



High-resolution accuracy-mass method for the screening of a wide range of pesticides in different fruit and vegetable matrices



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1. Introduction

The Orbitrap (QExactive) was evaluated for the analysis of pesticides. The evaluation was performed using QuEChERS extracts of tomato, pepper, orange and green tea. The extracts were spiked with 170 selected pesticides at four concentration levels (10 µg/kg, 50 µg/kg, 100 µg/kg and 500 µg/kg). Extracts were diluted 5 fold before the injection. Three different resolution settings (17,500, 35,000 and 70,000) were evaluated. This report presents working parameters of the LC-MS system and data base of the investigated pesticides.

2. Instrumentation and analytical conditions for the LC- MS system

UHPLC Dionex Ultimate 3000

- Column: Thermo Scientific Accucore aQ C18 150 mm x 2.1 mm and 2.6 m
- Mobile phase A: 98% water, 2% methanol, 5mM ammonium formate, 0.1% formic acid
- Mobile phase B: A: 98% methanol, 2% water, 5mM ammonium formate, 0.1% formic acid
- Flow rate: 0.4 mL/min
- Injection volume: 10 µL
- Gradient: From 0 to 4 minutes, the amount of mobile phase B increased to 20%, from 4 to 5.5 minutes to 40%, and from 5.5 to 10 minutes to 100%. 100% of B was maintained until 13 minutes. Following this, the mobile phase was changed to 100% A and maintained over 5 minutes for re-equilibration.

QExactive:

- sheath gas flow rate: 40
 - auxiliary gas flow rate: 5
 - sweep gas flow rate:1
 - spray voltage: 3.00 kV
 - capillary temperature: 280 °C
 - S-lens RF level: 55.0
 - heater temperature: 350 °C
-
- Scan mode: full scan
 - AGC target: 1e6
 - maximum IT: 200 ms
 - scan range: 100-800 m/z
 - resolution (FWHM at 200 m/z): 35,000 for easy matrices and 70,000 for difficult matrices



The parameters were the same for positive and negative polarity.

3. References

Ł. Rajski, M.M. Gomez-Ramos, and A.R. Fernandez-Alba, *Large pesticide multiresidue screening method by liquid chromatography-Orbitrap mass spectrometry in full scan mode applied to fruit and vegetables*. *J Chromatogr A*, 2014. 1360: p. 119-27

APPENDIX I: List of studied pesticides

Compound Name	Chemical Formula	Extracted Mass	Adduct	Polarity	Retention time
Acephate	C4H10NO3PS	184.0192	M+H	+	2.66
Acetamiprid	C10H11ClN4	223.0745	M+H	+	6.6
Aldicarb	C7H14N2O2S	208.1114	M+NH4	+	7.15
Azinphos-methyl	C10H12N3O3PS2	318.0131	M+H	+	8.93
Azoxystrobin	C22H17N3O5	404.1241	M+H	+	8.91
Bifenthrin	C23H22ClF3O2	440.1599	M+NH4	+	11.35
Bitertanol	C20H23N3O2	338.1863	M+H	+	10.02
Boscalid	C18H12Cl2N2O	343.0399	M+H	+	9.15
Bromuconazole	C13H12BrCl2N3O	375.9614	M+H	+	9.4
Bupirimate	C13H24N4O3S	317.1642	M+H	+	9.49
Buprofezin	C16H23N3OS	306.1635	M+H	+	10.48
Carbaryl	C12H11NO2	202.0863	M+H	+	8.14
Carbendazim	C9H9N3O2	192.0768	M+H	+	5.43
Chlorantraniliprole	C18H14BrCl2N5O2	481.9781	M+H	+	8.74
Chlorfenvinphos	C12H14Cl3O4P	358.9768	M+H	+	9.89
Chlorpyrifos	C9H11Cl3NO3PS	349.9336	M+H	+	10.75
Chlorpyrifos-methyl	C7H7Cl3NO3PS	321.9023	M+H	+	10.3
Clofentezine	C14H8Cl2N4	303.0199	M+H	+	10.32
Cymoxanil	C7H10N4O3	199.0826	M+H	+	6.65
Cyproconazole	C15H18ClN3O	292.1211	M+H	+	9.25
Cyprodinil	C14H15N3	226.1339	M+H	+	9.92
Cyromazine	C6H10N6	167.1040	M+H	+	2.33
Diazinon	C12H21N2O3PS	305.1083	M+H	+	9.92
Dichlorvos-d6	C4D6HCl2O4P	226.9908	M+H	+	7.73
Dicrotophos	C8H16NO5P	238.0839	M+H	+	5.87
Diethofencarb	C14H21NO4	268.1543	M+H	+	8.9
Difenoconazole	C19H17Cl2N3O3	406.0720	M+H	+	10.21
Diflubenzuron	C14H9ClF2N2O2	311.0393	M+H	+	9.75
Dimethoate	C5H12NO3PS2	230.0069	M+H	+	6.37
Dimethomorph	C21H22ClNO4	388.1310	M+H	+	9.02
Diniconazole	C15H17Cl2N3O	326.0821	M+H	+	10.19
Diphenylamine	C12H11N	170.0964	M+H	+	9.57
Dodine	C13H29N3	228.2434	M+H	+	10.25
Epoxiconazole	C17H13ClFN3O	330.0804	M+H	+	9.58
Ethion	C9H22O4P2S4	384.9949	M+H	+	10.6
Ethirimol	C11H19N3O	210.1601	M+H	+	7.18
Ethoprophos	C8H19O2PS2	243.0637	M+H	+	9.53
Etofenprox	C25H28O3	394.2377	M+NH4	+	11.35
Famoxadone	C22H18N2O4	392.1605	M+NH4	+	9.93
Fenamidone	C17H17N3OS	312.1165	M+H	+	9.02
Fenamiphos	C13H22NO3PS	304.1131	M+H	+	9.64
Fenarimol	C17H12Cl2N2O	331.0399	M+H	+	9.49
Fenazaquin	C20H22N2O	307.1805	M+H	+	11.34
Fenbuconazole	C19H17ClN4	337.1215	M+H	+	9.61
Fenhexamid	C14H17Cl2NO2	302.0709	M+H	+	9.38
Fenitrothion	C9H12NO5PS	278.0247	M+H	+	9.17
Fenoxycarb	C17H19NO4	302.1387	M+H	+	9.71
Fenpropathrin	C22H23NO3	350.1751	M+H	+	10.82
Fenpropimorph	C20H33NO	304.2635	M+H	+	9.04
Fenpyroximate	C24H27N3O4	422.2074	M+H	+	10.93
Fenthion	C10H15O3PS2	279.0273	M+H	+	9.96
Fonicamid	C9H6F3N3O	230.0536	M+H	+	4.72



Fluazifop	C15H12F3NO4	328.0791	M+H	+	8.95
Flubendiamide	C23H22F7IN2O4S	683.0306	M+H	+	9.67
Flufenoxuron	C21H11ClF6N2O3	489.0435	M+H	+	10.75
Fuopyram	C16H11ClF6N2O	397.0537	M+H	+	9.36
Fluquinconazole	C16H8Cl2FN5O	376.0163	M+H	+	9.43
Flusilazole	C16H15F2N3Si	316.1076	M+H	+	9.68
Flutriafol	C16H13F2N3O	302.1099	M+H	+	8.44
Formetanate	C11H15N3O2	222.1237	M+H	+	3.55
Fosthiazate	C9H18NO3PS2	284.0539	M+H	+	8.24
Haloxypop	C15H11ClF3NO4	362.0402	M+H	+	9.64
Hexaconazole	C14H17Cl2N3O	314.0821	M+H	+	10
Hexythiazox	C17H21ClN2O2S	353.1085	M+H	+	10.71
Imazalil	C14H14Cl2N2O	297.0556	M+H	+	8.48
Imidacloprid	C9H10ClN5O2	256.0596	M+H	+	6.11
Indoxacarb	C22H17ClF3N3O7	528.0780	M+H	+	10.15
Iprodione	C13H13Cl2N3O3	352.0226	M+Na	+	9.63
Iprovalicarb	C18H28N2O3	321.2173	M+H	+	9.37
Isocarbofos	C11H16NO4PS	312.0430	M+Na	+	9.75
Isofenphos-methyl	C14H22NO4PS	332.1080	M+H	+	9.75
Isoprocarb	C11H15NO2	194.1176	M+H	+	8.44
Kresoxim-methyl	C18H19NO4	314.1387	M+H	+	9.76
Linuron	C9H10Cl2N2O2	249.0192	M+H	+	9.16
Malathion	C10H19O6PS2	331.0433	M+H	+	9.22
Malathion-d10	C10D10H9O6PS2	341.1061	M+H	+	9.19
Mandipropamid	C23H22ClNO4	412.1310	M+H	+	9.1
Metconazole	C17H22ClN3O	320.1524	M+H	+	10.02
Methamidophos	C2H8NO2PS	142.0086	M+H	+	1.97
Methidathion	C6H11N2O4PS3	302.9691	M+H	+	8.79
Methiocarb	C11H15NO2S	226.0896	M+H	+	9.1
Methomyl	C5H10N2O2S	163.0536	M+H	+	4.86
Methoxyfenozide	C22H28N2O3	369.2173	M+H	+	9.27
Metobromuron	C9H11BrN2O2	259.0077	M+H	+	8.54
Monocrotophos	C7H14NO5P	224.0682	M+H	+	5.55
Myclobutanil	C15H17ClN4	289.1215	M+H	+	9.31
Nitenpyram	C11H15ClN4O2	271.0956	M+H	+	4.56
Oxadixyl	C14H18N2O4	279.1339	M+H	+	7.41
Oxamyl	C7H13N3O3S	237.1016	M+NH4	+	4.43
Oxydemeton-methyl	C6H15O4PS2	269.0042	M+Na	+	4.96
Paclbutrazol	C15H20ClN3O	294.1368	M+H	+	9.18
Penconazole	C13H15Cl2N3	284.0716	M+H	+	9.88
Pencycuron	C19H21ClN2O	329.1415	M+H	+	10.14
Pendimethalin	C13H19N3O4	282.1448	M+H	+	10.83
Phenthoate	C12H17O4PS2	321.0379	M+H	+	9.75
Phosalone	C12H15ClNO4PS2	367.9941	M+H	+	10.09
Phosmet	C11H12NO4PS2	318.0018	M+H	+	8.95
Phoxim	C12H15N2O3PS	299.0614	M+H	+	10.03
Pirimicarb	C11H18N4O2	239.1503	M+H	+	7.25
Pirimiphos-methyl	C11H20N3O3PS	306.1036	M+H	+	10.03
Prochloraz	C15H16Cl3N3O2	376.0381	M+H	+	10.05
Procymidone	C13H11Cl2NO2	301.0505	M+NH4	+	8.49
Profenofos	C11H15BrClO3PS	372.9424	M+H	+	10.44
Propamocarb	C9H20N2O2	189.1598	M+H	+	3.56
Propargite	C19H26O4S	373.1444	M+Na	+	10.77
Propiconazole	C15H17Cl2N3O2	342.0771	M+H	+	9.98
Propoxur	C11H15NO3	210.1125	M+H	+	7.72
Propyzamide	C12H11Cl2NO	256.0291	M+H	+	9.28
Prothioconazole	C14H15Cl2N3OS	344.0386	M+H	+	9.97
Prothiophos	C11H15Cl2O2PS2	344.9701	M+H	+	11.2



Pymetrozine	C10H11N5O	218.1036	M+H	+	3.75
Pyraclostrobin	C19H18ClN3O4	388.1059	M+H	+	10.02
Pyrethrin	C21H28O3	329.2111	M+H	+	10.84
Pyridaben	C19H25ClN2OS	365.1449	M+H	+	11.07
Pyrimethanil	C12H13N3	200.1182	M+H	+	9.08
Pyriproxyfen	C20H19NO3	322.1438	M+H	+	10.67
Quinoxyfen	C15H8Cl2FNO	308.0040	M+H	+	10.89
Rotenone	C23H22O6	395.1489	M+H	+	9.66
Spinosyn A	C41H65NO10	732.4681	M+H	+	10.07
Spirodiclofen	C21H24Cl2O4	411.1124	M+H	+	10.9
Spiromesifen	C23H30O4	371.2217	M+H	+	10.75
Spiroxamine	C18H35NO2	298.2741	M+H	+	9.26
Tebuconazole	C16H22ClN3O	308.1524	M+H	+	9.85
Tebufenozide	C22H28N2O2	353.2224	M+H	+	9.69
Tebufenpyrad	C18H24ClN3O	334.1681	M+H	+	10.46
Terbuthylazine	C9H16ClN5	230.1167	M+H	+	9.15
Tetraconazole	C13H11Cl2F4N3O	372.0288	M+H	+	9.49
Thiabendazole	C10H7N3S	202.0433	M+H	+	6.28
Thiacloprid	C10H9ClN4S	253.0309	M+H	+	7.03
Thiamethoxam	C8H10ClN5O3S	292.0266	M+H	+	5.27
Thiophanate-methyl	C12H14N4O4S2	343.0529	M+H	+	7.74
Tolclofos-methyl	C9H11Cl2O3PS	300.9616	M+H	+	10.18
TPP	C18H15PO4	327.0781	M+H	+	9.93
Triadimefon	C14H16ClN3O2	294.1004	M+H	+	9.27
Triazophos	C12H16N3O3PS	314.0723	M+H	+	9.4
Trichlorfon	C4H8Cl3O4P	256.9299	M+H	+	6.13
Trifloxystrobin	C20H19F3N2O4	409.1370	M+H	+	10.18
Triflumuron	C15H10ClF3N2O3	359.0405	M+H	+	10.02
Triticonazole	C17H20ClN3O	318.1368	M+H	+	9.46
Zoxamide	C14H16Cl3NO2	336.0319	M+H	+	9.98
3-hidroxicarbofuran	C12H15NO4	238.1074	M+H	+	6.39
Aldicarb Sulfone	C7H14N2O4S	223.0747	M+H	+	4.22
Aldicarb Sulfoxide	C7H14N2O3S	207.0798	M+H	+	3.83
Carbofuran	C12H15NO3	222.1125	M+H	+	7.8
Clothianidin	C6H8ClN5O2S	250.0160	M+H	+	6.15
Demeton-S-methylsulfone	C6H15O5PS2	263.0171	M+H	+	5.21
Desmethyl Pirimicarb	C10H16N4O2	225.1346	M+H	+	5.98
Fenamiphos Sulfone	C13H22NO5PS	336.1029	M+H	+	8
Fenamiphos Sulfoxide	C13H22NO4PS	320.1080	M+H	+	7.88
Fenthion Oxon	C10H15O4PS	263.0501	M+H	+	8.9
Fenthion Oxon Sulfone	C10H15O6PS	295.0400	M+H	+	6.78
Fenthion Oxon Sulfoxide	C10H15O5PS	279.0451	M+H	+	6.62
Fenthion Sulfone	C10H15O5PS2	311.0171	M+H	+	8.23
Fenthion Sulfoxide	C10H15O4PS2	295.0222	M+H	+	8.1
Malaoxon	C10H19O7PS	315.0662	M+H	+	7.86
Metalaxyl-M	C15H21NO4	280.1543	M+H	+	8.53
Methiocarb Sulfone	C11H15NO4S	258.0795	M+H	+	6.74
Methiocarb Sulfoxide	C11H15NO3S	242.0845	M+H	+	6.36
Omethoate	C5H12NO4PS	214.0297	M+H	+	3.33
Paraoxon Methyl	C8H10NO6P	248.0319	M+H	+	7.47
Phosmet Oxon	C11H12NO5PS	302.0247	M+H	+	7.43
Prothioconazole-desthio	C14H15Cl2N3O	312.0665	M+H	+	6.78
Thiodicarb	C10H18N4O4S3	355.0563	M+H	+	8.34
Triadimenol	C14H18ClN3O2	296.1160	M+H	+	9.38
2.4-D	C8H6Cl2O3	218.9621	M-H	-	8.34
Fipronil	C12H4Cl2F6N4OS	434.9314	M-H	-	9.64
Fludioxonil	C12H6F2N2O2	247.0325	M-H	-	9.23
Lufenuron	C17H8Cl2F8N2O3	508.9712	M-H	-	10.61



Teflubenzuron	C ₁₄ H ₆ Cl ₂ F ₄ N ₂ O ₂	378.9670	M-H	-	10.69
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