Splitless liners in gas chromatography

Inertia, durability and performance

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1. Aim and scope

This document reports the use of different commercially available liners for splitless injection in gas chromatography. The most common liner configurations from three manufacturers are herein compared in terms of inertia, durability and general performance. A mixture of 190 pesticide residues has been employed for the analysis in two different matrices -tomato and orange- and three concentration levels, from 0.005 to 0.200 mg/L.

2. Short description

With the exception of on-column injection, liners play an essential role in gas chromatography inlets, as the liquid samples are turned into gas phase inside them. Choosing an appropriate liner according to the sample and type of injection may determine the accuracy of the results. The internal geometry and the deactivation methods provided by different manufacturers should therefore be taken into consideration as an initial step in the method development. Moreover, liners are easily contaminated with the sample components and they should be frequently replaced, so a liner that maximizes the injections without losing its properties might save time, money and work to routine analytical laboratories.

Splitless injection, in which the split vent is closed and virtually all the injected volume is transferred to the GC column, is one of the most popular injection modes for the analysis of traces. A wide variety of liner geometries is available for this injection mode; the most common features of splitless liners are briefly described below.

Geometries

- Straight.
- Single taper. The presence of a taper at the bottom of the liner minimizes the possible interactions of the sample components with the inlet and focuses the analytes to the chromatographic column.
- Double taper. An additional taper at the top of the liner could reduce the loss of matrix components during the evaporation, increasing the amount of sample transferred to the column.
- Especial geometries. Some geometries, such as the spiral shape, may help the vaporization step and avoid the need of using glass wool (*see below*).

Packing

The glass wool provides a support for the sample during the evaporation step and prevents the non-volatile matrix components (as well as other contaminants such as septum particles) from reaching the GC columns. However, some labile analytes might be lost through interaction with this component, and the packing of the wool could not be homogeneous enough to provide a good reproducibility.

Deactivation

Some GC analytes -specially the most lipophilic ones- might interact with the glass walls of the liner, so a deactivation process minimizes the loss of sensitivity and reproducibility. Different commercial firms develop their own deactivation modes, such as the Premium deactivation from Restek® or the Ultra-inert liners of Agilent®.

Internal diameter

A reduced internal diameter helps transfer the sample to the GC column in a narrow band due to the increased flow and gas velocity (with the same inlet pressure). However, in splitless injection, the maximum capacity of these liners should be carefully considered. If the volume of sample after the evaporation is higher than the maximum capacity of the liner, the analytes will not be transferred to the system (loss of sensitivity and reproducibility) and might contaminate the inlet. There are useful calculators that can be used to confirm if a specific liner is amenable for a specific solvent, injection volume and inlet temperature/pressure.

3. Apparatus and consumables

- Liners included in the present study, all of them with 78.5 mm length and 6.4 mm external diameter:
    - Agilent 5190-5105 Inlet liner, universal, Ultra Inert, mid-frit
    - Agilent 5190-2293 Inlet liner, Ultra Inert, splitless, single taper, glass wool
    - Agilent 5190-5112 Splitless, UI, Fritted Liner, Low
    - Scharlab 032-092017 Split/Splitless with Single Taper
    - Scharlab 032-092019 Split/Splitless with Single Taper (Quartz Wool)
    - Restek 23310 Topaz 4.0 mm ID Cyclo Double Taper Inlet Liner
    - Restek 23303 Topaz 4.0 mm ID Single Taper Inlet Liner w/ Wool
    - Restek 23316 Topaz 2.0 mm ID Single Taper Inlet Liner w/ Wool

Liner #	Brand	Ref.	Geometry	Int. Diameter	Packing	Position
8	Agilent	5190-5105	Single taper	4	Glass-frit	Medium
1-2-3*	Agilent	5190-2293	Single taper	4	Glass wool	Low
7	Agilent	5190-5112	Single taper	4	Glass-frit	Low
9	Scharlab	032-092003	Tapered	4	Quartz wool	Medium
6	Scharlab	032-092017	Single taper	4	No	-
1-2-3*	Scharlab	032-092019	Single taper	4	Quartz wool	Low
5	Restek	23310	Cyclo Double Taper	4	No	-
1-2-3*	Restek	23303	Single taper	4	Quartz wool	Low
4	Restek	23316	Single taper	2	Quartz wool	Low

*One of the liners with single taper geometry and glass wool at the bottom was selected as the reference liner for the Sensitivity studies (*see section 5.1.2*)

- Automatic pipettes, suitable for handling volumes from 1 µL to 5 mL
- Vortex Shaker IKATM 4 Basic
- Concentration workstation
- Injection vials, 2 mL, suitable for LC and GC auto-sampler

4. Chemicals

- Acetonitrile ultra-gradient grade
- Ethyl acetate
- Pesticide analytical standards

5. Procedure

5.1. Experiment setup

5.1.1. 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 a standard mix containing 188 pesticides (10 mg/L in acetonitrile), which was diluted to 1 mg/L in ethyl acetate (3 mL final volume) and used throughout the experiment.

Each day of the study, this mix was employed to prepare three calibration levels in ethyl acetate: 0.200, 0.050 and 0.005 mg/L. The experiment involved two different matrices: tomato (high water content) and orange (high water and acid content). A blank extract of these matrices (QuEChERS extraction method [1]) was evaporated and reconstituted with the same volume of the calibration points. Three replicates of each sample were prepared, resulting in 18 injection vials prepared daily.

2 matrices · **3** calibration levels · **3** replicates

5.1.2. Injection sequence

1. A new "reference" liner (single taper with glass wool) was placed in the inlet.
2. A conditioning injection was performed and discarded (tomato matrix).
3. One replicate of each calibration level in tomato matrix (3 injections) was injected.
4. The "reference" liner was replaced by the liner to be studied.
5. A conditioning injection was performed and discarded (tomato matrix).
6. Four replicates of each sample were injected, following the sequence:
   - 0.005 mg/L, tomato, vial 1, R1-R4
   - 0.050 mg/L, tomato, vial 1, R1-R4
   - 0.200 mg/L, tomato, vial 1, R1-R4
   - 0.005 mg/L, orange, vial 1, R1-R4
   - 0.050 mg/L, orange, vial 1, R1-R4
   - 0.200 mg/L, orange, vial 1, R1-R4
   - 0.005 mg/L, tomato, vial 2, R1-R4
   - 0.050 mg/L, tomato, vial 2, R1-R4
   - 0.200 mg/L, tomato, vial 2, R1-R4
   - […]
   - 0.005 mg/L, orange, vial 3, R1-R4
   - 0.050 mg/L, orange, vial 3, R1-R4
   - 0.200 mg/L, orange, vial 3, R1-R4

5.2. 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 A.

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

5.3.1. Intuvo 9000 GC system (Agilent)

- Columns: 2 planar columns HP-5MS UI (15 m long × 0.25 mm i.d. × 0.25 µm film thickness)
- Injection mode: Splitless
- Sample injection volume: 1 µL
- Inlet 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 (hold for 3.5 min)
- Post Run: 2.1 min, 310 °C

5.3.2. 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

The experiment setup was designed to maximize the information obtained from different liner designs. With that purpose, nine different liners were tested, each one with unique features described in **Figure 1**. The first three liners had equivalent designs and were provided by different firms, so their respective manufacturers (Agilent, Restek or Scharlab) will be kept confidential. These liners have glass wool at the bottom and a single taper, which is the bestseller design for splitless injection (as reported by the three manufacturing companies). Liner #4 has the same geometry, but its internal diameter (I.D.) is smaller (2 mm instead of 4) and liner #5 has an especial geometry consisting of a double taper and a spiral in the lower half. Liner #6 was similar to #1-2-3, in this case without the glass wool. In liner #7, the glass wool was replaced by glass frit. Lastly, in liners #8 and #9, there was a glass frit or glass wool in an intermediate position; liner #9 contained also a double taper. The internal volume of some of these liners is smaller than

in other geometries, so a calculation was made to ensure the volume of the sample would be lower than the liner's maximum capacity.

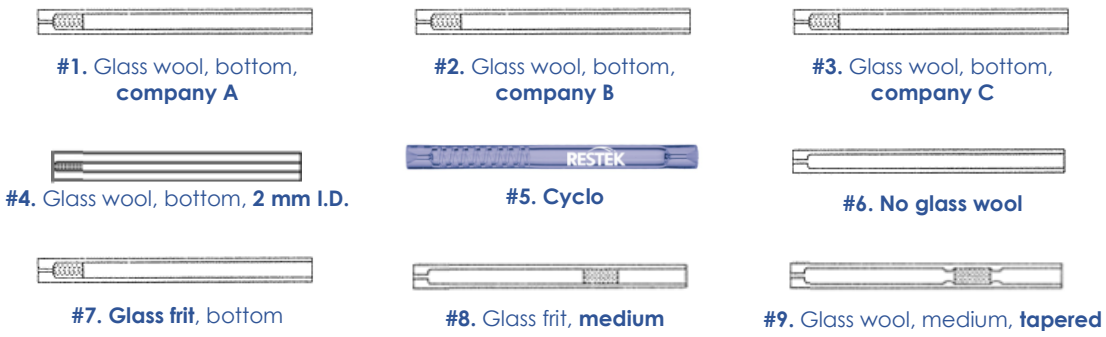

Figure 1. Schemes of the liner configurations tested

The presence of packing in middle position (liners #8 and #9) resulted in the loss of intensity and very wide peaks for most compounds. Therefore, these liners will be discussed separately.

6.1. Durability

The durability of these liners was assessed at three concentration levels (0.005, 0.050 and 0.200 mg/L) in two different matrices: tomato and orange. According to the experimental setup, 12 injections were performed to each type of sample. As these samples were injected alternately, there were 51 injections between the first and last injection of each type of sample. To assess the durability of the liners, the intensity of each compound (area of the chromatographic signal) in the last injection was compared to the one of the first injection. An area in the range 80-120 % regarding the first injection indicates that the liner was still suitable for further analysis of that compound. Conversely, values lower than 70 % when compared to the first injection -i.e. a loss of intensity higher than 30 %- were indicative that the liner was not in good condition anymore for that compound.

Figure 2 shows the performance of each individual liner in terms of durability. These 51 injections did not affect significantly the areas of the majority of compounds; however, some general observations should be considered:

- In general terms, orange samples provided better results than tomato samples. Orange matrix contains a larger number of constituents, which block the active sites of the liner and provide better and more homogeneous results (*see technical report EURL-FV 2020-M35, on dual layer injection, for more information*).
- The performance of the liner is not affected by the concentration of the analytes in the sample. In some cases, the loss of intensity was more intense at low concentration levels, whereas the opposite happened in other occasions.

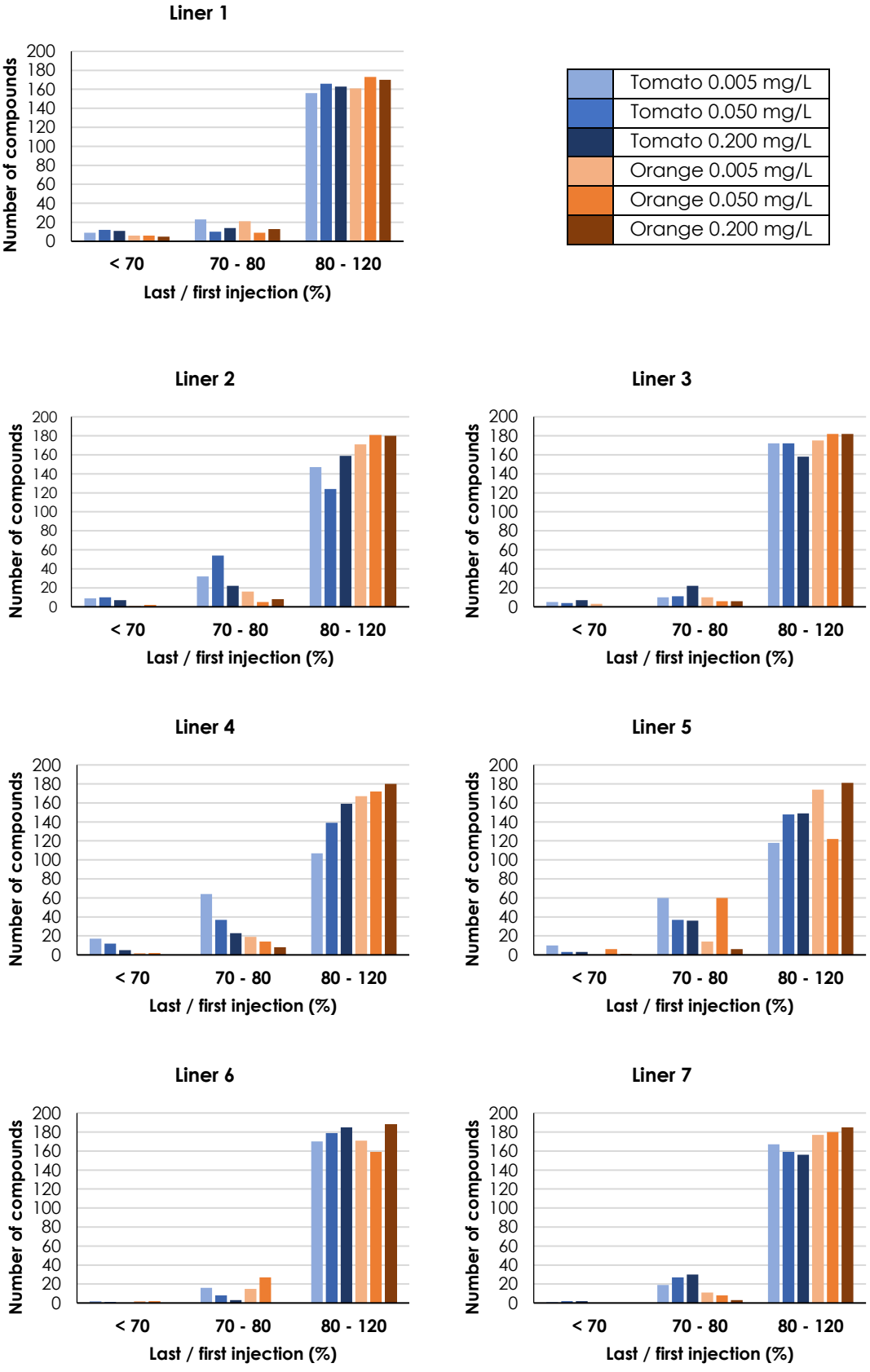

Figure 2. Relative response of the last and first injection (after 51 injections with the same liner) for all matrices (tomato, orange) and concentration levels (0.005, 0.050 and 0.200 mg/L). Total number of compounds: 188

The performance of liners # 1, 2 and 3 was expected to be similar (as they share the same configuration), and the differences can be attributed to their manufacture by different companies. It can be seen that, in general terms, the performance of liners # 1 and 3 was indeed very similar, but that liner #2 provided a shorter durability in tomato matrix. The deactivation procedure employed by each one of the companies might be related to the loss of sensitivity in certain labile compounds. Similar trends were observed for liner #4 and, to a lesser extent, liner #7 (smaller internal diameter and glass frit respectively). The absence of glass wool or frit in liner # 6 did not cause a reduced durability and, most interestingly, provided similar results for both tomato and orange. Conversely, the especial geometry in #5 could have resulted in shorter durability of this liner for both matrices.

As regards the individual pesticides, the vast majority (169 out of 188) were not severely affected in the reiterate injections, independently of the liner configuration -i.e. the loss of intensity was lower than 30 % in all cases. In some specific cases, such as pyraclostrobin and phosmet, there was a strong decrease in the signal regardless of the liner used, which could indicate a loss of the analyte in the vial (for instance, because of degradation in the injection solvent). In other cases, the liner configuration indeed influenced the signals obtained over time.

Figure 3 shows the ratio between the last and first injection for some representative compounds; each point represents one matrix (tomato, orange) and a specific concentration level (six points per liner). It can be seen, for instance, that chlorpyrifos did not undergo a loss of intensity with any of the liners tested, for any matrix nor calibration level. Conversely, the areas of pyraclostrobin decreased significantly with all liners (being this decrease more intense in tomato matrix). Lindane and dichlofluanid, for their part, underwent a decrease in their signals only with the use of some liners, whereas provided stable results with others.

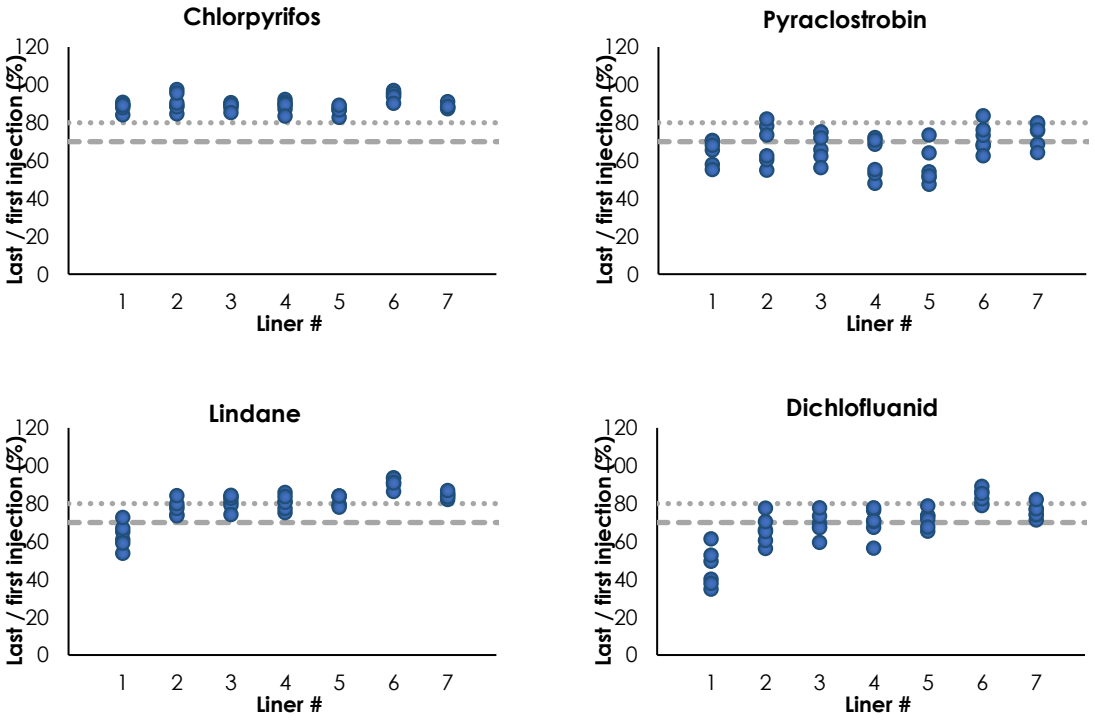

Figure 3. Liner durability for some specific compounds. For each liner, two matrices and three calibration levels are depicted (six balls per liner)

6.2. Signal intensity

The intensity of the chromatographic signals in tomato matrix was assessed at the three calibration levels included in the study in tomato matrix. With that purpose, liner #1 was selected as the reference liner and, every day, the areas obtained with this liner were compared to the ones obtained with the liner being assessed. In order to avoid deviations produced by the instrument drifting, three reference injections in tomato (one per calibration level) were done every day with a new liner #1, followed by the complete sequence with the corresponding liner to be compared. The first injections of each liner were compared to the reference injections so that the vial content and the instrument status were equal. No more than 90 minutes passed between the reference injections and the ones used for assessing the signal intensity.

Very similar results were obtained for all the calibration levels, with only minor differences for 0.005, 0.050 and 0.200 mg/L. Therefore, for simplicity reasons, the average sensitivity obtained with each liner was calculated, as shown in **Table 1**. Values above 100 % are related to an enhancement in the signal intensity when compared to liner #1 (reference values), whereas values lower than 100 % correspond to a reduction in the sensitivity.

It can be observed that, with very few exceptions, the responses provided by the first three liners (with the same geometry) are virtually the same. However, the vast majority of compounds undergo a remarkable increase in their signals with liner #4. A reduced internal diameter was expected to produce narrower peaks, but it turned out to affect the sensitivity. Conversely, the areas provided by liner #7 were in general lower than the ones obtained with the reference injections, which could indicate that glass wool performs more effectively than glass frit (for the injection parameters of the present study). The especial configuration of liner #5 and the absence of glass wool in liner #6 did not affect remarkably the sensitivity of these compounds.

Table 1. Average sensitivity of 188 compounds with the use different liners over a reference liner at three concentration levels (expressed as %)

Compound	Liner #							Compound	Liner #						
	1	2	3	4	5	6	7		1	2	3	4	5	6	7
2,4'-DDE	104	99	102	130	110	107	93	Heptenophos	95	98	101	127	111	101	92
2-Phenylphenol	96	97	98	119	104	101	92	Hexaconazole	98	101	103	139	104	101	86
4,4'-DDD	99	97	105	130	98	94	83	Indoxacarb	96	94	106	117	101	78	81
4,4'-DDE	103	99	102	131	111	106	93	Iprodione	96	87	99	141	102	98	77
Acrinathrin	103	93	109	132	88	104	70	Iprovalicarb	100	102	110	136	105	100	86
Alachlor	96	95	100	127	109	106	94	Isazofos	106	97	103	127	109	100	93
Ametryn	103	94	96	130	98	99	80	Isocarbophos	95	98	103	135	111	102	87
Anthraquinone	98	101	100	137	105	91	81	Isofenphos	102	96	101	126	107	104	93
Atrazine	100	98	98	129	108	98	88	Isofenphos-methyl	100	99	102	131	110	104	92
Azoxystrobin	99	100	111	124	96	90	81	Isopyrazam	104	99	109	134	100	94	76
Benalaxyl	102	101	98	126	100	96	79	Kresoxim-methyl	102	100	104	132	106	103	90
Bifenthrin	106	97	100	128	101	103	87	Lambda-Cyhalothrin	105	97	103	127	94	95	79
Biphenyl	102	95	101	122	106	101	97	Lindane	91	97	98	130	109	106	93
Bixafen	101	93	106	127	97	71	67	Lindane-d6	91	98	97	126	110	106	93
Boscalid	101	92	102	122	96	78	71	Malathion	102	99	105	135	118	105	94
Bromopropylate	101	97	101	133	100	99	80	Malathion-d10	101	99	106	136	115	105	95
Bupirimate	106	97	104	130	103	118	84	Mecarbam	111	97	101	129	107	101	89
Buprofezin	104	99	102	132	105	117	88	Mepanipyrim	95	101	105	140	110	99	82
Butralin	97	99	99	136	118	103	92	Metalaxyl	102	99	101	128	110	104	90
Butylate	103	95	102	115	102	104	94	Metazachlor	93	102	100	128	106	102	87
Cadusafos	100	97	101	125	110	103	94	Metconazole	104	98	103	134	102	94	79
Carbophenothion	107	98	99	126	100	95	77	Methidathion	98	103	112	149	122	108	88

Chinomethionate	104	103	109	152	112	91	78	Methiocarb	94	97	107	142	113	97	92
Chlorbromuron	101	97	103	113	97	86	72	Metolachlor	95	97	101	130	111	105	93
Chlorfenapyr	104	97	97	131	105	104	85	Mevinphos	93	99	112	126	114	101	90
Chlorfenvinphos	97	98	105	128	112	103	92	Molinate	104	97	98	118	107	101	93
Chlorobenzilate	99	103	104	128	103	92	88	Myclobutanil	100	98	105	137	105	99	85
Chlorothalonil	93	104	105	148	114	102	85	Napropamide	100	97	105	139	107	98	85
Chlorpropham	100	97	96	120	107	96	85	Novaluron	103	107	113	124	110	120	91
Chlorpyrifos	98	99	102	128	109	104	93	Nuarimol	101	97	101	130	100	98	82
Chlorpyrifos-methyl	99	98	102	130	109	103	92	Ofurace	92	96	100	127	101	94	80
Chlorthal-dimethyl	103	98	101	125	108	104	93	Oxadixyl	98	96	103	127	98	95	81
Chlozolinate	100	97	98	130	105	98	89	Paclobutrazol	95	110	113	162	123	114	89
Coumaphos	102	96	106	124	100	86	73	Parathion	93	101	104	141	112	101	95
Cyfluthrin	105	92	109	124	92	89	86	Parathion-methyl	96	99	105	134	115	98	90
Cypermethrin	103	100	96	124	91	84	68	Pebulate	104	98	103	127	103	94	100
Cyproconazole	98	100	103	136	104	99	83	Penconazole	101	100	101	131	105	98	87
Cyprodinil	101	98	102	131	101	93	81	Pendimethalin	89	98	103	135	112	107	92
Deltamethrin	100	96	110	127	99	83	77	Penthiopyrad	106	100	108	138	109	106	86
Diazinon	103	97	101	126	109	106	95	Permethrin	103	104	95	128	100	94	77
Dichlofluanid	96	100	100	133	119	108	96	Phenthoate	104	99	104	125	110	102	92
Dichloran	100	100	99	144	116	96	85	Phorate	107	97	98	124	108	105	92
Dichlorvos	99	95	105	92	102	110	90	Phosmet	97	101	111	136	107	88	72
Dichlorvos-d6	104	94	102	94	102	108	87	Picolinafen	101	97	107	131	100	93	81
Diclobutrazol	99	100	108	145	109	106	86	Picoxystrobin	99	102	106	142	117	113	96
Dicofol	99	97	103	133	104	102	85	Pirimicarb	108	104	103	135	110	126	94
Dieldrin	100	97	102	124	99	101	94	Pirimiphos-methyl	99	99	104	134	112	106	96
Dimethenamid	98	98	101	129	110	105	93	Procymidone	101	99	99	126	103	97	87
Dimethipin	105	99	99	129	106	102	89	Profenofos	95	99	110	137	118	104	92
Diphenylamine	102	108	98	122	106	102	88	Prometon	103	98	100	128	95	97	81
Disulfoton	112	94	106	125	110	107	95	Prometryn	104	95	101	128	96	103	85
Dodemorph	109	92	99	121	92	98	75	Propaphos	96	103	109	148	115	109	91
Endosulfan sulfate	98	98	95	117	100	99	89	Propazine	100	98	100	126	106	102	91
Endosulfan-alpha	101	98	104	133	107	105	93	Propiconazole	100	98	101	121	100	95	89
Endosulfan-beta	99	99	101	126	105	100	87	Propyzamide	102	99	103	130	109	99	91
Endrin	98	99	100	124	105	104	91	Prosulfocarb	101	98	95	127	104	95	96
EPN	98	97	106	134	104	100	85	Prothiofos	104	100	101	132	107	106	93
Epoxiconazole	97	96	98	126	102	97	81	Pyraclostrobin	92	95	112	136	103	70	67
Ethion	108	98	104	133	106	105	89	Pyrazophos	103	94	109	138	99	90	78
Ethofumesate	101	101	102	132	113	103	93	Pyridaben	103	97	104	140	99	92	74
Ethoprophos	100	97	101	127	110	104	93	Pyrifenox	101	95	101	132	97	96	80
Ethoxyquin	114	101	102	131	102	108	59	Pyrimethanil	103	97	101	132	103	95	84
Etofenprox	106	94	104	125	98	84	75	Pyriofenone	102	95	99	128	99	101	86
Etrimfos	103	97	102	126	109	105	94	Pyriproxyfen	102	94	98	126	95	87	78
Fenamidone	94	97	105	130	96	100	81	Quinalphos	105	95	96	129	105	92	90
Fenarimol	101	96	102	127	96	90	76	Quinoxyfen	103	97	98	121	96	90	82
Fenazaquin	102	98	106	122	93	94	94	Quintozene	95	98	98	127	107	106	93
Fenbuconazole	104	97	107	119	97	78	71	Secbumeton	102	94	103	135	97	100	78
Fenchlorphos	100	100	102	126	109	102	92	Spirodiclofen	101	97	103	129	100	97	79
Fenhexamid	96	90	99	142	105	97	74	Spiromesifen	103	98	102	129	100	105	85
Fenitrothion	95	101	104	143	116	102	92	Sulfotep	105	97	99	122	109	104	97
Fenpropathrin	104	96	102	125	100	98	81	Sulprofos	99	97	102	129	104	99	86
Fenpropidin	107	97	112	124	93	85	75	Tau-fluvalinate	100	92	108	130	103	81	104
Fenpropimorph	107	94	101	127	96	106	83	Tebuconazole	100	97	103	130	97	94	79
Fenthion	101	97	104	132	110	99	90	Tebufenpyrad	105	95	101	130	98	97	81
Fenvalerate	103	96	102	124	100	82	69	Tecnazene	102	95	99	120	106	101	93
Fipronil	94	98	100	143	107	110	87	Tefluthrin	103	98	102	122	110	104	96
Flamprop-isopropyl	101	97	104	133	106	104	89	Terbufos	113	98	102	129	113	110	99
Flamprop-methyl	101	99	103	130	105	104	91	Terbumeton	103	97	98	129	97	101	81
Fluacrypyrim	105	96	101	129	103	105	88	Terbutryn	101	101	106	136	105	107	87
Fluazifop-p-butyl	103	99	104	135	108	101	91	Tetrachlorvinphos	96	104	113	153	124	112	93
Flucythrinate	104	95	103	127	99	85	67	Tetraconazole	100	100	103	131	106	106	88
Fludioxonil	98	103	102	132	110	93	83	Tetradifon	105	95	101	121	98	87	82
Fluensulfone	98	95	99	124	107	98	93	Tetramethrin	107	99	104	133	103	93	83
Fluopicolide	98	98	100	125	99	92	87	Thiobencarb	99	100	103	128	107	97	91
Fluopyram	101	98	102	131	105	98	88	Tolclofos-methyl	103	98	100	126	108	102	94
Fluquinconazole	103	93	99	123	91	82	71	Tolylfluanid	92	96	97	133	112	106	93
Flusilazole	101	97	104	137	104	103	84	Triadimefon	99	100	101	131	109	102	92
Flutolanil	97	99	105	138	107	100	88	Triallate	102	97	101	125	111	105	96
Flutriafol	95	99	105	142	109	102	84	Triazophos	89	104	107	135	104	93	90
Formothion	98	97	102	133	110	96	85	Trifloxystrobin	100	101	100	130	103	100	85

Fosthiazate	95	100	104	146	116	102	94	Trifluralin	98	96	99	121	109	103	91
HCB	103	99	96	120	106	106	93	Triphenyl phosphate	105	96	102	128	100	95	85
Heptachlor	91	96	94	122	120	106	96	Vinclozolin	101	98	102	131	108	106	92

6.3. Peak shapes

The liner configuration did not affect the peak shapes for the compounds, with just one noticeable exception: biphenyl in tomato matrix. In this case, the use of a certain type of liner determined the peak shape to a high extent (**Figure 4**): the best results were obtained with the single taper geometry (with glass wool or without packing, liners # 1, 2, 3 and 6). Conversely, liner #4, with a smaller internal diameter resulted in a very peak. However, this effect was not observed in orange matrix, nor with any of the remaining 187 compounds.

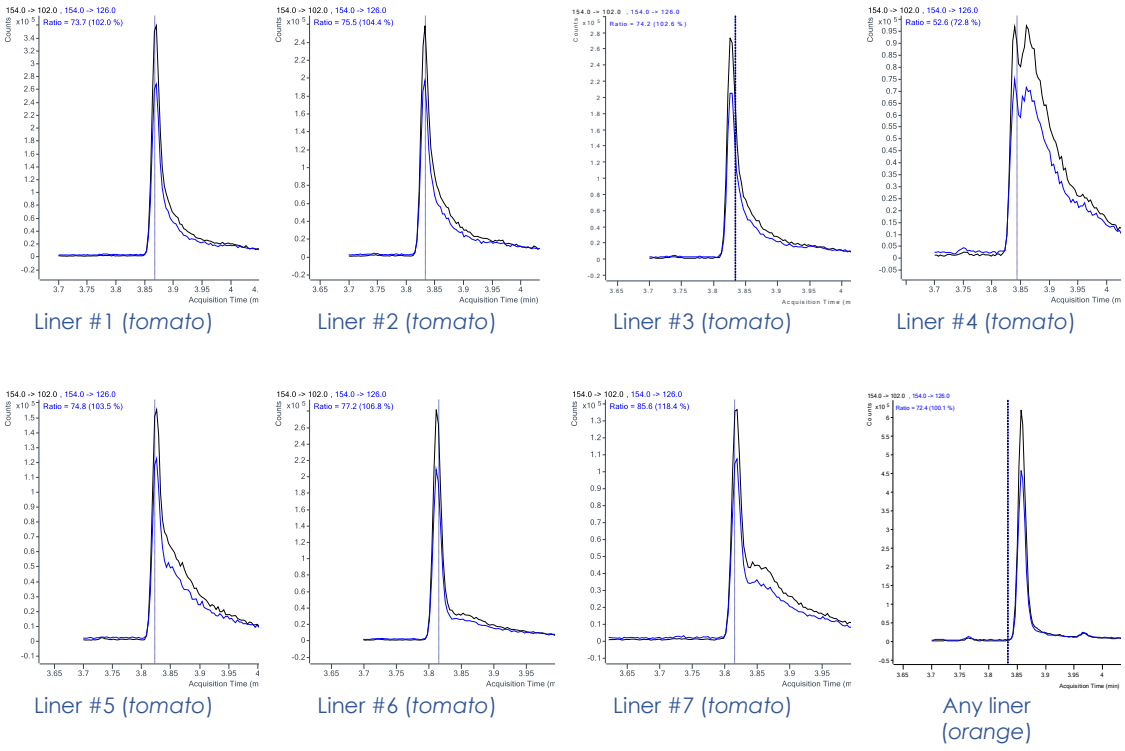

Figure 4. Peak shape of biphenyl in tomato and orange when using different liner configurations

6.4. Packing in middle position

The presence of glass wool or frit in middle position resulted in either a dramatic loss of signal intensity of the compounds (liner #8) or even the total disappearance of signals (liner #9). In the first case, the average signal intensity when compared to the reference liner was 9 %, with most compounds in the range of 3-15 %. The peak shapes were also affected in the majority of compounds, with broader peaks obtained with liner #8 than with the remaining liners (in some cases, the peak shapes were so poor that the quantitation was as well affected). For its part, the use of liner #9 resulted in no peaks obtained for most of the 188 compounds included in the study. **Figure 5** shows these effects for some representative compounds: diazinon has usually a very narrow peak and the main effect in liner #8 was the loss of sensitivity. However, dichloran provides usually a broader peak and, in this case, the quantitation with liner #8 was affected due to the

poor peak shape. *Please note that the chromatograms in* ***figure 5*** *are not scaled; the relative intensities have been calculated for each one of the peaks (4 to 14 %).*

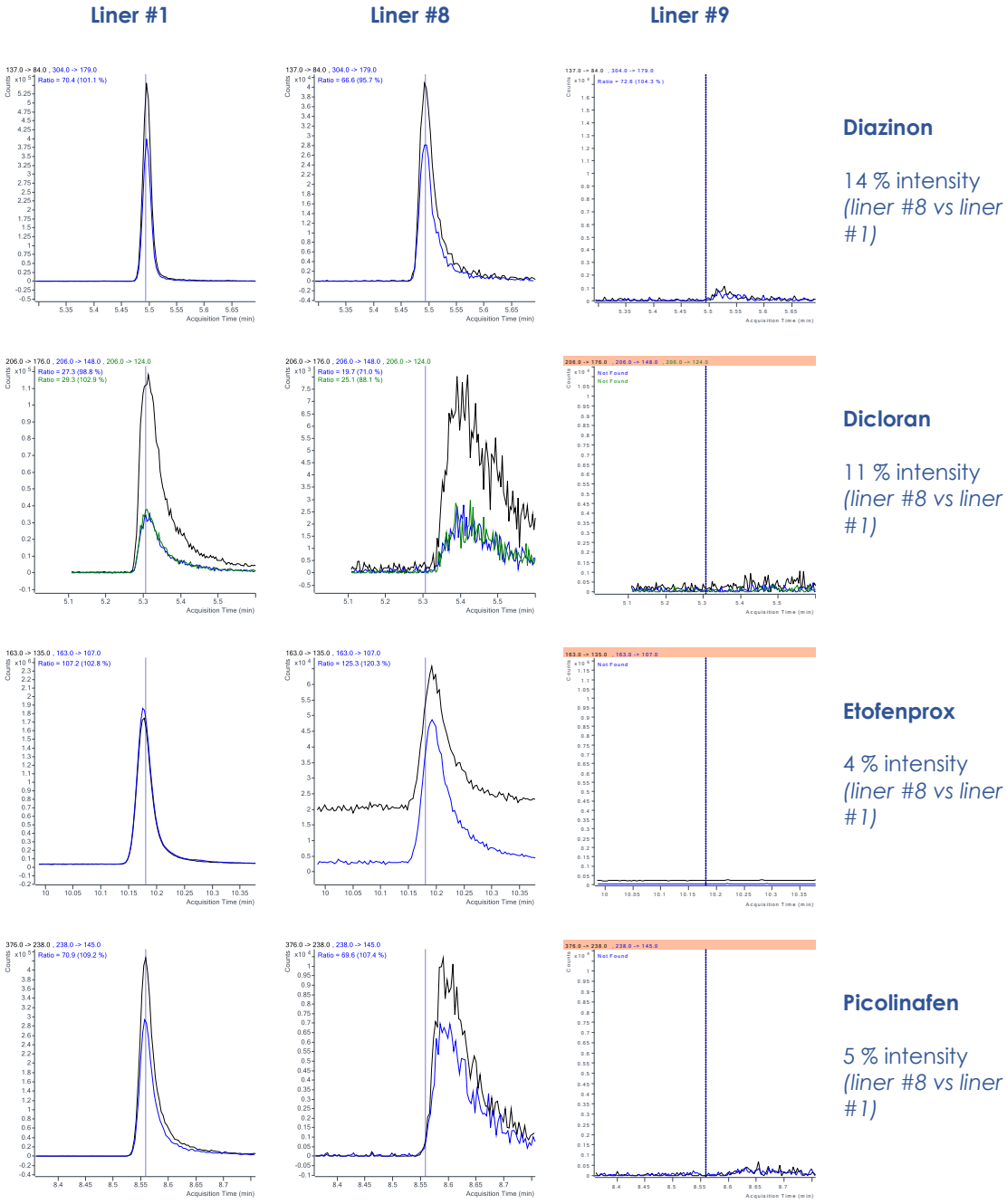

Figure 5. Chromatographic signals of four compounds when using liners #1, 8 or 9 (tomato, 0.050 mg/L)

In all cases, the injection volume was 1 µL (solvent ethyl acetate), the injector temperature was 80 °C and its pressure was 16.2 psi. This corresponds to a gas volume of 140 µL, which is significantly lower than the maximum capacity of these liners (for instance, 870 µL of internal volume for liner #8). However, the presence of packing in mid position provided very poor results and liners with this configuration should not be employed for splitless injection.

7. Conclusions

The selection of an adequate liner is essential in gas chromatography analysis. The deactivation processes employed by different companies affect their durability, especially for the analysis of clean matrices (more susceptible to the presence of active sites inside the liner). Also, in general terms, the presence of a complex matrix in the sample could help maximize the lifetime of any type of liner, so methods such as the dual layer injection could be a useful solution for durability issues.

Given the different behavior of distinct matrices throughout long sequences, and in order to avoid the liner condition to affect the quantification, samples with a positive detection close to the MRL value should be reanalyzed using the same matrix in the calibration curve (*Document SANTE/12682/2019, section D15* [2]).

A reduced internal diameter might not have an intense effect on peak shapes for the vast majority of compounds but, in turn, it provides an increase in their sensitivity of 20-30 %. Conversely, liners with packing in middle position might result in an intense loss of sensitivity when using splitless injection.

8. 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.

[2] Document N° SANTE/12682/2019 Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed

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
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
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
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
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
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
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
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
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	5.53	142.0	109.0	5	142.0	81.0	12
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
Fenpropidin	6.26	273.0	98.0	3	98.0	55.0	12
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
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
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
Heptachlor	6.30	272.0	237.0	10	272.0	143.0	40
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
Isocarbophos	6.59	230.0	212.0	8	136.0	108.0	15
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
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
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
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
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
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
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
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
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
Prosulfocarb	6.24	251.0	128.0	5	128.0	86.0	3
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
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