Use of L-ascorbic acid as a mean to prevent in-vial degradation of LC-amenable pesticides

Table of contents

1. Aim and scope

This document reports the effect different concentrations of L-ascorbic acid added to liquid chromatography (LC) injection vials has on the stability of selected pesticides.

2. Introduction and short description

Sample analysis in LC typically includes a step where a certain amount of water is added to an organic extract prior injection, or an organic extract is gently evaporated and then dissolved again in a solvent mixture that contains water. Afterwards, vials sit on an autosampler until it is time for their actual injection. This time can be anywhere between some minutes to several hours, depending on their batch order number. During this time, the analytes present in the acetonitrile-water-based solution can potentially undergo a myriad of reactions, which include oxidations and other degradation processes.

Most modern instruments include a refrigerated autosampler, which help prevent said processes from taking place by cooling the injection vials down to 5-10 °C (278.15 – 283.15 K). Nevertheless, plenty of instruments still in day-to-day use do not include a cooled autosampler, which means injection vials may sit at 20-30 °C (293.15 – 303.15 K) for several hours.

Whilst many pesticides are known to be stable during this length of time under the aforementioned conditions, not all of them will remain stable during batch analysis and, thus, an alternative to upgrading the autosampler is suggested.

For this experiment, five injection vials containing of a pesticide mixture at 0.050 mg/L (ppm) in acetonitrile:water (20:80, V/V) were repeatedly, non-consecutively injected for up to 18.3 h. To each aliquot, different concentrations of L-ascorbic acid were added, ranging from 0 to 600 ppm, and the stability of the analytical response was evaluated.

3. Apparatus and consumables

- 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 an LC auto-sampler

4. Chemicals

- Acetonitrile ultra-gradient grade
- Ammonium formate
- Ultra-pure water
- Methanol HPLC grade
- Formic acid
- Pesticide analytical standards
- L-Ascorbic acid

5. Procedure

5.1. L-Ascorbic acid solution

L-Ascorbic acid (CAS no. 50-81-7) is an organic molecule that readily undergoes oxidation processes (thus behaving as an antioxidant) and is soluble up to 30 % (w/V) in water. To prepare the initial solution, 30 g of L-Ascorbic acid were dissolved in 100 mL of ultra-pure water and shaken until the solute completely was completely dissolved. Then, a 10-fold dilution was prepared by mixing 25 mL of the 30 % (w/V) solution with an additional 225 mL of water, achieving a concentration of 3 % L-ascorbic acid (w/V).

5.2. Injection vials and L-ascorbic acid concentrations

Individual pesticide stock solutions (1000–2000 mg/L) were prepared in acetonitrile (AcN) or methanol (MeOH) and were stored in screw-capped glass vials in the dark at -20 °C. These solutions were combined into five different mixes at a concentration of 10 ppm. Then, these five solutions were combined and diluted down to 1 ppm in AcN, which was subsequently diluted down to 0.050 ppm in AcN.

Using the 0.050 ppm mixture in AcN and a combination of ultra-pure water and the 3 % L-ascorbic acid solution (w/V), five different injection vials were prepared:

(i) No L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, and 0.8 mL of water.

(ii) 12 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.796 mL of water, and 0.004 mL of the 3 % (w/V) L-ascorbic acid solution.

(iii) 60 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.78 mL of water, and 0.02 mL of the 3 % (w/V) L-ascorbic acid solution.

(iv) 300 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.7 mL of water, and 0.1 mL of the 3 % (w/V) L-ascorbic acid solution.

(v) 600 ppm L-ascorbic acid: 0.2 mL of the 0.050 ppm pesticide mixture, 0.6 mL of water, and 0.2 mL of the 3 % (w/V) L-ascorbic acid solution.

Once prepared, the vials were injected ten times, non-consecutively, in L-ascorbic acid concentration ascending order, i.e., first, the vial with 0 ppm of L-ascorbic acid; then, the vial containing 12 ppm; afterwards, the vial containing 60 ppm of L-ascorbic acid; then, the vial containing 300 ppm of L-ascorbic acid; and finally, the vial containing 600 ppm of L-ascorbic acid. The injection sequence was repeated, starting again with the vial containing 0 ppm of L-ascorbic acid. Each analysis lasted 20.5 min, and the batch elapsed 18.5 h until the end of the analyses.

5.3. Methodology

The LC-MS instrument was operated in selected reaction monitoring (SRM). First, full scan (FS) analyses were carried out to select the most sensitive precursor ions. Then, product ion scans (PIS) were performed to select the most abundant product ions. Finally, two SRM transitions and the correct ratio between the abundances of the two optimised SRM transitions (SRM1/SRM2) were used, alongside retention time matching to obtain the maximum sensitivity for the detection of the target molecules. The instrumental responses produced by the different constituents and/or isomers of a single pesticide were assessed and compared in terms of area and ratio between two transitions (quantitation and confirmation transitions). The mass transitions used are presented in the **Appendix** (**Table A1** for LC-MS/MS parameters).

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

5.4.1. 1290 UHPLC (Agilent)

- Column: Zorbax Eclipse Plus C8 2.1x100 mm and 1.8 µm particle size (Agilent)
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)

- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)
- Column temperature: 35 °C
- Flow rate: 0.300 mL/min
- Injection volume: 5 µL
- Autosampler: two were used, (1) no temperature control and (2) 10 °C.

Mobile phase gradient for pesticides analysis:

Time [min]	Mobile phase A	Mobile phase B
0	100 %	0 %
2	80 %	20 %
15	0 %	100 %
18	0 %	100 %

Re-equilibration time with the initial mobile phase was set to 2.5 minutes.

5.4.2. 6490A triple quadrupole system (Agilent)

- Ionisation mode: positive mode and negative mode
- Capillary (positive and negative): 3000 V
- Nebulizer: 45 psi
- Nozzle: 400 V
- Drying gas flow: 13 L/min
- Drying gas temperature: 120 °C
- Sheath gas flow: 10 L/min
- Sheath gas temperature: 375 °C
- High Pressure RF (positive): 150 V
- High Pressure RF (negative): 110 V
- Low Pressure RF (positive): 60 V
- Low Pressure RF (negative): 60 V

6. Results

Most of the 278 evaluated LC-amenable compounds presented little to no differences in their stability and instrumental response whether in the absence or presence of L-ascorbic acid. However, some compounds were found to be affected positively (stabilization) or negatively (degradation, decreased

instrumental response) by L-ascorbic acid. In broad terms, the net effect of this antioxidant was beneficial or neutral for the vast majority of the analytes.

6.1. Compounds positively affected by the addition of L-ascorbic acid

As discussed, some pesticides exhibit a decreased or halted degradation rate in the presence of L-ascorbic acid.

In this regard, 12 compounds were found to showcase a significant reduction in their in-vial degradation processes: bendiocarb, cymoxanil, dazomet, dithianon, amitraz metabolites DMA and DMPF, fenpicoxamid, formetanate, methiocarb-sulfone, methiocarb-sulphoxide, phosmet, and trichlorfon (**Figure 1**).

In the case of dazomet, dithianon, DMA, and methiocarb-sulfone, the absence of L-ascorbic acid results in a rapid degradation of these analytes. The instrumental response of these compounds dropped below the detection limits between 600 and 800 min (10 and 13.3 h) after the vials were first injected.

On the other hand, for the remaining 8 compounds, a decrease in instrumental response over time was observed, but detection was possible even after 1100 min (18.3 h).

While matrix coextractants and/or the solvent composition in the injection vial (in this case, acetonitrile:water 20:80, V/V) can potentially affect the degradation rate of these compounds, there exists the risk that, under the described conditions, a pesticide present in a sample will disappear from the injection vial before its analysis and thus go undetected during routine analysis. For those pesticides where degradation does not result in in-vial concentrations dropping below the instrumental detection limits, nevertheless, inaccurate concentrations can result from the in-vial degradation processes.

Concentrations of at least 300 ppm of L-ascorbic acid solve all the herein described issues associated to in-vial analyte degradation, whereas 12 ppm of L-ascorbic acid barely had any effect on said processes.

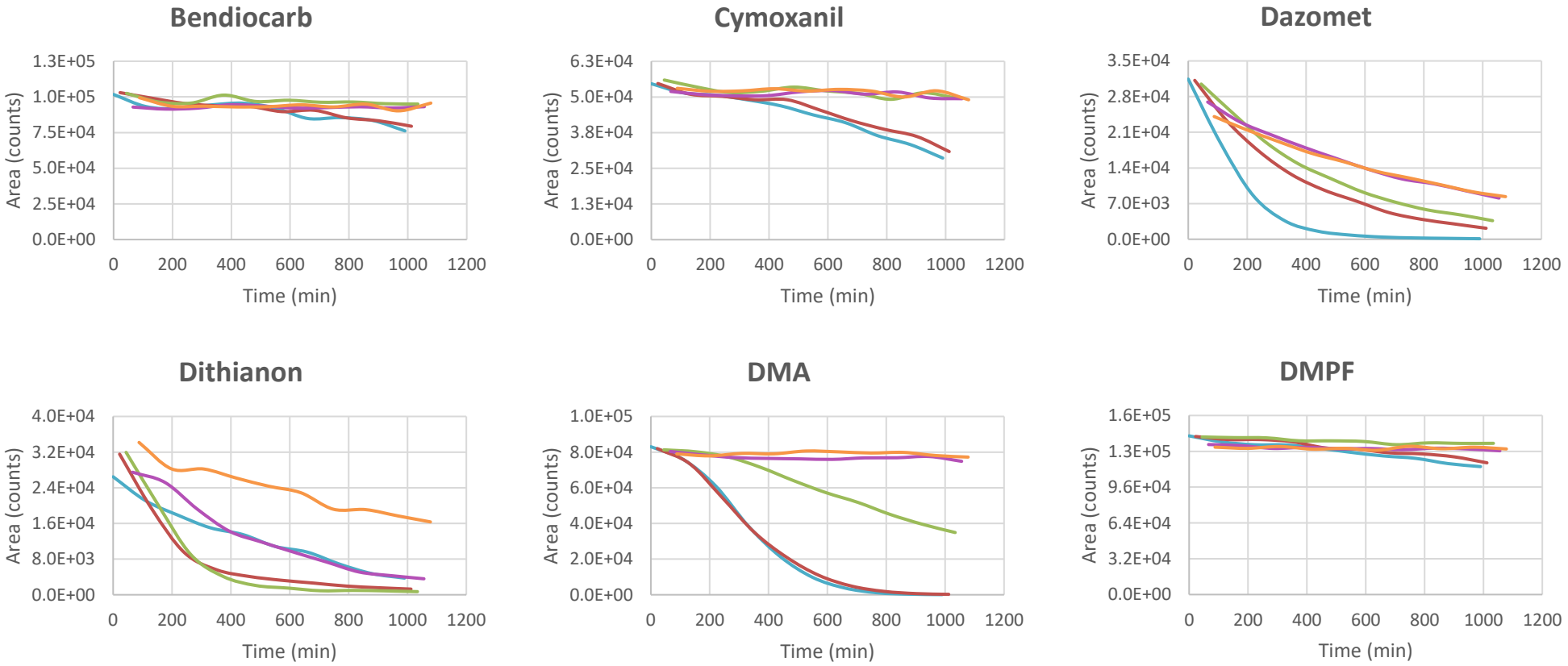

Figure 1. Instrumental response trend for LC-amenable pesticides positively affected by the presence of L-ascorbic acid (diminished or halted in-vial degradation) (*continues*).

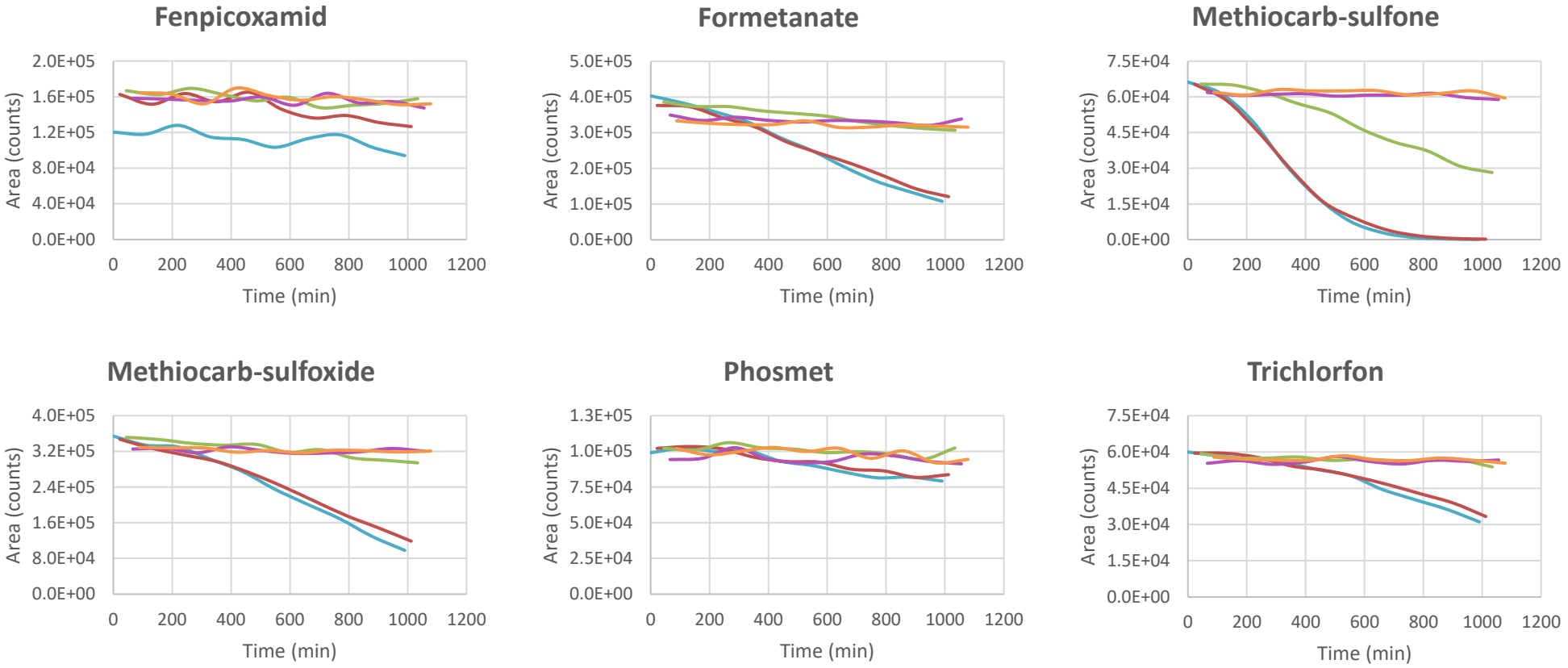

Figure 1. (*Continuation*) Instrumental response trend for LC-amenable pesticides positively affected by the presence of L-ascorbic acid (diminished or halted in-vial degradation).

6.2. Compounds negatively affected by the addition of L-ascorbic acid

6.2.1. Compounds whose instrumental response is decreased

There exists a group of compounds for which the addition of L-ascorbic acid results in a decreased instrumental sensitivity. These compounds are butoxycarboxm, carbendazim, cyromazine, demeton-*S*-methylsulfoxide (oxydemeton-methyl), flonicamid, methomyl, omethoate, oxamyl and pirimicarb-desmethyl (**Figure 2**).

The most probable source of decreased sensitivity is ion suppression due to the elution of L-ascorbic acid which, at 600 ppm and due to its chemical properties, is expected to show a large, broad chromatographic peak behaviour at the beginning of the analysis. This hypothesis is supported by the fact that these compounds are amongst the earliest eluting compounds within the method, with retention times from as low as 2.01 min (cyromazine) to 5.26 min (pirimicarb-desmethyl), with an average retention time of 3.84 min for all nine compounds.

6.2.2. Compounds which suffer from degradation

Three analytes, all of which belong to the sulphonylureas class of organic compounds, suffer from in-vial degradation in the presence of L-ascorbic acid (**Figure 3**). The three compounds found to be negatively affected by the addition of L-ascorbic acid are flazasulfuron, orthosulfamuron and oxasulfuron (**Figure 4**).

Other urea derivatives (such as chlorbromuron, chlorfluazuron, chlorotoluron, difenoxuron, diflubenzuron, diuron or flufenoxuron) did not showcase such a behaviour, indicating that the sulphonyl moiety in these sulphonylureas plays a critical role in their acid-based degradation process. Examples of sulfosulfuron degradation under acidic conditions (another member of the sulphonylureas chemical group) to yield the corresponding amine and sulphonamide -with the loss of the carbonyl moiety- has been reported in the literature and is the likely reason for the observed results for flazasulfuron, orthosulfamuron and oxasulfuron.

6.3. Special situations: bifenazate and clofentezine

There are two compounds that, due to their chemical structure, are deeply affected by the presence or absence of L-ascorbic acid in the injection vial: bifenazate, a carbazate; and clofentezine, a triazine.

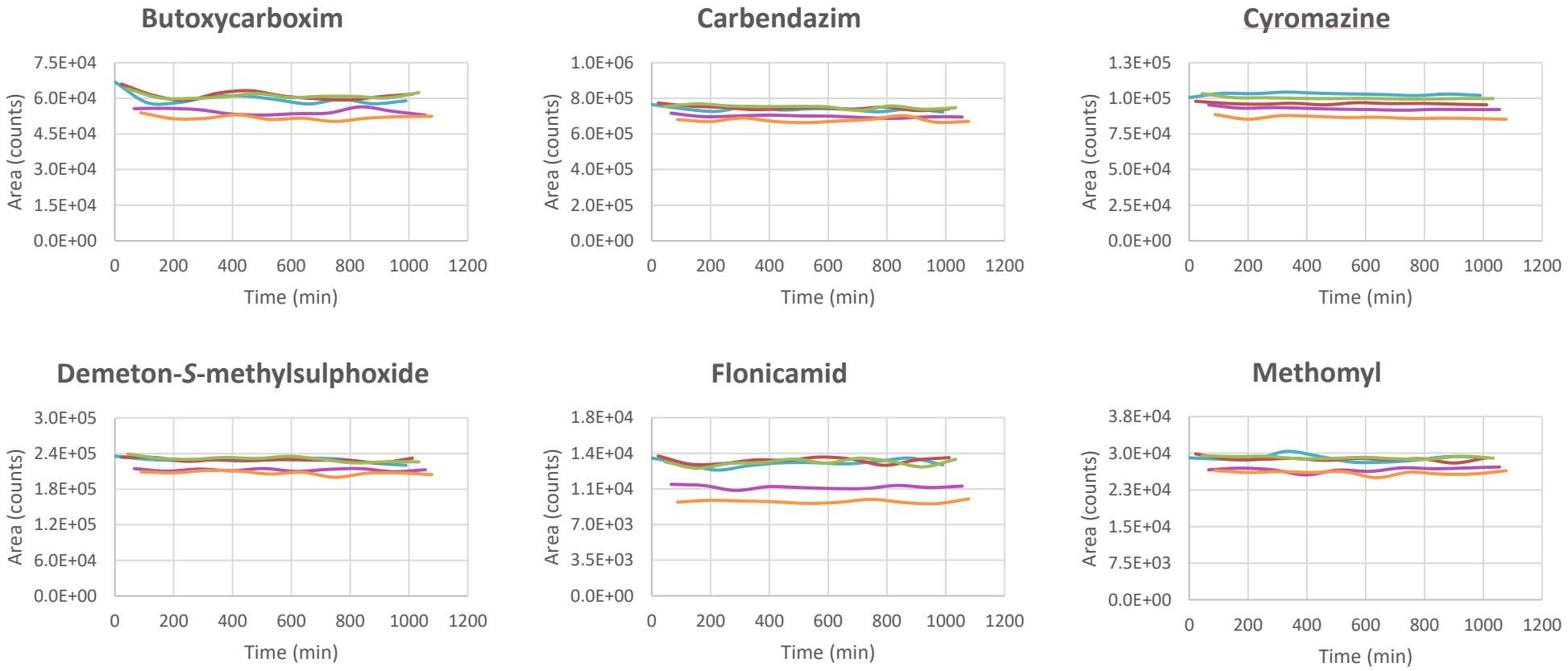

Figure 2. Instrumental response trend for LC-amenable pesticides negatively affected by the presence of L-ascorbic acid (decreased sensitivity) (*continues*).

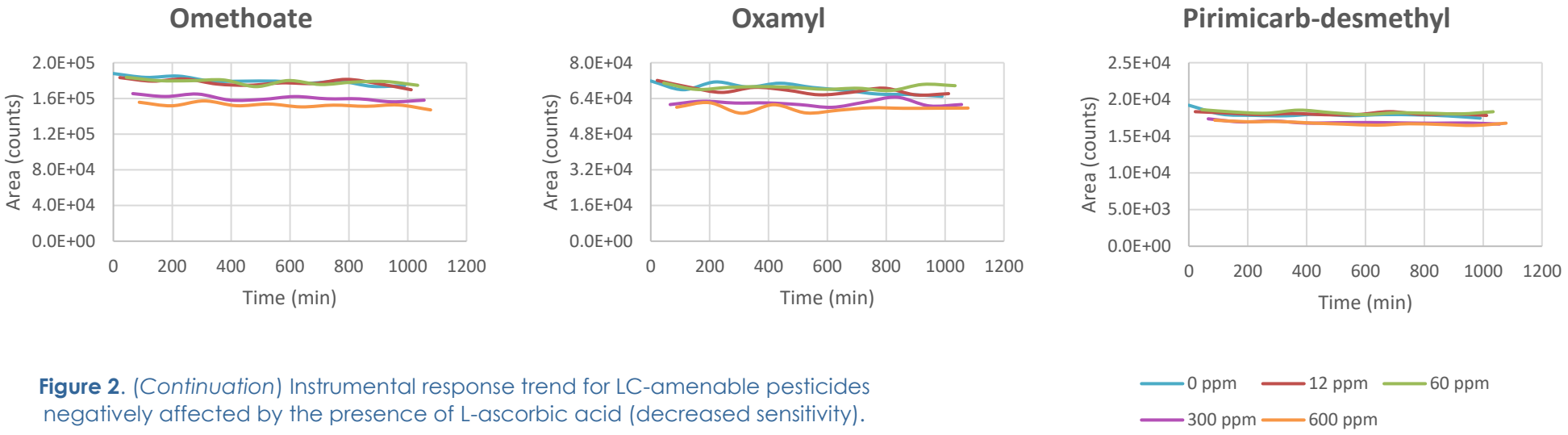

Figure 2. (*Continuation*) Instrumental response trend for LC-amenable pesticides negatively affected by the presence of L-ascorbic acid (decreased sensitivity).

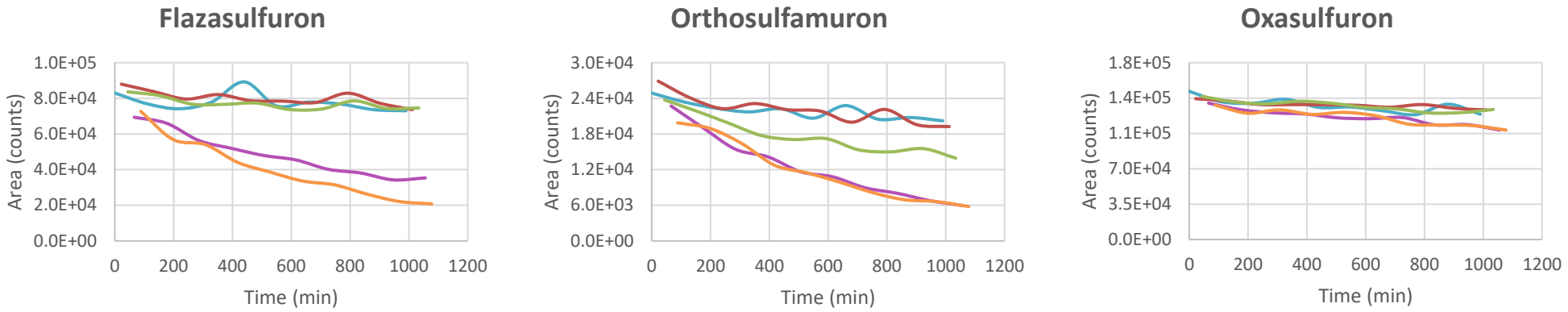

Figure 3. Instrumental response trend for LC-amenable pesticides negatively affected by the presence of L-ascorbic acid (increased in-vial degradation).

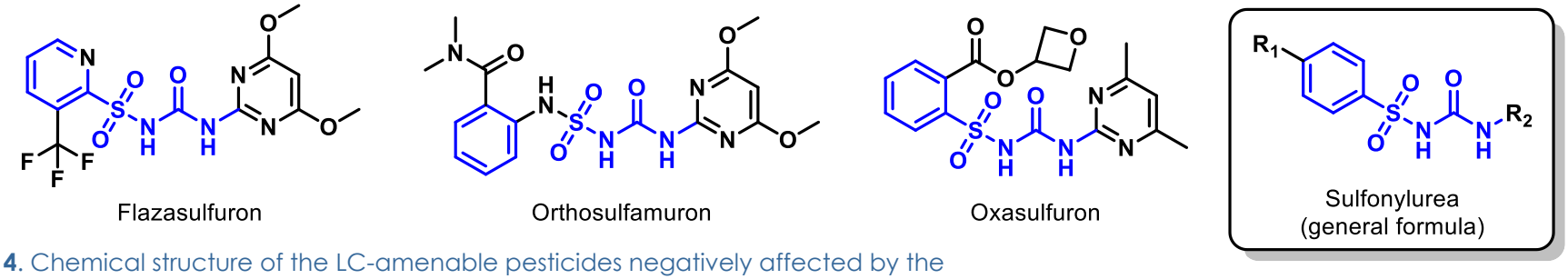

Figure 4. Chemical structure of the LC-amenable pesticides negatively affected by the presence of L-ascorbic acid, all of which belong to the sulphonylureas class of compounds.

Both bifenazate and clofentezine are present in solution as an equilibrium with another species: bifenazate and bifenazate-diazene, and clofentezine and 1,2-dihydroclofentezine. In the presence of an acid, such as L-ascorbic acid, the bifenazate equilibrium is displaced towards the bifenazate species, whereas clofentezine is displaced towards the 1,2-dihydroclofentezine species (**Figure 5**).

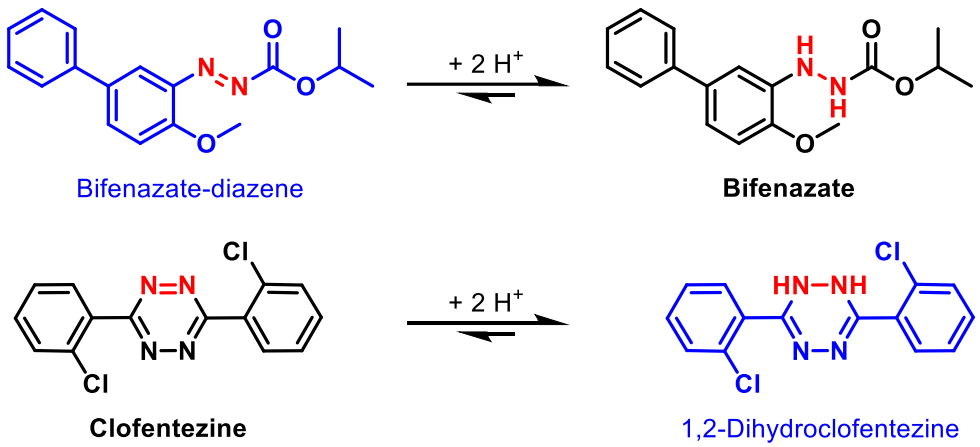

Figure 5. Equilibria between bifenazate and bifenazate-diazene (*top*) and clofentezine and 1,2-dihydroclofentezine (*bottom*).

Without the addition of L-ascorbic acid, the analysis of bifenazate within multiresidue methods is nigh impossible, with high abundances of the diazene species. Nonetheless, with the addition of L-ascorbic acid, virtually all bifenazate-diazene is transformed into bifenazate, which allows for excellent linearity in the calibration curve and also excellent reproducibility. Only very small traces of bifenazate-diazene can be detected with this approach (**Figure 6**).

In the case of clofentezine, however, L-ascorbic acid displaces the equilibrium towards the 1,2-dihydroclofentezine species, but not fully (or almost fully, as in the bifenazate situation), making clofentezine analysis within the scope of a multiresidue method very difficult.

6.4. Comparison with a thermostatted autosampler

As previously described, the original autosampler had no temperature control. Hence, the temperature at which the vials were kept was room temperature (20 – 30 °C). Since the temperature was suspected to be the major source of in-vial degradation processes, the same experiment was repeated using a thermostatted autosampler instead. This autosampler allowed to keep the injection vials at a temperature of 10 °C.

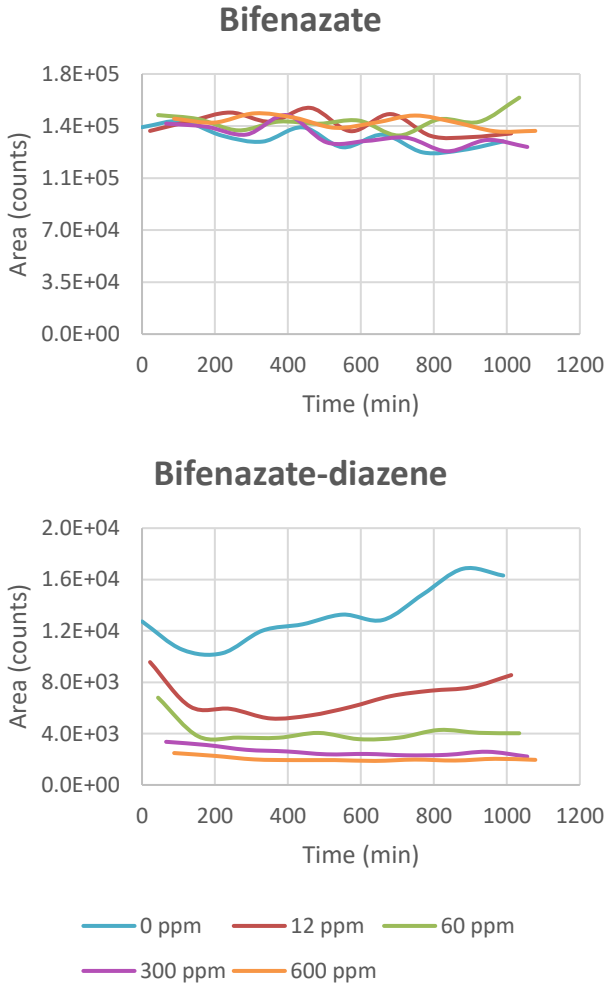

Figure 6. Evolution of bifenazate-diazene abundance over time at different L-ascorbic acid concentration levels. No bifenazate-diazene was added to the vials, i.e. all bifenazate-diazene is due to the bifenazate/bifenazate-diazene equilibrum

The results were in accordance with the hypothesis of uncontrolled temperatures as the main source of in-vial degradation. Out of all the compounds which showed in-vial degradation (**Figure 2**), only dazomet continued to exhibit a downtrend in the absence of L-ascorbic acid (**Figure 7**), whilst bendiocarb, cymoxanil, dithianon, DMA, DMPF, fenpicoxamid, formetanate, methiocarb-sulfone, methiocarb-sulfoxide, phosmet and trichlorfon exhibited stability over the 1100 min evaluated (18.3 h) independent of the L-ascorbic acid concentration.

7. Conclusions

Several compounds have been found to undergo degradation processes in injection vials with an acetonitrile:water (20:80, V/V) solvent at room temperature

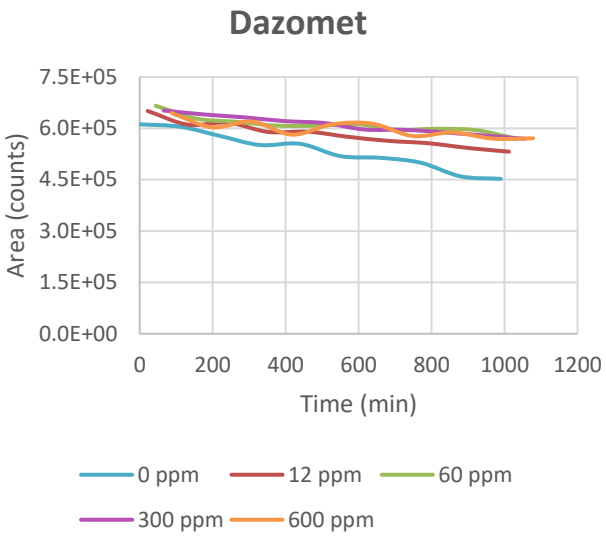

Figure 7. Instrumental response trend for dazomet pesticides positively affected by the presence of L-ascorbic acid (diminished or halted in-vial degradation).

(20-30 °C). These compounds are bendiocarb, cymoxanil, dazomet, dithianon, DMA, DMPF, fenpicoxamid, formetanate, methiocarb-sulfone, methiocarb-sulfoxide, phosmet and trichlorfon. Concentrations of at least 300 ppm of L-ascorbic acid have been shown to decrease or halt in-vial degradation processes, in some cases allowing for accurate quantitation, whilst in other cases allowing, at least, detection.

Other compounds, butoxycarboxm, carbendazim, cyromazine, demeton-*S*-methylsulfoxide (oxydemeton-methyl), flonicamid, methomyl, omethoate, oxamyl and pirimicarb-desmethyl, presented decreased instrumental response with the addition of L-ascorbic acid, with the lowest instrumental response achieved at 600 ppm of the antioxidant. The most probable cause is competing ionisation at the ion source, giving rise to ion suppression for the affected analytes.

Additionally, three sulphonylureas, stable when no L-ascorbic acid is present in the injection vial, presented in-vial degradation, which was faster the higher the L-ascorbic acid concentration was. Sulphonylureas have been described in the literature to react in acidic medium to yield the corresponding sulphonamides and amides, with the loss of the carbonyl group.

Furthermore, there are two specific situations regarding bifenazate and clofentezine. Bifenazate exists in an equilibrium with bifenazate-diazene, whereas clofentezine exists in an equilibrium with 1,2-dihydroclofentezine. At low pH values, as is the case with the addition of L-ascorbic acid, the bifenazate/bifenazate-diazene equilibrium is displaced towards bifenazate, and quantitative analysis is easily achievable. However, in the case of clofentezine/1,2-dihydrocofentezine, at low pH values, the equilibrium is displaced towards the 1,2-dihydroclofentezine species, making quantitation -and potentially detection- extremely difficult.

Finally, all experiments were replicated using a thermostatted autosampler, which kept the injection vials at a constant 10 °C temperature. Under these conditions, all the aforementioned issues were solved, except for the degradation of dazomet, which continued to take place, albeit at a slower rate. Even in thermostatted autosamplers, if accurate quantitation of bifenazate is desired, the addition of L-ascorbic acid is a requirement. On the other hand, even in thermostatted autosamplers, if L-ascorbic acid is added, clofentezine accurate quantitation and detection becomes difficult.

In summary, the use of thermostatted autosamplers is strongly recommended. In the case this is not an option, then, the addition of at least 300 ppm of L-ascorbic acid to the injection vials is suggested. However, in this situation, the effect of L-ascorbic acid on, at least, sulphonylureas and clofentezine, should be kept in mind.

8. References

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APPENDIX: MASS TRANSITIONS

Table A1. Detection and chromatographic parameters for the LC-MS/MS instrument.

Name	t_R (min)	Cone voltage (V)	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)	Polarity
2,4-D	9.59	380	220.96	162.95	15	218.96	160.96	15	Negative
8-Quinolinol	3.09	380	146.10	128.00	25	146.10	100.90	33	Positive
Acephate	2.82	380	184.00	143.00	5	184.00	125.00	15	Positive
Acetamiprid	6.04	380	223.00	126.00	20	223.00	56.00	15	Positive
Alachlor	11.87	380	270.10	238.10	10	270.10	162.00	20	Positive
Albendazole	10.10	380	266.20	234.10	15	266.20	191.00	20	Positive
Aldicarb	7.53	380	213.00	116.00	10	213.00	89.00	15	Positive
Ametoctradin	12.99	380	276.20	176.10	35	276.20	149.00	35	Positive
Anilofos	12.52	380	368.10	198.70	10	368.10	170.90	20	Positive
Atrazine	9.77	380	216.20	173.80	15	216.20	131.90	20	Positive
Avermectin B1a	14.69	380	890.30	567.10	10	890.30	305.10	15	Positive
Azinphos-ethyl	11.63	380	368.00	160.10	10	368.00	131.90	15	Positive
Azinphos-methyl	10.36	380	318.00	261.00	0	318.00	132.10	8	Positive
Azoxystrobin	10.75	380	404.00	372.00	10	404.00	344.00	20	Positive
BAC10	11.45	380	276.20	184.30	20	276.20	90.80	25	Positive
BAC8	9.79	380	248.30	156.20	15	248.30	91.20	35	Positive
Benalaxyl	12.58	380	326.20	208.00	15	326.20	148.00	15	Positive
Bendiocarb	8.72	380	224.10	166.70	5	224.10	109.10	20	Positive
Benzovindiflupyr	12.48	380	398.00	377.90	10	398.00	342.00	15	Positive
Bifenazate	11.57	380	301.10	198.20	10	301.10	169.90	20	Positive
Bifenazate-diazene	12.87	380	299.20	213.20	5	299.20	183.90	26	Positive
Bifenthrin	15.24	380	440.10	198.20	5	440.10	181.00	20	Positive
Bitertanol	12.71	380	338.20	269.20	5	338.20	99.10	10	Positive
Boscalid	11.06	380	343.00	307.10	16	343.00	272.10	32	Positive
Bromacil	8.61	380	261.00	204.80	25	261.00	81.10	25	Negative
Bromuconazole	11.83	380	378.00	159.00	20	378.00	70.00	20	Positive
Bupirimate	11.74	380	317.00	272.00	20	317.00	166.00	20	Positive
Buprofezin	13.65	380	306.00	201.00	10	306.00	116.00	15	Positive
Butoxycarboxim	3.60	380	240.10	222.70	5	240.10	165.90	5	Positive
Carbaryl	9.03	380	202.00	145.00	10	202.00	127.00	20	Positive
Carbendazim	4.17	380	192.00	160.00	15	192.00	132.00	20	Positive
Carbendazim-D_3	4.16	380	195.10	159.80	20	195.10	131.90	20	Positive
Carbofuran	8.72	380	222.00	165.00	10	222.00	123.00	15	Positive
Chlorantraniliprole	10.42	380	483.90	452.90	16	483.90	285.90	8	Positive
Chlorbromuron	11.00	380	292.90	203.90	20	292.90	181.90	15	Positive
Chlorbufam	10.93	380	223.90	172.00	5	223.90	125.80	25	Positive
Chlorfenvinphos	12.78	380	358.90	155.00	8	358.90	99.20	28	Positive

Chlorfluazuron	14.31	380	540.00	382.90	20	540.00	158.10	15	Positive
Chloridazon	5.98	380	222.10	104.10	20	222.10	92.00	20	Positive
Chlorotoluron	9.51	380	213.10	140.00	20	213.10	72.00	20	Positive
Chloroxuron	11.48	380	291.20	217.80	20	291.20	71.90	20	Positive
Chlorpropham	8.58	380	214.00	123.90	15	214.00	96.00	25	Positive
Chlorpyrifos	13.79	380	352.00	200.00	20	349.93	198.00	20	Positive
Chlorpyrifos-methyl	12.86	380	321.90	289.90	14	321.90	125.00	16	Positive
Chromafenozide	11.87	380	395.20	339.10	5	395.20	174.90	10	Positive
Cinerin I	14.30	380	317.00	149.00	5	317.00	107.10	10	Positive
Clofentezine	12.48	380	303.00	138.00	12	303.00	102.00	40	Positive
1,2-Dihydroclofen-tezine	8.95	380	303.00	138.00	12	303.00	102.00	40	Positive
Clomazone	10.54	380	240.10	127.80	10	240.10	124.90	20	Positive
Clopyralid	3.15	380	192.00	146.00	20	192.00	110.00	40	Positive
Coumaphos	12.37	380	363.00	307.00	20	363.00	227.00	28	Positive
Cyazofamid	11.92	380	325.00	261.20	10	325.00	108.10	15	Positive
Cyflufenamid	12.89	380	413.00	294.90	15	413.00	240.80	15	Positive
Cyflumetofen	13.35	380	465.30	248.80	10	465.30	173.10	25	Positive
Cyhalofop-butyl	13.12	380	375.10	256.00	15	375.10	120.10	15	Positive
Cymoxanil	6.44	380	199.10	128.00	4	199.10	110.90	12	Positive
Cyproconazole	11.52	380	292.10	125.00	32	292.10	70.00	16	Positive
Cyprodinil	11.67	380	226.20	92.90	40	226.20	76.90	40	Positive
Cyromazine	2.01	380	167.00	125.00	15	167.00	59.90	20	Positive
Dazomet	3.79	380	163.00	119.90	10	163.00	90.00	5	Positive
DEET	10.04	380	192.10	119.00	15	192.10	91.10	20	Positive
Deltamethrin	14.51	380	522.90	280.80	10	520.90	278.70	10	Positive
Demeton-*S*-methyl	8.76	380	230.90	89.10	5	230.90	61.10	20	Positive
Demeton-*S*-methyl-sulfone	4.40	380	263.02	169.00	12	263.02	109.00	24	Positive
Demeton-*S*-methyl-sulfoxide	4.13	380	247.00	169.00	8	247.00	109.00	24	Positive
Desethylterbuthylazine	9.06	380	202.10	146.10	15	202.10	110.10	20	Positive
Diazinon	12.60	380	305.00	169.00	15	305.00	153.00	20	Positive
Dichlorvos	8.56	380	220.80	108.80	15	220.80	78.90	30	Positive
Dichlorvos-D_6	8.51	380	226.90	132.90	20	226.90	115.00	20	Positive
Dicrotophos	5.15	380	238.09	112.10	8	238.09	72.10	28	Positive
Diethofencarb	10.70	380	268.00	226.00	5	268.00	180.00	15	Positive
Difenoconazole	12.94	380	406.00	337.00	15	406.00	251.00	20	Positive
Difenoxuron	9.94	380	287.20	123.10	15	287.20	72.10	15	Positive
Diflubenzuron	11.94	380	311.00	158.00	8	311.00	141.00	32	Positive
Dimethoate	6.07	380	230.00	199.00	5	230.00	171.00	10	Positive
Dimethoate-D_6	6.00	380	236.00	205.00	4	236.00	131.00	16	Positive
Dimethomorph	11.00	380	388.00	301.00	20	388.00	165.00	20	Positive
Dimethylvinphos	11.56	380	331.00	204.80	10	331.00	127.00	10	Positive
Diniconazole	13.05	380	326.10	159.00	28	326.10	70.00	28	Positive
Dinotefuran	3.28	380	203.10	129.10	9	203.10	114.10	9	Positive

Dithianon	10.91	380	295.90	264.00	20	295.90	163.60	30	Negative
Diuron	10.09	380	233.03	160.00	20	233.03	72.10	20	Positive
DMA	6.36	380	122.00	106.90	15	122.00	79.10	20	Positive
DMF	7.94	380	150.00	132.00	15	150.00	107.00	20	Positive
DMPF	4.73	380	163.00	131.90	15	163.00	122.00	15	Positive
Dodine	12.62	380	228.20	60.10	20	228.20	57.20	20	Positive
Edifenphos	12.40	380	311.10	282.80	10	311.10	110.90	20	Positive
Emamectin B1a benzoate	13.46	380	886.50	302.20	35	886.50	158.10	40	Positive
Epoxiconazole	11.80	380	330.10	121.00	16	330.10	101.20	52	Positive
Ethiofencarb	9.39	380	226.10	163.80	5	226.10	107.20	10	Positive
Ethion	13.80	380	385.10	199.00	5	385.10	171.00	10	Positive
Ethiprole	11.06	380	397.00	351.00	20	397.00	254.80	40	Positive
Ethirimol	7.35	380	210.16	140.10	20	210.16	43.10	52	Positive
Ethoprophos	11.91	380	243.10	130.90	15	243.10	97.00	30	Positive
Etofenprox	14.98	380	394.20	359.10	10	394.20	177.30	8	Positive
Etoxazole	14.11	380	360.00	304.00	20	360.00	140.90	30	Positive
Famoxadone	12.54	380	392.00	331.00	10	392.00	238.00	20	Positive
Fenamidone	11.06	380	312.00	92.20	28	312.00	65.10	56	Positive
Fenamiphos	12.12	380	304.10	234.00	12	304.10	217.10	20	Positive
Fenamiphos-sulfone	9.03	380	336.10	266.00	16	336.10	188.00	24	Positive
Fenamiphos-sulfoxide	8.81	380	320.11	292.10	8	320.11	108.10	44	Positive
Fenarimol	11.79	380	331.00	268.00	20	331.00	259.00	20	Positive
Fenazaquin	14.42	380	307.30	161.30	15	307.30	147.20	15	Positive
Fenbendazole	11.20	380	300.10	268.00	20	300.10	158.90	35	Positive
Fenbuconazole	11.97	380	337.10	125.10	40	337.10	70.00	33	Positive
Fenhexamid	11.70	380	302.00	97.00	25	302.00	55.00	30	Positive
Fenitrothion	9.61	380	278.00	125.00	10	278.00	108.90	16	Positive
Fenobucarb	10.88	380	208.20	151.90	5	208.20	95.10	20	Positive
Fenoxycarb	12.07	380	302.20	116.20	5	302.20	88.20	20	Positive
Fenpicoxamid	13.35	380	615.30	515.00	13	615.30	238.90	25	Positive
Fenpropidin	10.38	380	274.30	147.10	30	274.30	85.80	25	Positive
Fenpropimorph	10.66	380	304.30	147.10	30	304.30	130.00	25	Positive
Fenpyrazamine	11.55	380	332.20	272.10	10	332.20	230.20	20	Positive
Fenpyroximate	13.97	380	422.21	366.20	12	422.21	107.00	64	Positive
Fensulfothion	10.01	380	309.00	252.80	17	309.00	157.00	29	Positive
Fenthion	12.33	380	279.00	247.10	8	279.00	169.10	12	Positive
Fenthion-sulfone	9.29	380	310.70	125.00	15	310.70	108.80	15	Positive
Fenthion-sulfoxide	8.99	380	295.02	280.00	16	295.02	109.00	32	Positive
Fenuron	5.67	380	165.20	92.10	20	165.20	71.80	20	Positive
Fenvalerate	14.59	380	437.10	419.80	5	437.10	167.00	15	Positive
Fipronil	12.28	380	434.90	329.90	12	434.90	249.90	28	Negative
Flazasulfuron	10.46	380	408.00	227.00	20	408.00	182.10	20	Positive
Flonicamid	4.38	380	230.10	202.60	10	230.10	173.90	10	Positive
Fluacrypyrim	13.12	380	427.10	205.00	10	427.10	145.10	15	Positive

Fluazifop	10.97	380	328.20	282.20	15	328.20	254.20	20	Positive
Flubendiamide	12.46	380	680.90	273.90	15	680.90	254.00	20	Negative
Flucythrinate	14.08	380	469.10	412.10	10	469.10	198.90	20	Positive
Fludioxonil	11.13	380	265.90	228.90	5	265.90	158.00	20	Positive
Flufenacet	11.91	380	364.10	194.10	15	364.10	152.00	15	Positive
Flufenoxuron	14.07	380	489.10	158.00	20	489.10	140.90	56	Positive
Fluometuron	9.46	380	233.20	187.90	20	233.20	72.20	20	Positive
Fluopicolide	11.33	380	382.90	172.90	20	382.90	144.80	20	Positive
Fluopyram	11.77	380	397.10	208.00	20	397.10	173.10	20	Positive
Fluquinconazole	11.55	380	376.00	307.10	24	376.00	108.00	56	Positive
Flusilazole	12.16	380	316.10	247.10	12	316.10	165.00	24	Positive
Flutriafol	9.90	380	302.10	95.00	56	302.10	70.10	16	Positive
Fluxapyroxad	11.30	380	381.90	362.00	10	381.90	342.00	15	Positive
Formetanate Hydro-chloride	2.89	380	222.13	165.10	8	222.13	65.10	52	Positive
Fosthiazate	9.52	380	284.00	227.80	10	284.00	103.80	20	Positive
Haloxyfop	12.22	380	362.10	316.20	12	362.10	288.10	24	Positive
Hexaconazole	12.78	380	314.10	159.00	30	314.10	70.10	20	Positive
Hexaflumuron	13.12	380	459.00	439.00	5	459.00	276.10	20	Negative
Hexythiazox	13.98	380	353.10	228.20	10	353.10	168.20	20	Positive
Imazalil	9.51	380	297.00	255.00	15	297.00	159.00	20	Positive
Imidacloprid	5.29	380	256.00	209.00	15	256.00	175.00	15	Positive
Indoxacarb	13.13	380	528.10	218.00	20	528.10	203.00	45	Positive
Ioxynil	10.10	380	369.80	214.80	30	369.80	126.80	30	Negative
Iprovalicarb	11.88	380	321.20	202.90	0	321.20	119.00	16	Positive
Isocarbophos	10.14	380	290.10	121.00	28	290.10	65.20	60	Positive
Isofenfos-methyl	12.39	380	231.00	199.00	15	231.00	121.00	15	Positive
Isoprocarb	9.92	380	194.10	152.00	5	194.10	95.10	15	Positive
Isoprothiolane	11.25	380	291.00	230.70	10	291.00	189.10	15	Positive
Isoproturon	9.98	380	207.15	165.10	20	207.15	72.10	10	Positive
Isoxaflutole	10.17	380	360.00	250.90	15	360.00	219.70	50	Positive
Kresoxim-methyl	12.26	380	314.10	267.00	0	314.10	222.10	10	Positive
Lenacil	9.96	380	235.10	152.90	10	235.10	136.00	20	Positive
Linuron	10.78	380	249.02	160.10	20	249.02	133.00	36	Positive
Lufenuron	13.74	380	508.90	339.00	10	508.90	325.90	10	Negative
Malathion	11.28	380	331.00	285.00	5	331.00	127.10	15	Positive
Malathion-D_{10}	11.32	380	341.11	132.00	12	341.11	100.00	24	Positive
Mandipropamid	11.15	380	412.13	356.10	4	412.13	328.10	8	Positive
Matrine	2.47	380	249.20	247.10	29	249.20	150.10	37	Positive
Matrine-*N*-oxide	3.03	380	265.20	247.10	29	265.20	205.00	29	Positive
Mebendazole	9.23	380	296.10	263.90	21	296.10	105.00	37	Positive
Mepanipyrim	11.27	380	224.10	206.80	10	224.10	190.60	20	Positive
Meptyldinocap	14.49	380	295.10	248.10	30	295.10	193.80	30	Negative
Metaflumizone	13.38	380	505.00	328.00	10	505.00	302.00	10	Negative
Metalaxyl	10.10	380	280.30	220.00	5	280.30	192.40	10	Positive

Metamitron	5.66	380	203.20	174.90	15	203.20	104.10	15	Positive
Metconazole	12.73	380	320.10	125.00	48	320.10	70.10	24	Positive
Methamidophos	2.31	380	142.10	125.00	10	142.10	94.10	10	Positive
Methidathion	10.29	380	302.90	145.00	0	302.90	85.10	15	Positive
Methiocarb	10.96	380	226.10	121.10	12	226.00	169.00	5	Positive
Methiocarb-sulfone	6.35	380	275.00	201.10	5	275.00	122.00	15	Positive
Methiocarb-sulfoxide	5.79	380	242.00	185.00	10	242.00	170.00	20	Positive
Methomyl	4.11	380	163.10	106.00	4	163.10	88.00	0	Positive
Methoxyfenozide	11.57	380	369.30	149.00	15	369.30	133.00	20	Positive
Metobromuron	9.58	380	259.00	170.00	15	259.00	148.00	10	Positive
Metolachlor	12.01	380	284.20	252.10	15	284.20	175.90	20	Positive
Metolcarb	7.96	380	166.00	109.10	5	166.00	91.00	20	Positive
Metrafenone	12.83	380	409.10	226.90	16	409.10	209.10	8	Positive
Monocrotophos	4.73	380	224.20	193.10	5	224.20	127.00	10	Positive
Monolinuron	9.18	380	215.06	148.10	8	215.06	126.00	16	Positive
Monuron	8.20	380	199.10	125.80	20	199.10	71.90	15	Positive
Myclobutanil	11.52	380	289.20	125.10	20	289.20	70.20	15	Positive
Neburon	12.29	380	275.10	113.90	10	275.07	88.10	12	Positive
Nitenpyram	3.83	380	271.00	225.00	10	271.00	99.00	10	Positive
Novaluron	13.29	380	490.80	470.70	5	490.80	305.10	15	Negative
Omethoate	3.12	380	214.10	183.00	5	214.10	125.00	20	Positive
Orthosulfamuron	10.03	380	425.00	226.90	15	425.00	199.10	15	Positive
Oxadiargyl	12.74	380	341.05	222.90	13	341.05	150.90	33	Positive
Oxadixyl	7.80	380	279.10	219.20	5	279.10	132.30	32	Positive
Oxamyl	3.82	380	237.00	90.00	5	237.00	72.00	10	Positive
Oxasulfuron	8.14	380	407.10	209.70	24	407.10	150.10	16	Positive
Oxathiapipronil	11.22	380	540.20	522.00	29	540.20	500.00	29	Positive
Oxfendazole	7.98	380	316.10	284.10	20	316.10	159.10	35	Positive
Oxyfluorfen	13.52	380	362.00	252.00	25	362.00	237.10	30	Positive
Paclobutrazol	11.32	380	294.10	125.20	36	294.10	70.10	16	Positive
Penconazole	12.44	380	284.00	159.00	20	284.00	70.00	15	Positive
Pencycuron	12.97	380	329.10	125.10	24	329.10	89.10	60	Positive
Pendimethalin	13.89	380	282.10	212.10	4	282.10	194.10	16	Positive
Penflufen	12.37	380	318.10	234.00	10	318.10	141.00	20	Positive
Penthiopyrad	12.54	380	357.90	207.60	20	357.90	149.00	25	Negative
Permethrin	14.84	380	408.00	355.20	5	408.00	182.90	15	Positive
Phenthoate	12.29	380	321.00	247.10	4	321.00	79.10	44	Positive
Phosalone	12.74	380	368.00	182.00	8	368.00	110.90	44	Positive
Phosmet	10.46	380	317.99	160.00	8	317.99	133.00	36	Positive
Phoxim	12.67	380	299.00	129.10	4	299.00	77.10	24	Positive
Pirimicarb	7.62	380	239.20	182.10	15	239.20	72.20	20	Positive
Pirimicarb-desmethyl	5.26	380	225.10	168.10	8	225.10	72.10	20	Positive
Pirimiphos-methyl	12.66	380	306.20	164.20	20	306.20	108.20	20	Positive
Prochloraz	12.49	380	376.00	308.00	10	376.00	266.00	15	Positive

Procymidone	11.66	380	284.00	255.80	28	284.00	67.00	28	Positive
Profenofos	13.42	380	374.90	347.00	5	374.90	304.90	15	Positive
Promecarb	11.25	380	208.20	150.90	5	208.20	108.80	10	Positive
Prometryn	11.03	380	242.20	201.00	20	242.20	157.80	20	Positive
Propamocarb	3.27	380	189.20	144.10	10	189.20	102.10	15	Positive
Propaquizafop	13.45	380	444.10	371.00	15	444.10	99.90	20	Positive
Propargite	14.13	380	368.10	231.20	0	368.10	175.20	8	Positive
Propazine	10.87	380	230.20	187.90	15	230.20	146.00	20	Positive
Propiconazole	12.48	380	342.10	159.00	32	342.10	69.10	16	Positive
Propoxur	8.60	380	210.11	168.10	5	210.11	111.10	10	Positive
Propyzamide	11.31	380	256.00	190.00	10	256.00	173.00	20	Positive
Proquinazid	14.15	380	373.00	331.00	20	373.00	289.10	20	Positive
Prosulfocarb	13.32	380	252.10	128.00	10	252.10	90.90	20	Positive
Prothioconazole	12.60	380	341.90	306.10	15	341.90	99.80	20	Negative
Prothioconazole-desthio	11.92	380	312.10	125.00	40	312.10	70.00	20	Positive
Prothiofos	14.60	380	345.00	241.00	20	345.00	161.00	40	Positive
Pymetrozine	2.81	380	218.11	105.00	20	218.11	51.00	60	Positive
Pyraclostrobin	12.54	380	388.11	193.80	8	388.11	163.10	20	Positive
Pyridaben	14.54	380	365.20	309.20	10	365.20	147.30	20	Positive
Pyridalyl	15.32	380	490.00	203.90	20	490.00	108.80	20	Positive
Pyridaphenthion	11.50	380	341.10	205.00	20	341.10	189.00	15	Positive
Pyridate	14.78	380	379.10	351.10	5	379.10	206.80	10	Positive
Pyrimethanil	10.07	380	200.00	183.00	20	200.00	107.00	20	Positive
Pyriofenone	12.86	380	366.10	209.00	20	366.10	183.90	20	Positive
Pyriproxyfen	13.63	380	322.00	185.00	20	322.00	96.00	10	Positive
Quinalphos	12.12	380	299.10	270.80	10	299.10	242.80	10	Positive
Quinoclamine	7.70	380	208.00	105.10	25	208.00	77.00	40	Positive
Quinoxyfen	13.71	380	308.10	271.90	25	308.10	196.90	35	Positive
Quizalofop	11.83	380	345.00	299.00	20	345.00	254.90	35	Positive
Quizalofop-ethyl	13.25	380	373.09	271.20	24	373.09	255.10	36	Positive
Rotenone	11.89	380	395.00	213.10	20	395.00	192.10	20	Positive
Simazine	8.45	380	202.20	131.80	15	202.20	124.00	15	Positive
Spinetoram J	13.08	380	748.30	203.00	30	748.30	142.00	25	Positive
Spinetoram L	13.39	380	760.40	203.00	35	760.40	142.10	35	Positive
Spinosyn A	12.59	380	732.50	142.10	30	732.50	98.10	40	Positive
Spinosyn D	12.95	380	746.50	142.00	25	746.50	98.00	40	Positive
Spirodiclofen	14.43	380	411.10	313.00	5	411.10	71.20	15	Positive
Spiromesifen	14.22	380	371.00	273.00	5	371.00	255.00	20	Positive
Spirotetramat	11.72	380	374.20	330.30	15	374.20	270.10	20	Positive
Spiroxamine	11.02	380	298.00	144.00	20	298.00	100.00	20	Positive
Sulfoxaflor	6.49	380	278.00	153.90	20	278.00	105.10	10	Positive
Tebuconazole	12.45	380	308.00	125.00	20	308.00	70.00	20	Positive
Tebufenozide	12.35	380	353.20	296.90	5	353.20	133.10	15	Positive
Tebufenpyrad	13.58	380	334.20	145.10	20	334.20	117.00	47	Positive

Teflubenzuron	13.57	380	379.00	359.00	0	379.00	339.00	4	Negative
Terbutryn	11.15	380	242.20	186.20	15	242.20	91.00	20	Positive
Terbutylazine	11.07	380	230.00	174.00	15	230.00	146.00	20	Positive
Tetraconazole	11.92	380	372.00	159.00	36	372.00	70.00	20	Positive
Tetramethrin	13.47	380	332.10	163.90	15	332.10	135.10	15	Positive
Thiabendazole	4.83	380	202.00	175.00	30	202.00	131.00	40	Positive
Thiacloprid	6.75	380	253.00	186.00	10	253.00	126.00	20	Positive
Thiamethoxam	4.38	380	292.00	211.00	10	292.00	181.00	20	Positive
Thiobencarb	12.82	380	258.00	124.70	15	258.00	99.90	10	Positive
Tolclofos-methyl	12.62	380	300.90	269.00	10	300.90	125.00	15	Positive
Tolfenpyrad	13.53	380	384.10	197.00	25	384.10	170.90	20	Positive
Triadimefon	11.48	380	294.20	225.00	10	294.20	197.10	10	Positive
Triallate	13.94	380	306.01	145.00	25	306.01	86.00	15	Positive
Triazophos	11.52	380	314.10	286.20	10	314.10	162.20	20	Positive
Trichlorfon	5.96	380	258.90	222.50	5	258.90	108.80	20	Positive
Triclorcarban	13.10	380	313.00	160.00	20	313.00	126.00	20	Negative
Tricyclazole	7.03	380	190.10	163.00	25	190.10	136.10	35	Positive
Trifloxystrobin	13.20	380	409.20	206.20	10	409.20	186.20	20	Positive
Triflumizole	13.23	380	346.10	277.80	5	346.10	72.90	15	Positive
Triflumuron	12.71	380	359.00	156.00	8	359.00	139.00	32	Positive
Triticonazole	11.79	380	318.10	125.20	20	318.10	70.20	20	Positive
Tritosulfuron	10.61	380	446.00	195.00	20	446.00	145.00	40	Positive
Valifenalate	11.58	380	399.00	313.00	10	399.00	143.70	15	Positive
XMC	9.04	380	180.10	123.10	10	180.10	95.10	20	Positive
Zoxamide	12.59	380	336.00	187.00	16	336.00	159.00	44	Positive

t_R: retention time
CE: collision energy