

**EVALUATION OF SELECTED ACARICIDES RESIDUES
IN HONEY FROM VARIOUS PHYTOGEOGRAPHIC
REGIONS OF PAKISTAN**



By

SUMAIRA AKRAM

**Department of Earth and Environmental Sciences
Bahria University, Islamabad**

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ABSTRACT

This research work aimed to achieve highly sensitive, selective and economically feasible multi-residue technique for quantification of selected acaricides in honey by GC- μ ECD and GC-MSD. The two extraction procedures QuEChERS and SPE were compared and SPE was found more suitable for selected acaricides with recoveries ranged from $76\% \pm 1.3$ - $122\% \pm 2.1$ as recommended by SANCO. The Limits of quantification of both in-hive treated and environmentally extracted acaricides (LOQ) were lower than their MRLs which indicates that method was sufficiently sensitive. To make the clean-up process satisfactory, potential matrix effects and decrease in ion suppression/ enhancement was minimized by reducing the organic layer from 3 ml to 0.5 ml in SPE. In MSD, an enhancement of the signal was found for chlorpyrifos –methyl (ME > 200%). The Intra-day repeatability ($RSD_{r_{wd}}$) and inter-day repeatability ($RSD_{r_{dd}}$) for the selected acaricides by proposed method was observed to be lower than 16%. This was found to be within acceptable range as set by SANCO and Codex Alimentarius guidelines. The optimized chromatographic multi-residue method was practiced to assess pesticide residues in honey samples from different apiaries of Pakistan. Monitoring results indicate that 12% of the samples contained no detectable residues of the target acaricides while 88% of honey samples from different geographical regions of KP and Punjab were contaminated with at least one of selected acaricides. 6 selected acaricides residues were detected in the collected honey samples and only 5 honey samples had residues level above MRLs. In-hive treated acaricides i.e. coumaphos, t-fluvalinate and malathion were not detected in honey samples from any selected area while fipronil and mirex were detected in only two and one selected region respectively. Thus to provide safe honey to the consumers, it is essential to monitor it occasionally to eliminate the possibility of the presence of the residues of pesticides above prescribed levels.

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ABBREVIATIONS

DDT	Dichlor-Diphenyl-Trichlorethylene
EFSA	European Food Safety Authority
EU	European Union
FPBC	4-Fluoro-3-Phenoxybenzaldehyde Cyanohydrin
FPB	4-Fluoro-3-Phenoxy-Benzaldehyde
GC-ECD	Gas Chromatography – Electron Capture Detector
GC*GC-TOFMS	(GC × GC) two-dimensional Gas Chromatography -Time-of-Flight Mass Spectrometric Detector
GC-MS	Gas Chromatography–Mass Spectrometry
GC-MS/MS	Gas Chromatography–Mass Spectrometry/ Mass Spectrometry
GC-NPD	Gas Chromatography – Nitrogen Phosphorous Detector
HPLC	High performance Liquid Chromatography
LC-APCI-MS	Liquid chromatography– Atmospheric pressure Chemical Ionization–Mass Spectrometry
LLE	Liquid-Liquid Extraction
LC-MS	Liquid Chromatography–Mass Spectrometry
LC-MS/MS	Liquid Chromatography–Mass Spectrometry/ Mass Spectrometry
MRLs	Maximum Residue Levels
MSPD	Matrix Solid Phase Dispersion
PCB's	Polychlorinated Biphenyls
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe method

SBI	Sterol Biosynthesis Inhibitor
SBSE	Stir Bar Sorptive Extraction
SFE	Supercritical Fluid Extraction
SPE	Solid Phase Extraction
SPME	Solid Phase Micro Extraction

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