sc. in Chemistry
Faculty of Science, Ain Shams University
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For the degree of Doctor of Philosophy in chemistry
(Ph. D.)

Chemistry Department, Faculty of Science
Ain Shams University

Under Supervision of

Prof. Dr. Mohamed Mahmoud Mohamed Abo-Aly
Professor, Department of inorganic Chemistry, Faculty of science, Ain shams University

Prof. Dr. Mona Abd-el-Aziz Khorshed
Professor, Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center

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Approval sheet

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This thesis has been approved by:

- **Prof. Dr. Mohamed Mahmoud Mohamed Abo-Aly**

Professor, Department of Chemistry, Faculty of science, Ain shams University
Signature: ……..……

- **Prof. Dr. Mona Abd-el-Aziz Khorshed**

Professor, Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center
Signature: ……..……

Head of Chemistry Department

Prof. Dr. Ayman Ayoub Abdel-Shafi

2020

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Mostafa Soliman Abd-el-Ghaffar Abd-el-Megid Abd-ellah

Abstract

Name: Mostafa Soliman Abd-el-Ghaffar Abd-el-Megid Abd-Ellah

Title of the thesis: Determination of pesticide residues in food using some recent applications in gas chromatography coupled with tandem mass spectrometry.

Position: Research assistant

Degree: PhD, Faculty of science, Ain Shams University

Matrix effects (MEs) in gas chromatography (GC) usually occur due to undesired interactions with active sites in the inlet and column, which can lead to analyte loss and/or peak tailing. Analyte protectants (APs) are compounds added individually or in combination to interact with the active sites and minimize errors related to MEs. However, the current Aps mixtures/introducing approach cannot sufficiently compensate for MEs in all cases. In this study, a comparison (based on sensitivity and peak shape) between thirteen different Aps (2,3-Butanediol, 3-O-ethylglycerol, D-Fructose, D-Gluconic acid γ-lactone, D-Glucose, D-Ribonic acid γ-lactone, D-Ribose, D-Sorbitol, l-Gulonic acid γ-lactone, Menthol, Polyethylene glycol, Triglycerol and Vanillinin) with four different solvents (n-hexane, acetone, acetonitrile and ethyl acetate) for 224 pesticides is presented.

The comparison was done between solvent based calibration and extracts of one selected difficult matrix (strawberry), prepared according to the citrate-buffered QuEChERS (quick, easy, cheap, effective, rugged, and safe) procedure. Each Ap had different behavior for each solvent. In general, acetonitrile showed the most susceptibility to polar Aps, followed by acetone, then ethyl acetate and then n-hexane. However, in the absence of Aps, peak shapes were best in the following order: n-hexane, then ethyl acetate, then acetone and then acetonitrile. Based on these results, a mixture of seven Aps was chosen. To ease their introduction, the sandwich injection approach (SIA) was used. Several factors were studied such as the calibration solvent, Aps solvent and Aps concentration. For acetonitrile calibration, the ME of 213/224 (95%) pesticides were ≤ 20% in one Aps mixture compared to 36 pesticides (16%) in non-protected mixtures. For n-hexane:acetone (9:1) calibration, the ME of 221/224 (99%) pesticides were ≤ 20% in one Aps mixture compared to 102 pesticides (45%) in non-protected mixtures.

Key words

Pesticide residue analysis; QuEChERS; Matrix effect; GC-MS/MS; Analyte protectants; Sandwich injection approach (SIA)

Supervisors' approval:

- **Prof. Dr. Mohamed Mahmoud Mohamed Abo-Aly**
  Professor, Department of Chemistry, Faculty of Science, Ain shams University

  Signature: ……..……

- **Prof. Dr. Mona Abd-el-Aziz Khorshed**

Professor, Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food, Agricultural Research Center

Signature: ……

Head of Chemistry Department

Prof Dr. Ayman Ayoub Abdel-Shafi

Aim of study

The present study aimed to evaluate a variety of different additives that can be employed as analyte protectants in the GC analysis of pesticides and to demonstrate the effectiveness of these agents for improving the quality of the analysis.

So, the plan of work was:

1- Evaluation of the capability of thirteen different analyte protectants (2,3-Butanediol, 3-O-ethylglycerol, D-Fructose, D-Gluconic acid γ-lactone, D-Glucose, D-Ribonic acid γ-lactone, D-Ribose, D-Sorbitol, l-Gulonic acid γ-lactone, Menthol, Polyethylene glycol, Triglycerol and Vanillinin) using four different solvents (n-hexane, acetone, acetonitrile and ethyl acetate) for 224 different pesticides.

2- Choosing the most suitable analyte protectants based on their individual ability.

3- Injection of different analyte protectants mixtures (different solvents and concentrations)/pesticides' solvents combinations in the sandwich injection mode.

4- Evaluation of each analyte protectants' mix/pesticides' solvent combination.

List of abbreviations

ACN	:	Acetonitrile.
AOAC	:	Association of Analytical Chemistry.
AP	:	Analyte Protectant.
CAC	:	Codex Alimentarius Commission.
CE	:	Collision Energy.
DB-35MS	:	35% Phenyl- 65% dimethyl polysiloxane.
D-SPE	:	Dispersive Solid Phase Extraction.
EI	:	Electron Ionization.
EN-QuEChERS	:	Citrate-buffer-based QuEChERS
EU	:	European Union.
EURL	:	European Reference Laboratory.
FAO	:	Food and Agriculture Organization.
GAP	:	Good Agriculture Practice.
GC	:	Gas Chromatography.
IS	:	Internal Standard.
LOQ	:	Limit of Quantification.
ME	:	Matrix Effect.
MRL	:	Maximum Residue Limit
MRM	:	Multiple Reaction Monitoring.
MS	:	Mass Spectrometry.
PSA	:	Primary Secondary Amine bonded phase silica.

PTFE	:	Polytetrafluoroehtylene.
QuEChERS	:	Quick, Easy, Cheap, Effective, Rugged and Safe method.
SIA	:	Sandwich Injection Approach.
SPE	:	Solid Phase Extraction.
WHO	:	World Health Organization.

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