

Abstract

Gehad Mosad Khattab: Determination of Fingerprint and Impurities of Certain Generic and Original Pesticides. Unpublished M.Sc. Thesis, Department of plant protection, Faculty of Agriculture, Ain Shams University, 2012.

This study aims to assess the impurities in some generic pesticides recommended for use in Egyptian agrochemical market. It also calculates the violation percentage of the impurities present in the Technical compared to the allowed percentages by FAO, IUPAC. In addition, the study examines some physical and chemical properties for generic pesticides while comparing them to their equivalents in the FAO specifications.

The percentages of impurities were assessed within different chemical groups of 11 generic pesticides as following (carbosulfan, chlorpyrifos, chlorpyrifos-methyl, difenoconazole, fenamiphos, flusilazole, lambdacyhalothrin, metalaxyl, oxyfluorfen, prochloraz and thiobencarb).

The carbosulfan generic sample was assessed for the impurity (carbofuran) specified by the FAO and was found to be of higher percentage than that of the FAO specifications. Two samples from different sources (Denmark & China) of chlorpyrifos technical were assessed for impurities, along with 3 samples of chlorpyrifos methyl (1 from Denmark & 2 from China) as well as 2 samples of lambdacyhalothrin (1 from Denmark & 1 from China). The three following impurities were identified in the generic chlorpyrifos samples, 0,0-diethyl 0-6-chloro-2-pyridal phosphorothioate, 0,0-diethyl 0-5,6-dichloro-2-pyridyl phosphorothioate and 0-ethyl 0,0-bis (3,5,6-trichloropyridin-2-yl) phosphorothioate. In generic chlorpyrifos-methyl samples from China, four impurities were identified as following, (3,5,6-Trichloro-N-methyl-2-pyridone), (2-(5-chloro-2-methoxyphenyl)pyrrolidine), (O,O-dimethylO-(3-chloro-2-pyridinyl)phosphorothioate) and (2-hydroxy-3,5,6-trichloropyridine) while no impurities were found in the generic sample from Denmark. Though FAO and IUPAC specify the impurity 0,0,0',0'-tetramethyl dithiopyrophosphate, it was not identified in any of the generic samples.

3-phenoxy benzaldehyde was identified as an impurity in both generic samples of Lambdacyhalothrin.

Impurities were not detected in both flusilazole and difenoconazole technical under the conditions used in this study. However, the generic sample of difenoconazole showed a different ratio of diastereomers when compared to the original sample.

The impurities of the generic sample of Fenamiphos were assessed and identified as (ethyl 2- (s-methyl-2,4-bis(methylthio)phenyl)propan-2-yl phosphoromidate) as an impurity within the sample.

The impurities of the generic sample of metalaxyl were assessed and 2 impurities were identified to be: Methyl N-(2,6-dimethylphenyl)N-acetyl-DL alaninate and Methyl N-(2,6-dimethylphenyl)N-(2-chloro acetyl)DL alaninate Though FAO and IUPAC specify the 2,6-dimethylaniline as an impurity for metalaxyl.

The generic sample of Oxyfluorfen was assessed and identified α -(4-chlorophenyl)-4,6-dimethoxy-3-methylindole-7-methanol) as an impurity.

Hexachlorobenzene the specified impurity of prochloraz TC by IUPAC was identified in generic sample in addition to urea,N-(4-chlorophenyl)-N,N-dimethyl and 1,2,3,8,9-Penta chloro dibenzo [1,4] dioxine which not mentioned in IUPAC report.

Two following impurities were identified in the generic thiobencarb samples as following, (S-(2-chlorobenzyl)-N,N-diethyl thiol carbamat) and(N-[4-(acetylamino)phenyl]-1-methyl-4-nitro-1H-pyrazole-3-carboxamide).

The samples of the following generic pesticides, fenamiphos, chlorpyrifos-ethyl and methyl, lambda-cyhalothrin, metalaxyl, oxyfluorfen, prochloraz and thiobencarb; have been shown to have impurities that are not identified by FAO or IUPAC. It was also found that the acidity and alkalinity of these samples coincide with the values found in FAO, and the differences between the melting points of the generic samples and the original ones (specified by FAO) does not exceed 2-3°C.

Key words:

Pesticide, Fingerprint, Impurities, Identification, Mass Spectroscopy, ¹H-NMR, IR, GC-MS.

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LIST OF ABBREVIATIONS

FAO	Food and Agriculture organization
IUPAC	International Union of Pure and Applied Chemistry.
EPA	Environmental Protection Agency.
TEDP	Tetraethyl dithiopyrophosphate (sulfotepp).
TGAI	technical Grade Active Ingredients.
GC/MS	gas chromatography /mass spectrometry.
HPLC	high performance liquid chromatography.
LC/MS	liquid chromatography/mass spectrometry.
Ppm	Part per million.
LD₅₀	lethal dose 50%
CCC	countercurrent chromatography
TMP	trimethyl phosphorothioate
I-TMP	isotrimethyl phosphorothioate
TCPM	Tris(4-chlorophenyl)methanol
TCPMe	Tris(4-chlorophenyl)methane
MSD	The mass spectrometric detector.
µg/g	Microgram/gram.
mg/g	Milligram/gram.
mg/l	Milligram/liter.
ml/min	Milliliter/minute.
mg/kg	Milligram/kilogram.
OOS-TMP	O,O,S-trimethyl phosphorothioate
IC₅₀	50% inhibition of cholinesterase.
DNA	deoxyribonucleic acid.
EC	Emulsifiable concentrates
WP	wettable powder
HLB	Hydrophobic Lipophilic Balance.
LOD_s	Limits of detection
UV	Ultraviolet
OPT	Organophosphorothionates
ACHE	acetylcholinesterase
CYP	cytochrome P450
CSCA	the sperm chromatin structure assay
DETP	Diethylthiophosphate
PLE	pressurized liquid extraction
LOQ	limits of quantification

MP	a multi pesticide method
FID	flam ionization detector
SPE	solid – phase extraction
OPP_s	organophosphorus pesticides
MHZ	megahertz
DMSO	dimethyl sulphoxide
CDCL₃	deuterated chloroform
FTIR	Fourier transform infrared
m/z	mass-to-charge ratio
NMR	Nuclear magnetic resonance
TMS	Tetramethylsilane