

Determination of Pesticide Residues in Olive Oil Using QuEChERS Extraction and Liquid Chromatography–Orbitrap High-Resolution Mass Spectrometry: Comparison of Different Clean-Up Sorbents and Validation Study

Konstantina Iosif ¹ and Ioannis Konstantinou ^{1,2,*}

¹ Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece; iokonstantina97@gmail.com

² Institute of Environment and Sustainable Development, University Research Center of Ioannina (URCI), 45110 Ioannina, Greece

* Correspondence: iokonst@uoi.gr; Tel.: +30-2651008349

Supplementary information

Table S1. Operational parameters of LTQ-FT Orbitrap instrument.

Full scan	
Mass range	120-1000Da
Spray voltage	3,7 kV
Resolution	60.000 FWHM
Sheath gas	40 au
Auxiliary gas flow	15au
Capillary temperature	320 °C
Collision energy	45 Ev
Mass tolerance	<5mg/L
Data dependent scanning	
Fragmentation technique	CID (collision induced dissociation)
Normalized collision energy, NCE	35%
Resolution	15000
Data processing software	Thermo Xcalibur 2.1

Table S2. LC–HR-MS elution program

Time (min)	%A (H ₂ O,0,1% FA)	%B (MeOH,0,1% FA)	Flow rate (μL min ⁻¹)
0	70	30	250
1	70	30	250
2	30	70	250
5	0	100	250

7	0	100	250
7,10	70	30	250
10	70	30	250

Table S3. LC-MS analytical characteristics of the studied pesticides.

Pesticides	Class	Ion formula [M+H] ⁺	Theoretical mass (m/z)	Experimental mass (m/z)	t _R (min)	Error (Δ ppm)	RDBE	Daughter ions 35% NCE
Alachlor	Herbicide	C ₁₄ H ₂₁ ClNO ₂	270.1255	270.1247	4.72	-2.973	4.5	238.0987, 162.1273
Azoxystrobin	Fungicide	C ₂₂ H ₁₈ N ₃ O ₅	404.1241	404.1232	4.13	-2.220	15.5	372.0964, 345.1200
Benalaxyl	Fungicide	C ₂₀ H ₂₄ NO ₃	326.1751	326.1743	5.07	-2.300	9.5	294.1482, 208.1328, 266.1536, 148.1117
Boscalid	Fungicide	C ₁₈ H ₁₃ Cl ₂ N ₂ O	343.0399	343.0391	4.29	-2.580	12.5	307.0624, 139.9893
Chlorfenviphos	Insecticide	C ₁₂ H ₁₅ Cl ₃ O ₄ P	358.9758	358.9762	5.05	-1.769	4.5	115.0462, 127.0149, 98.9835
Chlorpyrifos	Insecticide	C ₉ H ₁₂ Cl ₃ NO ₃ PS	349.9336	349.9328	3.50	-2.086	3.5	321.9015, 293.8702, 197.9270, 275.8604
Diazinon	Insecticide	C ₁₂ H ₂₂ N ₂ O ₃ PS	305.1083	305.1078	5.11	-1.856	3.5	169.0789, 153.1017, 277.0762, 249.0447
Difenoconazole	Fungicide	C ₁₉ H ₁₈ Cl ₂ N ₃ O ₃	406.0720	406.0713	5.48	-1.609	11.5	337.0386, 251.0020
Dimethoate	Insecticide	C ₅ H ₁₃ NO ₃ PS ₂	230.0069	230.0063	2.85	-2.381	0.5	198.9641, 170.9692
Diuron	Herbicide	C ₉ H ₁₁ Cl ₁₂ N ₂ O	233.0243	233.0238	4.03	-2.210	4.5	187.1477, 159.0798
Deltamethin	Insecticide	C ₂₂ H ₂₃ Br ₂ NO ₃	523.0051	523.0030	6.67	-0.0021	13	304.1321
Fenbuconazole	Fungicide	C ₁₉ H ₁₈ ClN ₄	337.1215	337.1205	4.78	-2.880	12.5	194.0475, 125.0148
Fenoxycarb	Insecticide	C ₁₇ H ₂₀ NO ₄	302.1387	302.1381	4.82	-2.034	8.5	116.0699, 256.0959

Table S3. (continue)

Pesticides	Class	Ion formula [M+H] ⁺	Theoretical mass (m/z)	Experimental mass (m/z)	t _R (min)	Error (Δppm)	RDBE	Daughter ions 35% NCE
Florasulam	Herbicide	C ₁₂ H ₉ F ₃ N ₅ O ₃ S	360.0373	360.0364	3.19	-2.364	9.5	327.1191, 129.0378, 191.9919, 296.0743
Fluquinconazole	Fungicide	C ₁₆ H ₉ Cl ₂ FN ₅ O	376.0163	376.0152	4.59	-2.979	13.5	349.0043, 306.9825
Iodosulfuron methyl	Herbicide	C ₁₄ H ₁₄ IN ₅ NaO ₆ S	529.9602	529.9587	4.00	-2.864	9.5	389.8889
Imazalil	Fungicide	C ₁₄ H ₁₅ Cl ₂ N ₂ O	297.0556	297.0550	3.82	-1.970	7.5	255.0078, 158.9757, 176.0382, 109.0754
Isoproturon	Herbicide	C ₁₂ H ₁₉ N ₂ O	207.1492	207.1489	3.98	-1.254	4.5	165.1015, 162.0906
Kresoxim- methyl	Fungicide	C ₁₈ H ₂₀ NO ₄	314.1387	314.1382	4.91	-1.670	9.5	267.1008, 282.1110, 222.0910
Metalaxyl	Fungicide	C ₁₅ H ₂₂ NO ₄	280.1543	280.1539	3.96	-1.552	5.5	248.1274, 220.1326, 192.1378
Myclobutanil	Fungicide	C ₁₅ H ₁₈ ClN ₄	289.1215	289.1208	4.49	-2.182	8.5	220.0880, 125.0151
Mefenpyr- diethyl	Herbicide	C ₁₆ H ₁₉ Cl ₂ N ₂ O ₄	373.0716	373.0706	5.11	-2.651	7.5	299.0573, 327.0518
Nicosulfuron	Herbicide	C ₁₅ H ₁₉ N ₆ O ₆ S	411.1081	411.1070	3.53	-2.772	9.5	366.0491, 213.0322, 182.0554, 156.0764
Pirimicarb	Insecticide	C ₁₁ H ₁₉ N ₄ O ₂	239.1503	239.1496	3.54	-2.561	4.5	182.1282, 195.1597, 239.1496
Penoxsulam	Herbicide	C ₁₆ H ₁₅ F ₅ N ₅ O ₅ S	484.0709	484.0694	3.64	-3.009	9.5	444.0567, 195.0744, 464.0629

Phosmet	Insecticide	C ₁₁ H ₁₃ NO ₄ PS ₂	318.0018	318.0011	4.12	-2.146	6.5	160.0387, 133.0280
----------------	-------------	---	----------	----------	------	--------	-----	-----------------------

Table S3. (continue)

Pesticides	Class	Ion formula [M+H] ⁺	Theoretical mass (m/z)	Experimental mass (m/z)	t _R (min)	Error (Δppm)	RDBE	Daughter ions 35% NCE
Pyriproxyfen	Insecticide	C ₂₀ H ₂₀ NO ₃	322.1438	322.1429	5.97	-2.763	11.5	227.1061, 136.0751, 96.0438
Pyraclostrobin	Fungicide	C ₁₉ H ₁₉ ClN ₃ O ₄	388.1059	388.1049	5.15	-2.345	11.5	194.0805, 296.0576, 164.0701
Quizalofop-p-ethyl	Herbicide	C ₁₉ H ₁₈ ClN ₂ O ₄	373.0950	373.0945	5.68	-1.129	11.5	299.0573
Spinetoram	Insecticide	C ₄₂ H ₇₀ NO ₁₀	748.4994	748.4992	5.58	-0.286	8.5	688.0282
Spirotetramat	Insecticide	C ₂₁ H ₂₈ NO ₅	374.1962	374.1953	4.56	-2.297	8.5	330.2054, 302.1745, 270.1485
Terbutylazine	Herbicide	C ₉ H ₁₇ ClN ₅	230.1167	230.1162	4.34	-1.998	3.5	174.0537
Trifloxystrobin	Fungicide	C ₂₀ H ₂₀ F ₃ N ₂ O ₄	409.1370	409.1362	5.39	-1.951	10.5	186.0521
Thiabendazole	Fungicide	C ₁₀ H ₈ N ₃ S	202.0433	202.0427	2.69	-3.289	8.5	202.0425, 175.0318
Thiamethoxam	Insecticide	C ₈ H ₁₁ ClN ₅ O ₃ S	292.0266	292.0258	1.91	-2.548	5.5	211.0641, 246.0329
Tebuconazole	Fungicide	C ₁₆ H ₂₃ ClN ₃ O	308.1524	308.1517	5.01	-2.228	6.5	308.0031
Thiacloprid	Insecticide	C ₁₀ H ₁₀ ClN ₄ S	253.0309	253.0305	3.24	-1.863	7.5	126.0100, 186.0134, 226.0194
Tribenuron-methyl	Herbicide	C ₁₅ H ₁₈ N ₅ O ₆ S	396.0972	396.0962	3.87	-2.652	9.5	155.0922, 364.0698, 199.0053
λ-cyhalothrin	Insecticide	C ₂₃ H ₂₃ ClF ₃ N ₂ O ₃	467.1344	467.1334	6.20	-2.101	11.5	226.0854, 450.1074

Table S4. Calibration curve equation and correlation coefficient factor (r^2) of the compared protocols.

Pesticides	EMR-lipid			Z-Sep ⁺		
	Concentration range ($\mu\text{g/kg}$)	Calibration curve equation	r^2	Concentration range ($\mu\text{g/kg}$)	Calibration curve equation	r^2
Alachlor	5-500	$y = 124560x + 804357$	0.9906	5-500	$y = 135004x + 668460$	0.9968
Azoxystrobin	5-500	$y = 603222x - 1537979$	0.9993	5-500	$y = 562263x + 2701010$	0.9973
Benalaxyl	5-500	$y = 737851x + 5232620$	0.9980	5-500	$y = 757938x + 5635450$	0.9959
Boscalid	5-500	$y = 88184.9x + 417036$	0.9936	5-500	$y = 93402.1x + 336783$	0.9969
Chlorfenviphos	5-500	$y = 221608x + 1600880$	0.9967	5-500	$y = 235514x + 1731910$	0.9932
Chlorpyrifos	5-500	$y = 69066.9x + 17848$	0.9956	5-500	$y = 65190.9x - 325777$	0.9979
Diazinon	5-500	$y = 484532x + 3880110$	0.9989	5-500	$y = 493036x + 4450710$	0.9967
Difenoconazole	5-500	$y = 159341x + 414814$	0.9943	5-500	$y = 160944x + 333097$	0.9989
Dimethoate	5-500	$y = 377218x - 753254$	0.9986	5-500	$y = 409475x + 1662440$	0.9989
Diuron	5-500	$y = 179021x - 309348$	0.9994	5-500	$y = 169614x + 1821490$	0.9922
Deltamethin	5-500	$y = 68930.1x - 505005$	0.9942	5-500	$y = 72635x - 432389$	0.9985
Fenbuconazole	5-500	$y = 135721x + 938941$	0.9908	5-500	$y = 140389x + 744523$	0.9969
Fenoxycarb	5-500	$y = 293789x + 205782$	0.9998	5-500	$y = 247900x + 3255170$	0.9916
Florasulam	5-500	$y = 58991.6x - 591385$	0.9968	5-500	$y = 77664.1x - 549336$	0.9996
Fluquinconazole	5-500	$y = 16466.9x - 20846$	0.9919	5-500	$y = 17970.3x - 111375$	0.9994
Iodosulfuron methyl	5-500	$y = 6752.52x + 9302.52$	0.9988	5-500	$y = 8179.83x + 54011.2$	0.9918
Imazalil	5-500	$y = 400326x - 1346460$	0.9989	5-500	$y = 375994x + 4153590$	0.9936
Isoproturon	5-500	$y = 546296x + 579244$	0.9996	5-500	$y = 505525x + 7375950$	0.9924
Kresoxim- methyl	5-500	$y = 357156x + 920650$	0.9995	5-500	$y = 304773x + 4523270$	0.9917
Metalaxyl	5-500	$y = 596400x + 664695$	0.9995	5-500	$y = 546209x + 7461990$	0.9944
Myclobutanil	5-500	$y = 146017x + 914948$	0.9916	5-500	$y = 152531x + 468150$	0.9981
Mefenpyr- diethyl	5-500	$y = 291451x + 3000970$	0.9938	5-500	$y = 307398x + 3081860$	0.9904
Nicosulfuron	5-500	$y = 94620.3x - 622363$	0.9964	5-500	$y = 121555x - 410348$	0.9996
Pirimicarb	5-500	$y = 447556x - 1670240$	0.9990	5-500	$y = 548036x + 5141760$	0.9970
Penoxsulam	5-500	$y = 146087x - 644206$	0.9958	5-500	$y = 172535x - 562109$	0.9992
Phosmet	5-500	$y = 186207x - 592556$	0.9995	5-500	$y = 171776x + 894584$	0.9955
Pyriproxyfen	5-500	$y = 647790x - 582780$	0.9992	5-500	$y = 518602x + 3446090$	0.9961
Pyraclostrobin	5-500	$y = 413832x + 1754580$	0.9989	5-500	$y = 431273x + 1939070$	0.9974
Quizalofop-p- ethyl	5-500	$y = 415488x - 619015$	0.9997	5-500	$y = 366045x + 3167820$	0.9938
Spinetoram	5-500	$y = 283223x + 1615790$	0.9907	5-500	$y = 285220x + 1947550$	0.9962
Spirotetramat	5-500	$y = 349358x + 2919690$	0.9911	5-500	$y = 360465x + 1654900$	0.9981
Terbutylazine	5-500	$y = 351632x - 67717.7$	0.9994	5-500	$y = 306786x + 3201460$	0.9954
Trifloxystrobin	5-500	$y = 687383x + 1591120$	0.9996	5-500	$y = 587443x + 8106970$	0.9918
Thiabendazole	5-500	$y = 462727x + 297572$	0.9952	5-500	$y = 549922x + 609410$	0.9990

Table S4. (continue)

Pesticides	EMR-lipid			Z-Sep ⁺		
	Concentration range (µg/kg)	Calibration curve equation	r ²	Concentration range (µg/kg)	Calibration curve equation	r ²
Thiamethoxam	5-500	y = 143301x - 1283700	0.9955	5-500	y = 145286x - 734395	0.9994
Tebuconazole	5-500	y = 114033x + 1358240	0.9967	5-500	y = 118655x + 1558350	0.9922
Thiacloprid	5-500	y = 205644x - 1677590	0.9966	5-500	y = 309387x + 1090420	0.9975
Tribenuron-methyl	5-500	y = 221921x - 1219980	0.9978	5-500	y = 238735x + 1409400	0.9941
λ-cyhalothrin	5-500	y = 53377.4x - 379668	0.9974	5-500	y = 41603.3x + 51985	0.9973

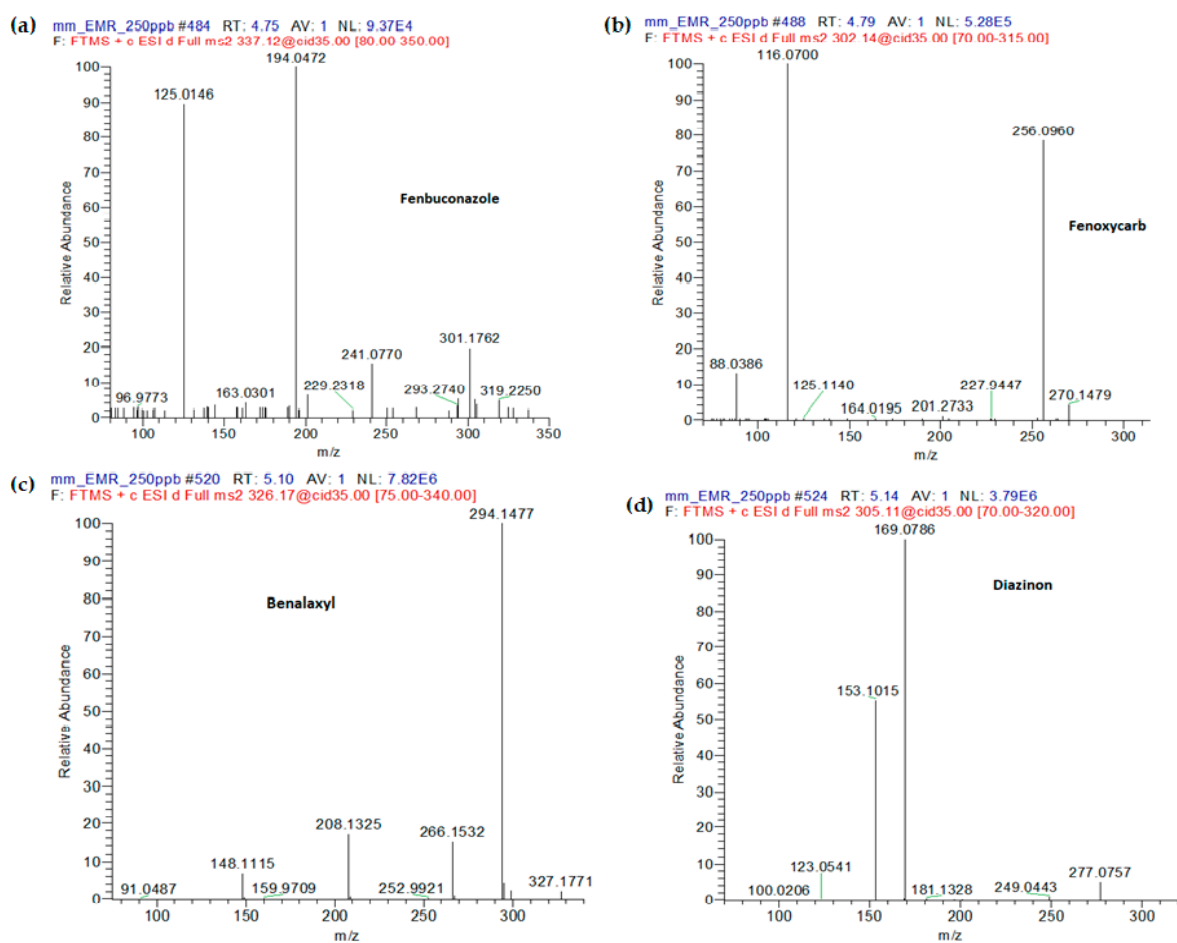


Figure S1. Representative MS/MS spectrum of pesticide analytes with close retention times.