

Fully automated analysis of 549 pesticides in oil with LCxGC and FOCUS auto sampler**Key Words:**

LCxGC
Large Volume Injection
OPTIC
Pesticides
Automation

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Introduction

Normally, the analysis of pesticides in oil, like olive oil and sunflower oil, is difficult. The whole application is also a time-consuming and expensive because of the necessary sample preparation prior the GC-MS analysis. However, we developed a relative new approach whereby the whole procedure is automated. For the sample preparation Size Exclusion Chromatography (SEC or GPC) is used. The oil is eluting earlier because of the bigger size of the oil-molecules. The later eluting pesticides are automated collected and injected using the side-port syringe.

In this application note, a sun-flower oil is analyzed containing 549 pesticides (spiked at a level of 10 ppb), 100 µl of the oil is injected into a SEC (mobile phase: ETAC/hexane mixture).

Instrumentation/Hardware:**SEC:**

- Pump: Shimadzu LC-20 AD
- Injection system: Focus LC-valve
- SEC column: PL mixed E
- Flow: 1 ml/min
- Injection vol. 100 µl

GC:

- Injector: Optic 3 PTV
- Liner: Sinter-bed (de-activated)
- Auto sampler: Focus Robotic Sample Processor
- GC-MS: Shimadzu 2010
- GC-program: 50 °C (5 min); 40 °C/min to 150 °C; 5 °C/min 280 for 20 min
- GC column: TC-5 MS (20 m; 0.18mm ID and 0.18 µm film)
- Interface: LC-GC interface kit
- Pesticides: The list of all the pesticides are given in appendix 1

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Results:

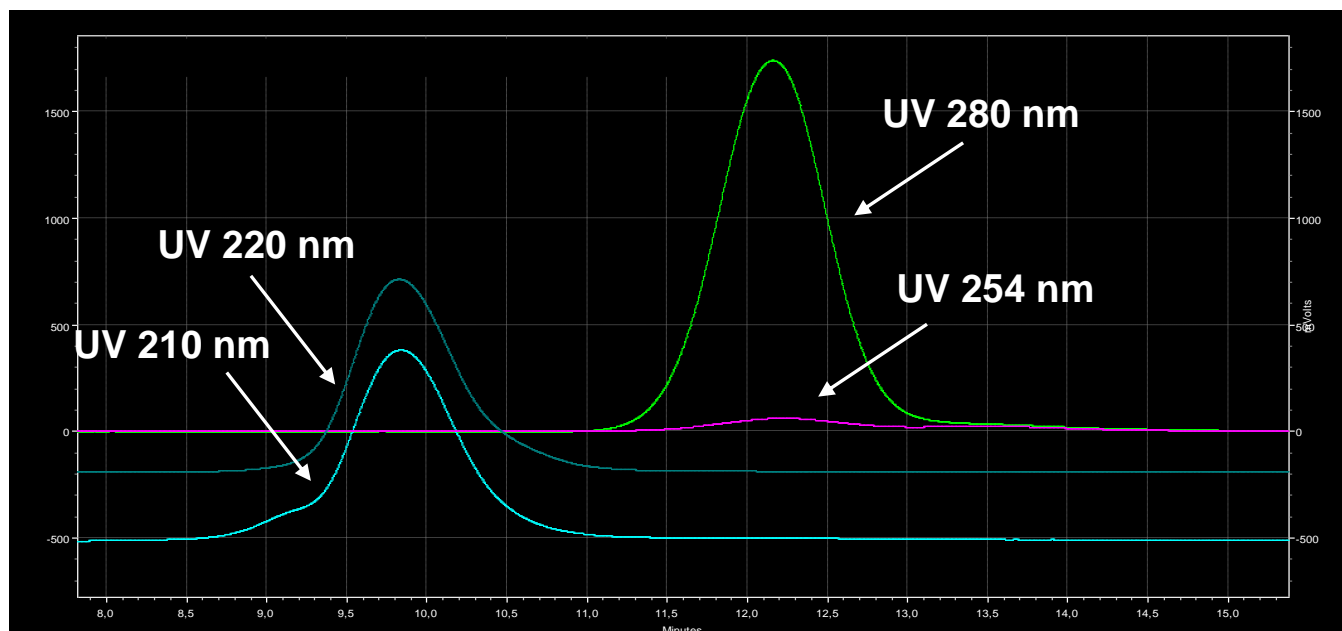


Figure 1: Size exclusion chromatogram of a crude oil with spiked pesticides (10ppb). The larger molecules of fat and oil were eluting first and the smaller pesticides components elute in the last part of the SEC. The pesticides were automated collected and LVI-injected into the PTV-GC-MS.

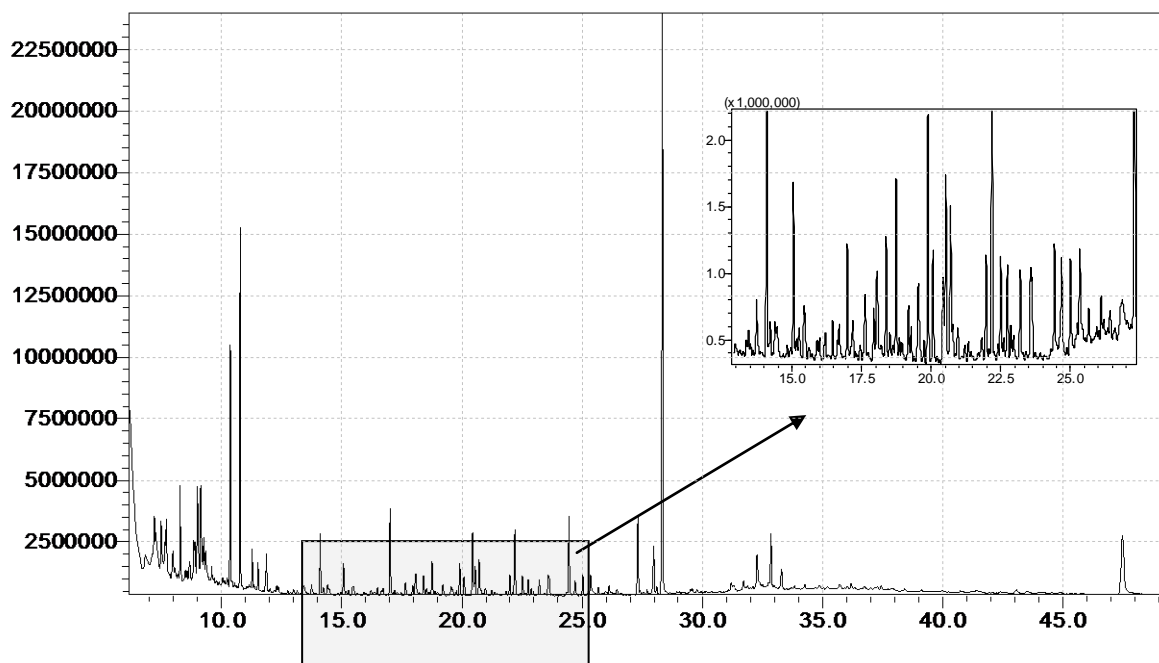


Figure 2: PTV-GC-MS TIC-chromatogram of the SEC-fraction including all the pesticides. Clearly, the injected fraction contains almost no components coming from the oil.

Conclusion:

Automated analysis of pesticides in oil is possible using the novel SEC-PTV-GC/MS method. At the level of 10 ppb, most of the pesticides had good recoveries and good peak shapes. The whole method is fast and reliable, however, if the oil contains too many small fatty acids, the SEC separation is becoming more critical or an automated SPE step is necessary.

Appendix 1: List of pesticides analyzed

Pesticide	Rt (min)	m/z	Pesticide	Rt (min)	m/z
Dimefox	5.33	110	Chlorfenvinphos	19.26	267
Metaldehyd	5.70	89	Pyrifenoxy-z	19.28	92
Diflubenzuron	6.28	153	Primicarb-desmethyl-formamido	19.28	72
Oxydemeton-Methyl	6.48	109	Penconazol	19.31	159
Hexachlor-1.3-butadien 1	6.71	225	Allethrin 1	19.31	123
Dimethylanilin (2.4-Xylidin)	6.78	121	Allethrin 2	19.31	123
Dimethylanilin-2.6 (Xylidin)	6.81	121	Oxychlordan	19.31	115
Hexachlor-1.3-butadien 2	7.27	225	Mecarbam	19.33	131
Dichlorvos	7.43	109	Bromfenvinphos-Methyl	19.33	109
Methamidophos (GC +LCQ)	7.62	94	Dinobuton	19.33	211
Thiofanox	7.65	55	Heptachlorepoxyd-cis	19.35	81
Neburon	8.04	124	Merphos	19.37	57
Dichlor-p-kresol-2.6	8.06	141	Tolyfluanid	19.43	137
Dichloranilin-3.5	8.21	161	Phentoate	19.46	121
EPTC	8.29	128	Heptachlorepoxyd-trans	19.50	81
Dichlobenil	8.31	171	Quinalphos	19.52	146
Nicotine	8.40	84	Furalaxyl	19.56	95
Biphenyl	8.63	154	Mephosfolan	19.59	140
Propamocarb (LCQ)	8.69	58	MCPA-butoxyethylester	19.59	57
Lufenuron	8.77	203	Triflumizole	19.67	73
Metosulam	8.98	188	Beflubutamid	19.67	91
Mevinphos	9.01	127	Crotoxyphos	19.71	127
Carbosulfan	9.02	118	Zoxamide 1	19.73	187
Dioxacarb	9.02	121	Triademenol 1	19.82	112
Chlormephos	9.16	121	Bromophos-E	19.82	174
Vernolate	9.17	128	Procymidon	19.84	96
Nitrapyrin	9.35	194	Haloxypop-methyl	20.03	316
Etridiazole	9.35	211	Thiabendazol	20.04	303
Propham	9.36	93	Chlordan-tr.	20.04	373
Pebulate	9.36	57	Phoxim +	20.10	109
Acephat (LCQ)	9.38	136	Propaphos	20.10	140
Metolcarb (LCQ)	9.45	108	Folpet	20.12	104
Carbofuran-3-hydroxy (LCQ)	9.46	137	Triademenol 2	20.14	112
Trichlorfon	9.76	109	Chlorbensid	20.21	125
Methacriphos	9.79	125	Triclosan	20.21	218
Pthalimide	9.79	147	Imazapyr 1	20.21	174
Chloroneb	9.97	191	Pyriphenox-e	20.29	92
Tetrahydrothalamide -1.2.3.6 cis	10.01	79	Methidathion	20.31	85
Crimidin	10.10	142	DDE-o,p	20.31	246
Phenylphenol-o	10.22	170	Tetrachlorvinphos	20.33	109
Pentachlorbenzol	10.28	250	Hexythiazox	20.36	156

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Isopropcarb	10.32	121	Chinomethionat	20.38	206
Triflusulfuron-Methyl	10.41	237	Vamidathion	20.42	87
Oxamyl (LCQ)	10.47	72	Paclobutrazol	20.46	125
Molinat	10.51	126	PCB 101	20.48	326
Demephion	10.52	74	MCPA-2-ethylhexylester	20.51	57
TEPP +	10.53	161	Chlordan-cis	20.55	373
Heptenophos	10.74	124	Picoxystrobin	20.59	145
DEET	10.85	119	Ditalimphos	20.78	130
Butocarboxim	10.99	87	Endosulfan-a	20.79	195
ETU (Ethlen-thiourea)	11.07	102	Mepanipirim	20.79	222
Chlorfenprop-methyl	11.09	125	Genite	20.81	77
Thionazin	11.17	97	Chlorfluazuron	20.81	321
Methomyl	11.17	58	Nonachlor-tr.	20.85	408
Fenobucarb	11.21	121	Bromfenvinphos-Ethyl	20.87	267
Cymoxanil	11.21	70	Flutriafol	20.91	123
Propoxur	11.26	110	Fenamiphos	20.92	154
Omethoat	11.29	203	Imidacloprid	20.92	211
Propachlor	11.33	120	Flubenzimine	20.94	135
Technazen	11.38	110	Naproamide	21.00	72
Hexaflumeron	11.41	176	Flutolanil	21.00	173
Phorat-oxon	11.41	74	Chlorflurenol +	21.02	215
Benzthiazuron	11.47	150	Flubenzimine	21.09	135
Demeton-S-methyl	11.54	88	Jodfenphos	21.13	125
Fluometuron	11.58	72	Imazapyr 2	21.15	174
Tetrachlor-m-xylo-2.4.5.6	11.62	209	Hexaconazol	21.19	83
Ethoprophos	11.70	97	Chlorfenson	21.19	111
Cycloate	11.78	83	Prothiophos	21.21	113
Diphenylamin	11.79	169	Imazalil (GC +LCQ)	21.26	215
DNOC	11.91	198	Fludioxonil	21.28	127
Trifluralin	12.00	264	Oxadiazon	21.49	175
Chlorpropham	12.04	127	Profenophos	21.54	97
Azobenzol	12.05	77	DDE-p,p	21.58	246
Benfluralin	12.08	292	Iprovalicarb 1 (LCQ)	21.58	116
Chlordimeform	12.12	117	DEF	21.60	57
Fenuron	12.20	72	Flamprop-methyl	21.64	105
Dicrotophos	12.21	127	Pymetrozine	21.65	98
Sulfotep	12.23	97	Oxyflurofen	21.71	252
Atrazin-desethyl	12.26	172	Myclobutanil	21.74	179
Bendiocarb	12.28	151	Bupirimate	21.78	208
Dichlorbenzamid-2.6	12.39	173	Flusilazol (LCQ)	21.78	233
Naled	12.42	109	Buprofezin	21.80	105
Methabenzthiazuron	12.42	136	Pyrethrin I a	21.80	123
Terbutylazin-desethyl	12.44	186	DDD-o,p	21.85	235
Monocrotophos	12.50	127	Dieldrin	21.87	79
Cadusaphos	12.50	159	Kresoxim-Methyl	21.96	116
Atrazin-desisopropyl	12.52	173	Diclobutrazol	21.96	270
Tebutam	12.52	91	Carboxin	22.00	143
DMSA	12.54	92	Iprovalicarb 2 (LCQ)	22.09	116
Promecarb	12.57	135	Dimefuron 2	22.09	105
Diallate 1	12.63	86	Chlorfenapyr	22.12	59
Diallate 2	12.63	86	Isoxathion	22.27	105
Phorat	12.68	75	Metamitron	22.27	104

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Pencycuron	12.73	125	Binapacryl	22.29	83
Sulfalat	12.84	188	USL 401	22.36	83
HCH-a	12.95	183	Fluazifop-butyl	22.40	282
Ethoxyquin	13.03	202	Cyproconazol	22.41	139
Thiometon	13.07	88	Cyproconazol	22.47	139
HCB	13.08	284	Dibrombenzophenon-4-4'	22.49	183
Demeton-S	13.18	88	Perthan	22.51	223
Flumethrin	13.21	216	Nitrofen	22.60	283
Pentachloranisol	13.21	237	Endrin	22.70	81
Prosulfuron	13.23	109	Chlorthiophos	22.76	269
Desmedipham	13.24	109	Chlorpropylat	22.80	139
Landrin (Trimetacarb-3.4.5)	13.28	121	Chlorbenzilat	22.83	139
Ethiofencarbsulfone	13.29	107	Flamprop-isopropyl	22.83	105
Dichloran	13.36	124	Metsulfuron-methyl	22.87	215
Dimethoat	13.45	87	PCB 118	22.90	326
Simazin	13.47	201	Carbofenthion-Methyl	22.94	157
Fenpyroximate	13.49	77	Fensulfothion	22.96	97
Carbofuran (LCQ)	13.50	164	Fenthionsulfoxid	22.98	125
Prometon	13.53	58	Nonachlor-cis	23.05	409
Chlorbufam	13.55	53	Ethion	23.07	268
Carbanolat	13.55	121	Fenthionsulfon	23.12	125
Atrazin	13.57	200	Diniconazol (LCQ)	23.14	231
Propazin	13.65	214	Endosulfan-b	23.14	159
Chlorsulfuron	13.65	111	Endosulfanalkohol +	23.19	69
Clomazone	13.70	125	DDD-p,p	23.25	235
Dazomet	13.70	89	Triamiphos	23.32	160
HCH-b	13.71	109	DDT-o,p	23.34	235
Profluralin	13.73	55	Pyrethrin I b	23.34	123
Flurenol	13.76	180	Pyrethrin I c	23.34	123
Aminocarb	13.81	151	Oxadixyl	23.39	132
PCP	13.82	266	Fluazinam 2	23.41	387
Dioxathion	13.86	97	PCB 153	23.56	360
Propetamophos	13.86	138	Thifensulfuron-Methyl	23.57	221
Propyzamid	13.95	142	Aclonifen	23.67	77
Terbuphos	13.95	57	Mepronil	23.72	119
Terbutylazin	13.99	214	Endrinaldehyd	23.72	67
Lindan	14.00	181	Triazophos	23.81	161
Cyromazine (LCQ)	14.08	151	Tetrasul	23.81	252
Benazolin	14.10	170	Sulprofos	23.85	156
Tetrachloranilin-2.3.4.5	14.13	231	Chlordecon	23.97	178
Fonofos	14.17	109	Ofurace	24.05	132
Phosphamidon 1	14.20	127	Carfentrazon-Ethyl	24.05	312
Quintozen	14.22	173	Isoxadifen-ethyl	24.08	165
Diazinon	14.22	137	Benalaxyl	24.14	148
Dinoterb	14.22	225	Trifloxystrobin	24.21	116
Pyrimethanil	14.39	198	Carbofenthion-Ethyl	24.26	97
Tefluthrin	14.48	177	Lenacil	24.26	153
Chloranil +	14.48	248	Cyanophenphos	24.35	141
Flzasulfuron	14.50	231	Norflurazon	24.39	145
Disulfoton	14.55	88	Propiconazol 1	24.43	69
Dinoseb	14.55	211	Edifenphos	24.45	109
Isazofos	14.59	161	Quinoxifen	24.52	237

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Aziprotryne	14.61	139	PCB 138	24.63	360
Paraoxon-M	14.66	109	Endosulfansulfate	24.68	272
Dichlone	14.66	191	Propiconazol 2	24.68	69
Chlorthalonil	14.70	266	DDT-p,p	24.77	235
Ethrimphos	14.70	153	Fenhexamid	24.77	97
Secbumeton	14.70	196	Clodinafop-propagylester	24.93	238
Chlorden-tr. (niet zur Berechnung !!!)	14.72	66	Chloridazon	24.97	77
Fenfuram	14.79	109	Hexazinon	25.03	171
Triallat	14.83	86	Propagite 1	25.26	135
Moschusambrett	14.86	253	Nuarimol	25.28	107
HCH-d	14.92	181	Diclofop-methyl	25.28	120
Flufenoxuron (GC +LCQ)	15.01	126	Tebuconazol	25.31	125
Sebutylazin	15.05	200	Diflufenican	25.31	266
Bromocyclen	15.09	359	Propagite 2	25.33	135
Oxabetrinil	15.14	73	Fluotrimazol	25.35	165
Pirimicarb (LCQ)	15.18	72	Dicofol	25.40	139
Silthiofam	15.20	252	Dicofol-2.4	25.40	139
Furmecycloz	15.27	123	Haloxyfop-ethoxyethylster	25.45	302
HCH-e	15.29	181	Piperonylbutoxid	25.51	176
Moschusxylool	15.34	282	Bioresmethrin	25.60	123
Formothion	15.36	93	Resmethrin 1	25.61	123
Ethiofencarb (LCQ)	15.40	107	Resmethrin 2	25.61	123
Pirimicarb-desmethyl	15.45	72	TPP	25.63	326
Pentachloranilin	15.54	265	Captafol	25.74	79
Phosphamidon 2	15.56	127	USL 402	25.85	83
Dichlofenthion	15.64	97	Mefenpyr-diethyl	25.86	253
Benfuresate	15.64	163	Zoxamide 2	25.88	187
Desmetryn	15.69	213	Epoxiconazol (LCQ)	25.92	192
Dimethenamid	15.69	154	Pyridaphenthion	26.31	199
Dimethachlor	15.69	134	Phosmet-oxon	26.38	160
Propanil	15.78	161	Iprodion	26.50	314
Chlorthiamid	15.87	170	Bromuconazol 1	26.61	173
Metribuzin	15.95	198	Endrin-keeton	26.66	67
PCB 31	15.97	256	Bifenthrin	26.71	181
PCB 28	15.99	256	EPN	26.75	157
Spiroxamin 1 (GC +LCQ)	16.02	100	Tetramethrin 1	26.77	164
Malaoxon	16.06	125	Tetramethrin 2	26.77	164
Tolcophos-Methyl	16.08	127	Picolinafen	26.77	238
Alachlor	16.15	160	Fenoxycarb (LCQ)	26.86	116
Vinclozolin	16.17	212	Cloquintocet-1-methylhexylester	26.93	192
Parathion-Methyl	16.17	109	Phosmet	26.94	183
Simetryn	16.30	213	Fenpiclonil	26.98	236
Chlorpyriphos-M	16.34	265	Tebuconazol (LCQ)	27.02	227
Cymiazol	16.34	119	Fenproprathrin	27.02	97
Ametryn	16.41	227	Phenkapton	27.02	121
Fenchlorphos	16.43	144	Fenamidone	27.18	238
Fuberidazole	16.43	184	Cycloxydim 1	27.18	136
Prometryn (GC +LCQ)	16.51	184	Bifenazate	27.21	199
Heptachlor	16.51	100	Methoxychlor	27.26	171
Metalaxyl-M	16.51	160	PCB 180	27.30	394
Carbaryl (LCQ)	16.53	285	Rimsulfuron	27.30	231
Metalaxyl	16.55	160	Bifenox	27.48	341

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Chlorden-cis	16.60	230 Fenazaquin (LCQ)	27.49	145
Acibenzolar-s-methyl	16.64	182 Metconazole	27.55	125
Paraoxon-E	16.73	109 Phenothrin 1	27.55	123
Triasulfuron	16.73	140 Bromuconazol 2	27.57	173
Prosulfocarb (LCQ)	16.79	128 Furathiocarb	27.64	135
S421	16.81	79 Phenothrin 2	27.81	123
Fenpropidin	16.90	98 Tetradifon	27.97	159
Methiocarbsulfon	16.92	121 Brompropylat	28.01	160
Oxychlorden	16.96	81 Triticonazole	28.19	83
Spiroxamin 2 (GC+LCQ)	16.99	100 Leptophos	28.22	171
Terbutryn	16.99	185 USL 403	28.22	83
Orbencarb	16.99	100 Flurtamone	28.24	120
Pirimiphos-Methyl	17.01	290 Amitraz	28.33	132
Demeton-s-methylsufon	17.05	169 Phosalon	28.35	182
Fenitrothion	17.07	125 Pyriproxyfen	28.51	136
Ethofumesat	17.09	161 Azinphos-Methyl	28.61	77
Methiocarbsulfoxid	17.11	107 Cyhalothrin-lambda	28.93	181
Methiocarb	17.12	168 Acrinathrin	29.05	93
PCB 52	17.22	292 TriFenmorph	29.08	243
Bromacil	17.31	205 Mirex	29.19	272
Malathion	17.46	127 Pyrazophos	29.23	221
Amidithion	17.46	131 Fluroglycofen-Ethyl	29.29	223
Phoratsulfoxid	17.48	97 Fluroglycofen-ethyl	29.32	75
Dichlofluanid	17.50	123 Benfuracarb	29.43	190
Moschusketon	17.54	279 Fenarimol	29.53	139
Metolachlor	17.55	162 Metrafenone	29.55	393
Diethiofencarb (LCQ)	17.61	124 Dialiphos	29.70	208
Quinoclamine	17.65	172 Azinphos-E	29.77	77
Phorat-sulfone	17.68	97 Fenoxaprop-Ethyl	29.96	288
Thiobencarb	17.68	100 Bitertanol	30.37	170
Chlorpyriphos-E	17.76	97 Spirodiclofen	30.37	71
Fenpropimorph	17.76	128 Permethrin 1	30.44	183
Fenthion	17.80	278 Cycloxydim 2	30.67	178
Chlorthaldimethyl	17.82	301 Permethrin 2	30.71	183
Isoxaben	17.82	163 Coumaphos	30.77	109
Asulam +	17.82	172 Pyridaben	30.80	147
Flufenacet	17.83	151 Fluquinconazol	30.82	340
Aldrin	17.85	66 Prochloraz	30.91	70
Isophenphos-oxon	17.93	229 Temephos	30.94	356
Cyanazin	17.93	225 Imazaquin 1	31.03	224
Tetraconazol	17.98	336 Warfarin +	31.19	265
Isocarbophos	18.02	120 Fentinhydroxid	31.50	120
Parathion-E	18.08	109 Cyfluthrin 1	31.55	163
Isoxaflutole	18.15	160 Fenbuconazol (LCQ)	31.62	129
Difenoxuron	18.17	241 Clotrimazole	31.67	165
Triademefon	18.19	57 Cyfluthrin 2	31.77	163
Butralin	18.25	266 Cyfluthrin 3	31.89	163
Flurochloridon	18.26	174 Cyfluthrin 4	31.97	163
Trichloronat	18.26	109 Imazaquin 2	32.16	224
Dichlorbenzophenon-4.4'	18.26	139 Cypermethrin 1	32.23	163
Crufomate	18.30	182 Cypermethrin 2	32.44	163
Anilazin	18.32	239 Boscalid (Nicobifen)	32.47	140

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Isobenzan	18.32	103	Flucytrinate 1	32.56	157
Pirimiphos-Ethyl	18.34	333	Cypermethrin 3	32.58	163
Imazethapyr	18.43	133	Quizalofop-Ethyl	32.63	299
Cinosulfuron	18.47	59	Cypermethrin 4	32.65	163
Bromophos-M	18.49	331	Etofenprox	32.92	163
Bentazon	18.49	119	Flucytrinate 2	32.99	157
Fenson	18.51	77	Prothioconazole	33.61	304
Diphenamid	18.51	72	Thiacloprid (LCQ)	34.00	101
Carbetamide	18.56	119	Pyridate	34.06	57
Isophenphos-Methyl	18.56	58	Fenvalerat	34.12	125
Fosthiazate 1	18.64	195	Flumioxazin	34.19	354
Octachlorstyrol	18.73	343	Fluvalinat-tau 1	34.33	250
Captan	18.77	79	Pyraclostrobin	34.42	132
Thiametoxam	18.83	182	Pyraclostrobin	34.42	132
Fosthiazate 2	18.85	195	Fluvalinat-tau 2	34.49	250
Pendimethalin	18.88	252	Esvenvalerat	34.76	125
Fluazinam 1	18.90	418	Sulfosulfuron	34.77	270
Cyprodinil	18.96	224	Difenconazol 1	35.14	265
Fipronil	18.96	367	Difenconazol 2	35.26	265
Isodrin	19.00	193	Tralomethrin 1	35.32	181
Metazachlor	19.00	133	Indoxacarb (LCQ)	35.41	59
Chlozolinate	19.15	188	Tralomethrin 2	35.74	181
Dimefuron 1	19.15	166	Deltamethrin	35.90	181
Isophenphos	19.16	58	Azoxystrobin	36.33	344
			Dimethomorph 1	36.42	165
			Famoxadone (LCQ)	36.55	330
			Dimethomorph 2	37.06	301