Application note | 002167

Food safety

Quantitation of pesticide residues in rice, grape, tomato, and chili powder using LC-MS/MS

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Keywords

TraceFinder software, pesticide residues, rice, grape, tomato, chili powder, QuEChERS, LC-MS/MS, TSQ Quantis Plus MS, polarity switching, minimum detection limit (MDL), targeted quantitation

Goal

The goal of this project is to demonstrate the performance and versatility of the Thermo Scientific™ TSQ Quantis™ Plus mass spectrometer for trace level quantitation of pesticide residues in samples of rice, grape, tomato, and chili powder. The optimized method must be validated as per the SANTE 2021 guidelines and evaluated for compliance with the Food Safety and Standards Authority of India (FSSAI) and the European Commission (EC) maximum residue levels (MRLs) for the specified matrices.

Introduction

In India, the commercial cultivation of crops involves frequent application of a large number of pesticides to control a variety of pests and diseases. Indirect sources such as contaminated soil and agro-inputs may also contribute to pesticide residue levels in crops.

The EC and FSSAI have set MRLs for pesticides in rice, grape, tomato, and chili powder.[1,2] Because of the ever-increasing number of pesticides included in monitoring programs, laboratories need to develop and implement comprehensive methods capable of analyzing a broad scope of pesticide chemistries in a wide variety of sample types. For generic extraction of pesticide residues in food matrices, the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction method has been adopted world-wide because of its simplicity, applicability for a range of pesticide-matrix combinations, increased productivity, and compatibility with both LC-MS and

GC-MS techniques.[3] To deliver accurate and precise analytical results for hundreds of pesticides in a single analysis, the LC system must deliver high peak capacity and gradient reproducibility and the mass spectrometer must perform fast and reproducible data acquisition across a wide linear dynamic range. Fast data acquisition must include fast polarity switching to maximize sample throughput without sacrificing the performance and while meeting regulatory requirements.

The aim of this work was to develop, optimize, and perform method validation of a multi-residue method for pesticides in rice, grape, tomato, and chili powder matrices using the Thermo Scientific™ Vanquish™ Flex UHPLC system coupled to the Thermo Scientific TSQ Quantis Plus triple quadrupole mass spectrometer. The data acquisition and processing steps were carried out using Thermo Scientific™ TraceFinder™ software. The optimized method was validated according to the SANTE guidelines.[4] This method was applied to real samples to demonstrate the application of a streamlined workflow in compliance with the EU and FSSAI MRLs requirements.[1,2]

Experimental

Chemicals, apparatus, and consumables

- Acetonitrile, Optima™ LC/MS grade, Fisher Scientific™ (P/N A955-4)
- Water, Optima™ LC/MS grade, Fisher Scientific™ (P/N W6-4)
- Acetic acid glacial (Certified ACS), Fisher Scientific™ (P/N A38S-500)
- Analytical balance (ACZET, CY2202, San Diego, CA) and precision balance (ACZET, CY205C, San Diego, CA)
- Vortex mixer (Thermo Scientific™, P/N 88880017TS)
- Refrigerated centrifuge (Thermo Scientific™ Sorvall™ ST8 ventilated benchtop centrifuge)
- Variable volume micropipettes (Thermo Scientific)
- QuEChERS Salts (2007.01) mylar pouch 6 g magnesium sulfate (anhydrous),1.5 g sodium acetate, 50 pk, Thermo Scientific™ (P/N S1-15-AOAC-POT)
- 50 mL extraction tubes (P/N LSC T50BS)
- 2 mL extraction tubes, Eppendorf Tubes™ (P/N 0030123620)
- Clean-up material: Anhydrous $MgSO_4$, Thermo Scientific™ (P/N 80020-432-1000), C18, Thermo Scientific™ (P/N 80020-430-100), and Primary Secondary Amine (PSA), Thermo Scientific™ (P/N 80020-429-100).

LC-MS/MS analysis

The Vanquish Flex UHPLC system was coupled with the TSQ Quantis Plus mass spectrometer using the heated electrospray ionization (HESI) source for all LC-MS/MS experiments. The optimized LC-MS/MS conditions are listed in Table 1.

Table 1. LC-MS/MS instrument conditions used for all data acquisition

Parameter	Value
Liquid chromatography method	
Instrumentation	Vanquish Flex Quarternary UHPLC system
Column	Thermo Scientific™ Accucore™ aQ column, 100 × 2.1 mm, 2.6 µm (P/N 17326-102130)
Sample compartment temp.	15 °C (Still air) (Vanquish Split Sampler FT, P/N VF-A10-A)
Column oven temp.	25 °C (Vanquish Column Compartment H, P/N VH-C10-A)
Injection volume	5 µL
Needle wash	90% methanol and 10% water
Seal wash	Water:methanol (50:50)
Mobile phase	A: 5 mM ammonium formate + 0.05% formic acid in water B: 5 mM ammonium formate + 0.05% formic acid in methanol
LC gradient program	Time (min) / Flow rate (mL/min) / %B / Curve 0.0 / 0.35 / 5.0 / 5 1.0 / 0.35 / 5.0 / 5 3.0 / 0.35 / 55.0 / 5 10.0 / 0.35 / 100.0 / 5 15.0 / 0.35 / 100.0 / 5 15.5 / 0.35 / 5.0 / 5 20.0 / 0.35 / 5.0 / 5
Total run time	20.0 min
Mass spectrometry method	
Instrumentation	TSQ Quantis Plus triple quadrupole mass spectrometer
Method type	Acquisition-Timed (t-SRM mode)
Ion source type	HESI
Spray voltage	Static Positive: 3,500 V Negative: 2,500 V
Sheath gas	45 Arb
Aux gas	10 Arb
Sweep gas	1 Arb
Ion transfer tube temp.	280 °C
Vaporizer temp.	350 °C

Sample preparation

The test samples were collected from the local market of Bangaluru, India, and homogenized to a uniform particle size using a heavy-duty mixer and grinder. Representative samples were extracted using the acetate buffered QuEChERS method; details are given below.[3] After the assurance of the pesticide-free matrices, homogenous sub-samples were utilized for recovery experiments as well as preparation of matrix-matched calibration standards. A total of 202 pesticides were included in the study.

Extraction and clean-up

- Weigh homogenized test sample into a 50 mL extraction tube [grape and tomato (15 g), rice (5 g), and chili powder (2 g)].
- Add internal standard triphenyl phosphate (TPP).
- For the recovery experiment, spike the samples before the addition of an extraction solvent.
- Add 10 mL of water for rice and chili powder only. (No water addition is required for grape and tomato.) Then vortex for 1 min at 2,500 rpm.
- Add 15 mL of acetonitrile (containing 1% acetic acid).
- Shake vigorously and vortex for 1 min on a vortex mixer at 2,500 rpm.
- Add salts (6 g $MgSO_4$ and 1.5 g sodium acetate) to the tube.
- Mix vigorously for 1 min on a vortex mixer at 2,500 rpm.
- Centrifuge at 5,000 rpm for 5 min at room temperature.
- Add 1 mL of supernatant to the 2 mL Eppendorf Tube.
- Add 150 mg $MgSO_4$ and 50 mg PSA to the tube (50 mg C18 and 7.5 mg GCB used for chili).
- Shake vigorously and vortex for 1 min on a vortex mixer at 2,500 rpm.
- Centrifuge at 10,000 rpm for 5 min.
- Dilute 0.3 mL supernatant with 0.6 mL water.
- Inject 5 µL of diluted extract into the LC-MS/MS.

Data acquisition and processing

Data acquisition and processing were performed using TraceFinder software, version 5.1. The data were acquired in t-SRM mode, which includes two or more transitions per analyte. The target list of analytes with their transitions, collision energies, and retention time (min) settings and timed acquisition duration is given in Table S1. An example of the acquisition method is presented in Figure 1, showing a sub-set of SRM transitions with the corresponding SRM settings. To ensure global detection of targeted pesticides for all matrices, the gradient used results in most pesticides eluting after 6 min. Automated dwell time determination was used to assign equal dwell time settings based on the expected retention times, average chromatographic peak width, timed SRM (t-SRM) acquisition duration, and number of data points per peak. Thus, the shortest dwell times correspond to pesticides eluting after 6 min.

For data processing in TraceFinder software, the ion ratio (±30%), retention time (±0.1 min), linearity (≥0.99 with back calculated concentration ±20), recovery (70–120%), and precision (±20%) were set as acceptance criteria as per the SANTE guidelines[4].

Results and discussion

LC-MS/MS data acquisition

The optimized liquid chromatographic method delivered excellent separation and peak shape for the target analytes while minimizing isobaric interference from the matrices. The extracted ion chromatogram (XIC) is shown for targeted compounds spiked at 0.05 mg/kg in grape and rice (Figure 2). Note the large difference in detector response for individual pesticides covering over three orders of magnitude for the equal molar pesticide mix. The same method was extended to tomato and chili powder. As per the gradient program, the distribution of analytes was observed in the range of 1–13 min, whereas the majority of analytes eluted in the range of 4–13 min. The acquisition method set was a user-defined input of 12 data points per peak and 12 s peak width enables the software to automatically determine the cycle time and consequently the dwell time settings per transition (Figure 2).

Experiment # 1 CLEAR

SRM Table ADD DELETE IMPORT EXPORT

	Compound	Retention Time (min)	RT Window (min)	Polarity	Precursor (m/z)	Product (m/z)	Collision Energy (V)	Min Dwell Time (ms)
91	Imazethapyr	6.75	1.5	Positive	290.2	177.1	30	6.9
92	Imazethapyr	6.75	1.5	Positive	290.2	245.1	23	6.9
93	Ethirimol	6.8	1.5	Positive	210.2	98.1	35	6.543
94	Ethirimol	6.8	1.5	Positive	210.2	140.1	30	6.543
95	Oxadixyl	6.81	1.5	Positive	279.1	132.1	43	6.543
96	Oxadixyl	6.81	1.5	Positive	279.1	219.1	15	6.543
97	Pirimicarb-Desmethy	6.85	1.5	Positive	225	72.1	20.04	6.543
98	Pirimicarb-Desmethy	6.85	1.5	Positive	225	168.1	14.52	6.543
99	Oxamyl [M+NH4]	6.85	1.5	Positive	237.1	72.3	17	6.543
100	Oxamyl [M+NH4]	6.85	1.5	Positive	237.1	192.1	8	6.543

Experiment # 1 CLEAR

SRM Table ADD DELETE IMPORT EXPORT

	Compound	Retention Time (min)	RT Window (min)	Polarity	Precursor (m/z)	Product (m/z)	Collision Energy (V)
390	Tebufenozide	9.6	1.5	Positive	353	133.1	19.32
391	Tebufenozide	9.6	1.5	Positive	353	297.2	8.5
392	Picoxystrobin	9.6	1.5	Positive	368	145.1	23.24
393	Picoxystrobin	9.6	1.5	Positive	368	205.2	9.38
394	Pendimethalin	9.65	1.5	Positive	282	118.1	22.1
395	Pendimethalin	9.65	1.5	Positive	282	194.1	19.36
396	Pendimethalin	9.65	1.5	Positive	282	212	12.5
397	Iprobenfos	9.65	1.5	Positive	289.1	91.1	21.98
398	Iprobenfos	9.65	1.5	Positive	289.1	204.9	10.73
399	Kresoxim methyl	9.65	1.5	Positive	314	116.1	16.16
400	Kresoxim methyl	9.65	1.5	Positive	314	206	5.25
401	Kresoxim methyl	9.65	1.5	Positive	314	267	7.32
402	Phenthoate	9.66	1.5	Positive	321	135.1	22
403	Phenthoate	9.66	1.5	Positive	321	246.8	12
404	Clodinafop-proparg	9.66	1.5	Positive	350	91.1	29.81
405	Clodinafop-proparg	9.66	1.5	Positive	350	266.1	15.7
406	Carfentrazone-Ethyl	9.66	1.5	Positive	412.1	346.1	23
407	Carfentrazone-Ethyl	9.66	1.5	Positive	412.1	366.1	19
408	Bromucanozole Isom	9.67	1.5	Positive	378	70	47
409	Bromucanozole Isom	9.67	1.5	Positive	378	159	37
410	Flubendiamide	9.67	1.5	Positive	683.1	274.1	32
411	Flubendiamide	9.67	1.5	Positive	683.1	408.2	9
412	Metolachlor-S	9.68	1.5	Positive	284.2	176.2	28.1

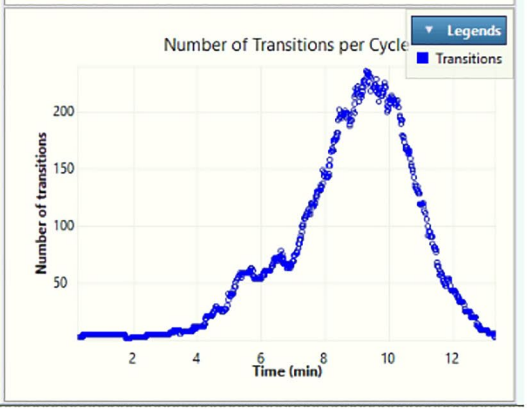

Figure 1. Screen capture from TraceFinder software showing the acquisition method. The list of pesticides and SRM transitions show the parameters used to manage the highly multiplexed method using t-SRM acquisition with equal dwell time settings accommodating polarity switching.

As shown in Figure 2, some pesticides have poor sensitivity that can create challenges for high-quality data acquisition, especially at low concentration. The poor sensitivity can prohibit compound quantitation and confirmation as the relative abundance of the second and third SRM transitions are often 2–10x lower than the quantifying SRM transition. In such cases, the new software feature Dwell Time Prioritization adjusts the SRM transition dwell times for identified compounds based on the user-defined priority setting. Following the initial method creation using the automated dwell time setting, all SRM transitions have an equivalent prioritization setting of 3 (normal) with a range of settings from 1 (highest) to 5 (lowest). This feature expedites method refinement, requiring only the priority of compromised transitions to be changed from normal to high priority. Adjustments for the specified SRM transitions automate re-determination of dwell time settings for those adjusted as well as all other transitions of equal priority settings within the timed retention time window. An example is presented in Figure 3. Changing the dwell time prioritization can improve the signal-to-noise ratio 2–3 times, enabling cconfident confirmation of identity and quantitation.

Due to excellent LC pump performance and optimal dwell time settings, most of the peaks were sharp and symmetrical with sufficient data points to enable excellent repeatability. This approach and new software feature reduce the time required for method optimization and allow the user to utilize the LC-MS/MS system to improve productivity in the lab.

Fast polarity switching

Contract testing labs (CTLs) expect high throughput from their LC-MS/MS workflow solutions to meet customer demands. Monitoring a large number of pesticides in a global method also requires fast polarity switching to maximize duty cycle and cycle times and provide high confidence in the data. The TSQ Quantis Plus mass spectrometer enables better stability and sensitivity for analyte measurements in both polarities by performing polarity switching at 5 ms. Figure 4 shows the comparative analysis of diflubenzuron and fipronil, both eluting at 9.55 min irrespective of their polarities and offering >12 scans per peak. This is evidence that the high scan speed and polarity switching do not compromise peak quality and fulfill the requirements.

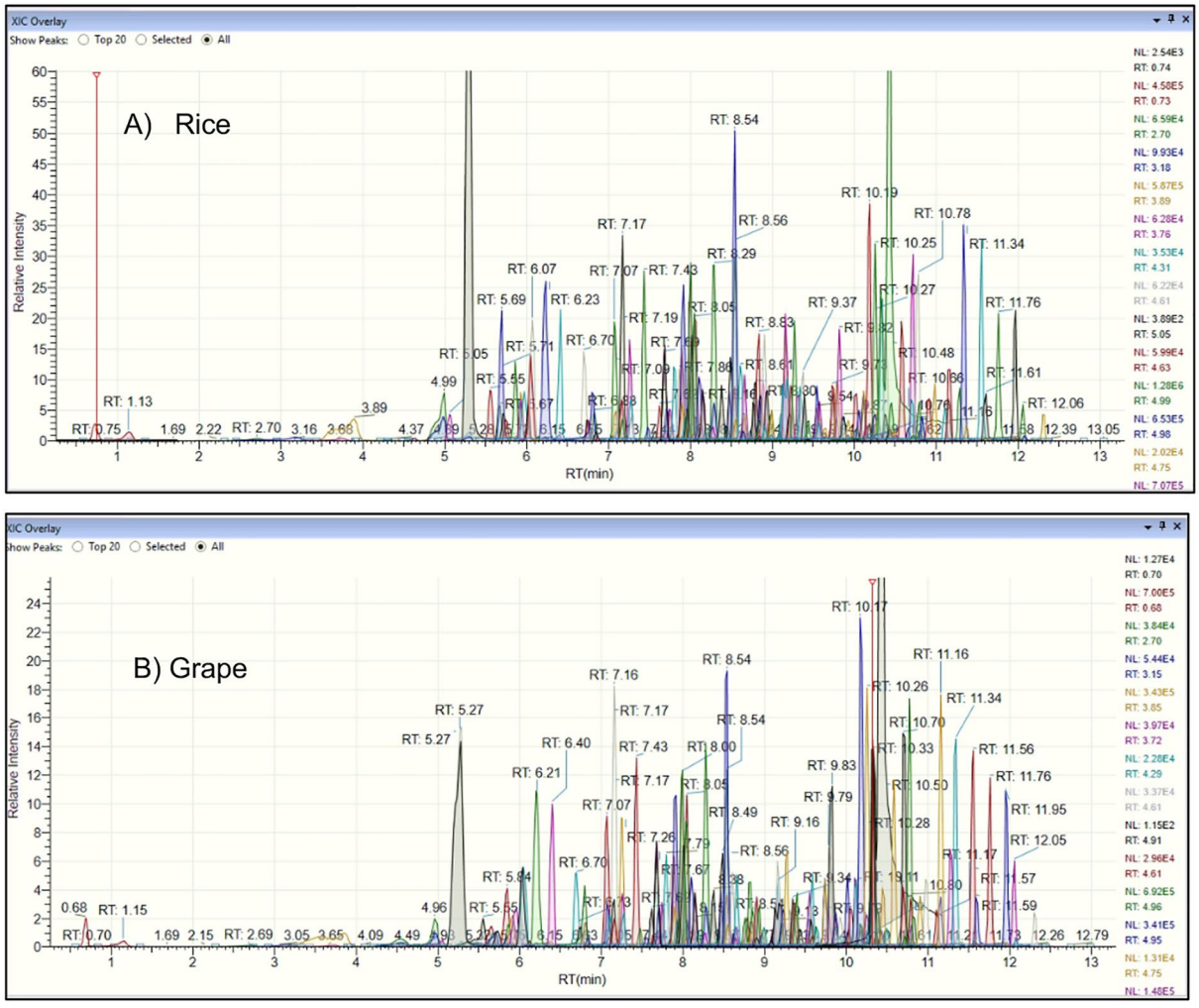

Figure 2. Extracted ion chromatogram for matrix-matched standard at 0.050 mg/kg in (A) rice and (B) grape

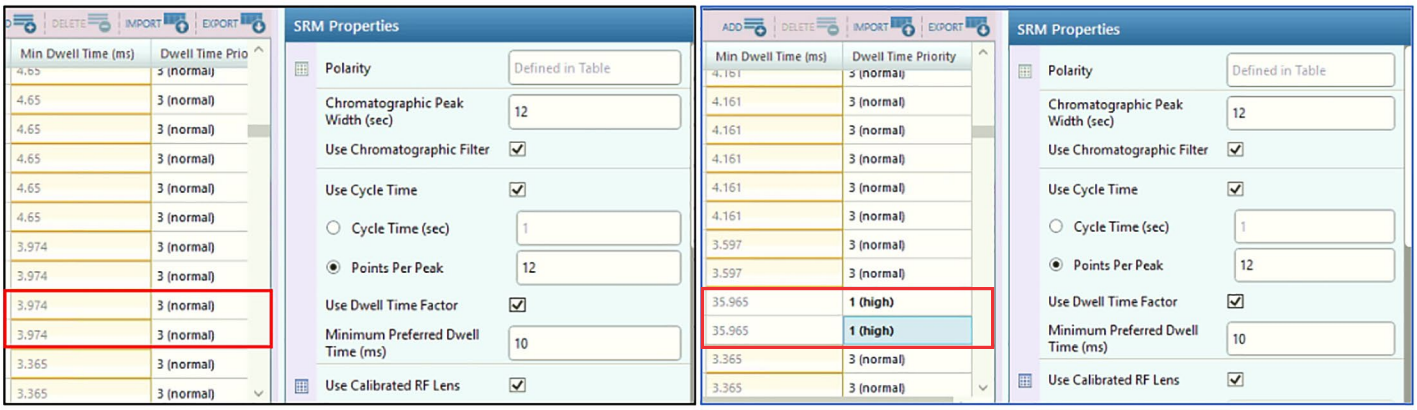

Figure 3. The dwell time priority feature in the new software enables rapid method refinement to confidence in results

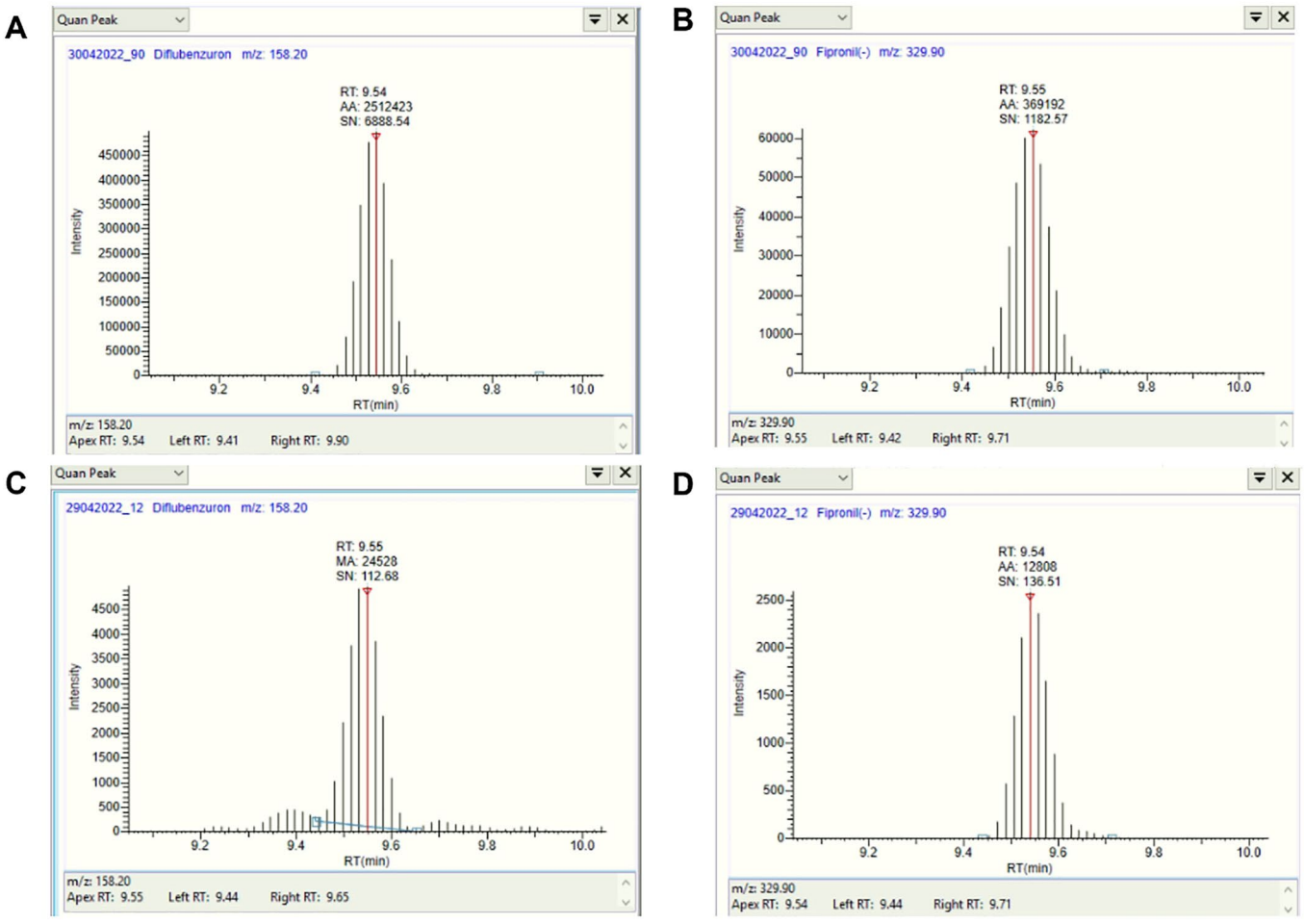

Figure 4. Chromatographic profiles for two coeluting pesticides measured using polarity switching. Diflubenzuron (+ESI) and fipronil (-ESI) were spiked at 0.05 mg/kg levels and measured in grape extract (A and B, respectively) and rice extract (C and D, respectively). Stick plots show the number of data points acquired across the elution profile.

Automated data processing for identification and quantitation

Robust automated data processing decreases sample turnaround time relying on well-established user parameters. Data processing in TraceFinder software performs data extraction and integration, enabling automated data analysis and scoring for rapid review and report generation. Figure 5A shows an example for carbaryl spiked at 0.00025 mg/kg in grape. Key metrics show the two transitions (202 → 145.10, quantifier ion and 202 → 127.20 qualifier ion) at the retention time (7.50 ± 0.1 min) and ion ratio within 30% to meet SANTE guidelines. To mitigate the matrix effect, the matrix-matched calibration was used. Further, the quantitation was performed based on the calibration curve plotted in the range of 0.00025–0.05 mg/kg. This calibration curve offered excellent linearity (r^2 ≥0.99) with ≤20% residuals using a 1/x weighting factor and linear equation.

As per user-defined parameters, the color-coded flags indicate whether results pass or fail according to the acceptance criteria defined in the processing method. Those results passing all the criteria are shown with a green flag (Figure 5), which minimizes the time required for review. Red-colored flags indicate manual investigation is required based on the reason provided by the flag. Identification in compliance with the SANTE guidelines, followed by the overlapping of both transitions at the same retention time is demonstrated in Figure 6.

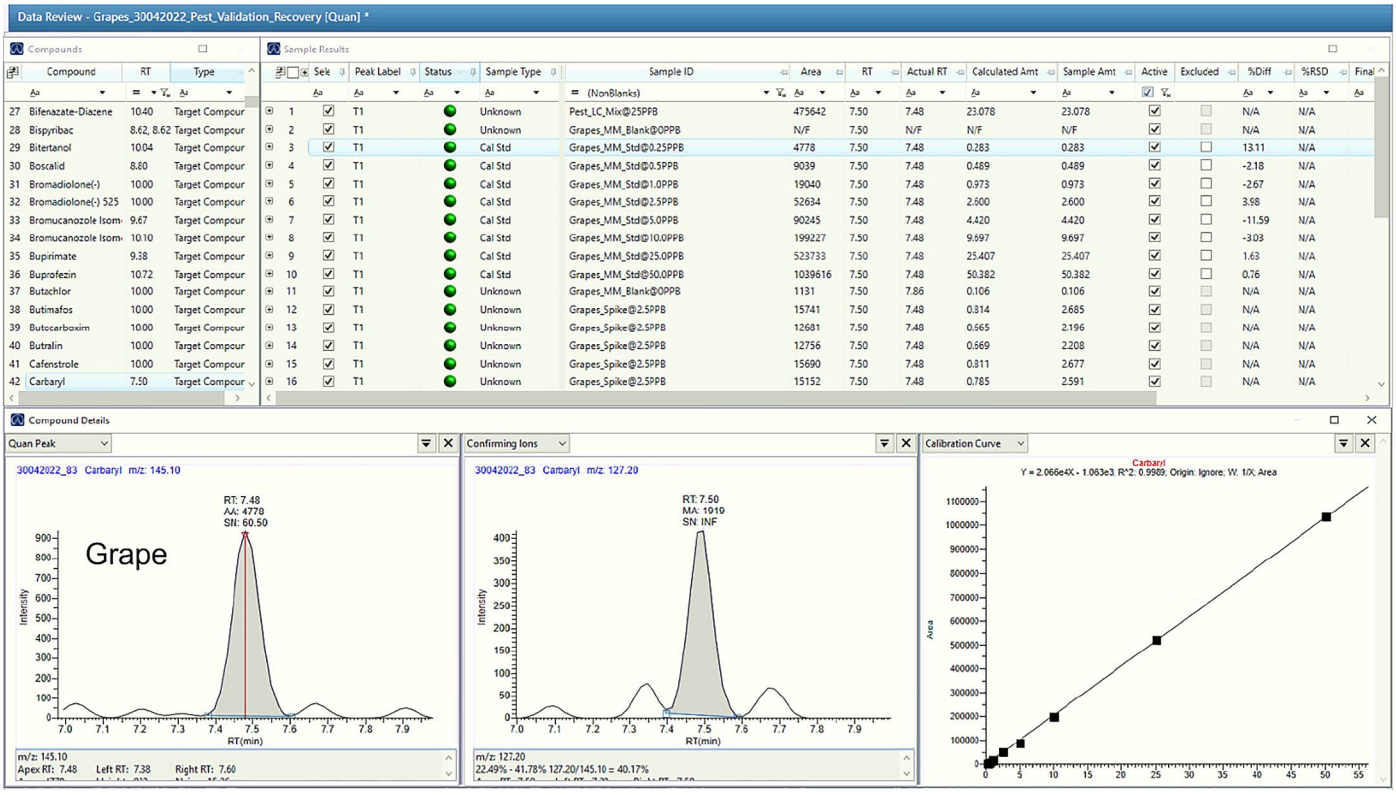

Figure 5A. Extracted ion chromatogram for quantifier ion of carbaryl at 0.00025 mg/kg, identification based on confirmatory ion with ion ratio, and calibration curve in the grape matrix

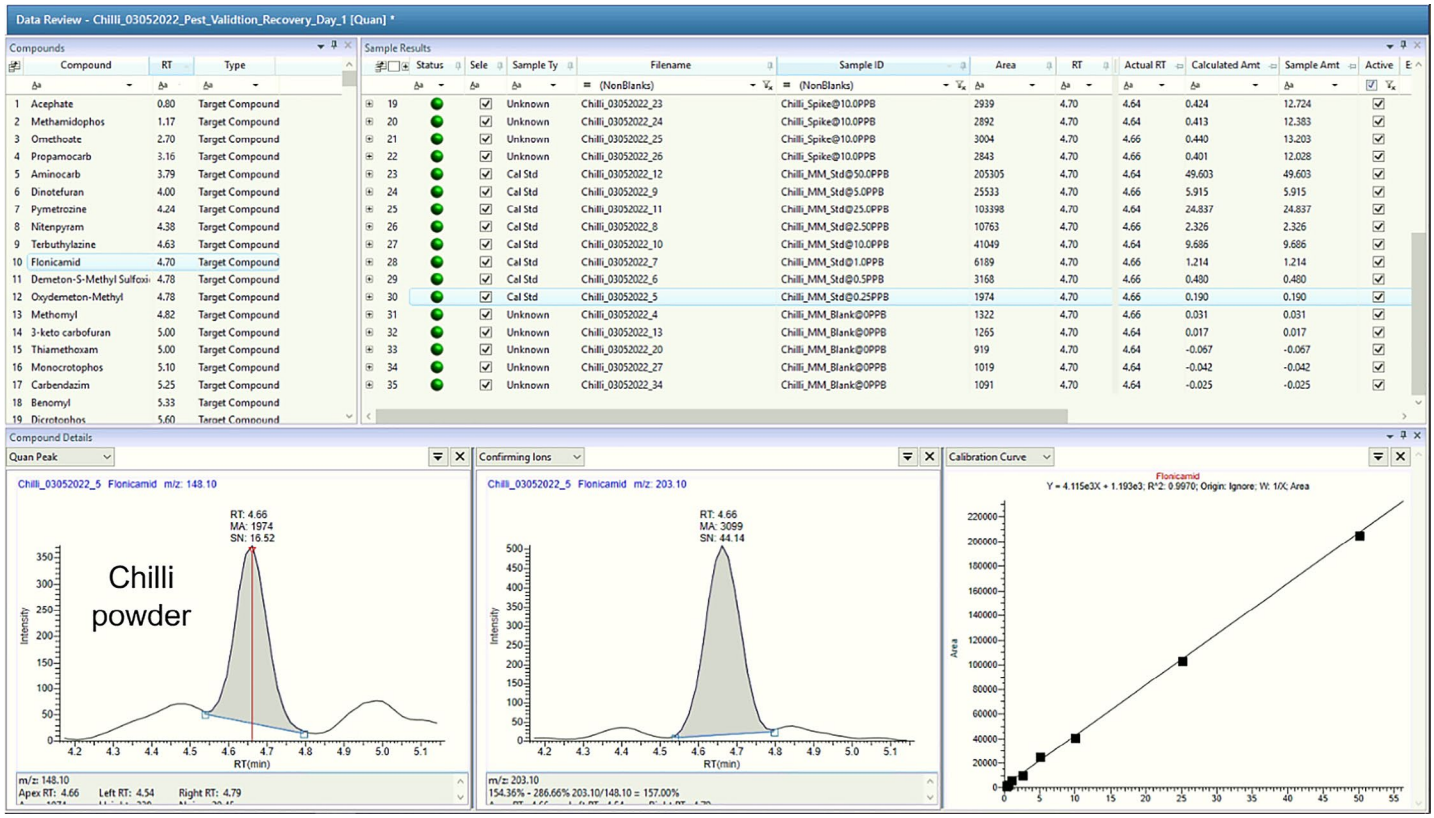

Figure 5B. Extracted ion chromatogram for quantifier ion of flonicamid at 0.00025 mg/kg, identification based on confirmatory ion with ion ratio and calibration curve in the chili powder matrix

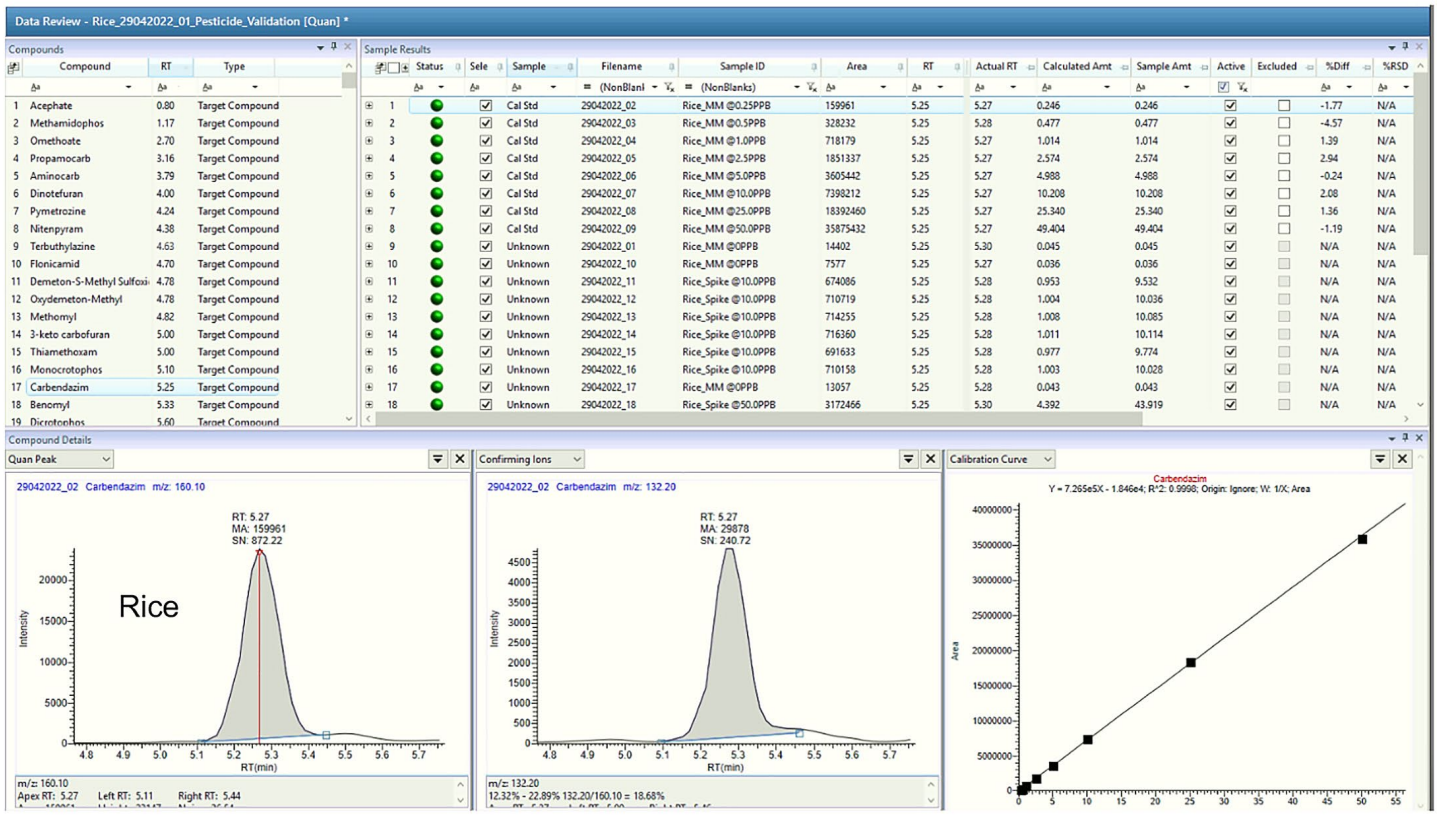

Figure 5C. Extracted ion chromatogram for quantifier ion of carbendazim at 0.00025 mg/kg, identification based on confirmatory ion with ion ratio and calibration curve in the rice matrix

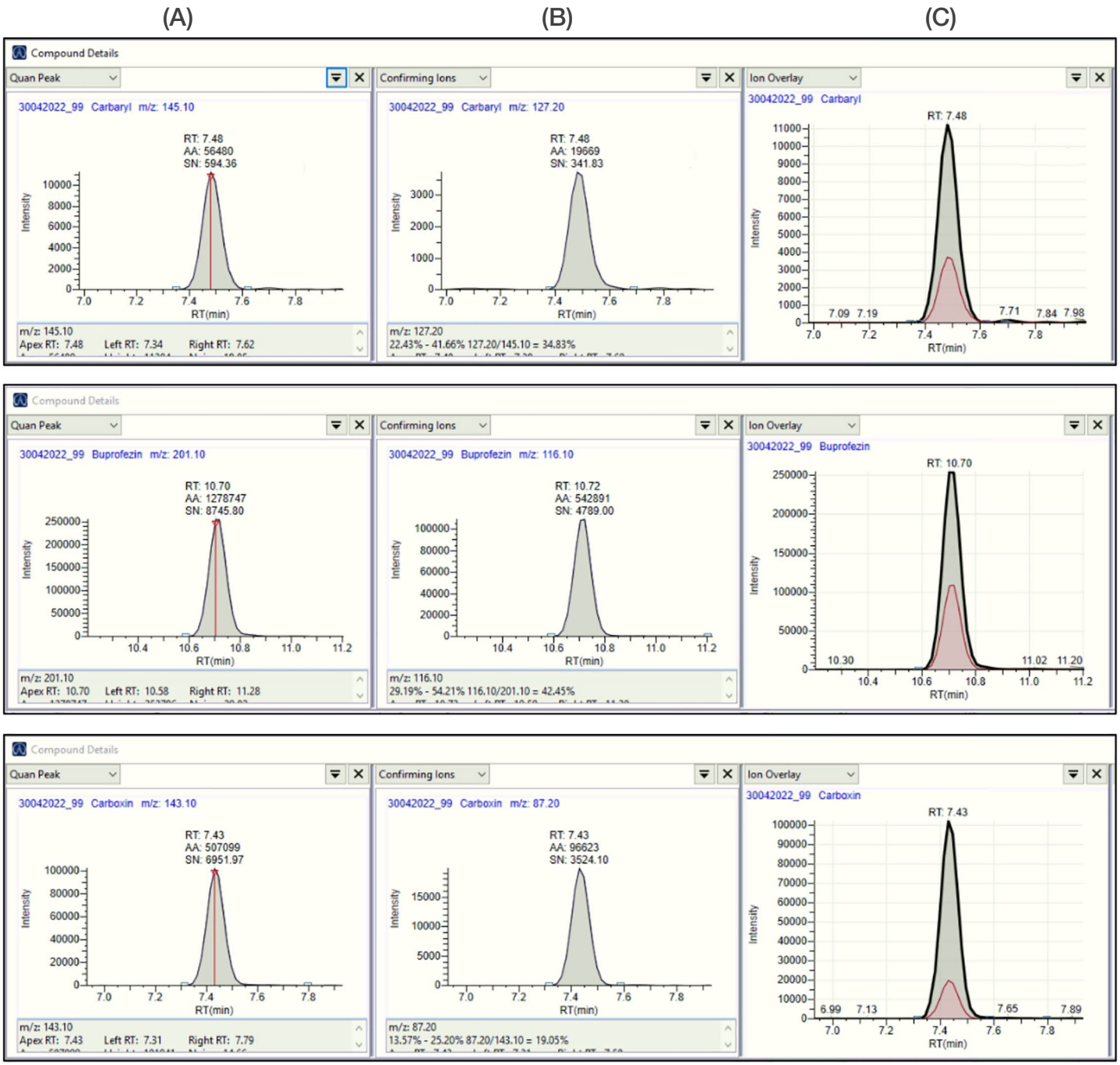

Figure 6. Extracted ion chromatograms for carbaryl, buprofezin, and carboxin showing the quantifier ion (A), confirmatory ion with ion ratio (B), and overlapping of both transitions at same retention time (C) at 0.01 mg/kg in grape

Method performance

Linearity

Excellent linearity over the range of 0.00025–0.05 mg/kg was achieved for all the target analytes (Supplementary Table S1) in all four matrices with correlation coefficients ≥0.99 with <20% residuals (back-calculated concentration) by following the linear equation and 1/X weighing factor.

Limit of quantitation

The LOQ was calculated from the lowest spike concentration in the target matrix that offered accuracy/recovery and precision within the acceptable criteria of the SANTE guidelines. In this study, the LOQ value was set at 0.01 mg/kg (rice), 0.005 mg/kg (chili powder and tomato), and 0.0025 mg/kg (grape), with excellent recoveries in the range of 70–120% with <20% RSD for six replicates in all four matrices. To evaluate the reproducibility of the stated workflow, the distribution of calculated RSD values at the LOQ and 0.05 mg/kg were compared per matrix (Figure 7). Almost all validated LOQ values are well below the established MRLs (default 0.01 mg/kg) by the FSSAI and EU Regulations.[1,2] Despite the short dwell times used for data acquisition, pesticide measurements show excellent reproducibility at the LOQ with about 50% of the pesticides showing %RSD at or below 10% and the remaining 50% of the pesticides within 10–20% RSD.

Recovery and precision

In this study, the recoveries were estimated through the measurements of additions of known amounts of the analyte(s) to a blank matrix against the spiked value. Recoveries were assessed at the stated LOQ and 0.05 mg/kg in targeted matrices with six replicates for each level. The quantitation was performed using matrix-matched calibration standards to harmonize the results. Most of the target analytes offered acceptable recoveries in the range of 70–120% with ≤20% RSD in the four matrices despite the range of compound polarity. The box and whisker plots in Figure 8 show recovery distribution profiles similar at the LOQ for rice, grape, and tomato, while the recovery distribution in chili powder is greater but still has an average recovery of 95%. Evaluation of the recovery distribution at 0.05 mg/kg again shows that measurements in chili powder present more challenges, but the universal method is still able to recover almost all pesticides within the stated acceptance range.

Triphenyl phosphate was used as an internal quality check standard (0.025 mg/kg) to demonstrate the overall performance of the system in the workflow. The TPP performance in terms of repeatability was <10% RSD for all the four matrices.

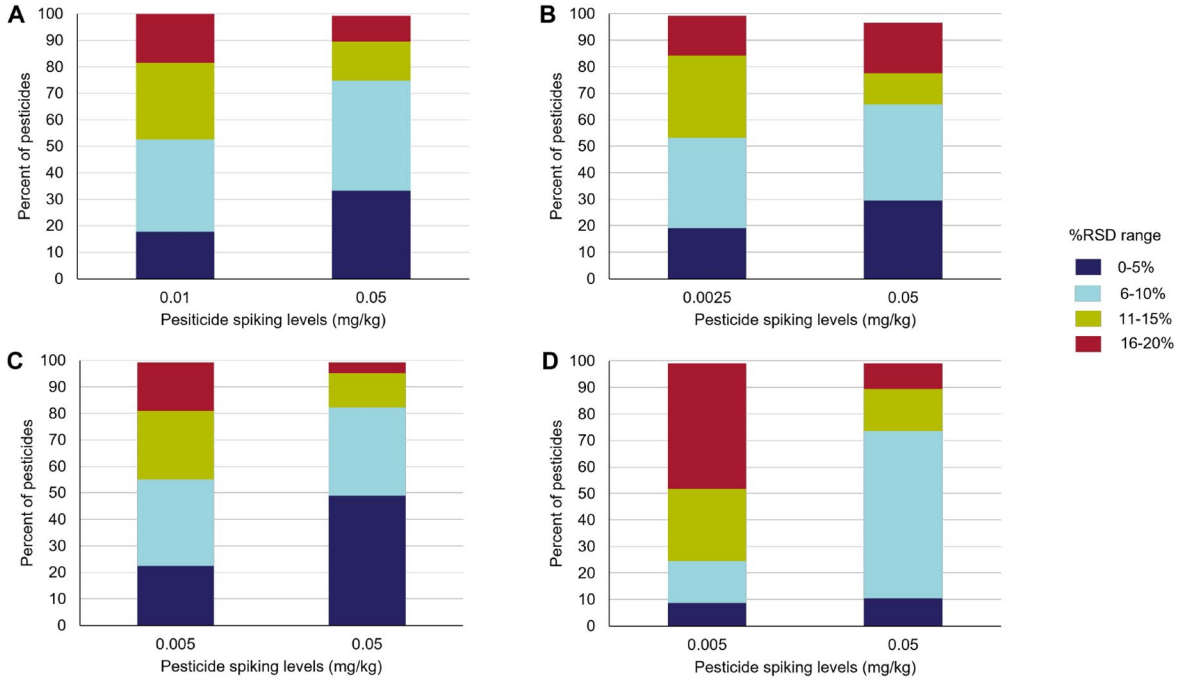

Figure 7. Precision (%) analysis for the set of pesticides spiked into (A) rice, (B) grape, (C) tomato, and (D) chili powder at the stated LOQ and highest levels

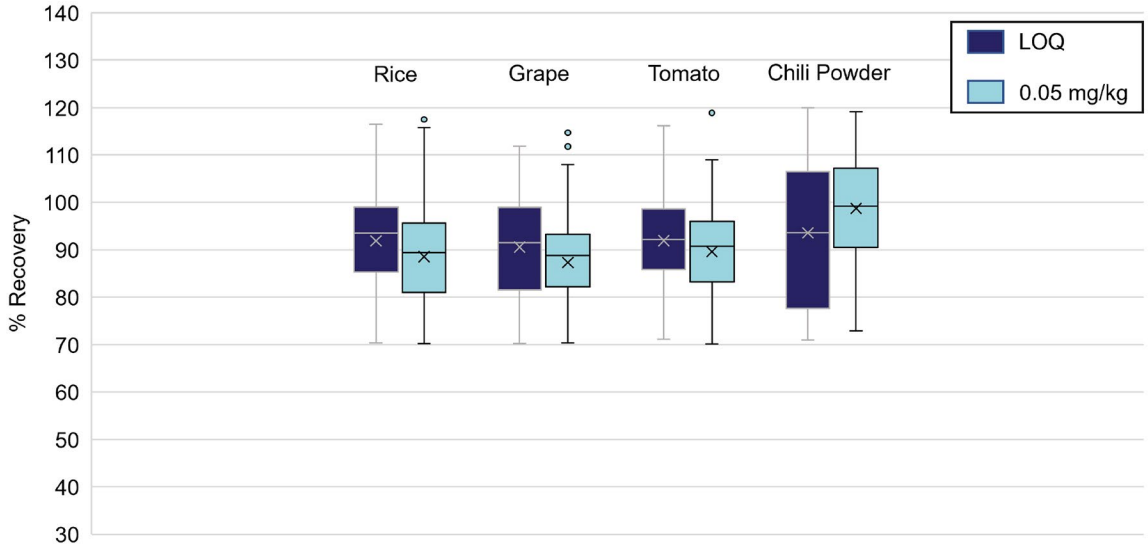

Figure 8. Recovery analysis for the set of pesticides spiked into the different matrices at the LOQ and highest levels

Conclusion

This work demonstrated an excellent analytical solution for trace-level quantitation of 202 pesticide residues in grape, tomato, rice, and chili powder by using a combination of acetate buffered QuEChERS (AOAC 2007.01) extraction followed by LC-MS/MS analysis with polarity switching. The method performance was evaluated at two different concentration levels with recoveries and precision in compliance with the SANTE guideline criteria. TraceFinder software offered flagging options that indirectly minimize the user's time required for data review and reporting. Based on the flagging option, the user can make quick decisions and move forward. The optimized method LOQs comply with the EU as well as the FSSAI MRL requirements. Use of this approach results in 70 injections of extraction (matrix matched samples, blanks, recovery checks, and samples) for highly confident results thus increasing the overall productivity of the commercial food testing laboratory.

References

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2. Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011. https://www.fssai.gov.in/upload/uploadfiles/files/Compendium_Contaminants_Regulations_28_01_2022.pdf
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4. SANTE guidelines https://www.eurl-pesticides.eu/userfiles/file/EurlALL/SANTE_11312_2021.pdf

Supplementary Table S1 (part 1). Compound-dependent parameters include the name of compounds, retention time, polarity, precursor, product ion, and collision energy (CE)

Name of compound	RT (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	CE (V)
3-Hydroxycarbofuran	5.94	Positive	238.0	163.2	17
3-Hydroxycarbofuran	5.94	Positive	238.0	181.1	12
3-Hydroxycarbofuran	5.94	Positive	238.0	220.2	7
Acetamiprid	6.06	Positive	223.0	99.1	39
Acetamiprid	6.06	Positive	223.0	126.0	21
Ametryn	8.29	Positive	228.2	68.3	38
Ametryn	8.29	Positive	228.2	186.1	21
Aminocarb	3.88	Positive	209.2	122.2	42
Aminocarb	3.88	Positive	209.2	152.2	16
Anilofos	9.83	Positive	368.1	125.1	32
Anilofos	9.83	Positive	368.1	171.0	23
Atrazine	6.19	Positive	216.1	104.2	31
Atrazine	6.19	Positive	216.1	174.1	20
Azimsulfuron	8.00	Positive	425.1	83.2	42
Azimsulfuron	8.00	Positive	425.1	156.1	26
Azimsulfuron	8.00	Positive	425.1	182.1	17
Azoxystrobin	8.57	Positive	404.1	344.1	27
Azoxystrobin	8.57	Positive	404.1	372.1	16
Benalaxyl	9.87	Positive	326.0	148.2	22
Benalaxyl	9.87	Positive	326.0	294.3	11
Bendiocarb	7.19	Positive	224.2	109.2	21
Bendiocarb	7.19	Positive	224.2	167.1	10
Bensulfuron methyl	8.41	Positive	411.1	119.1	38
Bensulfuron methyl	8.41	Positive	411.1	149.1	21
Bifenazate	9.15	Positive	301.0	170.2	20
Bifenazate	9.15	Positive	301.0	198.1	10
Bifenazate-diazene	10.40	Positive	299.0	184.1	19
Bifenazate-diazene	10.40	Positive	299.0	197.1	20
Bifenazate-diazene	10.40	Positive	299.0	213.1	12
Boscalid	8.80	Positive	343.0	140.0	34
Boscalid	8.80	Positive	343.0	307.1	21
Bromucanozole Isomer 1	9.67	Positive	378.0	70.0	47
Bromucanozole Isomer 1	9.67	Positive	378.0	159.0	37
Bromucanozole Isomer 2	10.01	Positive	378.0	70.1	47
Bromucanozole Isomer 2	10.01	Positive	378.0	159.1	37
Bupirimate	9.38	Positive	317.1	108.0	27
Bupirimate	9.38	Positive	317.1	166.2	25
Buprofezin	10.72	Positive	306.0	116.1	17
Buprofezin	10.72	Positive	306.0	201.1	13
Carbaryl	7.50	Positive	202.2	127.2	31
Carbaryl	7.50	Positive	202.2	145.1	11
Carbendazim	5.25	Positive	192.2	132.2	33
Carbendazim	5.25	Positive	192.2	160.1	20
Carbofuran	7.17	Positive	222.2	123.2	25
Carbofuran	7.17	Positive	222.2	165.1	15

Name of compound	RT (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	CE (V)
Carboxin	7.46	Positive	236.1	87.2	28
Carboxin	7.46	Positive	236.1	143.1	18
Carfentrazone-ethyl	9.66	Positive	412.1	346.1	23
Carfentrazone-ethyl	9.66	Positive	412.1	366.1	19
Carpropamid	9.89	Positive	334.1	103.2	43
Carpropamid	9.89	Positive	334.1	139.1	22
Chlorantraniliprole	8.30	Positive	482.0	284.1	14
Chlorantraniliprole	8.30	Positive	484.0	453.1	16
Chlorantraniliprole	8.30	Positive	486.0	455.0	17
Chloridazon	7.20	Positive	222.1	77.3	35
Chloridazon	7.20	Positive	222.1	104.2	26
Chlorimuron-ethyl	8.87	Positive	415.0	121.1	40
Chlorimuron-ethyl	8.87	Positive	415.0	186.1	19
Chlorotoluron	7.82	Positive	213.1	72.3	19
Chlorotoluron	7.82	Positive	213.1	140.1	25
Chloroxuron	9.17	Positive	291.1	72.4	23
Chloroxuron	9.17	Positive	291.1	218.1	27
Chromfenozide	9.26	Positive	395.2	175.1	13
Chromfenozide	9.26	Positive	395.2	339.1	10
Clethodim	10.45	Positive	360.0	164.2	20
Clethodim	10.45	Positive	360.0	268.3	12
Clethodim	10.45	Positive	362.0	164.2	20
Clodinafop-propargyl	9.66	Positive	350.0	91.1	30
Clodinafop-propargyl	9.66	Positive	350.0	266.1	16
Clothianidin	5.66	Positive	250.0	113.0	27
Clothianidin	5.66	Positive	250.0	132.0	17
Clothianidin	5.66	Positive	250.0	169.1	14
Cyantraniliprole	7.58	Positive	475.1	285.9	17
Cyantraniliprole	7.58	Positive	475.1	444.0	20
Cyazofamid	9.41	Positive	325.1	108.0	15
Cyazofamid	9.41	Positive	325.1	261.0	10
Cycluron	8.16	Positive	199.1	69.0	20
Cycluron	8.16	Positive	199.1	89.1	20
Cymoxanil	6.15	Positive	199.1	111.1	18
Cymoxanil	6.15	Positive	199.1	128.1	10
Cyproconazole	9.15	Positive	292.0	70.1	21
Cyproconazole	9.15	Positive	292.0	125.1	30
Cyproconazole	9.15	Positive	294.0	70.1	21
Cyprodinil	9.81	Positive	226.2	77.3	45
Cyprodinil	9.81	Positive	226.2	93.2	37
Demeton-S-methyl	8.92	Positive	231.1	61.3	30
Demeton-S-methyl	8.92	Positive	231.1	89.2	10
Demeton-S-methyl sulfone	8.06	Positive	263.0	108.9	23
Demeton-S-methyl sulfone	8.06	Positive	263.0	121.2	17
Demeton-S-methyl sulfone	8.06	Positive	263.0	169.1	17

Supplementary Table S1 (part 2). Compound-dependent parameters include the name of compounds, retention time, polarity, precursor, product ion, and collision energy (CE)

Name of compound	RT (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	CE (V)
Demeton-S-methyl Sulfoxide	5.03	Positive	247.0	109.1	26
Demeton-S-methyl Sulfoxide	5.03	Positive	247.0	169.1	14
Dichlorvos	7.13	Positive	221.0	109.0	18
Dichlorvos	7.13	Positive	223.0	109.0	18
Dicrotophos	5.60	Positive	238.1	112.2	15
Dicrotophos	5.60	Positive	238.1	127.1	20
Diethofencarb	8.50	Positive	268.1	124.0	40
Diethofencarb	8.50	Positive	268.1	226.1	13
Difenconazole	10.30	Positive	406.1	188.1	48
Difenconazole	10.30	Positive	406.1	251.0	28
Diflubenzuron	9.55	Positive	311.1	113.1	54
Diflubenzuron	9.55	Positive	311.1	158.2	16
Dimethoate	5.87	Positive	230.0	124.9	25
Dimethoate	5.87	Positive	230.0	171.1	16
Dimethoate	5.87	Positive	230.0	198.9	11
Dimethomorph E isomer	8.67	Positive	388.1	165.1	34
Dimethomorph E isomer	8.67	Positive	388.1	301.1	23
Dimethomorph Z isomer	8.90	Positive	388.2	165.1	34
Dimethomorph Z isomer	8.90	Positive	388.2	301.1	23
Dimoxystrobin	9.60	Positive	327.1	116.1	20
Dimoxystrobin	9.60	Positive	327.1	238.1	13
Diniconazole	10.20	Positive	326.2	70.3	27
Diniconazole	10.20	Positive	326.2	159.0	32
Dinotefuran	4.00	Positive	203.0	129.1	12
Dinotefuran	4.00	Positive	203.0	157.2	8
Disulfoton-sulfone	8.35	Positive	307.1	97.1	29
Disulfoton-sulfone	8.35	Positive	307.1	260.9	11
Diuron	7.70	Positive	233.1	72.3	21
Diuron	7.70	Positive	235.1	72.3	19
Emamectin-B1a-benzoate	10.92	Positive	886.5	82.3	47
Emamectin-B1a-benzoate	10.92	Positive	886.5	158.2	39
Emamectin-B1b-benzoate	10.71	Positive	872.5	82.3	46
Emamectin-B1b-benzoate	10.71	Positive	872.5	158.2	37
Epoxiconazole	9.37	Positive	330.1	101.2	45
Epoxiconazole	9.37	Positive	330.1	121.2	23
Etaconazole	9.32	Positive	328.1	123.2	59
Etaconazole	9.32	Positive	328.1	159.0	29
Ethiprole	8.68	Positive	397.0	255.0	39
Ethiprole	8.68	Positive	397.0	350.9	23
Ethirimol	6.80	Positive	210.2	98.1	35
Ethirimol	6.80	Positive	210.2	140.1	30
Ethofumesate	8.57	Positive	287.1	121.1	23
Ethofumesate	8.57	Positive	287.1	259.1	15
Fenamidone	8.68	Positive	312.2	92.3	26
Fenamidone	8.68	Positive	312.2	236.1	16
Fenbuconazole	9.45	Positive	337.2	70.3	22
Fenbuconazole	9.45	Positive	337.2	125.1	30
Fenobucarb	8.50	Positive	208.0	95.1	15
Fenobucarb	8.50	Positive	208.0	152.1	9
Fenuron	5.80	Positive	165.1	46.0	25
Fenuron	5.80	Positive	165.1	72.1	40
Fipronil(-)	9.56	Negative	434.9	249.9	29
Fipronil(-)	9.56	Negative	434.9	329.9	16
Fipronil(-)	9.56	Negative	437.0	331.9	16
Flonicamid	4.70	Positive	230.1	148.1	29
Flonicamid	4.70	Positive	230.1	203.1	18
Fludioxonil	8.86	Positive	266.1	158.1	35
Fludioxonil	8.86	Positive	266.1	229.1	12
Fludioxonil(-)	8.86	Negative	247.0	126.0	30
Fludioxonil(-)	8.86	Negative	247.0	169.0	33
Flufenacet	9.28	Positive	364.1	124.2	33
Flufenacet	9.28	Positive	364.1	152.1	21
Flufenoxuron	11.17	Positive	489.0	141.1	43
Flufenoxuron	11.17	Positive	489.0	158.1	21
Fluometuron 1	7.70	Positive	233.1	72.5	19
Fluometuron 1	7.70	Positive	233.1	188.2	15
Fluopicolide	8.91	Positive	383.0	109.0	55
Fluopicolide	8.91	Positive	383.0	145.0	52
Fluopicolide	8.91	Positive	383.0	173.1	29
Fluoxastrobin	9.18	Positive	459.2	188.1	36
Fluoxastrobin	9.18	Positive	459.2	427.0	18
Flupyradifuran	6.03	Positive	289.0	126.0	20
Flupyradifuran	6.03	Positive	291.0	127.9	21
Fluquinconazole	9.15	Positive	376.1	307.1	27
Fluquinconazole	9.15	Positive	376.1	349.1	19
Flusilazole	9.57	Positive	316.1	165.2	31
Flusilazole	9.57	Positive	316.1	247.1	20
Fluthiacet-methyl	8.55	Positive	404.1	274.1	29
Fluthiacet-methyl	8.55	Positive	404.1	331.1	29
Fluthiacet-methyl	8.55	Positive	404.1	344.1	22
Flutriafol	7.91	Positive	302.2	70.3	20
Flutriafol	7.91	Positive	302.2	123.1	30
Fluxapyroxad	8.92	Positive	382.2	342.1	22
Fluxapyroxad	8.92	Positive	382.2	362.1	14
Fuberidazole	6.00	Positive	185.2	129.2	39
Fuberidazole	6.00	Positive	185.2	157.1	25
Furalaxyl	8.56	Positive	302.2	242.1	18
Furalaxyl	8.56	Positive	302.2	270.1	11
Haloxyfop-R-methyl	10.27	Positive	376.0	316.0	17
Haloxyfop-R-methyl	10.27	Positive	378.0	318.2	17

Supplementary Table S1 (part 3). Compound-dependent parameters include the name of compounds, retention time, polarity, precursor, product ion, and collision energy (CE)

Name of compound	RT (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	CE (V)
Hexaconazole	9.94	Positive	314.1	70.0	22
Hexaconazole	9.94	Positive	314.1	159.0	31
Hexaconazole	9.94	Positive	316.1	70.1	21
Imazalil	7.94	Positive	297.1	159.0	26
Imazalil	7.94	Positive	297.1	255.0	20
Imidacloprid	5.70	Positive	256.1	175.1	21
Imidacloprid	5.70	Positive	256.1	209.1	19
Indoxacarb	10.33	Positive	528.0	150.0	23
Indoxacarb	10.33	Positive	528.0	203.1	37
Indoxacarb	10.33	Positive	528.0	249.2	17
Ipconazole	10.40	Positive	334.2	70.0	37
Ipconazole	10.40	Positive	334.2	125.0	47
Iprobenfos	9.65	Positive	289.1	91.1	22
Iprobenfos	9.65	Positive	289.1	204.9	11
Iprovalicarb	9.19	Positive	321.0	119.1	20
Iprovalicarb	9.19	Positive	321.0	186.2	11
Iprovalicarb	9.19	Positive	321.0	203.2	9
Isoprocarb	7.87	Positive	194.2	95.1	15
Isoprocarb	7.87	Positive	194.2	152.1	10
Isoprothiolane	8.90	Positive	291.0	145.1	34
Isoprothiolane	8.90	Positive	291.0	189.0	21
Isoprothiolane	8.90	Positive	291.0	231.1	11
Isoproturon	8.05	Positive	207.2	72.3	21
Isoproturon	8.05	Positive	207.2	132.0	15
Kresoxim methyl	9.65	Positive	314.0	116.1	16
Kresoxim methyl	9.65	Positive	314.0	206.0	5
Kresoxim methyl	9.65	Positive	314.0	267.0	7
Linuron	8.67	Positive	249.1	160.0	21
Linuron	8.67	Positive	249.1	182.1	18
Mandipropamid	8.85	Positive	412.1	328.1	15
Mandipropamid	8.85	Positive	412.1	356.0	11
Metalaxyl	8.01	Positive	280.2	192.2	21
Metalaxyl	8.01	Positive	280.2	220.2	16
Metalaxyl-M	8.01	Positive	280.2	160.2	26
Metalaxyl-M	8.01	Positive	280.2	220.1	16
Metconazole	10.01	Positive	320.1	70.0	40
Metconazole	10.01	Positive	320.1	125.0	50
Methabenzthiazuron	8.06	Positive	222.1	150.1	36
Methabenzthiazuron	8.06	Positive	222.1	165.1	19
Methamidophos	1.17	Positive	142.1	94.2	16
Methamidophos	1.17	Positive	142.1	125.0	16
Methoprotryne	8.29	Positive	272.2	198.0	30
Methoprotryne	8.29	Positive	272.2	240.2	25
Metribuzin	7.06	Positive	215.1	84.0	24
Metribuzin	7.06	Positive	215.1	187.1	20
Mevinphos	6.38	Positive	225.1	109.1	34
Mevinphos	6.38	Positive	225.1	127.1	19
Mexacarbate	6.15	Positive	223.0	151.1	25
Mexacarbate	6.15	Positive	223.0	166.3	15
Monocrotophos	5.30	Positive	224.0	127.1	10
Monocrotophos	5.30	Positive	224.0	193.0	9
Monolinuron	7.64	Positive	215.1	99.2	36
Monolinuron	7.64	Positive	215.1	126.1	20
Myclobutanil	9.01	Positive	289.2	70.3	21
Myclobutanil	9.01	Positive	289.2	125.1	33
Nitenpyram	4.60	Positive	271.2	126.1	30
Nitenpyram	4.60	Positive	271.2	225.0	18
Omethoate	2.70	Positive	214.0	108.9	28
Omethoate	2.70	Positive	214.0	124.9	23
Omethoate	2.70	Positive	214.0	183.0	11
Oxadiargyl	10.01	Positive	341.0	151.1	26
Oxadiargyl	10.01	Positive	341.0	223.1	18
Oxadixyl	6.81	Positive	279.1	132.1	43
Oxadixyl	6.81	Positive	279.1	219.1	15
Oxamyl [M+NH4]	6.85	Positive	237.1	72.3	17
Oxamyl [M+NH4]	6.85	Positive	237.1	192.1	8
Paclobutrazol	8.86	Positive	294.2	70.3	22
Paclobutrazol	8.86	Positive	294.2	125.1	36
Penconazole	9.75	Positive	284.1	70.4	20
Penconazole	9.75	Positive	284.1	159.0	30
Penoxsulum	8.29	Positive	484.0	139.1	29
Penoxsulum	8.29	Positive	484.0	164.1	35
Penoxsulum	8.29	Positive	484.0	194.1	37
Penoxsulum	8.29	Positive	484.0	195.1	29
Phenthoate	9.66	Positive	321.0	135.1	22
Phenthoate	9.66	Positive	321.0	246.8	12
Phorate-278	7.90	Positive	261.0	75.1	12
Phorate-278	7.90	Positive	261.0	171.1	12
Phorate-oxan-sulfone	7.76	Positive	277.0	97.0	39
Phorate-oxan-sulfone	7.76	Positive	277.0	127.0	15
Phorate-oxan-sulfone	7.76	Positive	277.0	155.1	12
Phorate-sulfone	7.87	Positive	293.1	97.0	20
Phorate-sulfone	7.87	Positive	293.1	171.0	13
Phorate-sulfoxide	7.76	Positive	277.0	142.9	21
Phorate-sulfoxide	7.76	Positive	277.0	199.1	10
Phosalone	9.81	Positive	368.0	111.1	42
Phosalone	9.81	Positive	368.0	182.0	10
Picoxystrobin	9.60	Positive	368.0	145.1	23
Picoxystrobin	9.60	Positive	368.0	205.2	9
Pinoxaden	10.07	Positive	401.3	57.3	26
Pinoxaden	10.07	Positive	401.3	317.1	23
Piperonyl-butoxide	10.80	Positive	356.3	119.2	35
Piperonyl-butoxide	10.80	Positive	356.3	177.1	10
Pirimicarb	7.05	Positive	239.2	72.3	23

Supplementary Table S1 (part 4). Compound-dependent parameters include the name of compounds, retention time, polarity, precursor, product ion, and collision energy (CE)

Name of compound	RT (min)	Polarity	Precursor (*m/z*)	Product (*m/z*)	CE (V)
Pirimicarb	7.05	Positive	239.2	182.2	18
Pirimicarb-desmethyl	6.85	Positive	225.0	72.1	20
Pirimicarb-desmethyl	6.85	Positive	225.0	168.1	15
Promecarb	8.81	Positive	208.0	109.3	16
Promecarb	8.81	Positive	208.0	151.2	9
Prometon	7.90	Positive	226.2	142.1	25
Prometon	7.90	Positive	226.2	184.1	20
Propamocarb	3.16	Positive	189.3	74.3	28
Propamocarb	3.16	Positive	189.3	102.2	20
Propiconazole	9.90	Positive	342.0	69.1	22
Propiconazole	9.90	Positive	342.0	123.2	53
Propiconazole	9.90	Positive	342.0	159.0	33
Propoxur	7.11	Positive	210.2	111.2	17
Propoxur	7.11	Positive	210.2	168.0	10
Pymetrozine	4.24	Positive	218.2	78.3	41
Pymetrozine	4.24	Positive	218.2	105.2	23
Pyracarbolid	7.30	Positive	218.2	97.2	28
Pyracarbolid	7.30	Positive	218.2	125.1	19
Pyrimethanil	8.65	Positive	200.2	82.2	28
Pyrimethanil	8.65	Positive	200.2	107.2	26
Pyrimethanil	8.65	Positive	200.2	183.1	25
Quinalphos	9.10	Positive	299.0	147.1	25
Quinalphos	9.10	Positive	299.0	163.1	24
Secbumeton	7.89	Positive	226.2	100.0	35
Secbumeton	7.89	Positive	226.2	170.1	25
Spinetoram	10.46	Positive	748.3	98.2	47
Spinetoram	10.46	Positive	748.3	142.2	33
Spinosyn A	10.14	Positive	732.5	98.3	41
Spinosyn A	10.14	Positive	732.5	142.2	26
Spinosyn D	10.45	Positive	746.5	98.3	43
Spinosyn D	10.45	Positive	746.5	142.2	27
Spiroxamine	8.86	Positive	298.3	100.2	30
Spiroxamine	8.86	Positive	298.3	144.1	20
Tebufenpyrad	10.68	Positive	334.0	117.0	45
Tebufenpyrad	10.68	Positive	334.0	145.0	35
Thiacloprid	6.41	Positive	253.0	125.9	23
Thiacloprid	6.41	Positive	253.0	186.1	15
Thiamethoxam	5.00	Positive	292.0	181.2	23
Thiamethoxam	5.00	Positive	292.0	211.2	13
Thiamethoxam	5.00	Positive	294.0	211.1	13
Thiobencarb	10.17	Positive	258.1	89.2	50
Thiobencarb	10.17	Positive	258.1	125.1	21
Thiodicarb	7.72	Positive	355.0	88.1	16
Thiodicarb	7.72	Positive	355.0	108.0	16
Thiophnate-methyl	7.10	Positive	343.0	151.1	22
Thiophnate-methyl	7.10	Positive	343.0	160.1	32
Triadimefon	8.99	Positive	294.0	69.2	22
Triadimefon	8.99	Positive	294.0	197.3	15
Triadimefon	8.99	Positive	294.0	225.1	14
Triadimenol	8.86	Positive	296.0	70.1	15
Triadimenol	8.86	Positive	296.0	227.2	10
Triasulfuron	7.12	Positive	402.1	141.1	21
Triasulfuron	7.12	Positive	402.1	167.1	18
Trichlorfon	5.72	Positive	257.0	109.1	17
Trichlorfon	5.72	Positive	257.0	127.1	14
Trichlorfon	5.72	Positive	257.0	221.0	10
Trichlorfon	5.72	Positive	274.0	109.0	23
Trichlorfon	5.72	Positive	274.0	221.0	15
Tricyclazole	6.71	Positive	190.1	136.0	29
Tricyclazole	6.71	Positive	190.1	163.0	24
Trifloxystrobin	10.35	Positive	409.1	186.1	20
Trifloxystrobin	10.35	Positive	409.1	206.0	44
Triflumizole	10.51	Positive	346.1	43.5	18
Triflumizole	10.51	Positive	346.1	278.0	11
Triticonazole	9.23	Positive	318.2	70.3	19
Triticonazole	9.23	Positive	318.2	125.1	30
Vamidothion	5.93	Positive	288.1	118.1	25
Vamidothion	5.93	Positive	288.1	146.1	15

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