Development and validation of analytical methods: Evaluation of the impact of the use of ascorbic acid during sample milling

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1. Aim and scope

Some compounds are known to degrade (generally by oxidative processes) during the sample comminution step. In previous years, the EURL-FV evaluated these processes in certain pesticides and was able to determine that the addition of ascorbic acid as an antioxidant prevented the degradation of these compounds. In this way, the addition of acid could be of great advantage by preventing the degradation of certain compounds. However, the addition of ascorbic acid before milling could have a negative impact on the other compounds of the multiresidue method. In this activity, the EURL-FV will assess this impact by validating the MRM compounds included in the EU-MACP [1] and in the working document [2]. The extraction method used during the validation will be the QuEChERS method as it is used by more than 90% of the OfLs.

2. Short description

In this study, the effect of adding ascorbic acid during homogenization was evaluated across different matrices, specifically potato, apple, and banana, to determine its influence on pesticide residue stability compared to processes without ascorbic acid. A total of 250 pesticides were examined using liquid chromatography coupled with mass spectrometry (LC-MS/MS). Key parameters, including linearity, matrix effects, and accuracy, were assessed to evaluate the method's effectiveness. Data were analyzed by comparing the results of milling and extraction with and without ascorbic acid.

3. Apparatus and consumables

- Ufesa 1450 Max Miller
- 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 at least 4000 rpm.
- Concentration workstation.
- Injection vials, 2 mL, suitable for LC and GC auto-sampler.

4. Chemicals

- Acetonitrile ultra-gradient grade
- Trisodium citrate dihydrate

- Disodium hydrogenocitrate sesquihydrate
- Sodium chloride
- Anhydrous magnesium sulphate
- Anhydrous calcium chloride
- Ammonium formate
- Ultra-pure water
- Methanol HPLC grade
- Formic acid
- Pesticide standards

5. Procedure

5.1. Sample preparation

Apple, potato, and banana samples were prepared using two different milling procedures prior to extraction. For each matrix, 200 g of the commodity was weighed, with 1% ascorbic acid added in one procedure and omitted in the other. Samples were then extracted following the QuEChERS extraction method, incorporating a conventional dispersive solid phase extraction (dSPE) clean-up step.

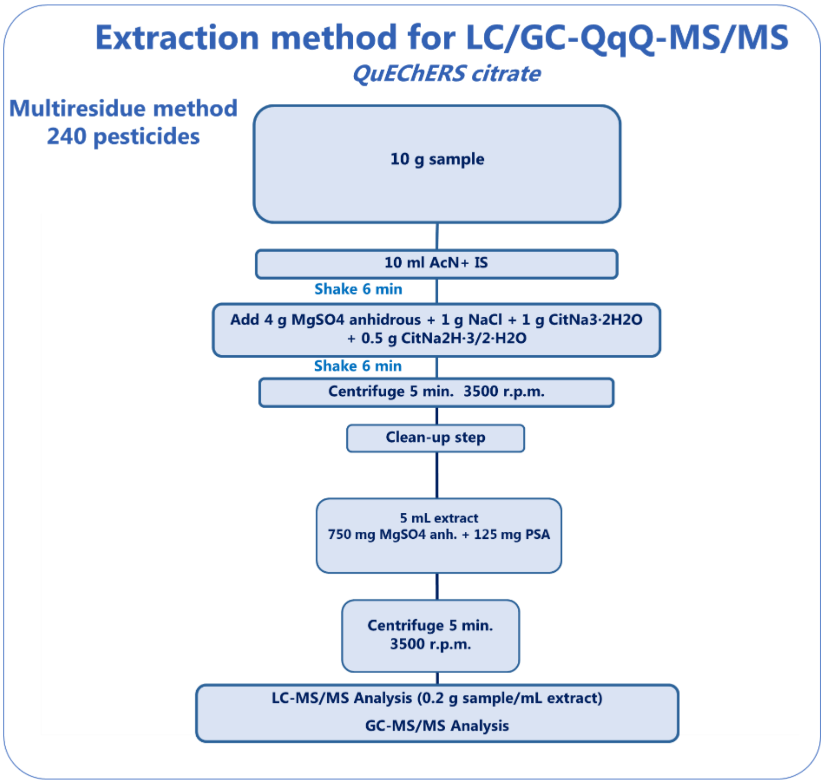

Figure 1. Diagram of the steps involved in the Quenchers extraction procedure

5.2. Pesticide stock solutions and working mix solutions

Individual pesticide stock solutions (1000–2000 mg/L) were prepared in acetonitrile or ethyl acetate and were stored in screw-capped glass vials in the dark at -20 °C. Working mixes were prepared in 10 mL volumetric flasks by pipetting the appropriate volume of each stock solution.

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

5.3.1. 1290 UHPLC (Agilent)

- Flow rate: 0.3 mL/min
- Injection volume: 5 µL
- Column: Zorbax Eclipse Plus C8 2.1x100 mm and a 1.8 µm particle size
- Column oven temperature: 35 °C
- 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)

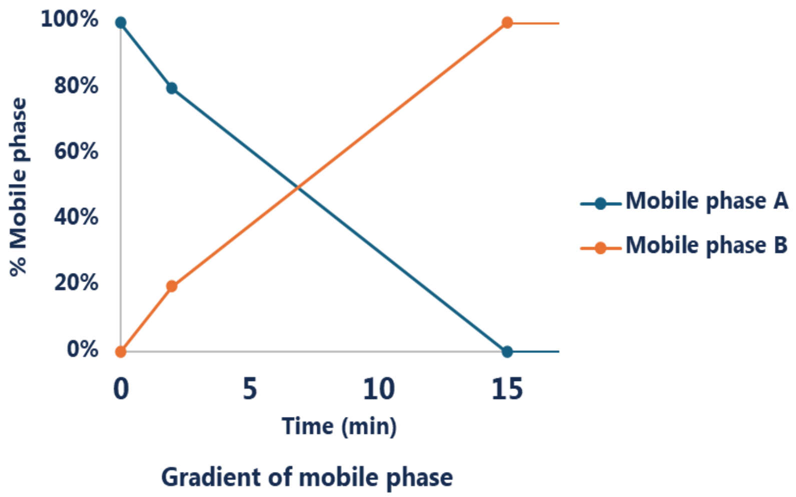

Figure 2. Mobile phase gradient of the LC-MS/MS instrument employed for the analysis.

5.3.2. 8060 triple quadrupole system (Shimadzu)

- Ionisation mode ESI: Positive mode and negative mode
- Ion spray voltage (+): 3500 V
- Ion spray voltage (-): 2500 V

- Nebulizer: 45 psi
- Nozzle: 400 V
- Working mode: MRM
- Drying gas Flow: 13 L/min
- Drying gas temperature: 120°C
- Sheath gas Flow: 10L/min
- Sheath gas temperature: 375°C

6. Results

6.1 Recoveries

Recoveries of the 250 pesticides were assessed following the sample treatment procedure outlined above, both with and without the addition of ascorbic acid. As shown in Figure 1, the majority of compounds in all matrices fall within the accepted recovery range of 70–120%. In the banana and apple matrices, the addition of ascorbic acid had little to no effect on recovery rates; apple samples showed identical recovery percentages with or without ascorbic acid, while banana samples displayed only slight differences.

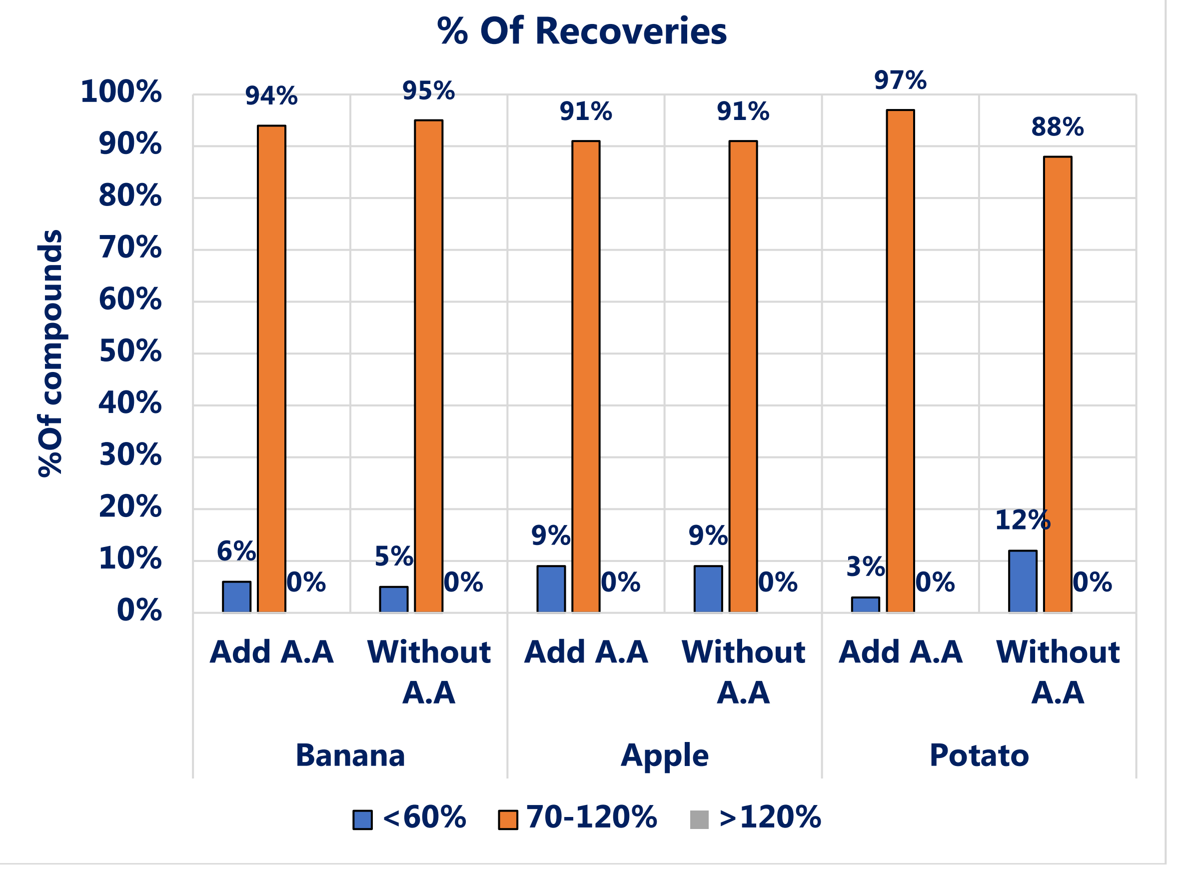

Figure 3. Recoveries of compounds analyzed in the three matrices with and without the addition of ascorbic acid.

In contrast, the potato matrix demonstrated a notable difference. Without ascorbic acid, the percentage of compounds recovered within the accepted range dropped from 97% to 88%, with 12% of compounds falling below the acceptable threshold. These findings indicate that, for potatoes, the use of an antioxidant like ascorbic acid significantly enhances the recovery of compounds within the acceptable range, highlighting its potential benefit in maintaining pesticide stability during sample preparation. The pesticides most affected by the addition of ascorbic acid in the potato matrix are shown in Table 1, along with the bifenazate chromatogram example in figure 4.

Table 1. Pesticides most affected by the addition of ascorbic acid in potato matrix.

Pesticide	Recovery value with addition of AA (%)	Recovery value without addition of AA (%)
Albendazole	86	44
Ametoctradin	91	66
Bifenazate	113	0
Bitertanol	95	67
Chloroxuron	85	68
Dichlorvos	88	9
Difenoconazole	84	68
Difenoxuron	86	64
Dimethomorph	78	62
Edifenphos	85	55
Ethiofencarb	77	58
Farmoxadone	96	53
Fenamidone	82	38
Fenamiphos	84	69
Fenhexamid	83	38
Flubendiamide	91	68
Haloxyfop	71	27
Imazalil	84	61
Ioxynil	70	59
Kresoxim-methyl	91	63
Malathion	77	6
Mefentrifluconazole	87	51
Metamitron	97	70
Methamidophos	78	29
Oxathiapipronil	78	59
Phenthoate	87	68

Propaquizafop	94	8
Pyrethrin I	85	37
Pyrethrin II	89	36
Quinoclamine	79	50
Spirotetramat	77	0
Triconazole	86	62
Tritosulfuron	81	69

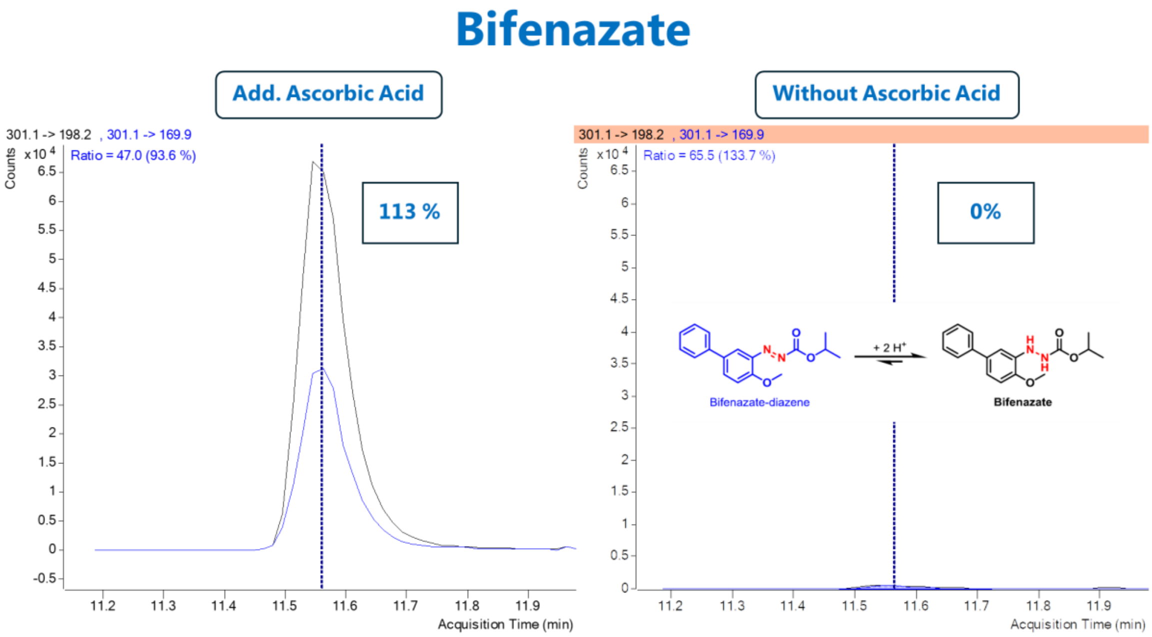

Figure 4. Bifenazate recoveries in the potato matrix. Bifenazate cannot be recovered without the addition of ascorbic acid, as it undergoes oxidation to bifenazate-diazene.

6.2 Matrix effects

The matrix effects were evaluated to determine how components within the matrix impact analytes and, specifically, whether the addition of ascorbic acid modifies these interactions. To assess these effects, calibration curves were prepared both in pure solvent and in the matrix, allowing a comparison of slopes between the two. Matrix components can introduce ion suppression, which reduces sensitivity and consequently affects the calibration curve slope, as shown in Figure 5. This suppression can lead to lower signal intensity for certain analytes, indicating that matrix effects must be carefully managed to ensure accurate quantification. Following DG-SANTE criteria [3], a signal modification within an absolute range of 0 and 20% is considered a low or non-existent matrix effect, while modifications between 20 and 50% and those greater than 50% (absolute values) are deemed medium and strong matrix effects, respectively.

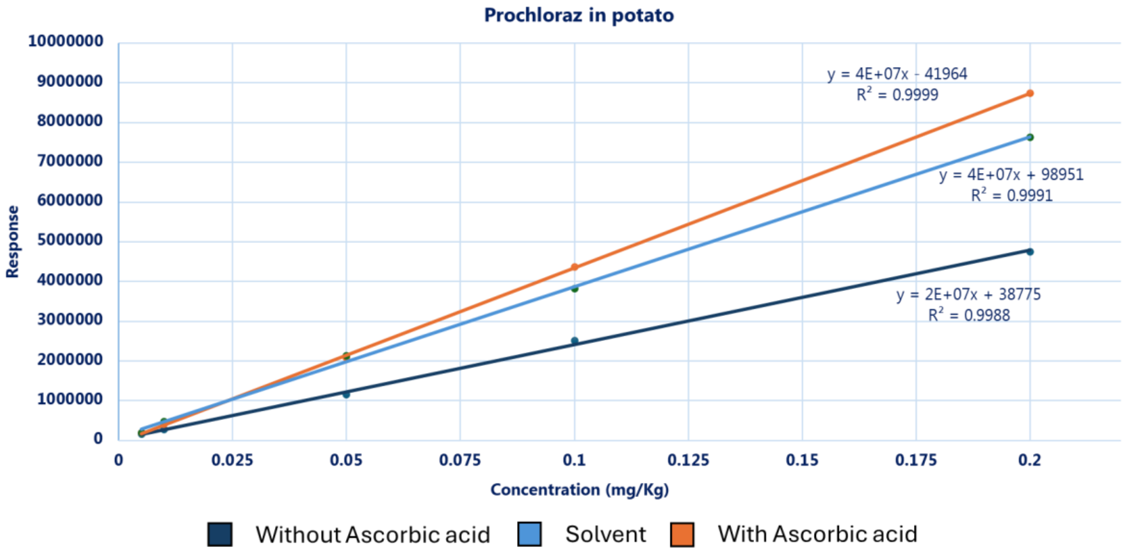

Figure 5. Calibration curves of Prochloraz pesticide in potato with and without ascorbic acid and solvent matrices.

6.2.1 Banana

As shown in figure 6, matrix effects are generally low for 86% of the compounds when ascorbic acid is not added to the sample. This indicates that, under these conditions, most analytes experience minimal interference from the matrix, allowing for reliable detection and quantification. However, after adding ascorbic acid, there is a noticeable change: the proportion of compounds with reduced matrix effects decreases by 30%, suggesting that ascorbic acid may alter the interaction between the analytes and the matrix components.

In particular, the banana matrix with ascorbic acid shows strong matrix effects for 12% of the compounds, which can lead to significant suppression or enhancement of analyte signals. Overall, results obtained from banana samples without added ascorbic acid are likely to be more precise and reliable, as they avoid substantial matrix-induced variations in analyte signal.

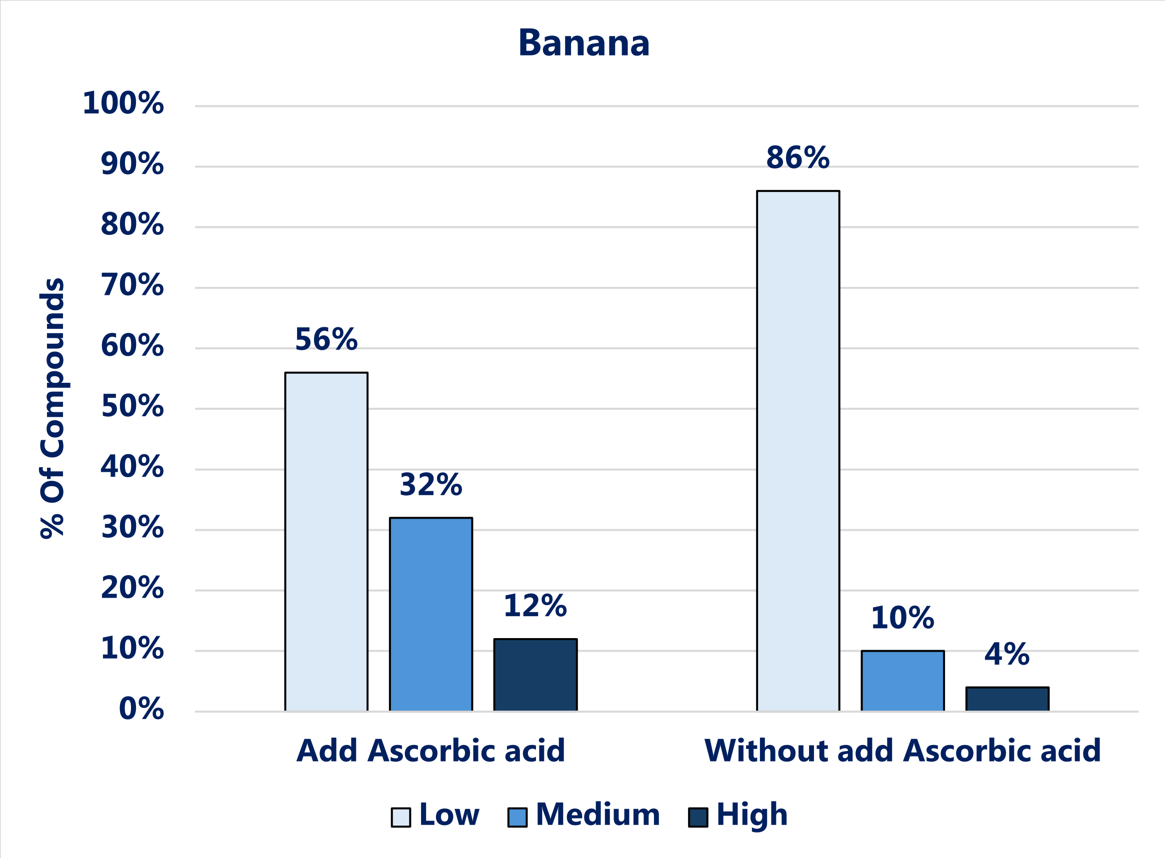

Figure 7. Matrix effect results expressed as percentages for the 250 pesticides evaluated in the banana matrix.

6.2.2 Apple

The matrix effects in the apple matrix showed notable differences depending on the addition of ascorbic acid. When ascorbic acid was added, matrix effects were predominantly low for 86% of the pesticides, while 9% showed medium matrix effects and only 5% exhibited strong matrix effects. This distribution suggests that the presence of ascorbic acid effectively minimized matrix interference for the majority of the compounds analyzed, supporting stable and accurate analyte detection.

In contrast, without the addition of ascorbic acid, the distribution of matrix effects shifted considerably. The proportion of pesticides experiencing low matrix effects dropped to 58%, while those with medium matrix effects rose to 40%. The percentage with high matrix effects also decreased slightly to 2%, but this shift towards increased medium matrix effects indicates greater interference in the analyte signal without the stabilizing influence of ascorbic acid. These findings suggest that ascorbic acid plays a crucial role in reducing matrix effects, particularly by increasing the percentage of pesticides with low matrix interference.

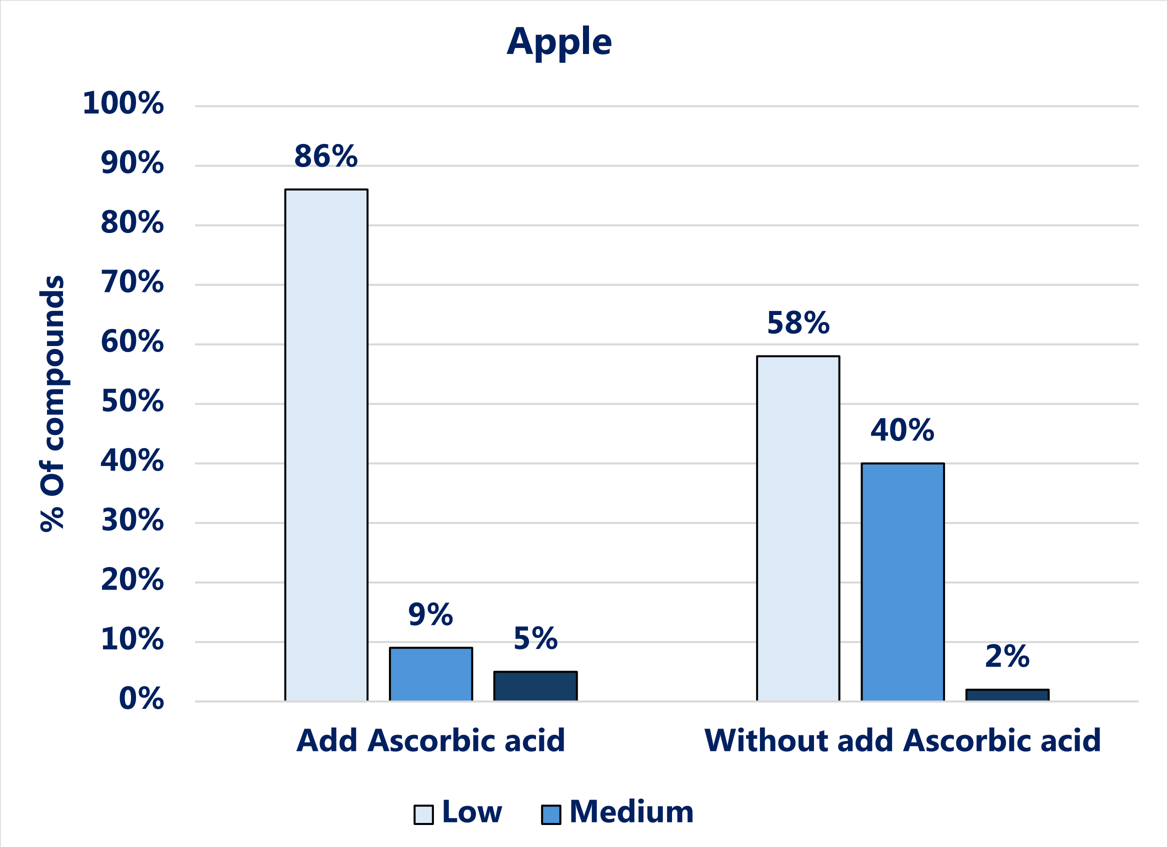

Figure 8. Matrix effect results expressed as percentages for the 250 pesticides evaluated in the apple matrix.

6.2.3 Potato

The matrix effects in the potato matrix exhibited significant differences depending on the presence of ascorbic acid. When ascorbic acid was added, 90% of the pesticides showed low matrix effects, with medium matrix effects observed in 7% of the compounds and strong matrix effects in 3%. This distribution suggests that ascorbic acid effectively reduces matrix interference for the majority of analytes, allowing for more stable and accurate measurements.

In contrast, without the addition of ascorbic acid, the proportion of pesticides with low matrix effects decreased to 50%, while medium and high matrix effects were 47% and 3%, respectively.. These findings highlight the role of ascorbic acid in minimizing matrix effects, particularly by increasing the proportion of compounds with low matrix interference. This suggests that the addition of ascorbic acid can improve the reliability of pesticide quantification in potato matrices by stabilizing analyte responses against matrix-induced variations.

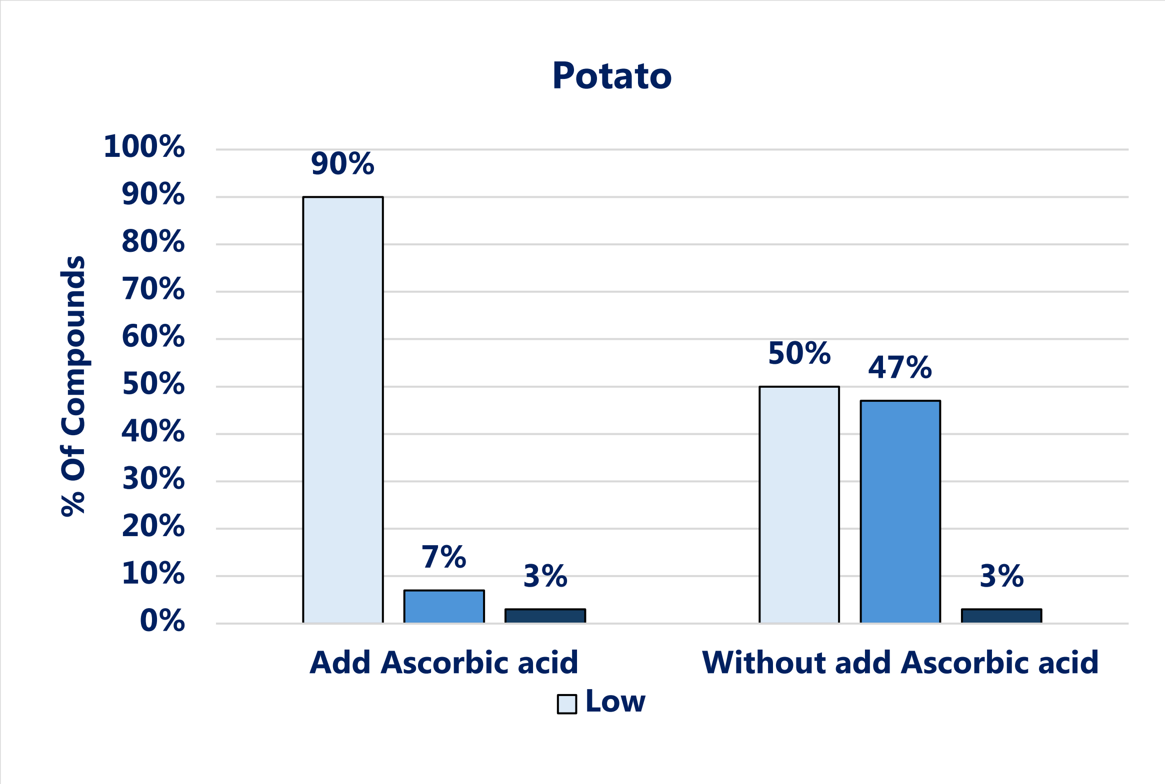

Figure 9. Matrix effect results expressed as percentages for the 250 pesticides evaluated in the potatomatrix.

7. Conclusion

The experiment evaluated the effect of ascorbic acid on the recoveries and matrix effects of 250 pesticides during the milling and extraction processes of banana, apple, and potato. Regarding recoveries, the addition of ascorbic acid had minimal impact on apple and banana, with little to no differences observed. However, for potato, the percentage of compounds within the acceptable recovery range (70–120%) increased significantly from 88% to 97% when ascorbic acid was added. These findings highlight that the influence of ascorbic acid on recoveries varies depending on the matrix.

In terms of matrix effects, the addition of ascorbic acid had a negative impact on banana, intensifying matrix effects. Conversely, in apple and potato matrices, ascorbic acid improved the results by reducing the severity of matrix effects, with many compounds transitioning from medium to low or negligible matrix effects. Overall, the study demonstrates that while the addition of ascorbic acid is not universally advantageous, it can be beneficial for specific analyte-matrix combinations.

8. References

[1] COMMISSION IMPLEMENTING REGULATION (EU) 2019/533 of 28 March 2019 concerning a coordinated multiannual control programme of the Union for 2020, 2021 and 2022 to ensure compliance with maximum residue levels of pesticides and

to assess the consumer exposure to pesticide residues in and on food of plant and animal origin.

[2] Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin (SANCO/12745/2013).

[3] E. Commission, SANTE 11312/2021 – Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed, 2021, pp. 1–51. https://www.eurl-pesticides.eu/userfiles/file/EurlALL/SANTE_11312_2021. pdf.

APPENDIX I: MASS TRANSITIONS

Table 1. Detection parameters for the selected compounds analysed by LC-MS/MS.

Name	tR (min)	Cone Voltaje (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)
Acephate	2.82	380	184.00	143.00	5	184.00	125.00	15
Acetamiprid	6.04	380	223.00	126.00	20	223.00	56.00	15
Alachlor	11.87	380	270.10	238.10	10	270.10	162.00	20
Albendazole	10.10	380	266.20	234.10	15	266.20	191.00	20
Ametoctradin	12.99	380	276.20	176.10	35	276.20	149.00	35
Anilofos	12.52	380	368.10	198.70	10	368.10	170.90	20
Atrazine	9.77	380	216.20	173.80	15	216.20	131.90	20
Azinphos-ethyl	11.63	380	368.00	160.10	10	368.00	131.90	15
Azinphos-methyl	10.36	380	318.00	261.00	0	318.00	132.10	8
Azoxystrobin	10.75	380	404.00	372.00	10	404.00	344.00	20
BAC10	11.45	380	276.20	184.30	20	276.20	90.80	25
BAC8	9.79	380	248.30	156.20	15	248.30	91.20	35
Benalaxyl	12.58	380	326.20	208.00	15	326.20	148.00	15
Bendiocarb	8.72	380	224.10	166.70	5	224.10	109.10	20
Benzovindiflupyr	12.48	380	398.00	377.90	10	398.00	342.00	15
Bifenazate	11.57	380	301.10	198.20	10	301.10	169.90	20
Bifenthrin	15.24	380	440.10	198.20	5	440.10	181.00	20
Bitertanol	12.71	380	338.20	269.20	5	338.20	99.10	10
Boscalid	11.06	380	343.00	307.10	16	343.00	272.10	32
Bromacil	8.61	380	261.00	204.80	25	261.00	81.10	25
Bromuconazole	11.83	380	378.00	159.00	20	378.00	70.00	20
Bupirimate	11.74	380	317.00	272.00	20	317.00	166.00	20
Buprofezin	13.65	380	306.00	201.00	10	306.00	116.00	15
Butoxycarboxim	3.60	380	240.10	222.70	5	240.10	165.90	5
Carbaryl	9.03	380	202.00	145.00	10	202.00	127.00	20
Carbendazim	4.17	380	192.00	160.00	15	192.00	132.00	20
Carbendazim-D3	4.16	380	195.10	159.80	20	195.10	131.90	20
Chlorantraniliprole	10.42	380	483.90	452.90	16	483.90	285.90	8
Chlorbromuron	11.00	380	292.90	203.90	20	292.90	181.90	15
Chlorfenvinphos	12.78	380	358.90	155.00	8	358.90	99.20	28
Chloridazon	5.98	380	222.10	104.10	20	222.10	92.00	20
Chlorotoluron	9.51	380	213.10	140.00	20	213.10	72.00	20
Chloroxuron	11.48	380	291.20	217.80	20	291.20	71.90	20
Chlorpyrifos	13.79	380	352.00	200.00	20	349.93	198.00	20
Chromafenozide	11.87	380	395.20	339.10	5	395.20	174.90	10
Clofentezine	12.48	380	303.00	138.00	12	303.00	102.00	40
Clomazone	10.54	380	240.10	127.80	10	240.10	124.90	20
Coumaphos	12.37	380	363.00	307.00	20	363.00	227.00	28

Name	tR (min)	Cone Voltaje (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)
Cyazofamid	11.92	380	325.00	261.20	10	325.00	108.10	15
Cyflufenamid	12.89	380	413.00	294.90	15	413.00	240.80	15
Cymoxanil	6.44	380	199.10	128.00	4	199.10	110.90	12
Cyproconazole	11.52	380	292.10	125.00	32	292.10	70.00	16
Cyprodinil	11.67	380	226.20	92.90	40	226.20	76.90	40
Cyromazine	2.01	380	167.00	125.00	15	167.00	59.90	20
DEET	10.04	380	192.10	119.00	15	192.10	91.10	20
Demeton-S-methyl	8.76	380	230.90	89.10	5	230.90	61.10	20
Desethylterbuthylazine	9.06	380	202.10	146.10	15	202.10	110.10	20
Diazinon	12.60	380	305.00	169.00	15	305.00	153.00	20
Dichlorvos	8.56	380	220.80	108.80	15	220.80	78.90	30
Dicrotophos	5.15	380	238.09	112.10	8	238.09	72.10	28
Diethofencarb	10.70	380	268.00	226.00	5	268.00	180.00	15
Difenoconazole	12.94	380	406.00	337.00	15	406.00	251.00	20
Difenoxuron	9.94	380	287.20	123.10	15	287.20	72.10	15
Diflubenzuron	11.94	380	311.00	158.00	8	311.00	141.00	32
Dimethoate	6.07	380	230.00	199.00	5	230.00	171.00	10
Dimethomorph	11.00	380	388.00	301.00	20	388.00	165.00	20
Dimethylvinphos	11.56	380	331.00	204.80	10	331.00	127.00	10
Diniconazole	13.05	380	326.10	159.00	28	326.10	70.00	28
Dinotefuran	3.28	380	203.10	129.10	9	203.10	114.10	9
Diuron	10.09	380	233.03	160.00	20	233.03	72.10	20
Dodine	12.62	380	228.20	60.10	20	228.20	57.20	20
Edifenphos	12.40	380	311.10	282.80	10	311.10	110.90	20
Emamectin B1a benzoate	13.46	380	886.50	302.20	35	886.50	158.10	40
Epoxiconazole	11.80	380	330.10	121.00	16	330.10	101.20	52
Ethiofencarb	9.39	380	226.10	163.80	5	226.10	107.20	10
Ethion	13.80	380	385.10	199.00	5	385.10	171.00	10
Ethiprole	11.06	380	397.00	351.00	20	397.00	254.80	40
Ethirimol	7.35	380	210.16	140.10	20	210.16	43.10	52
Ethoprophos	11.91	380	243.10	130.90	15	243.10	97.00	30
Etofenprox	14.98	380	394.20	359.10	10	394.20	177.30	8
Famoxadone	12.54	380	392.00	331.00	10	392.00	238.00	20
Fenamidone	11.06	380	312.00	92.20	28	312.00	65.10	56
Fenamiphos	12.12	380	304.10	234.00	12	304.10	217.10	20
Fenamiphos-sulfone	9.03	380	336.10	266.00	16	336.10	188.00	24
Fenamiphos-sulfoxide	8.81	380	320.11	292.10	8	320.11	108.10	44
Fenarimol	11.79	380	331.00	268.00	20	331.00	259.00	20
Fenbendazole	11.20	380	300.10	268.00	20	300.10	158.90	35
Fenbuconazole	11.97	380	337.10	125.10	40	337.10	70.00	33

Name	tR (min)	Cone Voltaje (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)
Fenhexamid	11.70	380	302.00	97.00	25	302.00	55.00	30
Fenobucarb	10.88	380	208.20	151.90	5	208.20	95.10	20
Fenoxycarb	12.07	380	302.20	116.20	5	302.20	88.20	20
Fenpicoxamid	13.35	380	615.30	515.00	13	615.30	238.90	25
Fenpropidin	10.38	380	274.30	147.10	30	274.30	85.80	25
Fenpropimorph	10.66	380	304.30	147.10	30	304.30	130.00	25
Fenpyrazamine	11.55	380	332.20	272.10	10	332.20	230.20	20
Fenpyroximate	13.97	380	422.21	366.20	12	422.21	107.00	64
Fensulfothion	10.01	380	309.00	252.80	17	309.00	157.00	29
Fenthion	12.33	380	279.00	247.10	8	279.00	169.10	12
Fenthion-sulfone	9.29	380	310.70	125.00	15	310.70	108.80	15
Fenthion-sulfoxide	8.99	380	295.02	280.00	16	295.02	109.00	32
Fenuron	5.67	380	165.20	92.10	20	165.20	71.80	20
Fipronil	12.28	380	434.90	329.90	12	434.90	249.90	28
Flazasulfuron	10.46	380	408.00	227.00	20	408.00	182.10	20
Flonicamid	4.38	380	230.10	202.60	10	230.10	173.90	10
Fluacrypyrim	13.12	380	427.10	205.00	10	427.10	145.10	15
Fluazifop	10.97	380	328.20	282.20	15	328.20	254.20	20
Flubendiamide	12.46	380	680.90	273.90	15	680.90	254.00	20
Fludioxonil	11.13	380	265.90	228.90	5	265.90	158.00	20
Flufenacet	11.91	380	364.10	194.10	15	364.10	152.00	15
Flufenoxuron	14.07	380	489.10	158.00	20	489.10	140.90	56
Fluometuron	9.46	380	233.20	187.90	20	233.20	72.20	20
Fluopicolide	11.33	380	382.90	172.90	20	382.90	144.80	20
Fluopyram	11.77	380	397.10	208.00	20	397.10	173.10	20
Fluquinconazole	11.55	380	376.00	307.10	24	376.00	108.00	56
Flusilazole	12.16	380	316.10	247.10	12	316.10	165.00	24
Flutriafol	9.90	380	302.10	95.00	56	302.10	70.10	16
Fluxapyroxad	11.30	380	381.90	362.00	10	381.90	342.00	15
Fosthiazate	9.52	380	284.00	227.80	10	284.00	103.80	20
Haloxyfop	12.22	380	362.10	316.20	12	362.10	288.10	24
Hexaconazole	12.78	380	314.10	159.00	30	314.10	70.10	20
Hexaflumuron	13.12	380	459.00	439.00	5	459.00	276.10	20
Hexythiazox	13.98	380	353.10	228.20	10	353.10	168.20	20
Imazalil	9.51	380	297.00	255.00	15	297.00	159.00	20
Imidacloprid	5.29	380	256.00	209.00	15	256.00	175.00	15
Indoxacarb	13.13	380	528.10	218.00	20	528.10	203.00	45
Ioxynil	10.10	380	369.80	214.80	30	369.80	126.80	30
Iprovalicarb	11.88	380	321.20	202.90	0	321.20	119.00	16
Isofenfos-methyl	12.39	380	231.00	199.00	15	231.00	121.00	15
Isoprocarb	9.92	380	194.10	152.00	5	194.10	95.10	15

Name	tR (min)	Cone Voltaje (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)
Isoprothiolane	11.25	380	291.00	230.70	10	291.00	189.10	15
Isoproturon	9.98	380	207.15	165.10	20	207.15	72.10	10
Kresoxim-methyl	12.26	380	314.10	267.00	0	314.10	222.10	10
Lenacil	9.96	380	235.10	152.90	10	235.10	136.00	20
Linuron	10.78	380	249.02	160.10	20	249.02	133.00	36
Malathion	11.28	380	331.00	285.00	5	331.00	127.10	15
Mandipropamid	11.15	380	412.13	356.10	4	412.13	328.10	8
Mebendazole	9.23	380	296.10	263.90	21	296.10	105.00	37
Metaflumizone	13.38	380	505.00	328.00	10	505.00	302.00	10
Metalaxyl	10.10	380	280.30	220.00	5	280.30	192.40	10
Metamitron	5.66	380	203.20	174.90	15	203.20	104.10	15
Metconazole	12.73	380	320.10	125.00	48	320.10	70.10	24
Methamidophos	2.31	380	142.10	125.00	10	142.10	94.10	10
Methidathion	10.29	380	302.90	145.00	0	302.90	85.10	15
Methiocarb	10.96	380	226.10	121.10	12	226.00	169.00	5
Methiocarb-sulfone	6.35	380	275.00	201.10	5	275.00	122.00	15
Methiocarb-sulfoxide	5.79	380	242.00	185.00	10	242.00	170.00	20
Methomyl	4.11	380	163.10	106.00	4	163.10	88.00	0
Methoxyfenozide	11.57	380	369.30	149.00	15	369.30	133.00	20
Metobromuron	9.58	380	259.00	170.00	15	259.00	148.00	10
Metolachlor	12.01	380	284.20	252.10	15	284.20	175.90	20
Metrafenone	12.83	380	409.10	226.90	16	409.10	209.10	8
Monocrotophos	4.73	380	224.20	193.10	5	224.20	127.00	10
Monolinuron	9.18	380	215.06	148.10	8	215.06	126.00	16
Monuron	8.20	380	199.10	125.80	20	199.10	71.90	15
Myclobutanil	11.52	380	289.20	125.10	20	289.20	70.20	15
Neburon	12.29	380	275.10	113.90	10	275.07	88.10	12
Nitenpyram	3.83	380	271.00	225.00	10	271.00	99.00	10
Omethoate	3.12	380	214.10	183.00	5	214.10	125.00	20
Orthosulfamuron	10.03	380	425.00	226.90	15	425.00	199.10	15
Oxadiargyl	12.74	380	341.05	222.90	13	341.05	150.90	33
Oxadixyl	7.80	380	279.10	219.20	5	279.10	132.30	32
Oxamyl	3.82	380	237.00	90.00	5	237.00	72.00	10
Oxasulfuron	8.14	380	407.10	209.70	24	407.10	150.10	16
Oxathiapipronil	11.22	380	540.20	522.00	29	540.20	500.00	29
Oxfendazole	7.98	380	316.10	284.10	20	316.10	159.10	35
Paclobutrazol	11.32	380	294.10	125.20	36	294.10	70.10	16
Penconazole	12.44	380	284.00	159.00	20	284.00	70.00	15
Pencycuron	12.97	380	329.10	125.10	24	329.10	89.10	60
Pendimethalin	13.89	380	282.10	212.10	4	282.10	194.10	16
Penflufen	12.37	380	318.10	234.00	10	318.10	141.00	20

Name	tR (min)	Cone Voltaje (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)
Penthiopyrad	12.54	380	357.90	207.60	20	357.90	149.00	25
Phenthoate	12.29	380	321.00	247.10	4	321.00	79.10	44
Phosalone	12.74	380	368.00	182.00	8	368.00	110.90	44
Phosmet	10.46	380	317.99	160.00	8	317.99	133.00	36
Phoxim	12.67	380	299.00	129.10	4	299.00	77.10	24
Pirimicarb	7.62	380	239.20	182.10	15	239.20	72.20	20
Pirimiphos-methyl	12.66	380	306.20	164.20	20	306.20	108.20	20
Prochloraz	12.49	380	376.00	308.00	10	376.00	266.00	15
Profenofos	13.42	380	374.90	347.00	5	374.90	304.90	15
Promecarb	11.25	380	208.20	150.90	5	208.20	108.80	10
Propamocarb	3.27	380	189.20	144.10	10	189.20	102.10	15
Propaquizafop	13.45	380	444.10	371.00	15	444.10	99.90	20
Propargite	14.13	380	368.10	231.20	0	368.10	175.20	8
Propazine	10.87	380	230.20	187.90	15	230.20	146.00	20
Propiconazole	12.48	380	342.10	159.00	32	342.10	69.10	16
Propoxur	8.60	380	210.11	168.10	5	210.11	111.10	10
Propyzamide	11.31	380	256.00	190.00	10	256.00	173.00	20
Proquinazid	14.15	380	373.00	331.00	20	373.00	289.10	20
Prosulfocarb	13.32	380	252.10	128.00	10	252.10	90.90	20
Pymetrozine	2.81	380	218.11	105.00	20	218.11	51.00	60
Pyraclostrobin	12.54	380	388.11	193.80	8	388.11	163.10	20
Pyridaben	14.54	380	365.20	309.20	10	365.20	147.30	20
Pyridalyl	15.32	380	490.00	203.90	20	490.00	108.80	20
Pyridaphenthion	11.50	380	341.10	205.00	20	341.10	189.00	15
Pyridate	14.78	380	379.10	351.10	5	379.10	206.80	10
Pyrimethanil	10.07	380	200.00	183.00	20	200.00	107.00	20
Pyriofenone	12.86	380	366.10	209.00	20	366.10	183.90	20
Pyriproxyfen	13.63	380	322.00	185.00	20	322.00	96.00	10
Quinalphos	12.12	380	299.10	270.80	10	299.10	242.80	10
Quinoclamine	7.70	380	208.00	105.10	25	208.00	77.00	40
Quinoxyfen	13.71	380	308.10	271.90	25	308.10	196.90	35
Quizalofop	11.83	380	345.00	299.00	20	345.00	254.90	35
Quizalofop-ethyl	13.25	380	373.09	271.20	24	373.09	255.10	36
Rotenone	11.89	380	395.00	213.10	20	395.00	192.10	20
Simazine	8.45	380	202.20	131.80	15	202.20	124.00	15
Spinetoram J	13.08	380	748.30	203.00	30	748.30	142.00	25
Spinetoram L	13.39	380	760.40	203.00	35	760.40	142.10	35
Spinosyn A	12.59	380	732.50	142.10	30	732.50	98.10	40
Spinosyn D	12.95	380	746.50	142.00	25	746.50	98.00	40
Spirodiclofen	14.43	380	411.10	313.00	5	411.10	71.20	15
Spiromesifen	14.22	380	371.00	273.00	5	371.00	255.00	20

Name	tR (min)	Cone Voltaje (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)
Spirotetramat	11.72	380	374.20	330.30	15	374.20	270.10	20
Spiroxamine	11.02	380	298.00	144.00	20	298.00	100.00	20
Sulfoxaflor	6.49	380	278.00	153.90	20	278.00	105.10	10
Tebuconazole	12.45	380	308.00	125.00	20	308.00	70.00	20
Tebufenozide	12.35	380	353.20	296.90	5	353.20	133.10	15
Tebufenpyrad	13.58	380	334.20	145.10	20	334.20	117.00	47
Teflubenzuron	13.57	380	379.00	359.00	0	379.00	339.00	4
Terbutryn	11.15	380	242.20	186.20	15	242.20	91.00	20
Terbutylazine	11.07	380	230.00	174.00	15	230.00	146.00	20
Tetraconazole	11.92	380	372.00	159.00	36	372.00	70.00	20
Tetramethrin	13.47	380	332.10	163.90	15	332.10	135.10	15
Thiabendazole	4.83	380	202.00	175.00	30	202.00	131.00	40
Thiacloprid	6.75	380	253.00	186.00	10	253.00	126.00	20
Thiamethoxam	4.38	380	292.00	211.00	10	292.00	181.00	20
Thiobencarb	12.82	380	258.00	124.70	15	258.00	99.90	10
Tolclofos-methyl	12.62	380	300.90	269.00	10	300.90	125.00	15
Tolfenpyrad	13.53	380	384.10	197.00	25	384.10	170.90	20
Triadimefon	11.48	380	294.20	225.00	10	294.20	197.10	10
Triallate	13.94	380	306.01	145.00	25	306.01	86.00	15
Triazophos	11.52	380	314.10	286.20	10	314.10	162.20	20
Trichlorfon	5.96	380	258.90	222.50	5	258.90	108.80	20
Triclorcarban	13.10	380	313.00	160.00	20	313.00	126.00	20
Tricyclazole	7.03	380	190.10	163.00	25	190.10	136.10	35
Trifloxystrobin	13.20	380	409.20	206.20	10	409.20	186.20	20
Triflumizole	13.23	380	346.10	277.80	5	346.10	72.90	15
Triflumuron	12.71	380	359.00	156.00	8	359.00	139.00	32
Triticonazole	11.79	380	318.10	125.20	20	318.10	70.20	20
Tritosulfuron	10.61	380	446.00	195.00	20	446.00	145.00	40
Valifenalate	11.58	380	399.00	313.00	10	399.00	143.70	15
XMC	9.04	380	180.10	123.10	10	180.10	95.10	20
Zoxamide	12.59	380	336.00	187.00	16	336.00	159.00	44
Aldicarb-sulfone	3.464	380	239.9	223	5	239.9	86	20
Avermectin B1a	14.643	380	890.3	305.1	15	890.3	567.1	10
Cyantraniliprole	9.206	380	474.9	285.8	25	474.9	444	15
Demeton-S-methylsulfone	4.401	380	230.9	169	12	230.9	109	24
Demeton-S-methylsulfoxide (Oxydemeton-methyl)	4.131	380	247	169	8	247	109	24
Emamectin B1b benzoate	13.132	380	827.5	157.9	30	827.5	82	35
EPN	12.967	380	324.1	296	10	324.1	156.99	20
Fenpropathrin	14.257	380	367.2	124.8	15	367.2	350	5

Name	tR (min)	Cone Voltaje (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)
Florpyrauxifen-benzyl	12.753	380	439.2	91.1	40	439.2	65	75
Flupyradifuron	6.077	380	289.2	126	20	289.2	72.9	75
Forchlorfenuron	9.907	380	248	128.9	20	248	93	30
Haloxyfop-methyl	13.019	380	375.9	316	15	375.9	287.9	25
Mefentrifluconazole	12.56	380	397.8	70	25	397.8	182	35
Pyrethrin I	14.306	380	329.1	161	5	329.1	143	20
Pyrethrin II	13.215	380	373.1	161	10	373.1	133	15
Triadimenol	11.336	380	296	70	10	296	227	5
Trinexapac-ethyl	10.158	380	253.1	185.1	5	253.1	41.1	45
Trinexapac-methyl	9.055	380	239.1	69	10	239.1	41.2	40