Dual layer injection

A way to improve the sensitivity of GC-amenable compounds

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1. Aim and scope

This document reports the use of dual layer injection as a simple way to improve the sensitivity of GC-amenable compounds in the analysis of clean matrices. The dual layer injection mode is available in the acquisition software of most chromatographic instruments and provides an improvement in both intensity and peak shape of a number of troublesome compounds.

2. Short description

In gas chromatography, samples are typically injected in liquid state and turned into gas state in the injector. With very few exceptions, such as the on-column injection, the evaporation takes place inside of the liner. However, the glass that constitutes these devices possesses active sites in which some sample components, including the analytes, can be retained.

When a clean sample –with few matrix components– is injected on a GC instrument, analytes will be retained in the injector at a higher proportion than those retained when injecting a complex matrix. This results in a loss of sensitivity and peak broadening for some compounds, whereas with complex matrices there is an enhancement in the signals and an improvement of the peak shapes. This is the main cause of the matrix effect in gas chromatography, and the lower sensitivities achieved in the analysis of clean matrices.

Dual layer injection mode allows to inject a certain amount of a different blank matrix together with all samples analyzed. The constituents of this blank matrix occupy the active sites of the injector, thus allowing more analytes from the sample to reach the detector. Consequently, higher sensitivities and narrower peaks are achieved with no need of additional experimental steps.

3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes from 1 µL to 5 mL
- Graduated 10 mL pipette
- 50 mL and 15 mL PTFE centrifuge tubes
- Vortex Shaker IKATM 4 Basic
- Axial shaker Agytax SR1 CP57
- Centrifuge Orto Alresa Consul 21, suitable for the centrifuge tubes employed in the procedure and capable of achieving 4000 rpm
- Concentration workstation
- Injection vials, 2 mL, suitable for LC and GC auto-sampler
- Amber vials, 7 mL

4. Chemicals

- Acetonitrile ultra-gradient grade
- Trisodium citrate dihydrate
- Disodium hydrogenocitrate sesquihydrate
- Sodium chloride
- Anhydrous magnesium sulphate
- Primary secondary amine (PSA)
- Ammonium formate
- Formic acid
- Ethyl acetate
- Pesticide analytical standards

5. Procedure

5.1. Extraction procedure

Blank samples of tomato, orange, onion, pepper and strawberry were extracted using the QuEChERS method [1], as detailed below:

1. Weigh 5 g of homogenate sample (after cryogenic milling) in a 50-mL PTFE centrifuge tube.
2. Add 5 mL of water, shake and let it sit for 30 min.
3. Add 10 mL acetonitrile.
4. Shake the samples in an Agitax axial extractor for 4 min.
5. Add 4 g anhydrous magnesium sulphate, 1 g sodium chloride, 1 g trisodium citrate dihydrate and 0.5 g disodium hydrogencitrate sesquihydrate.
6. Shake the samples in an Agitax axial extractor for 4 min.
7. Centrifuge at 4000 rpm for 5 min.
8. Transfer a 5-mL aliquot of the supernatant to a 15 mL PTFE tube containing 750 mg anhydrous magnesium sulphate, 125 mg PSA and 125 mg C18.
9. Vortex the tubes for 30 sec.
10. Centrifuge at 4000 rpm for 5 min.
11. Acidify with 10 µL formic acid 5 % per mL of extract.

5.2. Vial preparation

Individual pesticide stock solutions (concentrations ranging from 1000 to 2000 mg/L) were prepared in acetonitrile or ethyl acetate and were stored in screw-capped glass vials in the dark at -20 °C. These solutions were employed for the preparation of standard mixes (10 mg/L in acetonitrile), which were subsequently diluted with ethyl

acetate to different concentrations included in the calibration curve: 0.100, 0.050, 0.010, 0.005, 0.002 and 0.001 mg/L.

All sample extracts were evaporated and reconstituted with ethyl acetate prior to the injection in the GC instrument. The tomato samples were also employed to prepare a matrix-matched calibration curve with the concentrations indicated above.

5.3. Methodology

The GC instrument was operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target analytes. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimized SRM transitions (SRM2/SRM1) were used, along with retention time matching. The mass transitions used are presented in Appendix.

5.4. Instrumentation and analytical conditions for the GC- MS/MS system

5.4.1. Intuvo 9000 GC system (Agilent)

- Column: 2 Planar columns HP-5MS UI (15 m long × 0.25 mm i.d. × 0.25 µm film thickness)
- Injection mode: Splitless
- Ultra-inert inlet liner with a glass wool frit from Agilent
- Sample injection volume: 1 µL
- Injection type: reversed dual layer injection (L1 volume 1 µL, L2 volume 1 µL, air gaps 0.2 µL.
- Injector temperature: 80 °C hold for 0.1 min, then up to 300 °C at 600 °C/min, hold for 5 min and then to 250 °C at 100 °C/min.
- Carrier gas: Helium at constant flow = 1.28 mL/min column 1, 1.48 mL/min column 2.
- Carrier gas purity: 99.999 %
- Oven temperature: 60 °C for 0.5 min, up to 170 °C at 80 °C/min, and up to 310 °C at 20 °C/min.

5.6.2. 7410 triple quadrupole system (Agilent)

- Ionisation mode: electron impact ionisation
- Temperature of the transfer line: 280 °C
- Temperature of ion source: 280 °C
- Collision gas: nitrogen
- Collision gas purity: 99.999 %
- Solvent delay: 2.6 minutes

6. Results

6.1. Sensitivity and peak shapes

A 0.100 mg/L standard mix containing 209 GC-amenable compounds in tomato matrix was injected twice onto the GC instrument, using firstly the regular injection (1 µL sample, 0.2 µL air gap) and secondly the dual layer injection with orange matrix (1 µL sample, 0.2 µL air gap, 1 µL blank orange matrix, 0.2 µL air gap). **Table 1** shows the relative abundance of the 209 compounds injected with the dual layer mode over the regular mode, expressed as percentages. Values over 100 % imply an increase in the sensitivity. As can be seen, the vast majority of compounds undergo a noticeable increase in their sensitivity, with signals which in some cases are twice as intense as in the regular intense (values over 200 %).

Table 1. Sensitivity of 209 compounds in dual layer injection over regular injection at 0.100 mg/L (expressed as %)

2,4'-DDE	124	Fenarimol	128	Permethrin	150
2-Phenylphenol	138	Fenazaquin	129	Phenothrin	152
4,4'-DDD	136	Fenbuconazole	145	Phenthoate	158
4,4'-DDE	126	Fenchlorphos	135	Phorate	134
4,4'-DDT	215	Fenhexamid	254	Phosmet	274
Acrinathrin	162	Fenitrothion	217	Picolinafen	163
Alachlor	133	Fenpropathrin	144	Picoxystrobin	149
Ametryn	136	Fenpropimorph	103	Pirimicarb	90
Anthraquinone	177	Fenthion	122	Pirimiphos-methyl	130
Atrazine	131	Fenvalerate	134	Procymidone	133
Azoxystrobin	123	Fipronil	232	Profenofos	187
Benalaxyl	136	Flamprop-isopropyl	148	Prometon	134
Bifenox	179	Flamprop-methyl	145	Prometryn	137
Bifenthrin	142	Fluacrypyrim	149	Propaphos	165
Biphenyl	123	Fluazifop-p-butyl	163	Propazine	125
Bixafen	155	Flucythrinate	149	Propiconazole	156
Boscalid	131	Fludioxonil	204	Propyzamide	144
Bromopropylate	167	Fluensulfone	126	Prothiofos	139
Bupirimate	85	Fluopicolide	143	Pyraclostrobin	348
Buprofezin	121	Fluopyram	175	Pyrazophos	174
Butralin	186	Fluquinconazole	133	Pyridaben	155
Butylate	130	Flusilazole	155	Pyrifenox II	184
Cadusafos	142	Flutolanil	169	Pyrimethanil	149
Carbophenothion	180	Flutriafol	164	Pyriofenone	139
Chinomethionate	146	Fonofos	126	Pyriproxyfen	156
Chlorbromuron	112	Formothion	186	Quinalphos	154
Chlordane	116	Fosthiazate	263	Quinoxyfen	126
Chlorfenapyr	148	HCB	111	Quintozene	143
Chlorfenvinphos	168	Heptachlor	138	Secbumeton	128
Chlorfluazuron	50	Heptenophos	146	Spirodiclofen	140
Chlorobenzilate	147	Hexaconazole	154	Spiromesifen	134
Chlorothalonil	190	Indoxacarb	113	Sulfotep	126
Chlorpropham	152	Iprodione	242	Sulprofos	113
Chlorpyrifos	138	Iprovalicarb	214	Tau-fluvalinate	128
Chlorpyrifos-methyl	137	Isazofos	129	Tebuconazole	150
Chlorthal-dimethyl	121	Isofenphos	143	Tebufenpyrad	154
Chlozolinate	132	Isofenphos-methyl	142	Tecnazene	131
Coumaphos	204	Isoprothiolane	148	Tefluthrin	130

Cyfluthrin	154	Isopyrazam	159	Terbufos	151
Cypermethrin	144	Kresoxim-methyl	147	Terbumeton	122
Cyproconazole	166	Lambda-Cyhalothrin	149	Terbutryn	134
Cyprodinil	149	Lindane	123	Tetrachlorvinphos	218
Deltamethrin	140	Malathion	163	Tetraconazole	151
Diazinon	131	Malathion-d10	164	Tetradifon	132
Dichlofluanid	170	Mecarbam	169	Tetramethrin	158
Dichloran	168	Mepanipyrim	172	Thiobencarb	145
Dichlorvos	144	Merphos	178	Tolclofos-methyl	131
Dichlorvos-d6	145	Metalaxyl	136	Tolylfluanid	195
Diclobutrazol	192	Metazachlor	152	Triadimefon	151
Dicofol, o, p'-	170	Metconazole	152	Triallate	128
Dicofol, p, p'-	155	Methidathion	187	Triazophos	194
Dieldrin	121	Methiocarb	214	Trifloxystrobin	157
Diethofencarb	47	Methoxychlor, o,p'-	106	Trifluralin	148
Dimethenamid	131	Methoxychlor, p,p'-	269	Triphenyl phosphate	140
Dimethipin	133	Metolachlor	139	Vinclozolin	117
Diphenylamine	105	Mevinphos	155	Aldrin	119
Dodemorph	129	Molinate	131	Dichlorobenzophenone, 4,4'-	151
Endosulfan sulfate	116	Myclobutanil	150	Disulfoton-sulfoxide	115
Endosulfan-alpha	117	Napropamide	149	Fipronil sulfone	191
Endosulfan-beta	126	Novaluron	111	Fipronil-desulfinil	149
Endrin	158	Nuarimol	126	HCH-alpha	115
EPN	198	Ofurace	132	HCH-beta	124
Epoxiconazole	174	Oxadixyl	160	Heptachlor endo-epoxide	118
Ethion	164	Paclobutrazol	197	Heptachlor exo-epoxide	118
Ethofumesate	138	Parathion	212	Malaoxon	238
Ethoprophos	157	Parathion-methyl	223	Paraoxon-methyl	338
Ethoxyquin	108	Pebulate	140	Pentachloroaniline	120
Etofenprox	140	Penconazole	145	Phorate sulfone	172
Etrimfos	134	Pendimethalin	191	Tetrahydrophthalimide	108
Fenamidone	147	Penthiopyrad	175		

Only three pesticide residues were negatively affected by the dual layer injection in terms of intensity: bupirimate, chlorfluazuron and diethofencarb, with represent 1.4 % of the compounds included in the study.

Additionally, the use of dual layer injection provides a significant improvement of the peak shapes in analytes that typically produce broad signals in clean matrices. This is the case of compounds such as of chlorpropham, fludioxonil, phosmet and tetrahydrophthalimide, among others (**figure 1**).

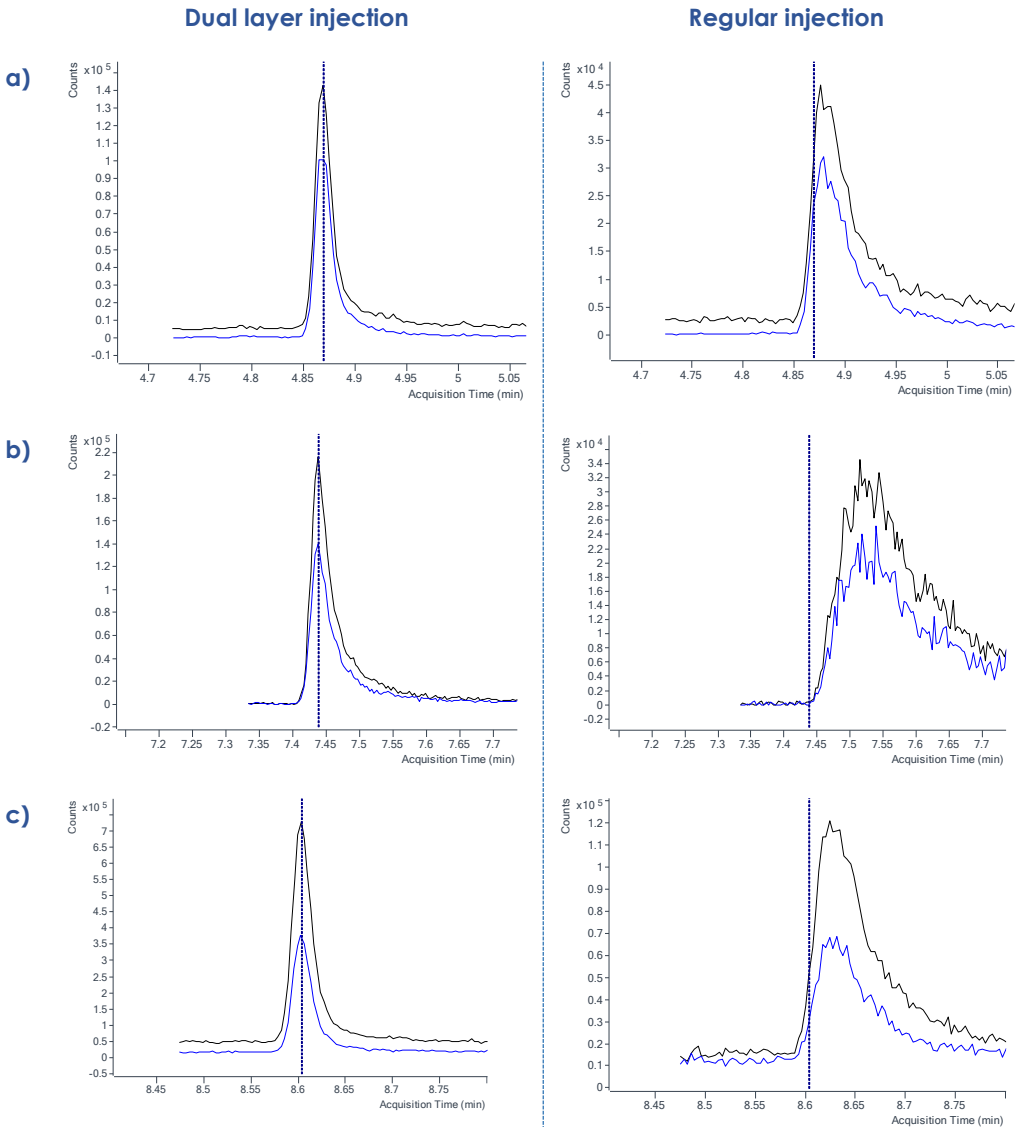

Figure 1. Chromatograms at 0.010 mg/L of **a)** chlorpropham; **b)** fludioxonil; **c)** phosmet when injected with dual layer injection type (left) and regular injection (right) in a tomato sample

6.2. Interferences and mixed blank matrices

The main disadvantage associated to the use of dual layer injection is the presence of interferences in the chromatograms. Complex matrices possess a higher number of components that coelute with the analytes and result in interfering signals that affect the identification of compounds, especially at low concentration levels.

A different approach can be adopted to overcome this situation. If a mixture of blank matrices is injected onto the instrument, the interferences caused by each one of them are diluted and their effect is less significant. With this purpose, four different blank matrices including orange, onion, pepper and strawberry were mixed at the same proportion in one vial and used for the dual layer injection. The total blank matrix volume was kept in 1 µL; thus, the total amount of each blank matrix was 0.25 µL (**figure 2**).

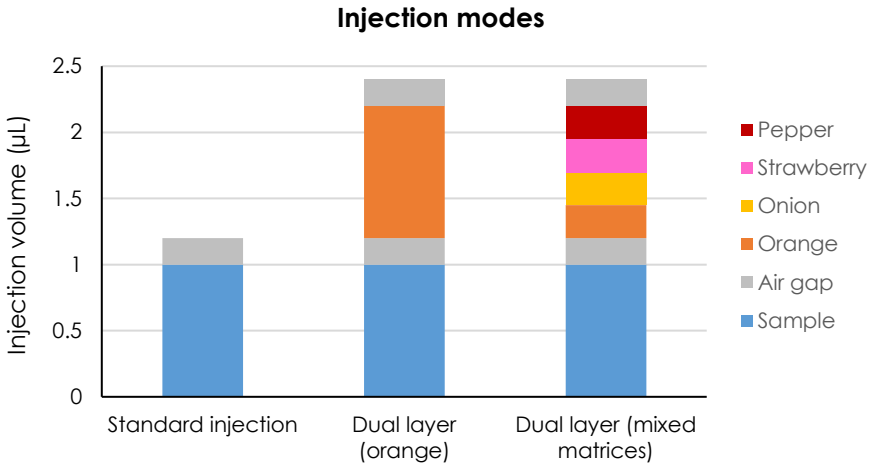

Figure 2. Volume and composition of the different injections tested

With this new strategy, the contribution of each blank matrix undergoes a 4-fold decrease. Therefore, the improvement in sensitivity and peak shapes is maintained (as there are still matrix components that occupy the active sites in the injector, allowing the analytes to reach the detector), but the effect of the interferences is 4 times less intense (as the matrices originating these effects are diluted). In **figure 3**, this effect is illustrated in the case of tecnazene at 0.002 mg/L. In this example, the compound underwent an increase in sensitivity of 1.4 (as can be observed in the scaled chromatograms **3a** and **3c**).

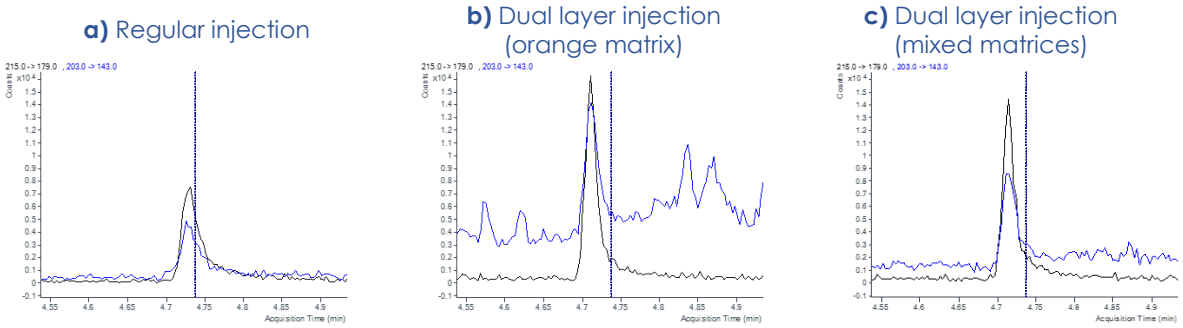

Figure 3. Scaled chromatograms of tecnazene at 0.002 mg/L in a tomato sample when using **a)** regular injection, **b)** dual layer injection with orange blank matrix and **c)** dual layer injection with a mixture of orange, onion, pepper and strawberry.

7. References

[1] Anastassiades, M.; Lehotay, S.; Štajnbaher, D.; Schenck, F. Fast And Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning And "Dispersive Solid-Phase Extraction" For The Determination Of Pesticide Residues In Produce. Journal of AOAC INTERNATIONAL 2003, 86 (2), 412-431.

APPENDIX : MASS TRANSITIONS

Table A1. Acquisition and chromatographic parameters for the compounds analyzed by GC-MS/MS.

Name	tR (min)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)
2,4'-DDE	7.24	246.0	211.0	20	246.0	176.0	30
2-phenylphenol	4.42	170.0	141.0	30	170.0	115.0	40
4,4'-DDD	7.95	235.0	199.0	15	235.0	165.0	20
4,4'-DDE	7.53	246.0	211.0	20	246.0	176.0	30
4,4'-DDT	8.30	235.0	199.0	20	235.0	165.0	20
Acrinathrin	9.31	289.0	93.0	5	208.0	181.0	5
Alachlor	6.24	188.0	160.0	10	188.0	130.0	40
Aldrin	6.48	293.0	257.0	8	293.0	186.0	40
Ametryn	6.24	227.0	212.0	8	227.0	185.0	5
Anthraquinone	6.69	208.0	180.0	5	208.0	152.0	20
Atrazine	5.49	215.0	173.0	5	215.0	58.0	10
Azoxystrobin	11.98	344.0	329.0	10	344.0	156.0	40
Benalaxyl	8.21	204.0	176.0	2	148.0	105.0	20
Bifenox	8.94	311.0	279.0	14	311.0	216.0	25
Bifenthrin	8.72	181.0	166.0	10	181.0	115.0	50
Biphenyl	3.96	154.0	126.0	40	154.0	102.0	40
Bixafen	10.69	413.0	159.0	12	159.0	139.0	15
Boscalid	10.43	140.0	112.0	10	140.0	76.0	25
Bromopropylate	8.77	341.0	185.0	20	341.0	155.0	20
Bupirimate	7.62	273.0	193.0	5	273.0	108.0	15
Buprofezin	7.61	305.0	172.0	5	172.0	57.0	15
Butralin	6.76	266.0	190.0	12	266.0	174.0	20
Butylate	4.08	156.0	57.0	5	146.0	57.0	10
Cadusafos	5.20	159.0	131.0	5	158.8	97.0	15
Carbophenothion	8.19	342.0	157.0	10	199.0	143.0	10
Carbosulfan	8.54	160.0	104.0	5	118.0	76.0	5
Chinomethionate	7.30	234.0	206.0	10	206.0	148.0	15
Chlorbromuron	4.06	233.0	205.0	12	233.0	124.0	25
Chlordane	7.29	373.0	301.0	10	373.0	266.0	20
Chlorfenapyr	7.76	247.0	227.0	15	247.0	200.0	25
Chlorfenvinphos	7.02	294.9	266.9	5	267.0	81.0	40

Chlorfluazuron	7.36	321.0	304.0	30	321.0	286.0	30
Chlorobenzilate	7.83	139.0	111.0	15	139.0	75.0	30
Chlorothalonil	5.93	266.0	231.0	20	266.0	133.0	40
Chlorpropham	5.02	213.0	171.0	5	213.0	127.0	5
Chlorpyrifos	6.62	314.0	286.0	5	314.0	258.0	15
Chlorpyrifos-methyl	6.18	288.0	93.0	26	286.0	271.0	16
Chlorthal-dimethyl	6.68	330.0	299.0	12	330.0	221.0	35
Chlozolinate	6.96	331.0	216.0	5	259.0	188.0	10
Coumaphos	9.90	362.0	226.0	10	362.0	109.0	15
Cyfluthrin	10.10	226.0	206.0	10	163.0	127.0	5
Cypermethrin	10.32	165.0	127.0	5	163.0	127.0	5
Cyproconazole	7.80	222.0	125.0	18	139.0	111.0	14
Cyprodinil	6.88	224.0	208.0	20	224.0	197.0	21
Deltamethrin	11.63	253.0	172.0	5	253.0	93.0	20
Diazinon	5.67	304.0	179.0	15	137.0	84.0	15
Dichlofluanid	6.53	224.0	123.0	8	167.0	124.0	5
Dichloran	5.50	206.0	176.0	5	206.0	124.0	25
Dichlorobenzophenone	6.57	250.0	139.0	8	139.0	111.0	10
Dichlorvos	3.44	185.0	109.0	15	185.0	93.0	15
Dichlorvos-D_6	3.43	191.0	115.0	20	191.0	99.0	15
Diclobutrazol	7.68	270.0	201.0	8	270.0	159.0	15
Dicofol, o, p'-	8.42	251.0	139.0	15	139.0	111.0	15
Dicofol, p, p'-	7.83	251.0	139.0	15	139.0	111.0	15
Dieldrin	7.62	345.0	263.0	8	279.0	243.0	8
Diethofencarb	6.52	207.0	151.0	10	151.0	123.0	10
Dimethenamid	6.12	232.1	154.0	5	230.0	154.0	10
Dimethipin	5.54	124.0	76.0	5	118.0	58.0	10
Diphenylamine	4.96	169.0	77.0	35	168.0	140.0	40
Disulfoton-sulfoxide	3.69	153.0	97.0	10	125.0	97.0	3
Dodemorph	6.77	281.0	154.0	15	154.0	82.0	20
Endosulfan sulfate	8.33	387.0	289.0	5	272.0	237.0	15
Endosulfan-alpha	7.37	241.0	206.0	10	195.0	160.0	5
Endosulfan-beta	7.93	240.9	205.9	10	207.0	172.0	15
Endrin	7.84	263.0	193.0	35	245.0	173.0	30
EPN	8.79	157.0	110.0	15	157.0	77.0	25
Epoxiconazole	8.61	192.0	138.0	10	192.0	111.0	35
Ethion	7.95	231.0	175.0	5	231.0	129.0	25
Ethofumesate	6.44	207.0	161.0	5	207.0	137.0	10

Ethoprophos	4.96	158.0	114.0	5	158.0	97.0	15
Ethoxyquin	5.229	202.0	174.0	15	202.0	145.0	30
Etofenprox	10.47	163.0	135.0	5	163.0	107.0	15
Etrimfos	5.83	292.0	181.0	5	292.0	153.0	20
Fenamidone	8.90	268.0	180.0	20	238.0	103.0	20
Fenarimol	9.44	219.0	107.0	10	139.0	111.0	15
Fenazaquin	8.92	160.0	145.0	5	145.0	117.0	10
Fenbuconazole	10.18	198.0	129.0	5	129.0	102.0	15
Fenchlorphos	6.32	285.0	270.0	15	285.0	240.0	30
Fenhexamid	8.33	177.0	113.0	10	177.0	78.0	20
Fenitrothion	6.44	277.0	260.0	5	277.0	109.0	20
Fenpropathrin	8.81	265.0	210.0	10	265.0	89.0	30
Fenpropimorph	6.58	128.0	110.0	10	128.0	70.0	12
Fenthion	6.61	278.0	169.0	20	278.0	109.0	20
Fenvalerate	10.98	167.0	125.0	12	125.0	89.0	20
Fipronil	7.04	369.0	215.0	30	367.0	213.0	30
Fipronil-sulfone	7.57	452.0	383.0	8	383.0	255.0	20
Fipronil-desulfinil	6.13	388.0	333.0	20	333.0	281.0	15
Flamprop-isopropyl	7.88	276.0	105.0	5	276.0	77.0	40
Flamprop-methyl	7.58	276.0	105.0	8	230.0	170.0	15
Fluacrypyrim	8.00	320.0	183.0	10	145.0	102.0	30
Fluazifop-p-butyl	7.70	282.0	238.0	20	282.0	91.0	15
Flucythrinate	10.42	199.0	157.0	5	157.0	107.0	15
Fludioxonil	7.62	248.0	154.0	25	248.0	127.0	30
Fluensulfone	4.64	226.0	206.0	20	119.0	92.0	10
Fluopicolide	8.33	209.0	182.0	20	173.0	109.0	25
Fluopyram	7.00	223.0	196.0	15	173.0	145.0	15
Fluquinconazole	9.89	340.0	298.0	20	340.0	286.0	30
Flusilazole	7.62	233.0	165.0	20	233.0	152.0	20
Flutolanil	7.41	323.0	281.0	5	323.0	173.0	15
Flutriafol	7.40	219.0	123.0	12	219.0	95.0	20
Fluvalinate-tau	11.11	250.0	200.0	20	250.0	55.0	15
Fonofos	5.68	246.0	137.0	5	137.0	109.0	5
Formothion	6.00	224.0	125.0	20	170.0	93.0	5
Fosthiazate	6.83	195.0	139.0	5	195.0	103.0	5
HCB	5.42	284.0	249.0	25	284.0	214.0	40
HCH-alpha	5.22	219.0	183.0	5	219.0	145.0	25
HCH-beta	5.51	219.0	183.0	5	219.0	145.0	25

Heptachlor	6.30	272.0	237.0	10	272.0	143.0	40
Heptachlor endo-epoxide	6.89	183.0	155.0	15	183.0	119.0	30
Heptachlor exo-epoxide	6.85	217.0	182.0	22	183.0	119.0	25
Heptenophos	4.71	126.0	89.0	10	124.0	89.0	15
Hexaconazole	7.46	214.0	172.0	20	214.0	159.0	20
Indoxacarb	11.53	264.0	148.0	25	203.0	134.0	10
Iprodione	8.59	244.0	187.0	5	187.0	124.0	25
Iprovalicarb	7.52	158.0	116.0	5	158.0	98.0	10
Isazofos	5.82	257.0	162.0	5	161.0	119.0	5
Isofenphos	7.00	213.0	185.0	3	213.0	121.0	15
Isofenphos-methyl	6.87	199.0	167.0	10	199.0	121.0	10
Isoprothiolane	7.47	162.0	134.0	5	162.0	85.0	15
Isopyrazam	9.55	359.0	303.0	8	159.0	139.0	10
Kresoxim-methyl	7.61	206.0	131.0	10	206.0	116.0	5
Lambda-Cyhalothrin	9.25	197.0	161.0	5	197.0	141.0	10
Lindane	5.64	219.0	183.0	5	219.0	145.0	25
Lindane-D_6	5.61	224.0	187.0	5	224.0	150.0	20
Malaoxon	5.99	195.0	125.0	15	127.0	99.0	5
Malathion	6.49	173.0	99.0	15	158.0	125.0	8
Malathion-D_{10}	6.45	183.0	151.0	3	183.0	132.0	5
Mecarbam	7.00	329.0	160.0	3	131.0	74.0	15
Mepanipyrim	7.31	222.0	207.0	30	222.0	158.0	30
Merphos	7.51	169.0	113.0	3	169.0	57.0	8
Metalaxyl	6.29	206.0	162.0	8	206.0	132.0	20
Metazachlor	6.96	209.0	133.0	10	133.0	117.0	25
Metconazole	8.98	125.0	99.0	20	125.0	89.0	20
Methidathion	7.22	145.0	85.0	5	145.0	58.0	15
Methiocarb	6.44	168.0	153.0	10	153.0	109.0	10
Methoxychlor, o,p'-	8.42	227.0	169.0	25	227.0	115.0	40
Methoxychlor, p,p'-	8.82	227.0	169.0	25	227.0	115.0	40
Metolachlor	6.60	238.0	162.0	8	162.0	133.0	10
Mevinphos	4.08	127.0	109.0	10	127.0	95.0	15
Molinate	4.58	187.0	126.0	3	126.0	55.0	12
Myclobutanil	7.62	179.0	152.0	5	179.0	125.0	10
Napropamide	7.43	271.0	128.0	3	128.0	72.0	3
Novaluron	3.49	335.0	168.0	35	168.0	139.9	10
Nuarimol	8.46	235.0	139.0	12	203.0	107.0	10
Ofurace	7.95	232.0	186.0	5	232.0	158.0	20

Oxadixyl	8.00	163.0	132.0	15	163.0	117.0	25
Paclobutrazol	7.28	236.0	132.0	15	236.0	125.0	10
Paraoxon-methyl	5.69	230.0	200.0	5	230.0	136.0	5
Parathion	6.64	291.0	109.0	10	139.0	109.0	10
Parathion-methyl	6.20	263.0	109.0	10	233.0	124.0	10
Pebulate	4.20	161.0	128.0	3	128.0	57.0	5
Penconazole	6.97	248.0	192.0	15	248.0	157.0	25
Pendimethalin	6.93	252.0	191.0	10	252.0	162.0	10
Pentachloroaniline	5.96	263.0	227.0	15	263.0	192.0	25
Penthiopyrad	7.94	302.0	177.0	20	177.0	101.0	20
Permethrin	9.69	183.0	153.0	15	163.0	127.0	5
Phenothrin	8.98	183.0	168.0	15	183.0	153.0	15
Phenthoate	7.05	274.0	246.0	5	274.0	121.0	10
Phorate	5.24	231.0	175.0	20	231.0	129.0	20
Phorate-sulfone	6.46	199.0	143.0	8	153.0	97.0	10
Phosmet	8.81	160.0	133.0	15	160.0	77.0	30
Picolinafen	8.78	376.0	238.0	25	238.0	145.0	25
Picoxystrobin	7.32	335.0	173.0	10	303.0	157.0	15
Pirimicarb	5.94	238.0	166.0	10	166.0	96.0	20
Pirimiphos-methyl	6.41	305.0	180.0	5	290.0	151.0	15
Procymidone	7.12	283.0	255.0	8	283.0	96.0	8
Profenofos	7.50	337.0	309.0	5	337.0	267.0	15
Prometon	5.42	225.0	183.0	3	225.0	168.0	10
Prometryn	6.26	241.0	226.0	8	241.0	184.0	12
Propaphos	7.17	220.0	140.0	12	220.0	125.0	25
Propazine	5.51	229.0	58.0	10	214.0	172.0	8
Propiconazole	8.25	259.0	191.0	8	259.0	173.0	10
Propyzamide	5.65	173.0	145.0	15	173.0	109.0	30
Prothiofos	7.46	309.0	239.0	15	309.0	221.0	25
Pyraclostrobin	11.15	164.0	132.0	10	132.0	77.0	20
Pyrazophos	9.42	232.0	204.0	5	221.0	193.0	10
Pyridaben	9.82	147.0	132.0	10	147.0	117.0	20
Pyrifenox	7.24	262.0	227.0	10	262.0	200.0	20
Pyrimethanil	5.72	198.0	156.0	25	198.0	118.0	25
Pyriofenone	8.62	365.0	350.0	5	350.0	320.0	5
Pyriproxyfen	9.13	136.0	96.0	10	136.0	78.0	20
Quinalphos	7.05	157.0	129.0	15	146.0	91.0	30
Quinoxyfen	8.26	307.0	272.0	5	307.0	237.0	25

Quintozene	5.68	295.0	265.0	10	295.0	237.0	15
Secbumeton	5.78	225.0	196.0	5	225.0	169.0	5
Spirodiclofen	9.74	312.0	259.0	10	312.0	109.0	20
Spiromesifen	8.64	272.0	254.0	3	272.0	209.0	12
Sulfotep	5.16	238.0	146.0	10	202.0	146.0	10
Sulprofos	8.08	322.0	156.0	10	156.0	141.0	15
Tebuconazole	8.45	250.0	153.0	12	250.0	125.0	20
Tebufenpyrad	8.85	333.0	276.0	5	333.0	171.0	20
Tecnazene	4.90	215.0	179.0	10	203.0	143.0	20
Tefluthrin	5.74	177.0	137.0	15	177.0	127.0	15
Terbufos	5.62	231.0	175.0	10	231.0	129.0	25
Terbumeton	5.53	225.0	169.0	3	169.0	154.0	5
Terbutryn	6.39	241.0	185.0	3	241.0	170.0	10
Tetrachlorvinphos	7.28	329.0	109.0	25	329.0	79.0	35
Tetraconazole	6.69	336.0	218.0	30	336.0	204.0	30
Tetradifon	9.06	356.0	229.0	10	356.0	159.0	10
Tetrahydrophthalimide	4.35	151.0	136.0	8	151.0	122.0	8
Tetramethrin	8.74	164.0	107.0	15	164.0	77.0	30
Thiobencarb	6.54	125.0	89.0	15	100.0	72.0	3
Tolclofos-methyl	6.24	265.0	250.0	15	265.0	220.0	25
Tolylfluanid	7.01	240.0	137.0	10	238.0	137.0	10
Triadimefon	6.66	208.0	181.0	5	208.0	127.0	15
Triallate	5.85	268.0	184.0	20	143.0	83.0	15
Triazophos	8.10	161.0	134.0	5	161.0	106.0	10
Trifloxystrobin	8.20	222.0	190.0	3	222.0	130.0	15
Trifluralin	5.07	306.0	264.0	10	264.0	160.0	15
Triphenyl phosphate	8.47	326.0	233.0	10	326.0	169.0	35
Vinclozolin	6.17	212.0	172.0	15	212.0	109.0	40

t_R: Retention time

CE: collision energy