Application note | 002215

Food safety

A multi-residue method for quantitation of pesticides in chicken, lamb, and fish using LC-MS/MS

Authors

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Keywords

TraceFinder software, pesticide residues, QuEChERS, LC-MS/MS, TSQ Quantis Plus MS, polarity switching

Goal

The goal of this project is to demonstrate the performance and versatility of the LC-MS/MS workflow featuring the Thermo Scientific™ TSQ Quantis™ Plus mass spectrometer for trace-level quantitation of pesticide residues in lamb, chicken, and fish. The optimized method was validated as per the SANTE guidelines and evaluated for the Food Safety and Standards Authority of India (FSSAI) as well as the European Commission (EC) Maximum Residue Levels (MRLs) compliance for the specified matrices. The MRLs under consideration cover fish and fish products, while the MRLs for meat apply to muscle (trimmed fat), fat, kidneys, liver, etc.

Introduction

Pest control in intensive agriculture involves treatment with a variety of synthetic chemicals generically known as pesticides. These chemicals are transferred from plants to animals via the food chain. Additionally, animals and their accomodations can be sprayed with pesticide products to prevent infestations in the overcrowded and unsanitary conditions that may exist on factory farms. Consequently, both contamination routes lead to the bioaccumulation of pesticides in food products of animal origin.

There has been a gradual increase in the consumption of lamb, chicken, and fish in India, with chicken arguably the most popular low-cost meat consumed. Therefore, monitoring pesticde residues in meat becomes essential, and LC-MS/MS is the best technique for accurate quantitation of LC-amenable analytes. The challenge presented to researchers and food control laboratories is to minimize the amount of work needed to modify the LC-MS/MS method to satisfy regulatory requirements for different meat matrices. The aim of this work was the optimization and validation of a single multi-residue method for pesticides in meat (chicken and lamb) and fish by using LC-MS/MS featuring the Thermo Scientific™ Vanquish™ Flex UHPLC system and the TSQ Quantis Plus mass spectrometer. The data acquisition and processing were carried out using Thermo Scientific™ TraceFinder™ software. The optimized method performance was evaluated as per the SANTE/11312/ 2021 guidelines[1] specifically focusing on linearity, matrix effects, limits of quantitation, recovery and precision.

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 centrifuge tubes
- 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).

Pesticide standards were purchased from Restek.

LC-MS/MS analysis

Liquid chromatographic separation was performed using a Vanquish Flex UHPLC system coupled with the TSQ Quantis Plus triple quadrupole mass spectrometer. The heated electrospray ionization (HESI) source was used for desolvation and ionization. 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	Thermo Scientific™ Vanquish UHPLC Flex Binary Pump F (P/N VF-P10-A)
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	10 µL
Needle wash	80% methanol and 20% water
Mobile phase	A: 5 mM ammonium formate + 0.1% formic acid in water:methanol (98:2) B: 5 mM ammonium formate + 0.1% formic acid in methanol:water (98:2
Set inline filter	Vanquish Pump mixer, VF-P1 (10 µL mixer kit) (P/N 6044.3870)
Total run time	15.0 min
LC gradient program	Time (min) / Flow rate (mL/min) / %B / Curve 0.0 / 0.300 / 0 / 5 0.5 / 0.300 / 0 / 5 7.0 / 0.300 / 70 / 5 9.0 / 0.300 / 100 / 5 12.0 / 0.300 / 100 / 5 12.1 / 0.300 / 0 / 5 15.0 / 0.300 / 0 / 5
Mass spectrometry method	
Instrumentation	TSQ Quantis Plus triple quadrupole mass spectrometer
Method type	Acquisition-Timed (t-SRM mode)
Ion source type	HESI-II
Spray voltage	Static Positive: 3,500 V Negative: 2,500 V
Sheath gas	40 Arb
Aux gas	7 Arb
Sweep gas	1 Arb
Ion transfer tube temp.	300 °C
Vaporizer temp.	350 °C

Sample preparation

The lamb, chicken, and fish samples were collected from the local market and were individually homogenized using a heavy-duty mixer and grinder to create uniform slurries. The acetate buffered QuEChERS method (AOAC 2007.01) detailed below[2] was used for extraction. The control samples were verified for the positive detection of target analytes. The pesticide residue-free matrix was then used for recovery experiments as well as matrix-matched calibration standards preparation. The details of the matrix-matched calibration standards preparation are given below in Table 2.

Extraction and clean-up

- Weigh 5 g homogenized sample into a 50 mL extraction tube.
- Add internal standard triphenyl phosphate (TPP).
- For the recovery experiment, spike the samples before the addition of an extraction solvent.
- A final set of 158 pesticide reference standards were spiked per matrix.
- Add 10 mL of water and vortex for 1 min on a vortex mixer 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 Na-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 and add 1 mL of supernatant to the 2 mL centrifuge tube containing 150 mg $MgSO_4$, 50 mg PSA, and 50 mg C18.
- Shake vigorously and vortex for 30 s on a vortex mixer at 2,500 rpm.
- Centrifuge at 10,000 rpm for 5 min.
- Dilute the supernatant (0.500 mL) with 0.5 mL water (1:1 ratio, v/v).
- Inject 5 µL of diluted extract into the LC-MS/MS.

Data acquisition and processing

The data acquisition and processing were carried out 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 is given in supplementary Table S1 with their transition, collision energies, and retention time (min). For data processing, the ion ratio (±30%), retention time (±0.1 min), linearity (>0.99 with residuals ±20), recovery (70–120%), and precision (±20%) were set as acceptance criteria as per SANTE guidelines[1].

Results and discussion

LC-MS/MS analysis

The liquid chromatographic method was selected from the previously published application note,[5] which offered excellent separation and peak shape for the target analytes and the absence of an isobaric interference from the matrix. As per the gradient program, the distribution of analyte elution was predominantly measured between 4 and 12 minutes requiring t-SRM acquisition (Figure 1).

Fast polarity switching

The large number of pesticide residues monitored in the method requires ionization and detection in both positive and negative ESI and polarity switching. The TSQ Quantis Plus mass spectrometer performs fast polarity switching with stabilization, enabling uncompromised sensitivity for both positive and negative polarity analytes. In this study, sensitivity of pesticide residues like fipronil, fluazinam, hexaflumuron, and teflubenzuron ionized in negative polarity showed an LOQ of 0.005 mg/kg in the lamb matrix, equivalent to 0.00083 mg/kg in all other matricesmatrices (Figure 2). Each of the pesticide residues displayed in Figure 2 eluted in the most crowded elution window of the method, required polarity switching, and had a low measured intensity value relative to other co-eluting compounds. Nevertheless, reproducible measurements were achieved based on calculated coefficients of variance (%CV) despite dwell time settings of 5, 8, 10, 15 ms being used, respectively.

Table 2. Preparation of matrix-matched standard

Matrix (µL)	Std stock (µg/mL)	Std volume (µL)	Water (µL)	Final conc. (µg/mL)	Final conc. (mg/kg)
500	0.1	5	495	0.0005	0.003
500	0.1	10	490	0.001	0.006
500	0.1	25	475	0.0025	0.015
500	0.1	50	450	0.005	0.030
500	0.1	100	400	0.010	0.060
500	1.0	25	475	0.025	0.150
500	1.0	50	450	0.050	0.300

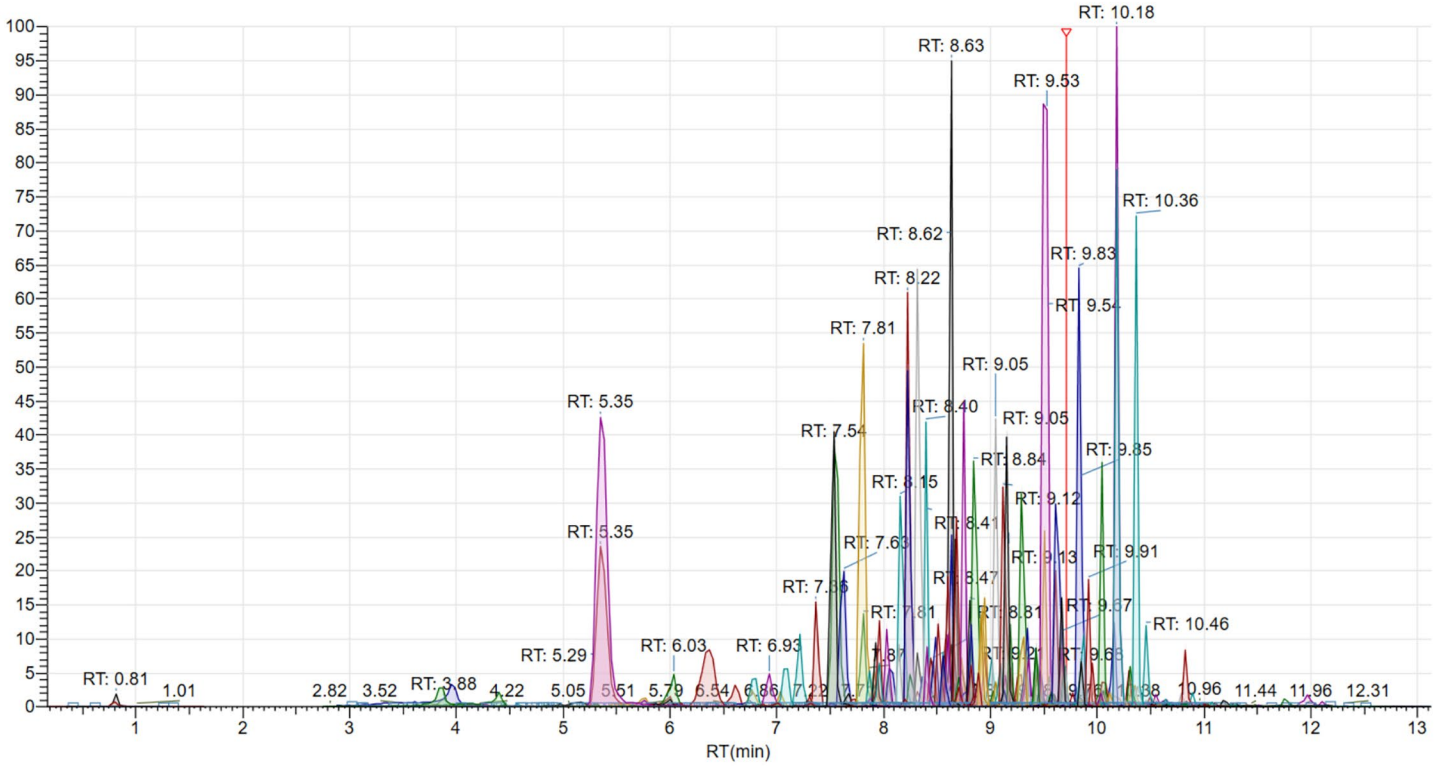

Figure 1. Overlaid extracted ion chromatogram for all target pesticides in a standard solution

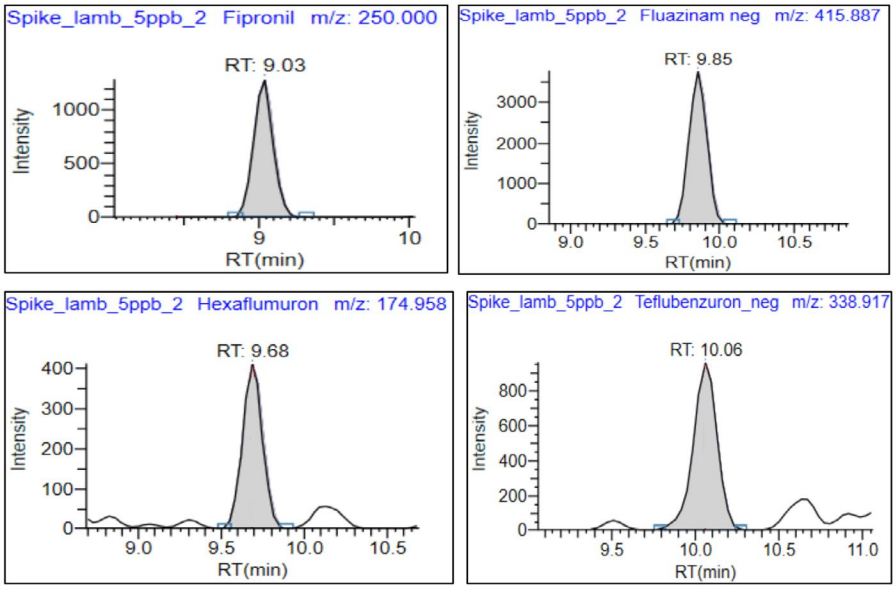

Figure 2. The sensitivity of fipronil, fluazinam, hexaflumuron, and teflubenzuron at LOQ level (0.005 mg/kg) in lamb matrix analyzed in negative ion mode

Identification and quantitation

As per user-defined parameters, the data was processed with the automatic flagging feature in TraceFinder software. Using color codes, these flags indicate whether results pass or fail against the acceptance criteria defined in the processing method. The results passing all the criteria are shown with a green flag while those failing have red flags (Figure 3). Color-coded flags minimizes the time required for manual data reviewing, enhancing the speed of reporting. Red-colored flags not only indicate compounds needing further investigation, but hovering the mouse over the flag displays the reason for the flag. For example, the red flag in Figure 3 indicates the absence of targeted pesticides in a solvent blank.

Identification criteria have been demonstrated for pencycuron with three transitions (quantifying ion at 329.05 → 124.988 and qualifying ions at 329.05 → 218.071, 329.05 → 261.071) at the expected retention time (9.46 ± 0.1 min) and ion ratio within 30% in comparison with the matrix-matched standards at 0.0005 mg/kg in lamb (Figures 3A and 3B). Further, the quantitation was performed based on the calibration curve plotted in the range of 0.0005–0.05 mg/kg. This calibration curve offered excellent linearity (r^2=0.9990) with <20% residuals by following the 1/x weighting factor and linear equation (Figure 3C).

Method performance

Linearity

Excellent linearity was achieved for all 158 target analytes over the range 0.0005–0.05 mg/kg with regression values ≥0.99 and lower than 20% residuals in all matrices. As stated above, a linear equation and 1/x weighting factor was used to evaluate measured response per spiking level. Regardless of meat matrix, all pesticide residues had a measured regression value ≥0.99 and about 50% were greater than 0.995.

Matrix effect

Co-eluting matrix components can cause an ion suppression or enhancement of the analytical signal. The intensity of the matrix effect (ME) is expressed in % ion enhancement or suppression compared to the peak of the analyte in pure solvent against the target matrix and becomes an important parameter in evaluating quantitative performance. A measured matrix effect within ±20% was considered to be acceptable as per the SANTE guidelines.[1] Measured values between ±20% and ±50% were considered a medium matrix effect, and a strong matrix effect was greater than +50% (Figure 4). Even with a high level of matrix effects, all compounds could be easily identified in compliance with the SANTE criteria. Based on the observed matrix effect, all the target analytes were quantified using the matrix-matched calibration curve to harmonize the results.

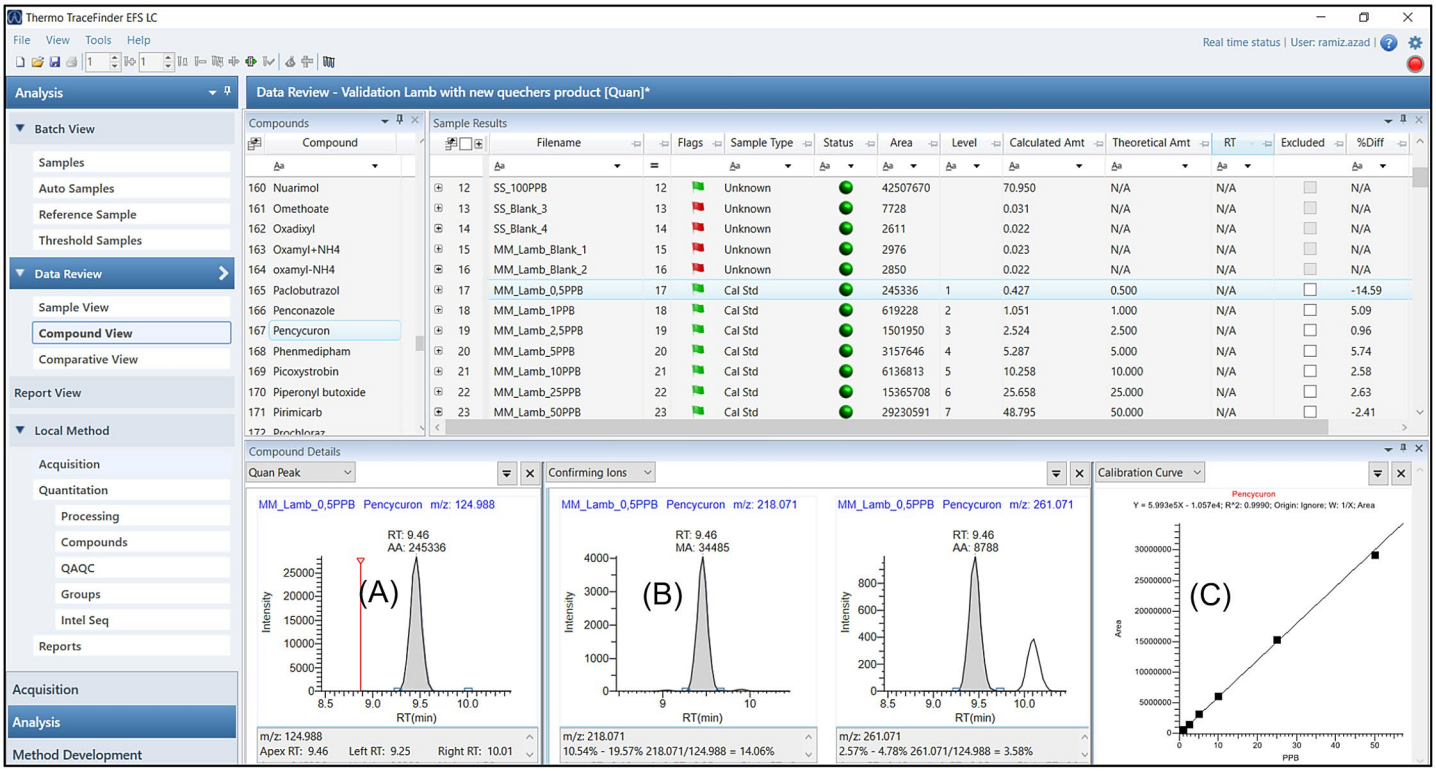

Figure 3. (A) Extracted ion chromatogram for pencycuron at 0.0005 mg/kg, showing quantifier ion (B) confirming ions with ion ratio, and (C) calibration curve

Limit of quantitation (LOQ)

Excellent recoveries (within 70–120%) with associated RSDs (<15%) were achieved at an LOQ of 0.005 mg/kg for six replicates in all three matrices (Figure 5). Almost all LOQ values are well below the established MRLs from the Food Safety Standards Authority of India (FSSAI) and the European Union (EU) Regulations for default MRL.[3,4]

Recovery and precision

Trueness was estimated at three different levels using certified reference materials (CRM). In this study, recovery was assessed at 0.005 (LOQ), 0.01 (LOQ x2) and 0.025 (LOQ x5) mg/kg in lamb, chicken, and fish based on six replicates for each level. The calculations were performed using matrix-matched calibration standards to consider the matrix effect in quantitation. The majority of the target analytes offered acceptable recoveries in the range of 70–120% while being measured with <20% RSD in the three matrices except for a few pesticides (120–150%), despite their different polarity (Figure 5). Figure 6 shows the breakdown of the measured RSD values at the three concentration ranges for the pesticides spiked into the different meat matrices.

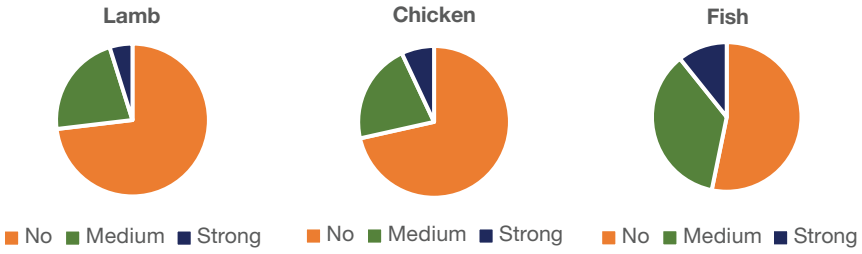

Figure 4. Matrix effect observed in lamb, chicken, and fish for the measured pesticide residues

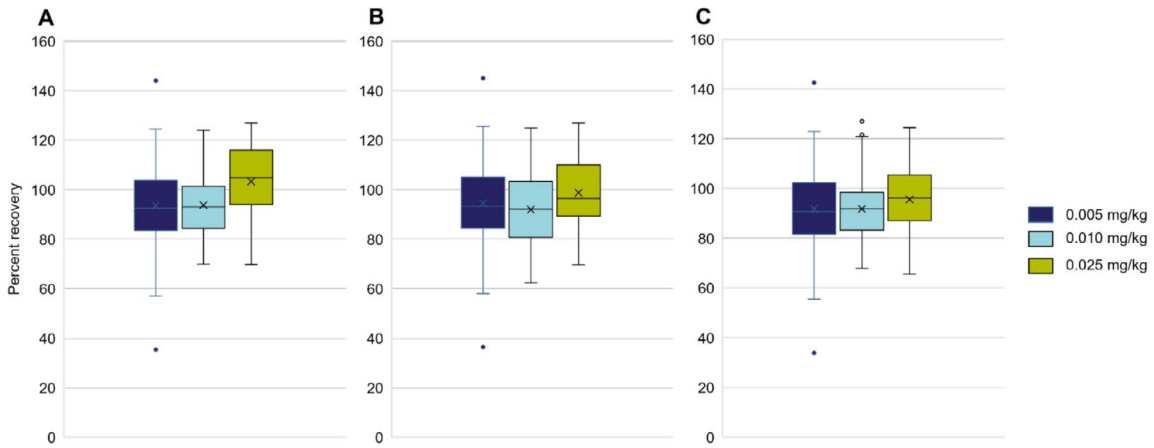

Figure 5. Comparative recovery analysis for the set of pesticides analyzed in (A) lamb, (B) chicken, and (C) fish at three different levels

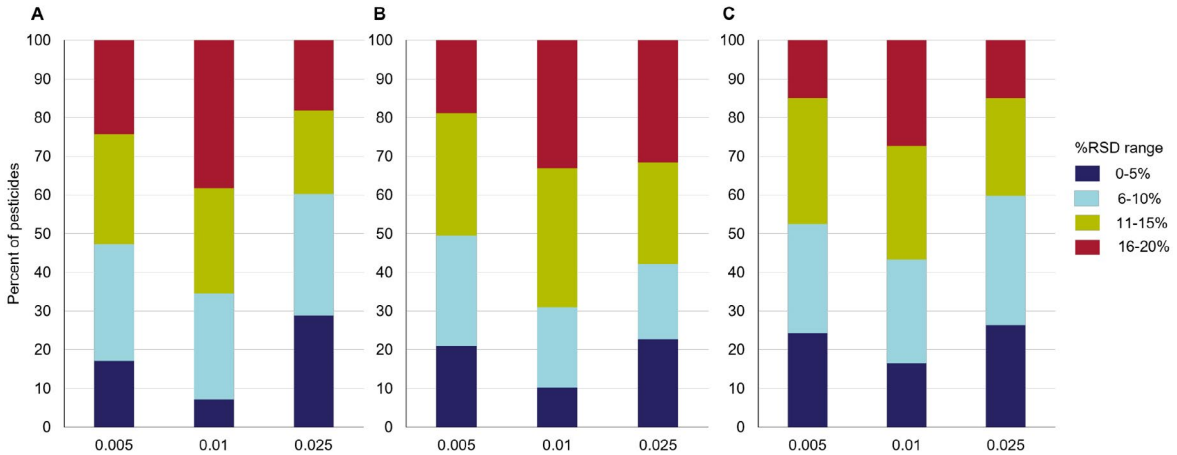

Figure 6. Precision (%) analysis for the set of pesticides spiked in (A) lamb, (B) chicken, and (C) fish at 0.005, 0.01, and 0.025 mg/kg

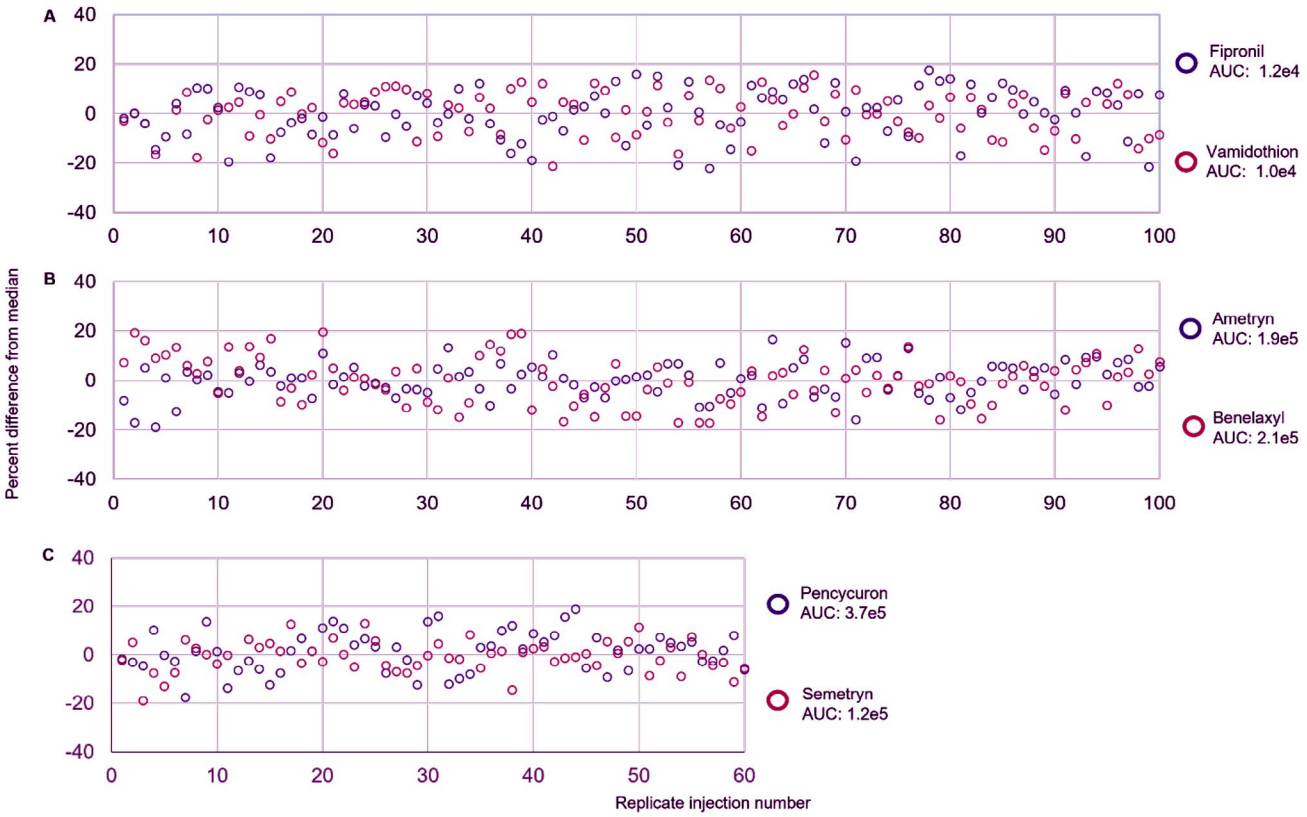

Figure 7. Reproducibility and ruggedness analysis for pesticide residue measurements in the different meat matrices. The set of pesticides were spiked at LOQ levels and repetitively analyzed following 100 injections for (A) lamb and (B) chicken as well as 60 replicate injections in (C) fish. The pesticide residues extracted are listed per meat matrix as well as the median AUC value measured.

The optimized method was tested for long-term repeatability through a large batch of spiked meat matrices at the LOQ level. One hundred replicate injections were performed for the spiked lamb and chicken samples while sixty replicate injections were performed for the spiked fish sample to simulate a commercial food testing laboratory schedule for 24 h. Figure 7 shows the integrated peak area values for two pesticides per meat matrix. The area repeatability was <15% RSD without internal standard correction, demonstrating excellent repeatability for the optimized method. Also note the randomness in measured response across the replicate injections for each set of pesticide residues. The robustness study was performed with successive replicate injections per meat matrix without cleaning the ion transfer tube or sweep cone to truly measure instrument robustness.

Conclusion

This work offered an excellent analytical solution for trace level quantitation of pesticide residues in high fatty matrices (lamb, chicken, and fish) by using a combination of acetate buffered QuEChERS extraction followed by Thermo Scientific LC-HESI-MS/MS analysis. The optimized method showed effective LC separations, in combination with t-SRM windows, allowing several transitions monitored in a single injection by auto-optimized dwell time without compromising data quality. In such high fatty matrices, the matrix effect was minimized using the dilution approach. This also helped to reduce the lipid solubility in the presence of water and minimized the carryover in injection to injection. Using this approach, at least 90–100 injections (standards, samples, blank) could be completed in a day (24 h cycle) providing high sample throughput for commercial food testing laboratories. The method performance was evaluated at three different levels including LOQ (0.005 mg/kg). Average recoveries and precision meet the SANTE guideline criteria. TraceFinder software offers flagging options that help minimize the time required for data review and reporting. Based on the flagging option, the user can make quick decisions and move forward. Also, this method complies with the EU as well as the FSSAI MRLs requirement by achieving the excellent LOQ.

References

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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
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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