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Nota de aplicación

Determination of Pesticide Residues in Black Peppercorns Using LC-MS/MS After Extraction and Clean up Using QuEChERS and Pass-Through SPE

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Abstract

Applying a generic QuEChERS protocol without clean-up is challenging when faced with complex food commodities due to the abundance of endogenous components, such as fats, phospholipids, pigments, and other phytochemicals. These components are known to cause matrix effects and isobaric interference, which negatively impact detection and quantitation of pesticide residues. Adding a clean-up step after extraction helps to remove matrix components to obtain more reliable results, improving sensitivity and selectivity, and maintaining instrument robustness. Using Solid-Phase Extraction (SPE) with a pass-through protocol allows pesticides to pass through the stationary phase, whereas the matrix components are retained on the SPE sorbent material.

The objective of this work was to establish the performance of a method for pesticide residues in peppercorn, based upon QuEChERS but using a simple pass-through SPE cleanup with an Oasis™ PRiME HLB cartridge prior to UPLC-MS/MS using an ACQUITY™ UPLC I-Class PLUS System coupled with a Xevo™ TQ-S micro Tandem Quadrupole Mass Spectrometer. We optimized a two-step protocol whereby the QuEChERS extract was pushed

through the cartridge, the first 0.25 mL discarded, and the remaining eluate collected for LC-MS/MS. The performance of the method has been successfully evaluated. 84% of the compounds exhibited values for Lowest Calibrated Level (LCL) at 0.005 mg/kg and 85% of the analytes exhibited recovery at all three concentrations within the tolerances set in the SANTE guidelines: 70–120%. A simple pass-through SPE protocol with an Oasis PRiME HLB cartridge was proven to be a quick but effective alternative to dilute and shoot or dispersive SPE and has been shown to be suitable for checking MRL compliance for pesticide residues in peppercorns.

Benefits

- Pass-through cleanup with the Oasis PRiME HLB cartridge is an effective and quick means for removal of fats, phospholipids, and pigments from QuEChERS extracts whilst maintaining excellent recoveries for the pesticides of interest
- The performance of the method in terms of sensitivity and recovery has been successfully evaluated using the SANTE acceptance criteria
- This method has been demonstrated as suitable for analysis of peppercorns, for checking compliance with MRLs

Introduction

Black and white pepper, ubiquitous in table shakers and takeout packets, comes from the peppercorn, the dried berry of a flowering vine native to Southeast Asia but now mainly produced commercially in Vietnam, Indonesia, India, Malaysia, Sri Lanka, and Brazil. Pepper is one of the most valuable spices in the world and brings significant revenue to those countries involved in its export. Pesticides are often widely applied for pest and disease control during black pepper planting, storage, and production. Various countries have established maximum residue levels (MRLs) for pesticides approved for use on pepper vines. These are the maximum concentration of pesticide residues in peppercorn (black, green, and white) that is legally tolerated when a pesticide is applied correctly to the pepper vine, following good agricultural practice. The excessive use of pesticides may result in residues that exceed the MRLs if the pre-harvest intervals and correct dosages are not adhered to by the growers or illegal pesticides are used. Not only is this a possible health risk, but it also has a negative impact on trade due to rejections of imported consignments and product recalls. In the EU, the “default MRL” applies for pesticides without an approved use on pepper vines, which is equal to the limit of quantification

(LOQ) achievable with analytical methods used for MRL enforcement. For peppercorns, the value of the default MRL in the EU varies depending on the pesticide and is between 0.01 and 0.1 mg/kg. India has adopted a similar system; if no MRL is specified by the Codex, then the MRL of 0.1 mg/kg shall apply.[1]

Compliance with these MRLs is checked by the monitoring for residues in peppercorn samples, by governments and the food and agriculture industries. Hence, reliable analytical methods are needed for detection, quantification, and identification of hundreds of pesticide residues in this complex commodity. The implementation of multiresidue methods has made a significant contribution to not only extending the scope of analyses but their effective and efficient implementation. Applying the typical QuEChERS protocol to the analysis of peppercorns without clean-up is challenging due to the abundance of endogenous components, such as fats, phospholipids, pigments, and other phytochemicals. These components are known to cause matrix effects and isobaric interference, which negatively impact detection and quantitation of pesticide residues. Adding a clean-up step after extraction helps to remove matrix components to obtain more reliable results, improving sensitivity and selectivity, and maintaining instrument robustness. Using Solid-Phase Extraction (SPE), in either dispersive (dSPE) or pass-through mode of action, allows pesticides to partition into the solvent, whereas the matrix components are retained on the SPE sorbent material.[2]

The objective of this work was to establish the performance of a method based upon QuEChERS prior to UPLC-MS/MS using the ACQUITY UPLC I-Class PLUS System coupled with the Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer. The performance of a conventional dSPE approach was compared using a simple pass-through SPE cleanup protocol with Oasis PRiME HLB and some initial validation work completed.

Experimental

Sample Preparation, Extraction, and Cleanup

A sample of ground black peppercorns was purchased from a local retail store. Samples were extracted using a modification of the CEN QuEChERS method.[3] The dSPE step (150 mg $MgSO_4$, 25 mg PSA, 25 mg C_{18}, and 7 mg GCB) was compared with a simple pass-through SPE protocol with an Oasis PRiME HLB cartridge, optimized for this analysis. An overview of the sample extraction and cleanup procedures used is given in Figure 1.

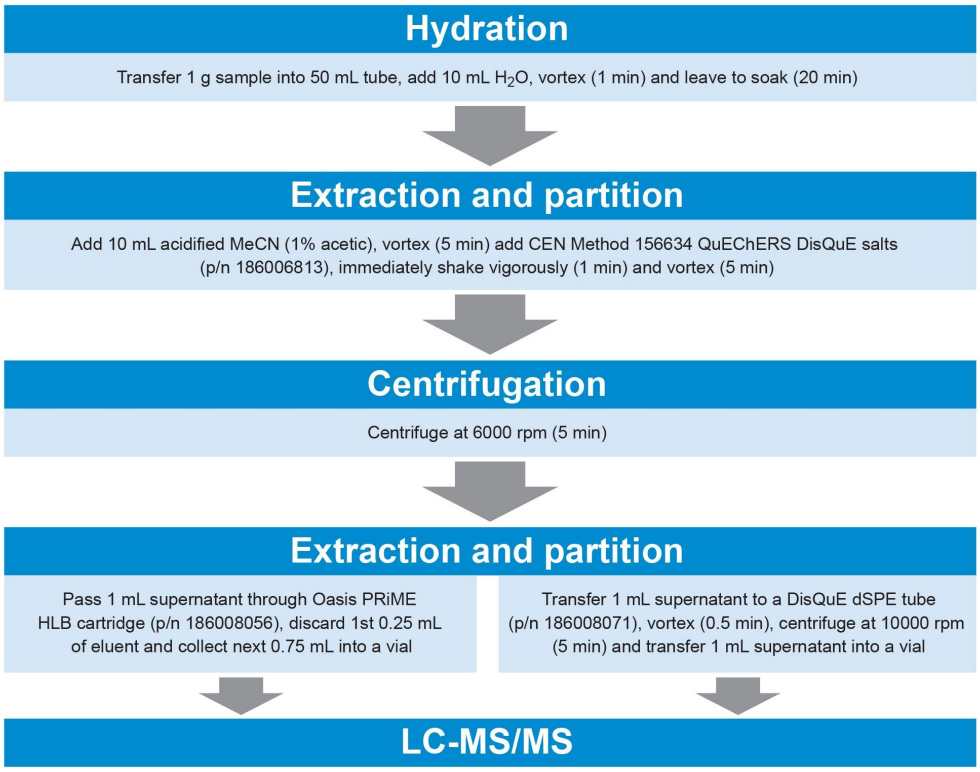

Figure 1. Overview of the details of sample preparation and cleanup for pesticide residues in black peppercorns.

The LC Multiresidue Pesticide Kit (Restek p/n: 31971), containing 204 pesticides, was used to prepare working solutions to create matrix-matched calibration standards and for spiking the black peppercorn test portions (0.01, 0.05, and 0.2 mg/kg). The calibration standards were prepared over the range 0.005 to 1.0 mg/kg.

LC Conditions

LC system:	ACQUITY UPLC I-Class Plus with BSM and FTN SM fitted with 50 µL Extension Loop Assembly (p/n: 430002012)
Vials:	Clear Glass 12 x 32 mm Screw Neck Vial, (p/n:

	186000273)
Column:	ACQUITY™ Premier HSS T3, 1.8 µm, 2.1 x 100 mm (p/n: 186009468)
Post injector mixing kit:	50 µL Extension Loop Assembly (p/n: 430002012)
Column temperature:	40 °C
Sample temperature:	10 °C
Injection volume:	2 µL
Wash solvent:	25/25/25/25 water/acetonitrile/methanol/isopropanol
Purge solvent:	95/5 water/acetonitrile
Seal wash:	95/5 water/acetonitrile
Mobile phase A:	10 mM ammonium formate + 0.1% formic acid in water
Mobile phase B:	10 mM ammonium formate + 0.1% formic acid in methanol

Gradient Table

Time (min)	Flow rate (mL/min)	%A	%B	Curve
0	0.5	100	0	Initial
0.2	0.5	100	0	6
0.5	0.5	50	50	7
2.5	0.5	45	55	7
7.5	0.5	15	85	6
8.3	0.5	0	100	6
12.0	0.5	0	100	6
12.1	0.5	100	0	6
15.0	0.5	100	0	6

MS Conditions

MS system:	Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer
Ionization mode:	Electrospray (positive and negative ion mode using polarity switching)
Capillary voltage:	0.5 and -1.0 kV
Source temperature:	120 °C
Desolvation temperature:	300 °C
Desolvation gas flow:	1000 L/hr
Cone gas flow:	0 L/hr

Data Mangement

Software:	waters_connect™ for Quantitation

The LC-MS/MS method for 204 pesticide analytes was created using the Acquisition Method Editor (AME) application in waters_connect for Quantitation and by importing MRMs previous created in MassLynx™ from a Quanpedia™ database. A list of the compounds included in the method can be found in the Annex.

Method Validation

Initially, the performance of two approaches to clean-up were evaluated for matrix effects, sensitivity, and recovery. The performance of the final method was then evaluated by analysis of spiked black peppercorn. The following factors were assessed: selectivity, sensitivity, calibration graph characteristics, and recovery. No assessment of within-laboratory repeatability was made in this work.

Results and Discussion

Clean-up

Dispersive SPE with multiple sorbents can be used to remove matrix co-extractives during QuEChERS but can lead to losses of certain pesticides. Here the crude extract was loaded into a 2 mL tube containing DisQuE sorbent comprising $MgSO_4$ to remove excess moisture, PSA (primary secondary amine) to remove fatty acids, sugars, and lipids, C_{18} to remove fats, waxes and other non-polar components and GCB (graphitized carbon black) to remove pigments. After shaking, the contents were centrifuged, and the supernatant collected.

The pass-through SPE protocol inverts the classical SPE approach by passing through the analytes of interest and retaining co-extracted fats, phospholipids, and pigments on the sorbent. Clean-up of the extracted sample on the Oasis HLB PRiME SPE cartridge was optimized by evaluating the stage at which the analytes pass through the cartridge. Here, the first 0.25 mL of eluant was discarded before collecting the next 0.75 mL containing most of the analytes with satisfactory recovery, whilst effectively removing matrix co-extractives.

Black peppercorns are associated with significant matrix effects.[4] Neither of the two clean-up options were able to remove all the co-extractives but matrix effects were effectively reduced for almost 50% of the analytes. There was little difference between the sensitivity, linearity, and matrix effects of the two approaches, but the Oasis

HLB PRiME approach provided better performance in terms of recovery: 86% of analytes within SANTE tolerance compared with 67% when using the dSPE approach.

Chromatography

Chromatography was shown to be stable with no significant change in retention times across the batches analyzed. The ACQUITY Premier HSS T3 Column provided sufficient retention for all but the most polar analytes and resulted in good separation and distribution of the 203 peaks within a 15-minute run time. Some of the pesticides in the method comprised multiple isomers that were quantified as separate peaks and evaluated separately. Despite the large number of compounds included, data quality, in terms of a sufficient number of data points across each peak, was not compromised.

QuEChERS has been used for the routine determination of pesticide residues using LC-MS/MS in numerous laboratories for many years. Those making direct injections of acetonitrile extracts typically observe fronting and/or split peaks for the early eluting compounds. The local concentration of the strong injection solvent is not in equilibrium with the high aqueous mobile phase, *i.e.* not immediately diluted by the mobile phase. Some of the analyte molecules migrate down the column with the stronger solvent whereas other molecules of the same analyte are diluted and migrate with the mobile phase. The impact is loss of sensitivity, peak detection issues, the need for manual intervention for peak integration and at data review and failure to pass typical peak shape acceptance criteria. Dilution of the batch of extracts with aqueous solvent can result in losses of analytes during storage. This can be avoided by using a post-injection mixing kit. A 50 µL extension loop is fitted in the SM-FTN, between position six of the injection pod and the column inlet tubing, to add more volume to aid dispersion of the acetonitrile prior to injection. Figure 2 shows the influence of post-injection mixing on peak shape of early eluting polar pesticides after injection of peppercorn extract in acetonitrile.

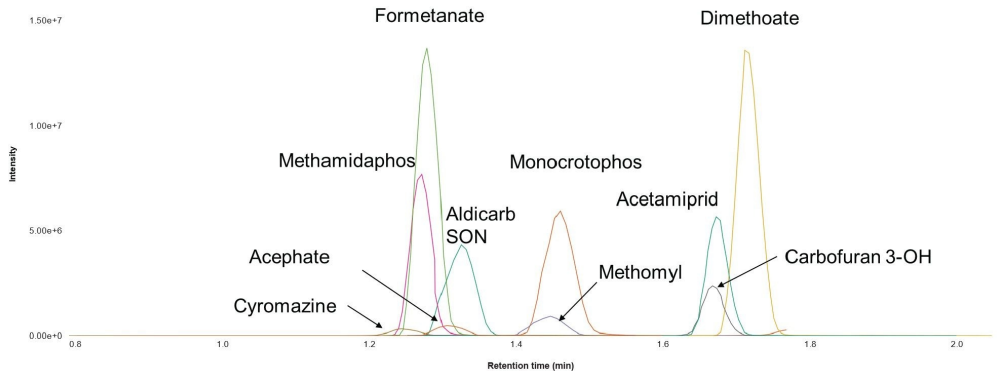

Figure 2. Chromatograms showing the influence of post-injection mixing on peak shape of early eluting polar pesticides after injection of peppercorn extract in acetonitrile.

Sensitivity, Selectivity, and Calibration Criteria

Representative samples of black peppercorn were prepared as blanks. In some cases, signal was detected in the blanks that impacted the sensitivity of the method. This was either due to co-eluting isobaric interference or incurred residues. Values for the Lowest Calibrated Level (LCL) were adjusted accordingly. The LCL is the concentration at which the LC-MS/MS system was successfully calibrated, throughout the analysis batch, ***i.e.*** meets the acceptance criteria for response (S/N >3), and contribution from blanks and residuals (± 20%). Despite the complexity of the sample extract, 84% of the compounds exhibited values for LCL at 0.005 mg/kg with a further 10% at 0.01 mg/kg.

Bracketed, calibration curves were prepared in black peppercorn extract. Linear or quadratic fits were applied, with 1/x weighing, and in all but two cases correlation of determination (R^2) values from the calibration graphs were ≥0.99, with individual residuals all <20%, demonstrating reliable quantification to check compliance with MRLs. Examples of typical calibration curves are given in Figure 3.

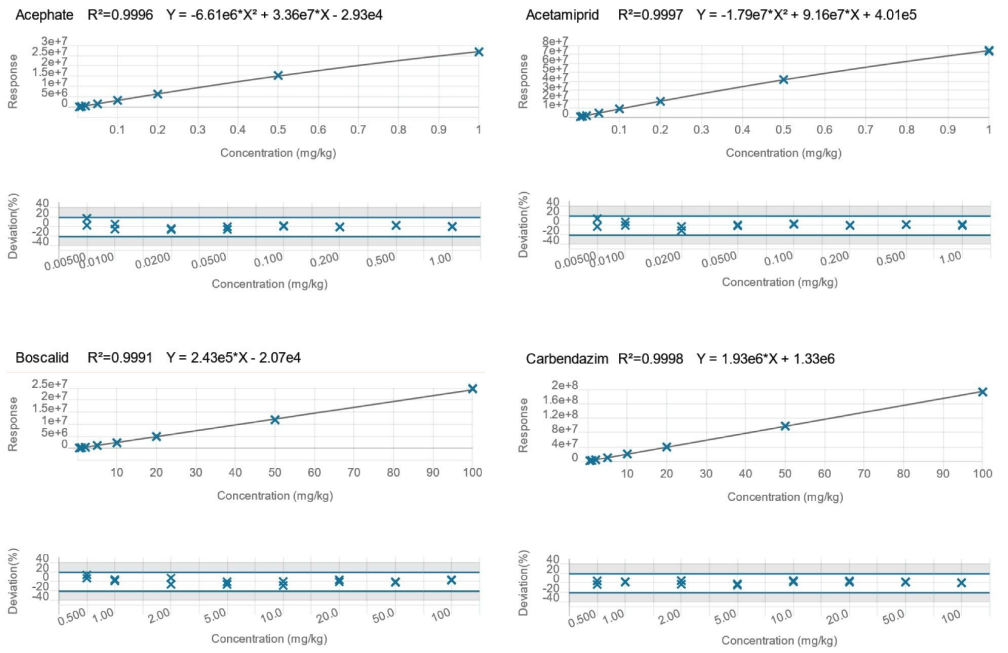

Figure 3. Typical calibration graphs for a selection of pesticides over the range 0.005–1.0 mg/kg (5–1000 µg/kg) in black peppercorn.

Evaluation of Performance

The two transitions for 83% of the analyte in the spikes at 0.01 mg/kg gave peaks with ion ratios and retention times within the tolerances in the SANTE guidelines, when compared with the standards. This rate improved at the higher concentrations; 94% at 0.05 mg/kg and 98% at 0.2 mg/kg.

The SANTE guidelines specify an average recovery for each spike level tested to be between 70 and 120%.[5] The data from the duplicate spikes analyzed here were used to create a mean value for each of the three concentrations. No attempt was made to evaluate precision from these data. It was not possible to generate adequate data for 6.5% of the original 217 components due to insufficient sensitivity or stability issues. Not all the remaining 203 pesticides were detected in peppercorn at 0.05 (201) and 0.01 mg/kg (197). When detected, most of the analytes were within tolerance for recovery at all three concentrations (85% overall). Figure 4 shows the distribution of all measured recoveries, at the three concentrations.

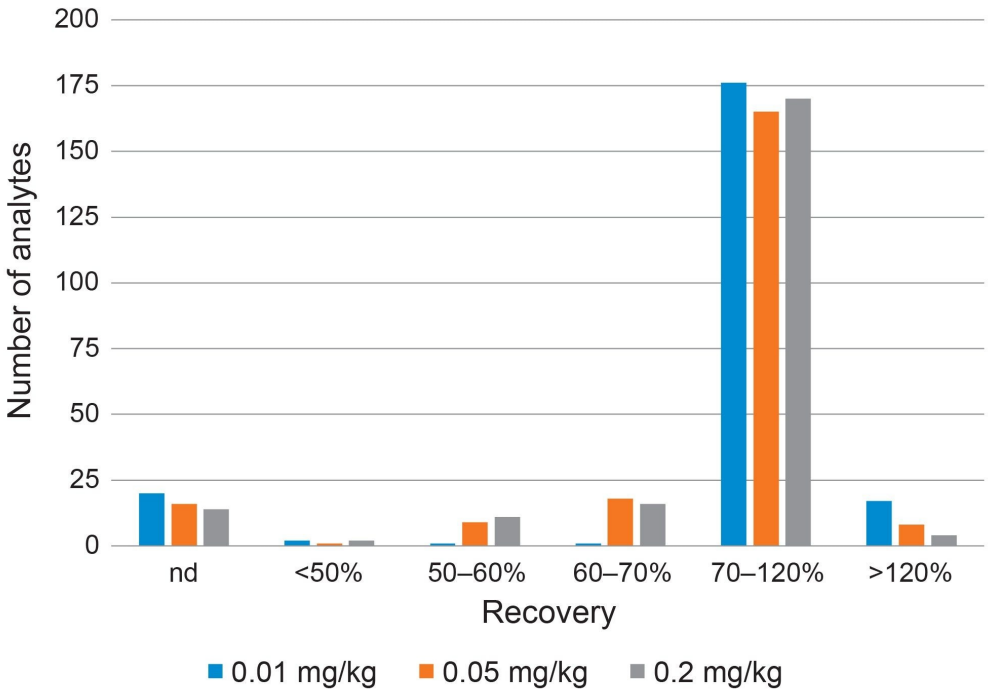

Figure 4. Distribution of the recoveries from the peppercorn validation data, at three concentrations.

Conclusion

This application note has described a sensitive multiresidue method for the determination of pesticide residues in peppercorns, using UPLC-MS/MS. A simple pass-through SPE protocol with Oasis PRiME HLB has proven to be a quick but effective alternative to dilute and shoot or dSPE. The performance of the method has been successfully evaluated using the SANTE acceptance criteria, with most analytes exhibiting values for LCL at 0.005 mg/kg and recovery within the tolerance of 70–120%. This method has been shown that, once fully validated, it could be suitable for determination of pesticide residues in peppercorns for checking compliance with MRLs.

References

1. https://fssai.gov.in/upload/advisories/2024/04/6616351c775b5Order%20MRL%20Spices%20and%20culinary%20herbs.pdf < https://fssai.gov.in/upload/advisories/2024/04/6616351c775b5Order%20MRL%20Spices%20and%20culinary%20herbs.pdf >

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4. Zhu Y *et al.* (2021). Evaluation of Clean-up Procedures and Sample Dilution in Multi-Residue Pesticide Analysis of Spices and Herbs By UPLC-MS/MS. *Food Addit. Contam: Part A* 38(2): 326–338.

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Annex

*List of analytes and retention time and compound-specific MS parameters (*isomers numbered according to elution order).*

Analyte name	RT (min)	CV	Precursor (*m/z*)	Product (*m/z*)	CE (eV)	Precursor (*m/z*)	Product (*m/z*)	CE (eV)
Abamectin	8.93	10	890.5	567.4	12	890.5	307.1	16
Acephate	1.31	20	183.9	142.8	10	183.9	49.0	25
Acetamiprid	1.67	25	223.0	126.0	20	223.0	56.1	15
Acibenzolar-S-methyl	1.45	60	211.0	181.0	17	211.0	69.1	26
Alanycarb	6.34	10	400.1	238.1	8	400.1	91.1	56
Aldicard	2.11	15	208.0	116.1	8	208.0	89.0	20
Aldicarb SOX	1.35	6	207.1	89.0	12	207.1	65.0	20
Aldicarb SON	1.36	35	223.1	86.0	15	223.1	148.0	10
Ametryn	4.06	38	228.1	186.2	18	228.1	68.0	35
Aminocarb	1.41	25	209.1	152.1	12	209.1	137.0	24
Amitraz	8.58	25	294.2	163.0	12	294.2	122.0	32
Azoxystrobin	4.60	20	404.1	372.0	15	404.1	328.9	30
Benalaxyl	6.53	30	326.2	148.0	20	326.2	91.0	35
Bendiocarb	2.50	15	224.1	109.0	15	224.1	167.0	10
Benfuracarb	7.63	18	411.0	195.1	32	411.0	190.1	15
Benzoximate	6.76	15	364.0	199.1	15	364.0	105.0	25
Bifenazate	5.30	30	301.2	198.1	4	301.2	170.1	24
Bitertanol	6.66	6	338.2	269.3	8	338.2	70.0	6
Boscalid	4.84	45	343.0	307.0	20	343.0	139.9	20
Bromuconazole I	5.25	36	378.0	159.0	30	378.0	70.0	18
Bromuconazole II	5.92	36	378.0	159.0	30	378.0	70.0	18
Bupirimate	5.77	50	317.2	108.0	25	317.2	166.0	25
Buprofezin	7.70	5	306.1	201.0	10	306.1	115.9	15
Butafenacil	5.61	15	492.1	180.0	45	492.1	331.0	30
Butocarboxim	3.23	33	213.0	72.1	26	213.0	140.0	26
Butocarboxim SON	1.37	15	223.0	106.0	10	223.0	166.0	5
Carbaryl	2.79	25	202.2	145.0	10	202.2	117.0	25
Carbendazim	1.63	25	192.1	160.1	15	192.1	132.1	30
Carbetamide	2.28	5	237.0	118.0	15	237.0	192.0	10
Carbofuran	2.58	25	222.1	123.0	20	222.1	165.1	10
Carbofuran-3-OH-	1.68	30	238.1	181.0	10	238.1	163.0	15
Carboxin	2.85	30	236.0	143.0	15	236.0	87.0	25
Carfentrazone-ethyl	4.97	55	411.9	328.1	18	411.9	125.1	46
Chlorantraniliprole	4.24	25	481.9	283.9	15	481.9	450.9	15
Chlorfluazuron	8.54	20	540.0	158.0	24	540.0	382.9	28
Chlorotoluron	3.24	25	213.0	72.0	15	213.0	46.0	15
Chloroxuron	5.18	20	291.1	72.0	15	291.1	164.1	15
Clethodim I	5.14	10	360.0	164.0	15	360.0	268.1	10
Clethodim II	7.35	10	360.0	164.0	15	360.0	268.1	15
Clofentezine	6.66	25	303.0	138.0	15	303.0	102.0	35
Clothianidin	1.61	25	250.0	169.0	10	250.0	132.0	15
Cyazofamid	5.69	20	325.1	108.0	14	325.1	261.1	8
Cycluron	3.84	25	199.2	89.1	15	199.2	69.2	20
Cymoxanil	1.86	15	199.0	127.9	10	199.0	110.9	14
Cyproconazole I	5.03	40	292.1	70.2	20	292.1	125.1	20
Cyproconazole II	5.27	40	292.1	70.2	20	292.1	125.1	20
Cyprodinil	5.87	40	226.1	93.0	35	226.1	108.0	25
Cyromazine	1.26	15	167.1	85.0	20	167.1	68.0	25
Desmedipham	3.98	30	318.0	182.0	10	301.0	136.0	15
Diclobutrazol	6.11	15	328.0	70.0	20	328.0	158.9	38
Dicrotophos	1.51	30	238.0	112.0	10	238.0	193.0	10
Diethofencarb	4.52	15	268.1	226.0	10	268.1	124.0	30
Difenoconazole	6.94	8	406.2	251.0	24	406.2	111.0	58
Diflubenzuron	5.76	25	311.0	158.2	15	311.0	141.1	30

Analyte name	RT (min)	CV	Precursor (*m/z*)	Product (*m/z*)	CE (eV)	Precursor (*m/z*)	Product (*m/z*)	CE (eV)
Dimethoate	1.73	15	230.0	198.8	10	230.0	124.8	20
Dimethomorph I	4.70	30	388.1	300.9	20	388.1	165.0	30
Dimethomorph II	5.00	30	388.1	300.9	20	388.1	165.0	30
Dimoxystrobin	6.04	15	327.1	205.2	10	327.1	116.1	20
Diniconazole	6.75	20	326.1	70.0	36	326.1	159.1	36
Dinotefuran	1.36	15	203.1	129.0	10	203.1	113.0	10
Dioxacarb	1.72	10	224.1	123.1	20	224.1	167.1	12
Diuron	3.08	35	233.0	72.1	15	233.0	46.3	15
Doramectin	9.10	15	916.5	331.2	24	916.5	113.1	52
Emamectin B1a	8.02	50	886.5	158.0	35	886.5	82.0	55
Emamectin B1b	7.70	26	872.5	158.1	34	872.5	82.0	72
Epoxiconazole	5.68	40	330.0	121.0	20	330.0	101.0	40
Eprinomectin B1a	8.83	10	914.5	186.1	24	914.5	153.9	44
Etaconazole I-II	5.54	20	328.1	159.0	31	328.1	205.0	23
Ethiofencarb	3.03	15	226.1	107.0	15	226.1	164.0	10
Ethiprole	4.70	20	397.0	351.1	25	397.0	255.1	44
Ethirimol	2.44	40	210.1	98.0	25	210.1	140.0	20
Ethofumesate	4.47	25	287.1	121.1	15	287.1	259.1	10
Etoxazole	8.35	44	360.2	141.0	32	360.2	304.1	20
Famoxadone	6.49	30	392.1	238.1	16	392.1	93.0	44
Fenamidone	4.70	10	312.1	92.0	25	312.1	236.1	10
Fenarimol	5.47	20	331.0	81.0	30	331.0	268.0	20
Fenazaquin	8.71	15	307.2	57.1	28	307.2	161.1	14
Fenbuconazole	5.76	35	337.0	70.1	15	337.0	125.0	30
Fenhexamid	5.47	40	302.1	97.1	20	302.1	55.2	30
Fenobucarb	4.31	25	208.1	94.9	15	208.1	152.0	5
Fenoxycarb	5.91	10	302.1	116.1	10	302.1	88.0	15
Fenpropimorph	4.70	35	304.2	147.1	25	304.2	57.2	30
Fenpyroximate	8.53	20	422.2	366.1	16	422.2	135.1	36
Fenuron	1.74	20	165.1	71.9	15	165.1	45.9	10
Fipronil*	5.95	50	434.6	330.0	20	434.6	249.9	36
Flonicamid	1.47	35	230.0	203.1	15	230.0	148.1	25
Fluazinam*	7.77	13	462.6	46.0	34	462.6	398.0	28
Flubendiamide	6.29	45	682.8	407.9	9	682.8	274.0	52
Fludioxonil	4.62	5	266.1	229.1	8	266.1	158.1	36
Flufenacet	5.57	15	364.0	194.1	10	364.0	152.1	20
Flufenoxuron	8.28	15	489.1	158.1	16	489.1	141.1	56
Fluometuron	3.66	30	233.0	72.2	15	233.0	46.4	15
Fluoxastrobin	5.56	40	459.0	427.0	15	459.0	188.0	35
Fluquinconazole	5.40	60	376.0	108.0	48	376.0	307.0	26
Flusilazole	5.88	45	316.1	247.0	15	316.1	165.0	25
Flutolanil	4.97	25	324.1	262.1	15	324.1	65.0	40
Flutriafol	3.41	30	302.1	70.1	15	302.1	122.9	25
Forchlorfenuron	3.68	36	248.1	129.0	15	248.1	93.1	35
Formetanate HCl	1.29	10	222.1	165.0	15	222.1	46.0	25
Fuberidazole	1.90	25	185.0	157.0	20	185.0	65.0	48
Furalaxyl	4.58	25	302.1	95.0	25	302.1	242.1	15
Furathiocarb	7.69	15	383.2	194.9	15	383.2	252.0	10
Halofenozide	4.68	2	331.1	104.9	16	331.1	274.9	8
Hexaconazole	6.42	45	314.0	70.1	15	314.0	159.0	35
Hexaflumuron*	7.24	35	458.6	438.9	15	458.6	42.0	34
Hexythiazox	8.04	25	353.0	228.0	16	353.0	168.0	28
Hydramethylnon	7.17	20	495.2	323.2	32	495.2	170.9	48
Imazalil	3.36	30	297.0	69.0	15	297.0	159.0	25

Analyte name	RT (min)	CV	Precursor (*m/z*)	Product (*m/z*)	CE (eV)	Precursor (*m/z*)	Product (*m/z*)	CE (eV)
Imidacloprid	1.57	20	256.1	209.0	15	256.1	174.9	20
Indoxacarb	7.12	35	528.0	203.0	40	528.0	150.0	50
Ipconazole I	7.03	35	334.2	70.0	20	334.2	125.0	35
Ipconazole II	7.19	35	334.2	70.0	20	334.2	125.0	35
Iprovalicarb	5.54	25	321.2	119.1	25	321.2	203.1	10
Isocarbofos	3.72	20	307.0	231.1	19	307.0	121.1	42
Isoprocarb	3.38	15	194.1	95.1	15	194.1	137.1	10
Isoproturon	3.59	20	207.0	72.0	20	207.0	46.0	15
Ivermectin B1a	9.23	30	892.5	307.2	24	892.5	569.0	12
Kresoxim-methyl	6.13	8	314.2	267.2	6	314.2	222.2	12
Linuron	4.37	20	249.0	182.0	15	249.0	160.1	15
Lufenuron	7.97	40	511.0	158.1	20	511.0	141.1	44
Mandipropamid	4.97	20	411.8	328.1	15	411.8	125.0	30
Mefenacet	5.27	20	299.1	120.1	24	299.1	148.1	8
Mepanipyrim	5.34	35	224.1	106.0	25	224.1	77.0	35
Mepronil	5.05	20	270.1	119.1	31	270.1	228.0	21
Mesotrione	1.70	55	339.9	228.1	24	339.9	104.0	44
Metaflumizone	7.71	20	507.1	116.0	52	507.1	178.0	36
Metalaxyl	3.77	25	280.2	220.1	15	280.2	192.1	15
Metconazole	6.56	25	320.1	70.0	20	320.1	125.0	35
Methabenzthiazuron	3.42	10	222.0	165.0	15	222.0	150.0	30
Methamidophos	1.27	25	142.0	93.9	15	142.0	124.9	15
Methiocarb	4.50	20	226.1	169.0	10	226.1	121.0	15
Methomyl	1.44	15	162.9	88.0	10	162.9	105.9	10
Methoprotryne	4.16	15	272.2	198.2	20	272.2	170.2	25
Methoxyfenozide	5.26	2	369.3	148.9	22	369.3	90.8	40
Metobromuron	3.29	15	259.0	148.1	15	259.0	170.0	20
Metribuzin	2.60	40	215.1	89.0	15	215.1	131.0	20
Mevinphos I	1.69	20	225.1	127.1	15	225.1	193.1	10
Mevinphos II	1.88	20	225.1	127.1	15	225.1	193.1	10
Mexacarbate	2.80	30	223.2	166.1	15	223.2	151.0	25
Monocrotophos	1.46	20	224.1	127.1	15	224.1	98.0	10
Monolinuron	2.99	25	215.0	126.0	15	215.0	99.0	30
Moxidectin	9.07	5	640.4	528.0	4	640.4	478.1	8
Myclobutanil	5.08	25	289.1	124.9	30	289.1	150.9	25
Neburon	5.98	30	275.0	57.0	20	275.0	88.0	15
Nitenpyram	1.40	30	271.1	225.0	10	271.1	125.9	30
Novaluron	7.38	45	493.0	158.0	20	493.0	141.0	52
Nuarimol	4.52	40	315.0	81.1	25	315.0	252.0	20
Omethoate	1.33	30	214.0	182.8	10	214.0	124.8	25
Oxadixyl	2.10	6	279.1	219.1	10	279.1	102.0	8
Oxamyl	1.37	15	237.1	72.0	15	237.1	90.0	5
Paclobutrazol	4.91	20	294.1	70.2	15	294.1	125.1	40
Penconazole	6.10	40	284.0	70.1	15	284.0	159.0	10
Pencycuron	6.86	15	329.1	125.2	24	329.1	218.0	16
Phenmedipham	4.13	25	301.0	136.0	20	301.0	168.0	5
Picoxystrobin	6.00	10	368.0	205.1	10	368.0	145.1	25
Piperonyl butoxide	7.88	25	356.2	176.9	10	356.2	119.0	35
Pirimicarb	2.78	15	239.1	72.0	20	239.1	182.1	15
Prochloraz	6.55	25	376.0	307.9	10	376.0	265.9	15
Promecarb	4.72	15	208.1	109.0	15	208.1	151.0	10
Prometon	3.57	15	226.2	86.1	25	226.2	184.1	15
Prometryn	5.05	40	242.2	158.0	25	242.2	200.1	15
Propamocarb	1.34	30	189.1	102.0	15	189.1	144.0	10

Analyte name	RT (min)	CV	Precursor (m/z)	Product (m/z)	CE (eV)	Precursor (m/z)	Product (m/z)	CE (eV)
Propargite	8.31	15	368.1	231.1	12	368.1	175.1	16
Propham	3.33	20	180.1	120.0	16	180.1	92.1	28
Propiconazole	6.40	45	342.0	159.0	35	342.0	69.0	15
Propoxur	2.52	15	210.1	110.9	15	210.1	92.9	25
Prothioconazole	6.35	23	343.8	189.0	30	343.8	125.1	48
Pymetrozine	1.36	25	218.1	105.0	15	218.1	79.0	25
Pyracarbolid	2.73	25	218.1	125.1	15	218.1	97.1	25
Pyraclostrobin	6.64	10	388.1	193.9	10	388.1	163.0	25
Pyridaben	8.72	20	365.2	147.1	28	365.2	309.1	12
Pyrimethanil	4.25	30	200.1	107.2	24	200.1	82.0	28
Pyriproxyfen	7.86	15	322.2	96.1	20	322.2	77.1	48
Quinoxyfen	7.89	35	308.0	197.1	40	308.0	162.1	56
Rotenone	5.93	10	395.1	213.1	20	395.1	192.1	25
Secbumeton I	3.50	5	226.0	170.1	20	226.0	113.9	24
Secbumeton II	3.74	5	226.0	170.1	20	226.0	113.9	24
Siduron I	4.56	25	233.2	93.8	20	233.2	137.0	15
Siduron II	4.57	25	233.2	93.8	20	233.2	137.0	15
Simetryn	3.07	50	214.0	124.0	20	214.0	95.9	25
Spinosyn J	7.46	35	748.5	142.1	30	748.5	98.1	66
Spinosyn L	7.82	35	760.5	142.1	30	760.5	98.1	66
Spinosyn A	6.94	50	732.6	142.0	30	732.6	98.1	50
Spinosyn D	7.35	45	746.5	142.0	30	746.5	98.1	50
Spirodiclofen	8.59	31	411.1	71.1	15	411.1	313.1	10
Spiromesifen	8.36	4	388.2	273.0	8	388.2	255.0	28
Spirotetramat	5.57	24	374.3	216.1	32	374.3	302.2	16
Spiroxamine I	4.58	10	298.0	144.0	20	298.0	100.0	32
Spiroxamine II	4.70	10	298.0	144.0	20	298.0	100.0	32
Sulfentrazone	2.74	55	387.0	307.0	20	387.0	145.8	40
Tebuconazole	6.21	25	308.1	70.1	20	308.1	125.0	40
Tebufenozide	6.05	2	353.3	133.1	16	353.3	72.1	16
Tebufenpyrad	7.65	15	334.1	117.0	40	334.1	145.0	28
Tebuthiuron	2.74	25	229.1	172.0	15	229.1	116.0	25
Teflubenzuron*	7.61	18	378.6	42.0	30	378.6	338.9	15
Temephos	7.82	35	467.0	125.0	44	467.0	404.9	16
Terbumeton I	3.51	35	226.1	170.1	20	226.1	114.1	25
Terbumeton II	3.75	35	226.1	170.1	20	226.1	114.1	25
Terbutryn	5.20	5	242.0	186.2	20	242.0	71.1	36
Tetraconazole	5.52	15	372.0	159.0	30	372.0	70.1	20
Thiabendazole	1.80	50	202.0	174.9	25	202.0	130.9	30
Thiacloprid	1.82	35	253.0	125.8	20	253.0	90.0	35
Thiamethoxam	1.44	25	292.0	211.2	10	292.0	132.0	30
Thidiazuron	2.49	15	221.0	102.0	30	221.0	93.9	15
Thiobencarb	6.69	25	258.1	124.9	16	258.1	89.0	35
Thiofanox	3.19	35	241.0	57.0	15	241.0	184.0	20
Thiophanate-methyl	2.46	25	343.0	151.0	20	343.0	93.0	45
Triadimefon	5.10	30	294.1	69.1	20	294.1	196.9	15
Triadimenol	5.25	16	296.1	70.0	8	298.1	70.0	12
Trichlorfon	1.74	35	256.9	109.0	15	256.9	79.0	30
Tricyclazole	2.04	50	190.0	163.0	20	190.0	136.0	25
Trifloxystrobin	7.17	15	409.2	185.9	20	409.2	145.0	40
Triflumizole	7.10	15	346.1	278.0	10	346.1	73.1	15
Triflumuron	6.62	35	359.0	156.1	15	359.0	139.1	35
Triticonazole	5.54	35	318.1	70.1	15	318.1	124.9	30
Vamidothion	1.66	20	288.0	118.0	25	288.0	146.0	20
Zoxamide	6.34	20	336.0	187.1	20	336.0	159.0	40

* negative ion mode

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