

Trace level quantitation of pesticide residues in leafy vegetables using LC-MS/MS

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Goal

The goal of this project is to demonstrate the performance and versatility of the Thermo Scientific™ TSQ Quantis™ mass spectrometer for trace level quantification of pesticide residues in leafy vegetables. The optimized method, validated as per the SANTE guideline, can deliver MRLs in spinach and cabbage that meet regulatory levels of the Food Safety and Standards Authority of India (FSSAI) and the European Commission (EC).

Introduction

Recently, the consumption of green leafy vegetables has increased. Bioactive compounds, such as vitamins, minerals, antioxidants, and pigments (chlorophylls and carotenoids), are available in vegetables.¹ Spinach and cabbage are the most planted vegetables worldwide. High chlorophyll content makes spinach a highly complex matrix for pesticide residue analysis using LC-MS/MS.² The EC and FSSAI have set maximum residue levels (MRLs) in spinach.^{3,4} The QuEChERS (quick, easy, cheap, effective, rugged, and safe) method with dispersive solid-phase extraction (dSPE) is very popular for pesticide residue



analysis. This procedure involves several simple analytical steps that are fast and easy to perform and provides high recoveries for an extensive scope of pesticides belonging to various chemical classes. Acetonitrile is the final solvent, which provides more flexibility in the choice of the quantitative analytical technique.^{5,6}

The aim of this work was the optimization and method validation of a multi-residue method for pesticides in spinach and cabbage by using a LC-MS/MS method with the Thermo Scientific™ Vanquish™ UHPLC and TSQ Quantis mass spectrometer. The data acquisition and processing were carried out using Thermo Scientific™ TraceFinder™ software. The optimized method was validated as per the SANTE/12682/2019 guideline.⁷ This method was applied to real samples to demonstrate that this workflow is fit for this purpose and meets the SANTE guideline requirement in terms of identification and quantitation of residues.

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,) and precision balance (ACZET, CY205C, San Diego, CA)
- Vortex mixer, Thermo Scientific™ (P/N 88880017TS)
- Refrigerated centrifuge (Thermo Scientific™ Sorvall™ ST8 ventilated benchtop centrifuge)
- Thermo Scientific™ Finnpiquette™ F2 variable volume pipette, (100–1000 µL, P/N 4642090; 10–100 µL, P/N 4642070 and 0.5–5 mL, P/N 4642100)
- Thermo Scientific™ 9 mm Wide Opening Clear Vial Convenience kit (P/N 60180-599)
- Thermo Scientific™ SPE QuEChERS Sample Prep pouch (P/N S1-15-AOAC-POT): 6000 mg anhydrous magnesium sulfate, 1500 mg anhydrous sodium acetate
- Thermo Scientific™ Nunc™ 2, 15, and 50 mL extraction/ conical sterile polypropylene centrifuge tubes (P/N 339652)
- Clean up material: MgSO₄-anhydrous (Fisher Scientific, P/N 80020-432-1000), Primary Secondary Amine (Thermo Scientific, P/N 80020-429-100), Graphitized Carbon Black (Thermo Scientific, P/N 80020-431-50)

LC-MS/MS analysis

The Vanquish UHPLC liquid chromatography system was coupled with the TSQ Quantis tandem mass spectrometer with heated electrospray (HESI) ionization probe. The optimized LC-MS/MS conditions are given in Table 1. The UHPLC gradient program was used from a previously reported application note⁶.

Table 1a. LC instrument conditions

Liquid chromatography method				
Instrumentation	Thermo Scientific™ Vanquish™ Flex Binary UHPLC system, consisting of: <ul style="list-style-type: none"> • Vanquish Split Sampler FT, P/N VF-A10-A • Vanquish Column Compartment, P/N VH-C10-A • Binary Pump F, P/N VF-P10-A • Vanquish Pump Mixer Set, Vanquish F Pumps, P/N 6044.3870 			
Column	Thermo Scientific™ Accucore™ aQ column, 100 mm × 2.1 mm, 2.6 µm (P/N 17326-102130)			
Sample compartment temp.	10 °C			
Column oven temp.	35 °C			
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	35 µL, VF-P1 (10 µL mixer kit)			
Total run time	15.0 min			
LC gradient program	<i>Time (min)</i>	<i>Flow rate (mL/min)</i>	<i>%B</i>	<i>Curve</i>
	0.0	0.3	0	5
	0.5	0.3	0	5
	7.0	0.3	70	5
	9.0	0.3	100	5
	12.0	0.3	100	5
	12.1	0.3	0	5
15.0	0.3	0	5	

Table 1b. MS/MS instrument conditions

Mass spectrometry method	
Instrumentation	TSQ Quantis triple quadrupole mass spectrometer
Method type	Timed (t-SRM mode)
Ion source type	H-ESI II
Spray voltage	Static Positive: 3,700 V Negative: 2,500 V
Sheath gas	50 Arb
Aux gas	6 Arb
Sweep gas	1 Arb
Ion transfer tube temp.	325 °C
Vaporizer temp.	350 °C

Sample preparation

The spinach and cabbage samples were collected from a local market and homogenized by using a mixer and grinder to get small and uniform particle sizes. The QuEChERS method⁵ used for extraction is detailed below. The control samples are verified for the positive detection of target analytes. After ensuring that the matrix was free of pesticide residues, the same procedure was utilized for recovery experiments as well as matrix-matched calibration standards preparation. The details of the matrix-matched calibration standards preparation are given in Table 2.

Table 2. Preparation of matrix-matched standards

Matrix (μL)	Std stock (μg/mL)	Std volume (μL)	Water (μL)	Final conc. (ng/mL)
250	0.1	5	745	0.5
250	0.1	10	740	1.0
250	0.1	25	725	2.5
250	0.1	50	700	5.0
250	0.1	100	650	10.0
250	1.0	25	725	25.0
250	1.0	50	700	50.0
250	1.0	100	650	100.0

Extraction and clean-up

- Weigh 15 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.
- 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, i.e., 6 g MgSO₄ and 1.5 g Na-acetate, to the tube.
- Mix vigorously for 1 min on a vortex mixer at 2,500 rpm.
- Centrifuge with 5,000 rpm for 5 min at room temperature.
- Add 1 mL of supernatant to the 2 mL Eppendorf tube.

- Add 50 mg PSA with 150 mg MgSO₄ and 5 mg GCB.
- Shake vigorously and vortex for 1 min on a vortex mixer at 2,500 rpm.
- Centrifuge at 10,000 rpm for 5 min.
- Dilute supernatant (0.250 mL) with 0.75 mL water (1:4 ratio, v/v).
- Transfer the diluted extract into the LC vial for instrumental analysis.

Data acquisition and processing

The data acquisition was performed using the instrument conditions in Table 1. The data acquisition and processing were carried out using TraceFinder software. The data was acquired in t-SRM (timed-selective reaction monitoring) mode, which includes two or three transitions per analyte. The target list of analytes in this experiment with their transitions, collision energies, and retention times (min) were optimized. For data processing, the ion ratio ($\pm 30\%$), retention time (± 0.1 min), linearity (>0.99 with residuals ± 20), recovery (70–120%) and precision ($\pm 20\%$) were set as acceptance criteria as per the SANTE guideline⁷.

Results and discussion

LC-MS/MS analysis

The liquid chromatographic method was selected from the previously published application note,⁶ which offered excellent separation and peak shape for the target analytes and absence of isobaric interferences from matrix. The extracted ion chromatogram (XIC) is shown for the selected top 20 compounds in a matrix-matched calibration standard in spinach (Figure 1). As per the gradient program, the distribution of analytes predominantly is observed between 4 and 12 min. The Instrument Method editor has a provision to auto-optimize the dwell time for all transitions in t-SRM mode. This feature is useful when the laboratory wants to analyze hundreds of analytes in a single method. Auto-optimized dwell times maintain a consistent scan rate, which along with water dilution, enables symmetrical and sharp peak shapes with the help of Accucore aQ C18 chemistry. Auto-optimized dwell time was in the range of 0.3 to 50 ms per transition (Figure 2) and offered more than 12 data points per peak.

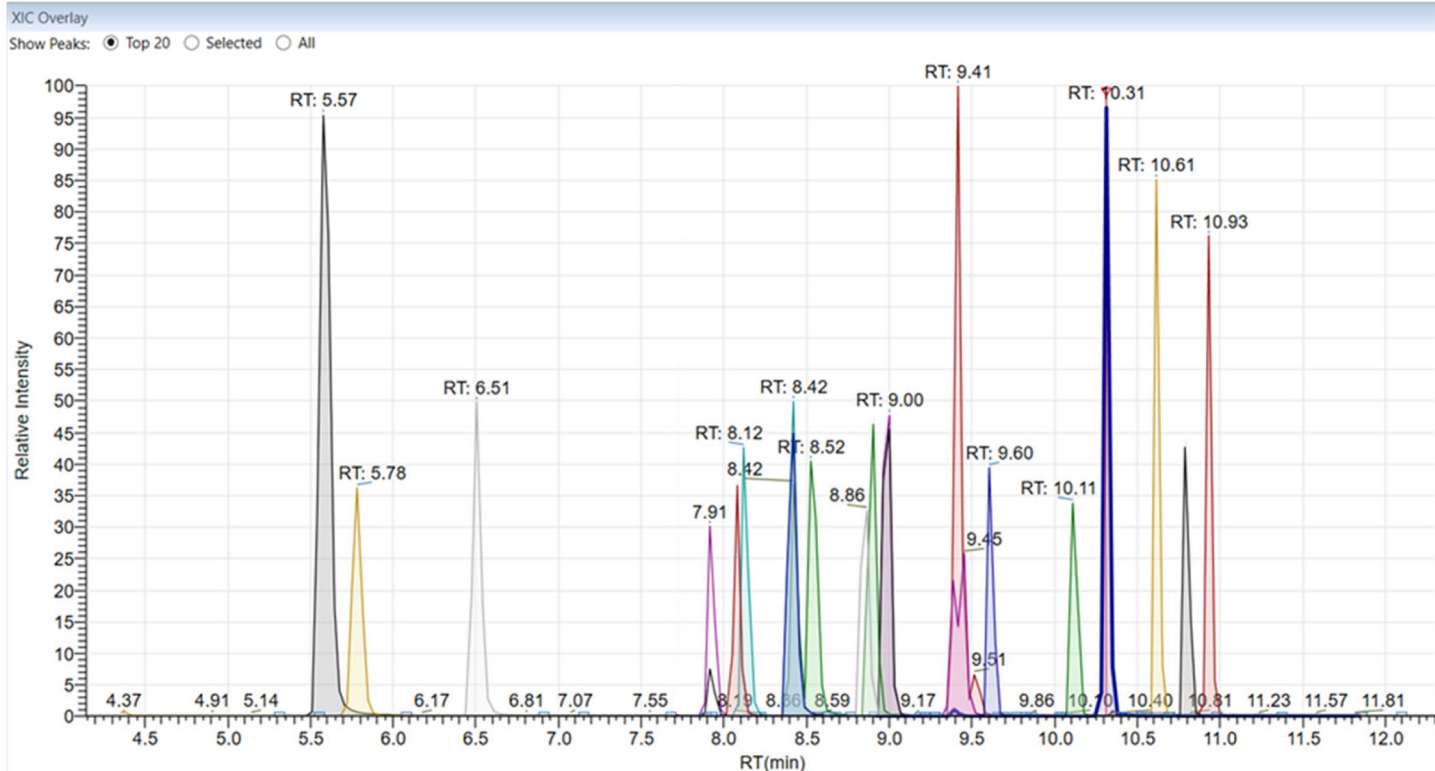


Figure 1. Extracted ion chromatogram for the top twenty most intense analytes at 5 ng/mL matrix-matched standard (MMS) in spinach

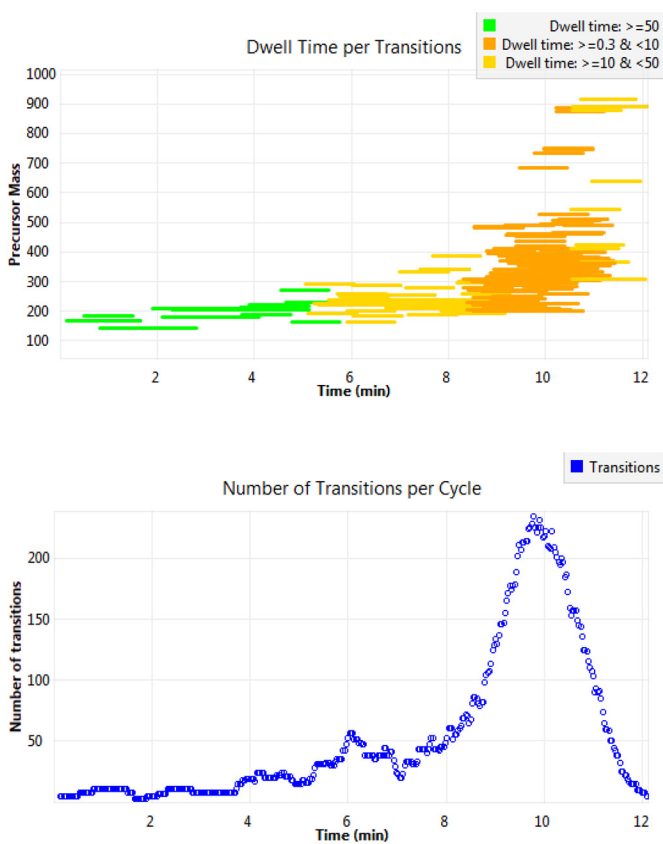


Figure 2. Representation of SRM transitions with auto-optimized dwell time

Identification and quantitation

As per user-defined parameters, the data was processed with an automatic flagging feature within TraceFinder software. These flags use color codes, alerting the user whether results pass or fail per the acceptance criteria defined in the processing method. Those results passing all criteria are shown with a green flag (Figure 3), which minimizes the time required for review; red flags indicate that there is an additional requirement for further investigation based on the reason viewed by hovering the mouse over the flag. As expected in the case of a matrix blank or solvent blank, the red color indicates the absence of pesticides. Here identification and confirmation criteria have been demonstrated for dimethoate with two transitions (m/z 229.82 \rightarrow 198.815, quantifier ion and m/z 229.82 \rightarrow 124.917, qualifier ion) at the retention time (6.42 ± 0.1 min) and an ion ratio of 68.66% (range = 47.04–87.35%), which is within $\pm 30\%$ in comparison with the matrix-matched standards (Figures 3A and 3B). Further, the quantitation was performed based on the calibration curve plotted in the range of 0.0005 to 0.1 mg/kg (0.5 to 100 ppb). This calibration curve offered excellent linearity ($r^2 = 0.9966$) with $<20\%$ residuals by following $1/x$ weighting fraction and linear equation (Figure 3C).

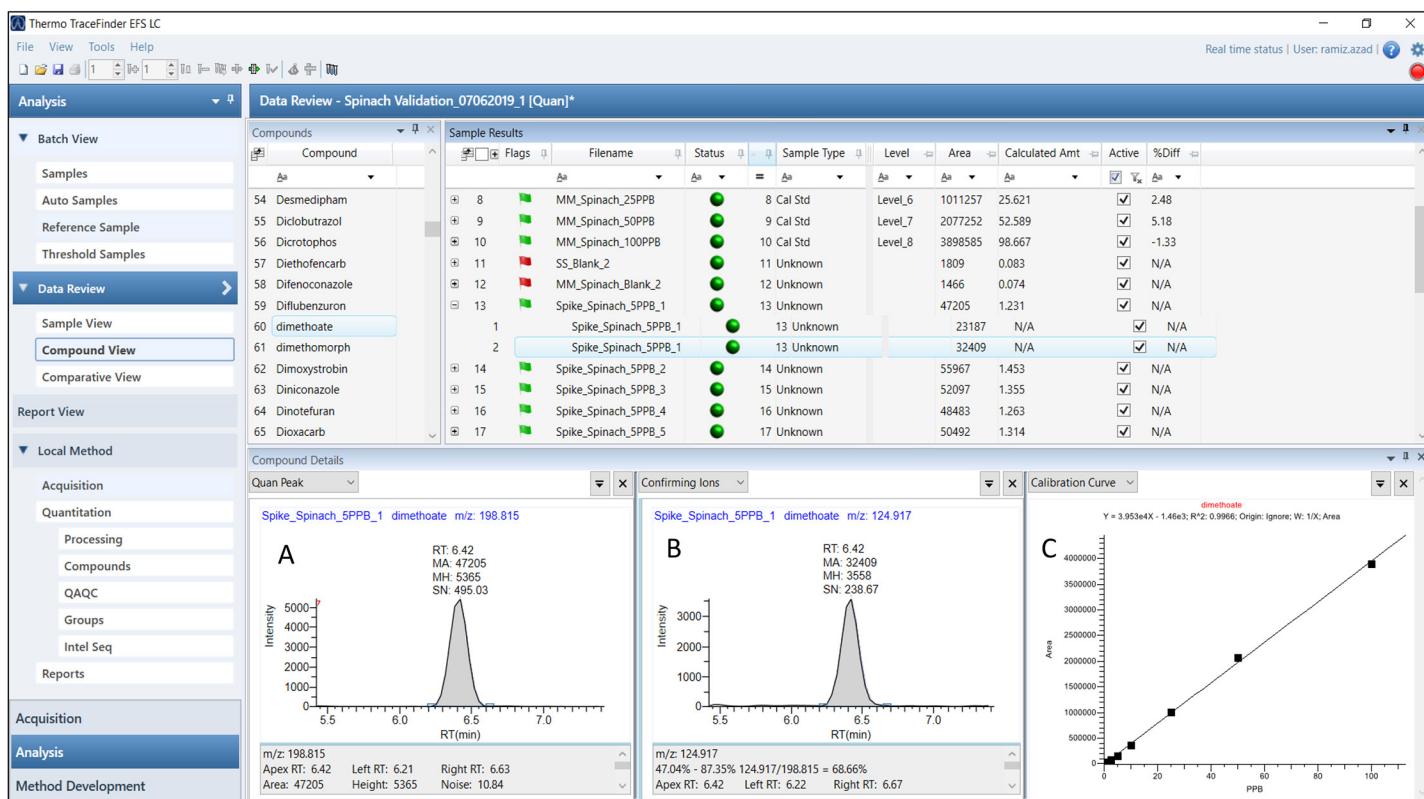


Figure 3. (A) Extracted ion chromatogram for quantifier ion of dimethoate, (B) identification based on confirmatory ion with ion ratio, and (C) calibration curve

Method performance

Linearity

In this method, the linearity was plotted in the range of 0.0005 to 0.100 mg/kg (0.5 to 100 ppb). Excellent linearity was achieved for all target analytes with correlation coefficients greater than 0.995 and lower than 20% residuals in both matrices and solvent by using a linear equation and $1/x$ weighting factor. For 5 or 6 compounds, the quadratic equation was utilized. The detailed results are shown in (Table 3, Appendix).

Limit of quantification (LOQ)

In this study, the LOQ value was calculated to be 0.005 mg/kg in spinach and cabbage except for a few (8–9%) of the analytes in spinach and 1% of the analytes in cabbage (LOQ = 0.01 mg/kg) shown in Table 3, which offered recoveries within 70–120% with <15% RSD for six replicates in both matrices. The matrix from the heavy dark green colored spinach limited the ability to achieve LOQs of 0.005 mg/kg for a few analytes. The extracted ion chromatogram for selected compounds (cyromazine, bifentazate, and aminocarb) is shown in Figure 8. Almost all LOQ values are well below the established MRLs from the FSSAI and the EU Regulations.

Matrix effect

Matrix effect is normally considered as an ion suppression or enhancement of the analytical signal due to co-eluting matrix components. Matrix effect is very much an important parameter, especially in quantitative mass spectrometry methods, and considered as a source of error. The intensity of the matrix effect (ME) is expressed in percentage ion enhancement or suppression compared to the peak of the analyte in pure solvent against the target matrix. The negative values of the matrix effect represent ion suppression, and positive values represent enhancements of analyte signal induced by the matrix. Matrix effects are known to be both compound and matrix dependent. The matrix effect observed in both matrices within $\pm 20\%$ was considered here as low matrix effect within acceptance criteria of the SANTE guideline. ME values from $\pm 20\%$ to $\pm 50\%$ were considered medium, and those with ME greater than $\pm 50\%$ were considered high (Figure 4). A medium matrix effect was observed for 52% of compounds, demonstrating that the analysis of spinach samples poses a challenge regarding high matrix complexity. Even with these matrix effects, all compounds can easily be identified at legislative limits and quantified using the matrix-matched calibration curve. The detailed matrix effects observed in these matrices for the target analytes were in Table 3.

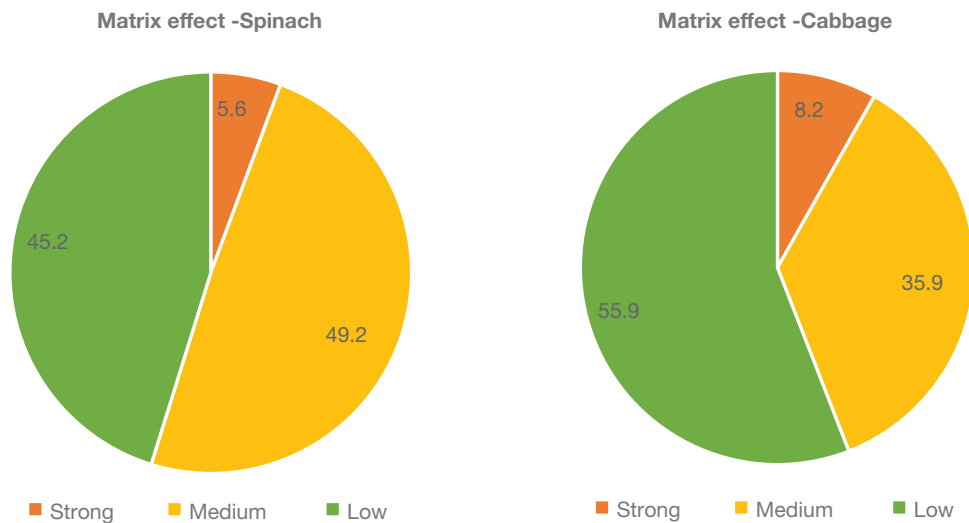


Figure 4. Matrix effect observed in spinach and cabbage (Low: $\lt; \pm 20\%$; Medium: $\pm 20\% - \pm 50\%</math>; High: $> \pm 50\%</math>)$$

Recovery and precision

Recovery is one of the important elements to be assessed for method performance by considering common errors. Recovery is defined in terms of accuracy or trueness. It can be estimated using certified reference materials (CRM). In this study, the recovery is assessed through the measurements of additions of known amounts of the analyte(s) to a blank matrix against the true value. Recovery was assessed at 0.005 (LOQ), 0.01 (LOQ $\times 2$),

and 0.025 (LOQ $\times 5$) mg/kg in spinach and cabbage as leafy vegetable matrix representatives in 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 had acceptable recoveries in the range of 70–120% with $< 20\%$ RSD in both matrices except a few analytes (120–150%) given in Table 3, despite their different polarities (Figure 5).

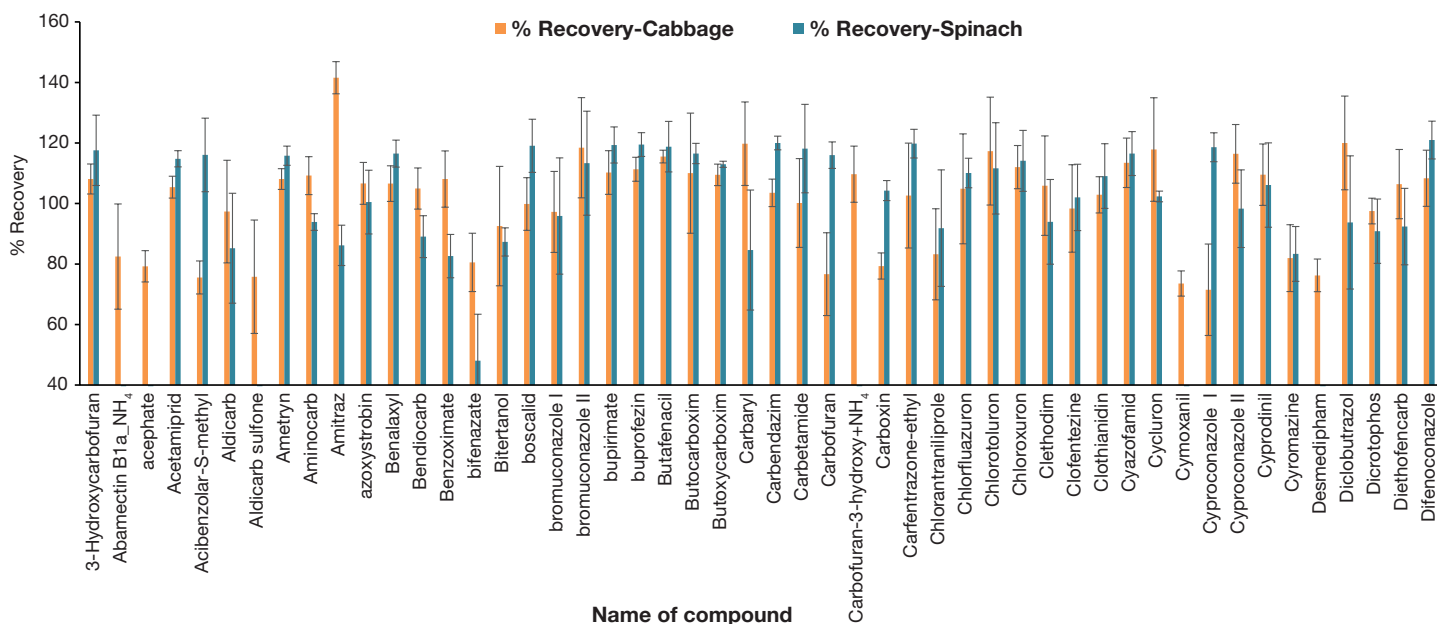


Figure 5 (part 1). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

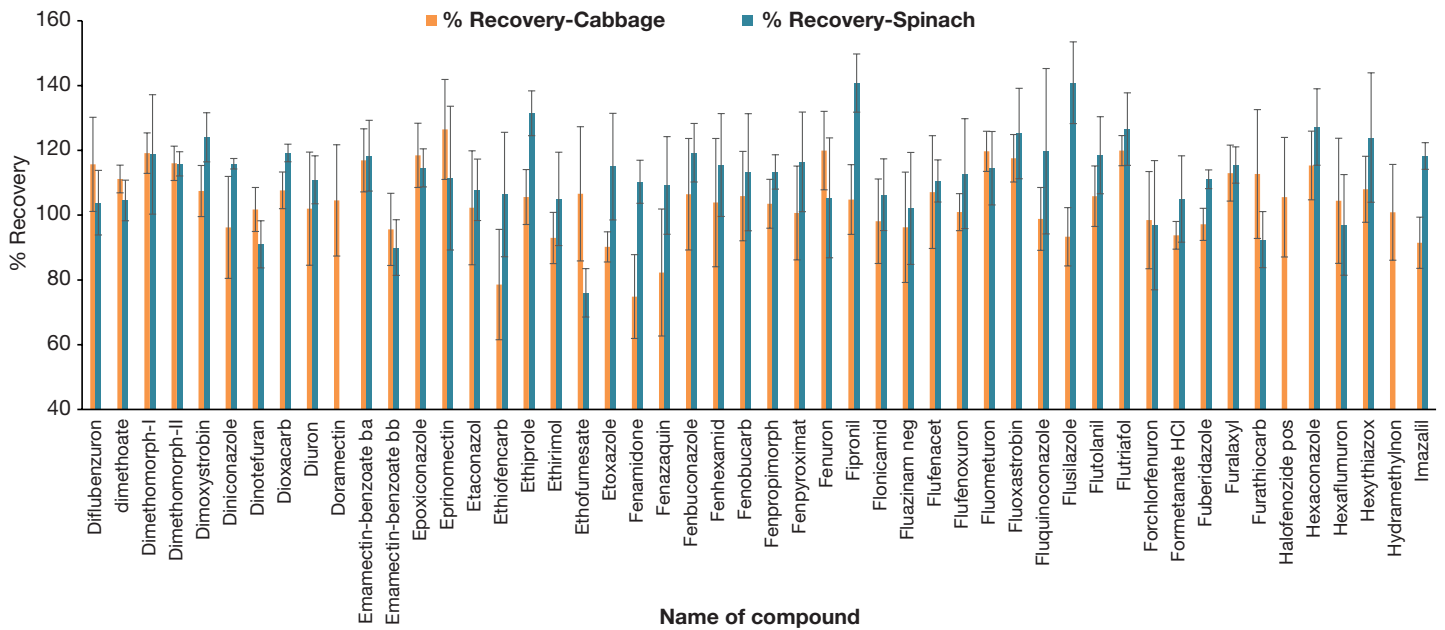


Figure 5 (part 2). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

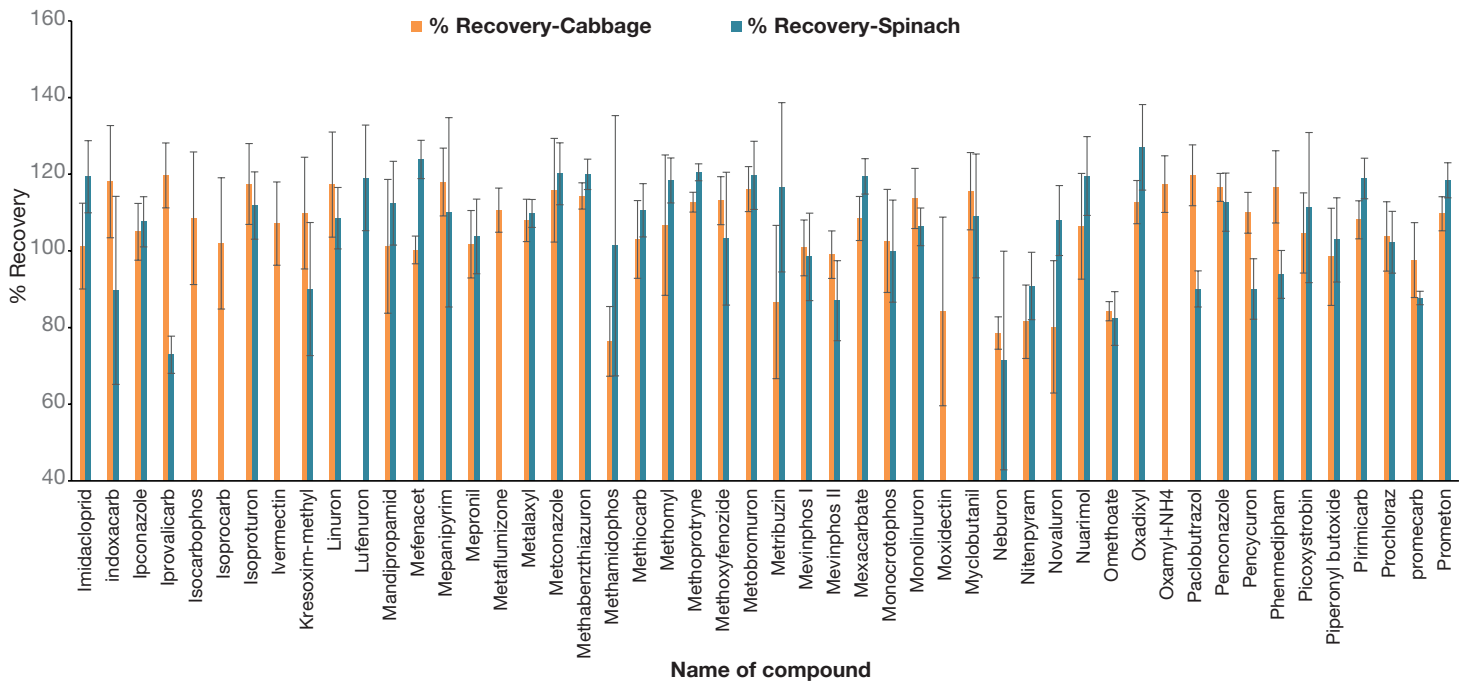


Figure 5 (part 3). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

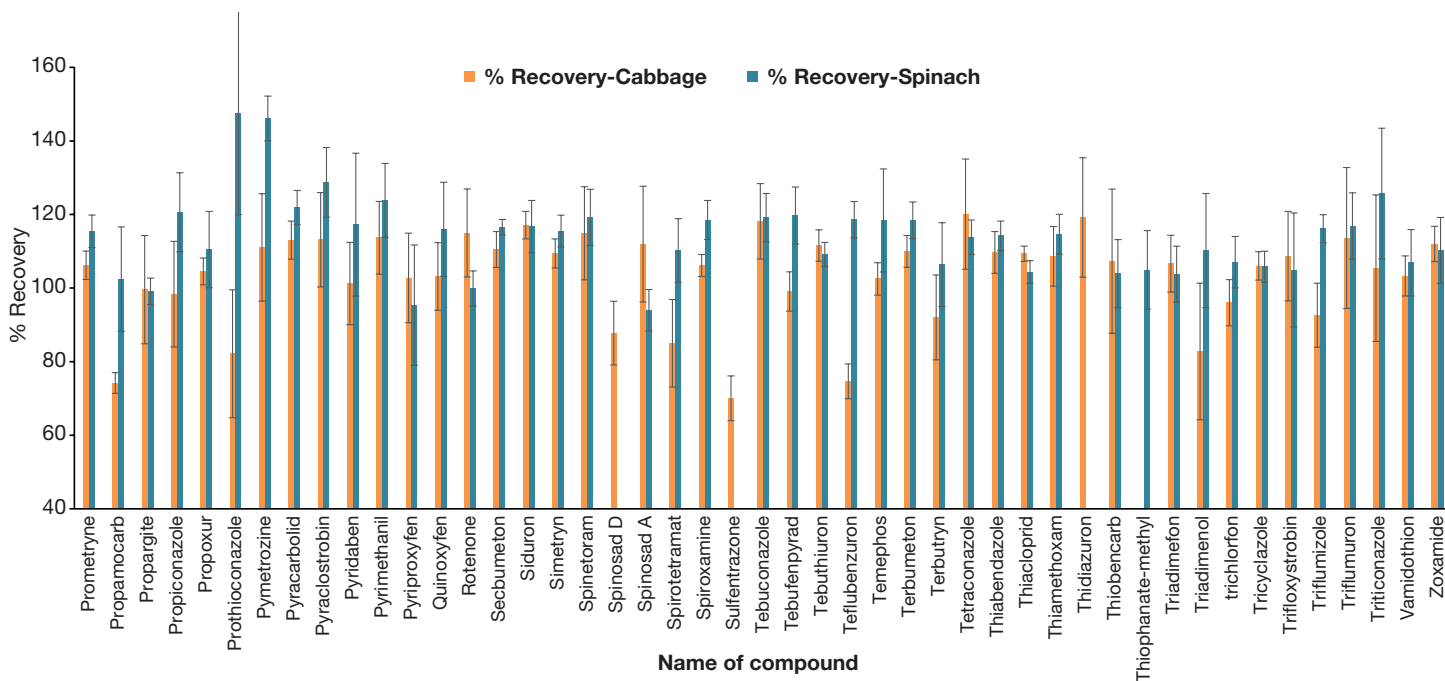


Figure 5 (part 4). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

A total of six replicates at each concentration level were used for the determination of the precision for spinach and cabbage. The precision (%RSD) results were <15% for both concentration levels, with all target analytes in both matrices. The optimized method was tested for repeatability of results obtained through large batches for spiked spinach (n=67) and cabbage (n=100) samples with replicate injections by considering the commercial food testing lab schedule for 24 hr. The area repeatability was <15% RSD without internal standard correction and <±0.05 min for the retention time in both matrices. This reveals that the optimized method offered excellent repeatability in results. Compound peak area repeatability examples are shown in Figures 6A and 6B.

Fast polarity switching

The TSQ Quantis mass spectrometer offers fast polarity switching (<20 ms), enabling uncompromised sensitivity for both positive and negative polarity analytes. In this study, the impact of polarity switching has been demonstrated the sensitivity at 0.005 mg/kg for temephos (pos) and fluazinam (neg) in spinach and difenoconazole (pos) and hexaflumeron (neg) in cabbage. This sensitivity was sufficient at LOQ 0.005 mg/kg (equivalent to 0.00125 mg/kg) in both the matrices (Figure 7).

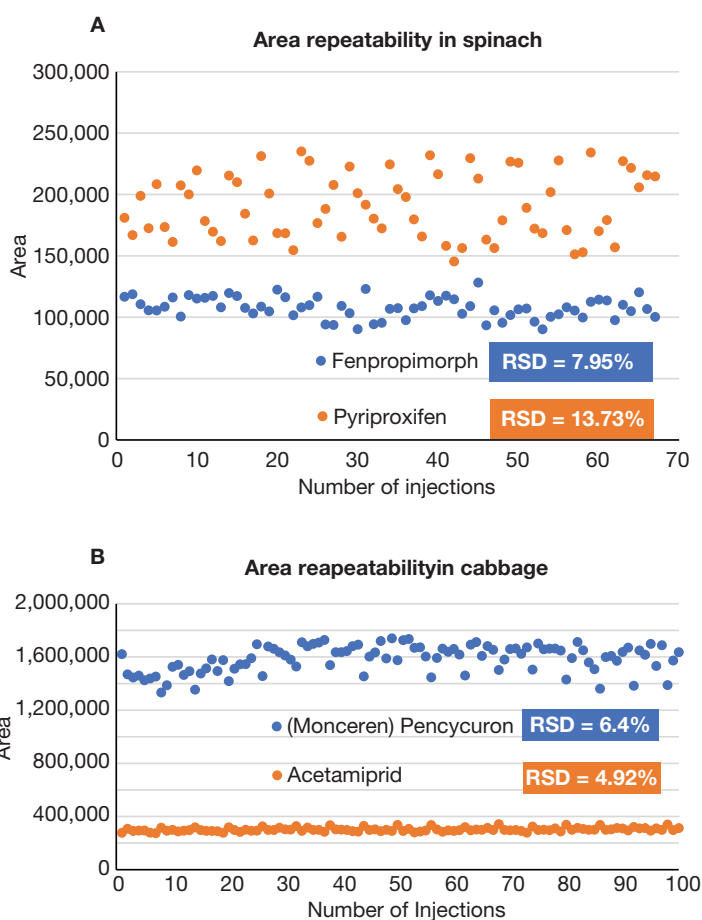
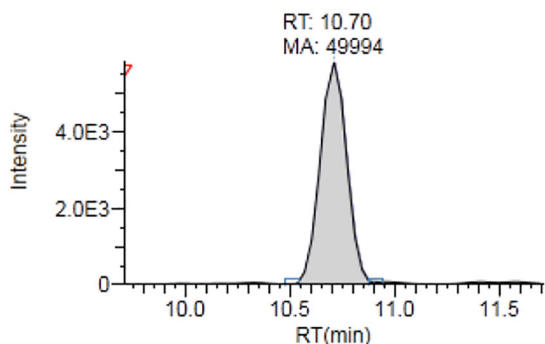


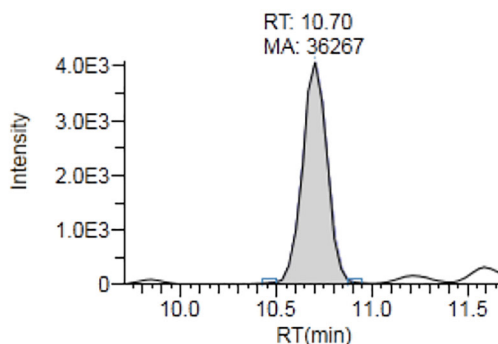
Figure 6. (A) Area repeatability shown for fenpropimorph and pyriproxyfen in spinach (n=67) at 0.005 mg/kg (spiked sample); (B) Area repeatability shown for (monceren) pencycuron and acetamidrid in cabbage (n=100) at 0.005 mg/kg (spiked sample)

(A) Spinach

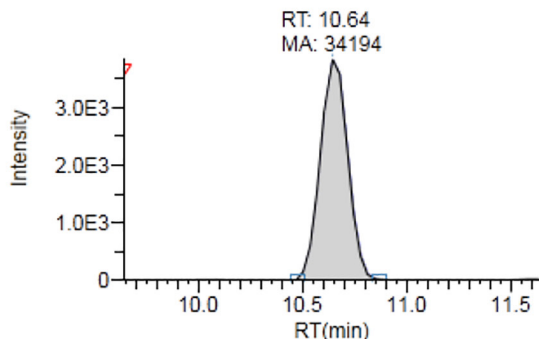
Spike_5PPB_1 Temephos m/z: 419.100
F: + c ESI SRM ms2 467.000 [404.999-405.001, 419.099-41 ...



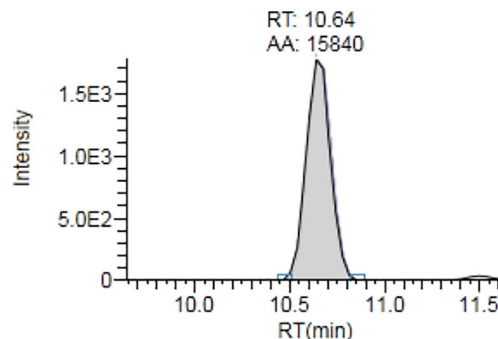
Spike_5PPB_1 Temephos m/z: 405.000
F: + c ESI SRM ms2 467.000 [404.999-405.001, 419.09 ...



Spike_5PPB_1 Fluazinam m/z: 415.700
F: - c ESI SRM ms2 462.700 [397.799-397.801, 415.699-41 ...

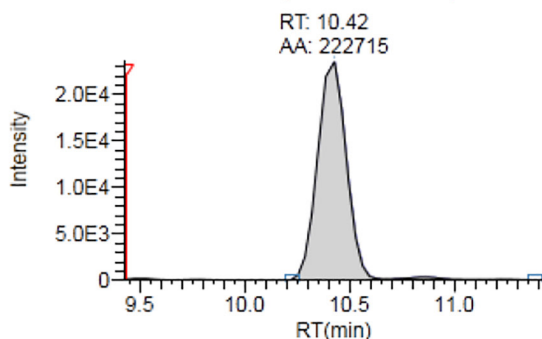


Spike_5PPB_1 Fluazinam m/z: 397.800
F: - c ESI SRM ms2 462.700 [397.799-397.801, 415.699 ...

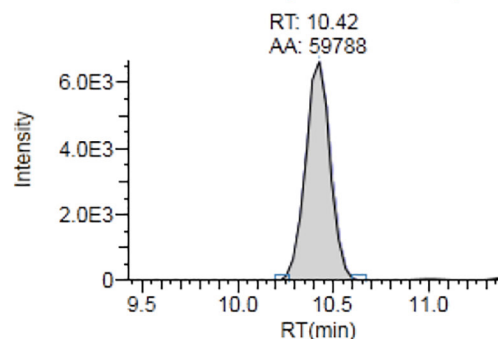


(B) Cabbage

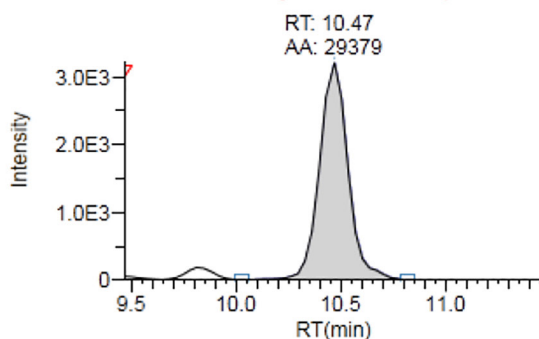
Spike_Spinach_5PPB_2 Difenconazole m/z: 250.970
F: + c ESI SRM ms2 406.012 [187.987-187.989, 250.969-25 ...



Spike_Spinach_5PPB_2 Difenconazole m/z: 337.042
F: + c ESI SRM ms2 406.012 [187.987-187.989, 250.96 ...



Spike_Spinach_5PPB_2 Hexaflumuron m/z: 438.917
F: - c ESI SRM ms2 458.832 [174.957-174.959, 275.916-27 ...



Spike_Spinach_5PPB_2 Hexaflumuron m/z: 275.917
F: - c ESI SRM ms2 458.832 [174.957-174.959, 275.916 ...

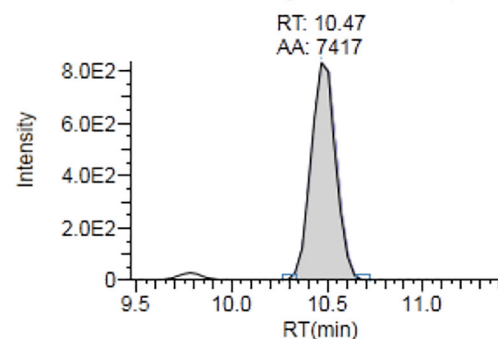


Figure 7. The sensitivity observed for temephos, fluazinam, difenoconazole, and hexaflumuron at 0.005 mg/kg in spinach (A) and cabbage (B)

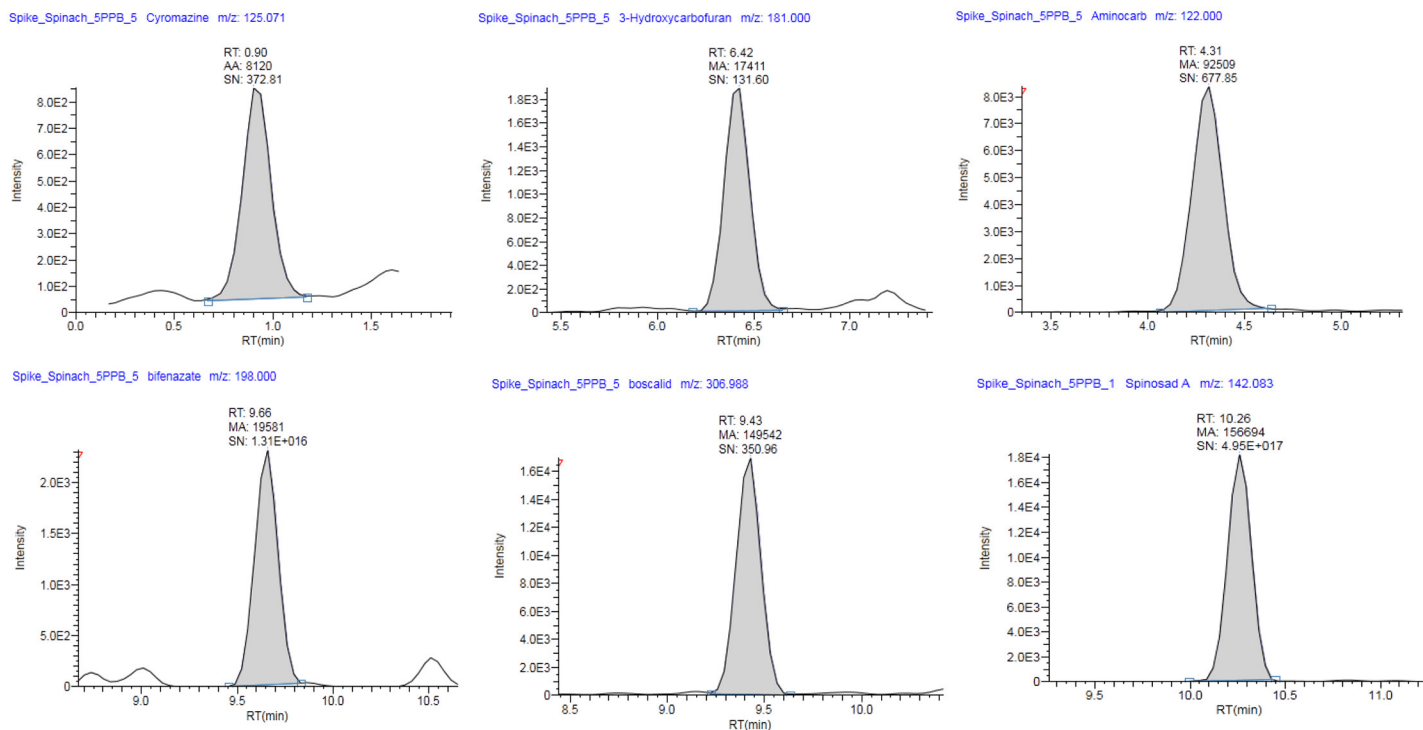


Figure 8. Extracted ion chromatogram for the selected compounds at LOQ level with the signal-to-noise ratio

Conclusion

This application note demonstrates an analytical solution for the detection and quantitation of pesticide residues in spinach and cabbage, using a combination of QuEChERS extraction followed by LC-MS/MS analysis. The optimized method results showed that LC separations, in combination with t-SRM windows, maintained the number of transitions monitored in single injection by auto-optimized dwell time without compromising data quality. Use of this approach, for at least 70 injections (standards, samples, blank) could be completed in a day and increase the overall high throughput of a commercial food testing laboratory. The method performance was evaluated at three different levels including LOQ (0.005 mg/kg). Average recoveries and precision data meet the SANTE guideline criteria. TraceFinder software has flagging options that minimize the user's time required for data review and reporting. Based on the flagging option, the user can make quick decisions on data quality. This method complies with the EU as well as the FSSAI MRLs requirement by achieving the excellent lower limit of quantitation (LOQ).

References

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Appendix

Table 3. Method validation data includes linearity, LOQ, recovery, and precision (% RSD) for spinach and cabbage matrix

Sr. No.	Analyte	Spinach								Cabbage							
		R ²	LOQ (mg/kg)	0.005 mg/kg		0.01 mg/kg		0.025 mg/kg		R ²	LOQ (mg/kg)	0.005 mg/kg		0.01 mg/kg		0.025 mg/kg	
				% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD			% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
1	3-Hydroxycarbofuran	0.9952	0.005	118	11.6	104	6.1	102	4.5	0.9940	0.005	108	5.0	109	4.2	108	5.5
2	Abamectin B1a	0.9912	0.01	ND	ND	119	6.1	118	1.7	0.9914	0.005	82	17.4	103	17.5	92	17.7
3	Acephate	0.9902	0.01	ND	ND	92	19.9	87	8.3	0.9944	0.005	79	5.2	71	4.2	71	5.6
4	Acetamiprid	0.9967	0.005	115	2.7	109	1.6	105	1.6	0.9968	0.005	105	3.6	103	3.0	108	3.7
5	Acibenzolar-S-methyl	0.9926	0.005	116	12.2	95	18.5	99	11.1	0.9944	0.005	76	5.5	114	18.9	104	15.9
6	Aldicarb	0.9904	0.005	85	18.2	81	12.6	94	8.6	0.9985	0.005	97	17.0	97	8.5	99	6.9
7	Aldicarb sulfone	0.9916	0.025	ND	ND	ND	ND	88	17.5	0.9942	0.005	76	18.7	104	14.9	96	8.5
8	Ametryn	0.9972	0.005	116	3.2	115	4.4	107	1.7	0.9975	0.005	108	3.4	108	4.9	112	3.6
9	Aminocarb	0.9927	0.005	94	2.8	95	3.2	98	1.6	0.9975	0.005	109	6.3	102	4.2	103	4.1
10	Amitraz	0.9929	0.005	86	6.6	87	9.5	108	3.5	0.9968	0.005	142	5.3	142	8.1	131	5.7
11	Azoxystrobin	0.9940	0.005	100	10.5	111	6.4	105	2.2	0.9957	0.005	107	6.9	107	8.1	110	5.3
12	Benalaxyl	0.9977	0.005	116	4.4	119	3.5	120	3.6	0.9996	0.005	107	5.9	112	6.5	112	1.7
13	Bendiocarb	0.9954	0.005	89	6.9	88	13.8	94	13.0	0.9989	0.005	105	6.8	101	3.6	105	3.2
14	Benzoximate	0.9977	0.005	83	7.2	99	10.4	103	3.6	0.9920	0.005	108	9.3	71	15.8	96	10.0
15	Bifenazate	0.9938	0.005	48	15.4	44	12.6	58	7.0	0.9891	0.005	81	9.6	84	3.9	91	19.6
16	Bitertanol	0.9925	0.005	87	4.7	89	8.7	111	12.0	0.9940	0.005	93	19.7	113	9.5	99	6.3
17	boscalid	0.9900	0.005	119	8.8	133	6.1	132	3.7	0.9915	0.005	100	8.7	115	3.7	119	1.9
18	Bromucanazole-I	0.9934	0.005	96	19.2	119	5.9	119	4.4	0.9945	0.005	97	13.4	108	7.3	119	2.9
19	Bromucanazole-II	0.9934	0.005	113	17.2	112	10.3	112	10.4	0.9950	0.005	118	16.6	96	8.4	97	11.2
20	Bupirimate	0.9954	0.005	119	6.0	113	4.5	114	3.0	0.9975	0.005	110	7.2	105	7.4	114	4.0
21	Buprofezin	0.9971	0.005	119	3.9	119	2.2	110	2.1	0.9930	0.005	111	4.0	113	5.4	111	2.7
22	Butafenacil	0.9974	0.005	119	8.4	116	7.2	118	4.6	0.9920	0.005	116	2.1	116	7.6	119	1.4
23	Butocarboxim	0.9968	0.005	117	3.4	100	4.9	102	9.4	0.9950	0.005	110	19.8	120	16.9	114	9.4
24	Butoxycarboxim	0.9879	0.005	113	1.0	109	1.4	105	2.1	0.9982	0.005	109	3.5	110	2.8	111	2.2
25	Carbaryl	0.9966	0.005	85	19.8	105	9.8	107	3.3	0.9967	0.005	120	13.8	108	16.1	112	10.0
26	Carbendazim	0.9958	0.005	120	2.3	116	0.8	110	1.6	0.9895	0.005	104	4.6	114	4.0	118	3.2
27	Carbetamide	0.9935	0.005	118	14.6	101	9.4	107	3.1	0.9991	0.005	100	14.7	107	18.1	108	5.4
28	Carbofuran	0.9990	0.005	116	4.4	115	1.3	120	2.5	0.9939	0.005	77	13.7	82	12.2	90	5.3
29	Carboxin	0.9969	0.005	104	3.3	105	3.4	101	5.2	0.9969	0.005	79	4.3	82	3.9	85	7.4
30	Carfentrazone-ethyl	0.9963	0.005	120	4.7	111	8.2	117	3.3	0.9899	0.005	103	17.3	116	11.3	118	6.6
31	Chlorantraniliprole	0.9934	0.005	92	19.3	111	7.3	120	4.0	0.9967	0.005	83	15.0	120	8.9	115	16.6
32	Chlorfluzuron	0.9978	0.005	110	4.9	77	13.7	72	7.8	0.9934	0.005	105	18.2	92	16.9	94	13.4
33	Chlorotoluron	0.9949	0.005	112	15.1	114	13.7	112	6.3	0.9979	0.005	117	17.8	104	7.5	111	4.6
34	Chloroxuron	0.9979	0.005	114	10.1	108	4.2	118	4.6	0.9958	0.005	112	7.2	117	5.6	112	15.2
35	Clethodim	0.9930	0.005	94	14.0	84	6.5	75	2.9	0.9953	0.005	106	16.4	88	12.4	72	12.3
36	Clofentezine	0.9939	0.005	102	11.0	95	14.5	94	3.9	0.9979	0.005	98	14.5	102	15.8	103	11.3
37	Clothianidin	0.9985	0.005	109	10.7	112	10.6	109	8.7	0.9973	0.005	103	6.0	96	5.1	97	4.9
38	Cyazofamid	0.9958	0.005	116	7.2	107	5.0	109	5.6	0.9974	0.005	113	8.2	99	10.1	99	5.7
39	Cycluron	0.9958	0.005	102	1.8	96	10.2	101	8.5	0.9983	0.005	118	17.1	117	10.7	105	12.1
40	Cymoxanil	0.9959	0.025	ND	ND	ND	ND	115	4.3	0.9909	0.005	74	4.2	75	12.8	113	15.1
41	Cyproconazole I	0.9940	0.005	119	4.8	114	1.5	120	3.8	0.9900	0.005	72	15.1	77	7.6	79	7.0
42	Cyproconazole II	0.9935	0.005	98	12.8	104	6.5	119	0.8	0.9910	0.005	116	9.7	120	7.6	114	9.4
43	Cyprodinil	0.9942	0.005	106	13.9	94	8.8	101	5.7	0.9997	0.005	110	10.2	101	5.1	102	4.6
44	Cyromazine	0.9930	0.005	83	9.1	59	3.5	56	4.3	0.9960	0.005	82	11.0	70	6.3	70	13.3
45	Desmedipham	0.9910	0.025	ND	ND	ND	ND	105	4.9	0.9926	0.005	76	5.4	113	14.6	120	14.2
46	Diclobutrazol	0.9950	0.005	94	22.0	127	8.1	119	7.1	0.9943	0.005	120	15.5	102	19.1	113	3.3
47	Dicrotophos	0.9929	0.005	91	10.6	87	8.8	88	4.6	0.9985	0.005	98	4.2	92	3.1	89	3.2
48	Diethofencarb	0.9925	0.005	92	12.6	108	2.5	109	11.6	0.9925	0.005	106	11.4	96	6.0	101	5.9
49	Difenoconazole	0.9961	0.005	121	6.2	107	4.8	107	3.3	0.9948	0.005	108	9.3	109	10.4	116	6.4
50	Diflubenzuron	0.9902	0.005	104	10.0	119	6.6	119	3.8	0.9942	0.005	116	14.5	118	14.5	118	12.4

Table 3 (continued). Method validation data includes linearity, LOQ, recovery, and precision (% RSD) for spinach and cabbage matrix

Sr. No.	Analyte	Spinach								Cabbage							
		R ²		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg		R ²		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg	
		LOQ (mg/kg)	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	LOQ (mg/kg)	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
51	Dimethoate	0.9970	0.005	105	6.3	103	2.0	110	2.2	0.9974	0.005	111	4.3	110	3.2	108	3.1
52	Dimethomorph-I	0.9930	0.005	119	18.4	108	12.6	115	3.4	0.9971	0.005	119	6.2	116	2.9	117	3.4
53	Dimethomorph-II	0.9942	0.005	116	3.7	113	6.2	118	1.6	0.9969	0.005	114	7.0	110	9.3	106	8.8
54	Dimoxystrobin	0.9969	0.005	124	7.6	117	4.4	111	1.6	0.9936	0.005	107	7.9	115	3.4	121	2.0
55	Diniconazole	0.9911	0.005	116	1.6	126	7.4	137	2.5	0.9970	0.005	96	15.7	113	5.9	119	4.4
56	Dinotefuran	0.9949	0.005	91	7.3	89	4.0	94	7.0	0.9939	0.005	102	6.8	99	3.1	98	4.7
57	Dioxcarb	0.9944	0.005	119	2.7	107	2.4	104	2.9	0.9991	0.005	108	5.7	104	3.8	106	4.6
58	Diuron	0.9938	0.005	111	7.4	108	5.2	106	3.2	0.9954	0.005	102	17.5	97	12.1	109	8.5
59	Doramectin	ND	ND	ND	ND	ND	ND	ND	ND	0.9947	0.005	105	17.2	116	4.0	71	14.9
60	Emamectin benzoate	0.9938	0.005	118	10.9	97	12.8	102	6.0	0.9968	0.005	117	9.7	98	14.9	98	5.2
61	Epoxiconazole	0.9978	0.005	115	5.9	116	2.9	122	5.6	0.9920	0.005	118	9.9	116	5.4	115	2.4
62	Eprinomectin	0.9949	0.005	111	22.2	91	12.6	85	22.9	0.9968	0.005	126	15.4	113	17.6	102	15.8
63	Etaconazol	0.9919	0.005	108	9.5	103	4.4	105	3.3	0.9958	0.005	102	17.6	103	19.3	111	8.9
64	Ethiofencarb	0.9958	0.005	106	19.2	90	11.6	103	4.2	0.9931	0.005	79	17.0	72	14.7	96	16.9
65	Ethiprole	0.9925	0.005	131	6.9	147	3.3	152	2.9	0.9905	0.005	106	8.5	135	5.4	143	5.2
66	Ethirimol	0.9944	0.005	105	14.4	97	7.0	82	8.6	0.9988	0.005	93	7.9	87	6.7	86	2.9
67	Ethofumesate	0.9952	0.005	76	7.5	78	6.7	110	6.2	0.9905	0.005	107	20.7	116	7.0	99	9.7
68	Etoxazole	0.9922	0.005	115	16.5	88	19.5	75	5.6	0.9901	0.005	90	4.7	53	10.5	34	23.3
69	Fenamidone	0.9976	0.005	110	6.6	116	5.2	120	4.5	0.9943	0.005	75	12.9	102	17.9	111	1.9
70	Fenazaquin	0.9926	0.005	109	15.1	86	21.0	73	6.8	0.9869	0.005	82	19.6	80	17.3	69	16.7
71	Fenbuconazole	0.9983	0.005	119	9.0	115	3.5	120	4.6	0.9944	0.005	106	17.2	111	8.2	111	9.7
72	Fenhexamid	0.9921	0.005	115	15.9	114	8.4	119	5.2	0.9977	0.005	104	19.8	109	19.1	113	8.5
73	Fenobucarb	0.9979	0.005	113	18.1	103	10.9	109	9.3	0.9978	0.005	106	13.8	102	2.8	103	8.9
74	Fenpropimorph	0.9950	0.005	113	5.3	108	8.3	103	5.0	0.9988	0.005	104	7.5	106	6.4	109	3.4
75	Fenpyroximate	0.9916	0.005	116	15.4	90	14.1	74	4.8	0.9972	0.005	101	14.5	96	6.0	102	3.0
76	Fenuron	0.9965	0.005	105	18.5	102	2.8	97	8.6	0.9942	0.005	120	12.1	112	8.1	114	7.6
77	Fipronil	0.9926	0.005	141	9.0	122	10.6	109	8.7	0.9981	0.005	105	10.8	112	1.7	103	6.5
78	Flonicamid	0.9961	0.005	106	11.1	98	8.8	97	6.1	0.9992	0.005	98	13.1	105	6.9	104	6.5
79	Fluazinam	0.9985	0.005	102	17.3	84	2.7	71	2.4	0.9959	0.005	96	17.0	81	12.1	73	9.4
80	Flufenacet	0.9959	0.005	111	6.5	119	2.8	117	1.6	0.9925	0.005	107	17.4	111	14.5	117	7.3
81	Flufenoxuron	0.9930	0.005	113	17.0	78	31.0	80	13.9	0.9930	0.005	101	5.7	95	7.8	95	5.9
82	Fluometuron	0.9953	0.005	114	11.3	107	5.4	107	1.9	0.9958	0.005	120	6.2	114	14.3	111	11.8
83	Fluoxastrobin	0.9990	0.005	125	14.0	124	9.8	123	5.6	0.9965	0.005	118	7.3	118	5.8	120	8.7
84	Fluquinconazole	0.9974	0.005	120	25.5	125	13.7	120	11.3	0.9955	0.005	99	9.7	126	10.6	123	5.8
85	Flusilazole	0.9945	0.005	141	12.6	136	3.2	136	3.3	0.9904	0.005	93	9.0	113	3.5	126	3.2
86	Flutolanil	0.9981	0.005	118	11.9	128	2.7	126	2.1	0.9946	0.005	106	9.4	109	4.4	115	2.5
87	Flutriafol	0.9910	0.005	127	11.2	135	3.9	134	4.6	0.9982	0.005	120	4.7	116	4.5	120	5.6
88	Forchlorfenuron	0.9903	0.005	97	19.9	132	7.8	143	2.7	0.9905	0.005	98	15.0	118	7.1	115	3.1
89	Formetanate	0.9943	0.005	105	13.3	100	14.3	101	7.3	0.9904	0.005	94	4.3	94	11.2	89	9.0
90	Fuberidazole	0.9938	0.005	111	2.9	102	1.0	99	2.1	0.9983	0.005	97	5.0	100	3.2	102	2.7
91	Furalaxyl	0.9979	0.005	115	5.6	121	3.9	122	3.2	0.9905	0.005	113	8.6	114	5.0	119	2.4
92	Furathiocarb	0.9932	0.005	92	8.6	99	11.2	101	4.0	0.9954	0.005	113	19.9	117	8.4	116	5.4
93	Halofenozide	0.9965	ND	ND	ND	ND	ND	ND	ND	0.9956	0.005	106	18.5	113	6.5	113	6.5
94	Hexaconazole	0.9957	0.005	127	11.8	127	3.7	131	2.5	0.9922	0.005	115	10.6	116	9.7	119	8.9
95	Hexaflumuron	0.9956	0.005	97	15.5	91	22.2	72	8.4	0.9964	0.005	104	19.3	96	16.7	86	11.0
96	Hexythiazox	0.9937	0.005	124	20.0	98	25.5	86	6.3	0.9974	0.005	108	10.2	118	8.2	119	4.2
97	Hydramethylnon	NA	NA	118	4.1	111	4.4	104	2.8	0.9915	0.005	101	14.8	71	8.0	70	0.0
98	Imazalil	0.9950	0.005	119	9.4	116	4.4	109	3.5	0.9986	0.005	91	7.9	92	8.2	95	4.9
99	Imidacloprid	0.9969	0.005	90	24.5	102	13.9	92	11.2	0.9992	0.005	101	11.2	97	5.5	98	4.1
100	Indoxacarb	0.9912	0.005	127	11.8	127	3.7	131	2.5	0.9910	0.005	118	14.6	85	16.7	118	10.5
101	Ipconazole	0.9964	0.005	108	6.5	91	10.3	95	4.0	0.9988	0.005	105	7.4	109	10.3	110	5.2

Table 3 (continued). Method validation data includes linearity, LOQ, recovery, and precision (% RSD) for spinach and cabbage matrix

Sr. No.	Analyte	Spinach								Cabbage							
		LOQ (mg/kg)		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg		LOQ (mg/kg)		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg	
		R ²		% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	R ²		% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
102	Iprovalicarb	0.9969	0.005	73	4.9	90	8.6	109	6.1	0.9933	0.005	120	8.5	94	16.9	109	1.9
103	Isocarboxiphos	ND	ND	ND	ND	ND	ND	ND	ND	0.9968	0.005	109	17.3	105	9.1	109	7.6
104	Isoprocarb	ND	ND	ND	ND	ND	ND	ND	ND	0.9958	0.005	102	17.1	107	10.5	108	13.2
105	Isoproturon	0.9962	0.005	112	8.8	123	2.2	116	5.1	0.9916	0.005	117	10.6	119	6.1	118	1.7
106	Ivermectin	ND	ND	ND	ND	ND	ND	ND	ND	0.9986	0.005	107	10.9	92	19.9	87	8.3
107	Kresoxim-methyl	0.9945	0.005	90	17.4	90	10.0	114	8.8	0.9929	0.005	110	14.6	98	16.8	110	9.7
108	Linuron	0.9966	0.005	109	8.0	118	8.9	128	7.4	0.9904	0.005	117	13.7	115	12.9	119	5.8
109	Lufenuron	0.9966	0.005	119	13.8	102	7.5	90	16.6	0.9956	0.005	101	7.3	96	6.6	100	2.6
110	Mandipropamid	0.9922	0.005	112	10.9	93	5.8	96	6.5	0.9968	0.005	101	17.5	109	18.5	104	11.3
111	Mefenacet	0.9973	0.005	124	5.0	120	4.8	125	6.0	0.9915	0.005	100	3.6	114	3.6	120	1.4
112	Mepanipyrim	0.9953	0.005	110	24.7	105	7.7	104	7.0	0.9944	0.005	118	8.8	112	9.2	116	5.1
113	Mepronil	0.9964	0.005	104	9.7	112	4.9	116	3.1	0.9914	0.005	102	8.8	115	2.8	118	4.2
114	Metaflumizone	ND	ND	ND	ND	ND	ND	ND	ND	0.9910	0.005	111	5.8	72	16.7	72	9.8
115	Metalaxyl	0.9981	0.005	110	3.6	113	4.9	112	2.8	0.9991	0.005	108	5.5	108	3.4	108	5.3
116	Metconazole	0.9930	0.005	120	8.1	131	5.6	136	3.8	0.9925	0.005	116	13.5	119	4.2	120	4.5
117	Methabenzthiazuron	0.9973	0.005	120	4.0	124	2.1	128	1.8	0.9951	0.005	114	3.4	115	5.0	115	3.8
118	Methamidophos	0.9909	0.005	101	34.0	83	5.1	86	2.2	0.9960	0.005	76	9.1	76	4.1	74	3.7
119	Methiocarb	0.9959	0.005	111	7.0	111	6.4	106	1.2	0.9985	0.005	103	10.1	104	9.1	98	3.3
120	Methomyl	0.9959	0.005	118	5.9	103	8.3	103	3.9	0.9978	0.005	107	18.3	97	8.8	98	6.1
121	Methoprotryne	0.9968	0.005	121	2.2	113	2.2	115	3.2	0.9970	0.005	113	2.6	115	6.4	115	2.1
122	Methoxyfenozide	0.9950	0.005	103	17.3	115	9.7	114	3.8	0.9985	0.005	113	6.3	113	9.6	109	8.0
123	Metobromuron	0.9975	0.005	120	8.9	117	4.7	113	3.7	0.9919	0.005	116	5.9	112	4.1	117	2.9
124	Metribuzin	0.9925	0.005	117	22.1	122	6.2	109	7.6	0.9986	0.005	87	20.0	118	16.5	113	7.2
125	Mevinphos	0.9979	0.005	98	11.4	106	3.3	106	3.1	0.9977	0.005	101	7.3	96	6.6	100	2.6
126	Mexacarbate	0.9951	0.005	119	4.6	114	0.4	106	1.1	0.9977	0.005	108	5.7	108	4.1	111	2.3
127	Monocrotophos	0.9909	0.005	90	7.9	105	8.4	93	4.5	0.9995	0.005	103	13.4	98	9.1	92	5.0
128	Monolinuron	0.9964	0.005	100	13.3	101	4.8	103	3.1	0.9952	0.005	114	7.8	107	8.8	112	3.3
129	Moxidectin	0.9955	0.010	ND	ND	104	6.0	108	7.9	0.9965	0.010	84	24.6	101	22.2	82	23.5
130	Myclobutanil	0.9970	0.005	109	16.2	117	7.5	110	6.9	0.9971	0.005	116	10.1	120	7.9	119	5.5
131	Neburon	0.9905	0.005	71	28.5	74	18.8	82	4.5	0.9956	0.005	79	4.2	104	13.1	112	10.2
132	Nitenpyram	0.9956	0.005	91	8.8	72	4.2	73	21.8	0.9978	0.005	82	9.6	82	7.0	83	1.8
133	Novaluron	0.9906	0.005	108	9.1	81	13.3	70	5.6	0.9908	0.005	80	17.3	91	19.0	92	17.0
134	Nuarimol	0.9962	0.005	120	10.3	145	8.0	149	3.3	0.9951	0.005	106	13.8	120	9.5	118	3.5
135	Omethoate	0.9930	0.005	82	7.0	83	4.7	93	1.7	0.9912	0.005	84	2.5	88	7.3	86	6.2
136	Oxadixyl	0.9984	0.005	127	11.2	118	7.8	109	5.8	0.9980	0.005	113	5.6	105	2.5	106	5.8
137	Oxamyl	ND	ND	ND	ND	ND	ND	ND	ND	0.9929	0.005	117	7.4	120	12.9	120	5.4
138	Paclobutrazol	0.9926	0.005	90	4.7	114	3.5	120	4.4	0.9945	0.005	120	7.9	111	6.7	111	1.9
139	Penconazole	0.9974	0.005	113	7.6	114	5.9	115	5.3	0.9930	0.005	117	3.7	113	5.2	112	3.7
140	Pencycuron	0.9975	0.005	111	5.8	72	16.7	72	9.8	0.9926	0.005	110	5.3	112	2.7	111	2.8
141	Phenmedipham	0.9926	0.005	94	6.2	91	12.6	93	10.8	0.9957	0.005	117	9.4	114	16.2	116	9.9
142	Picoxystrobin	0.9916	0.005	111	19.6	103	10.0	104	8.1	0.9964	0.005	105	10.4	108	10.5	114	6.9
143	Piperonyl butoxide	0.9969	0.005	103	11.0	105	7.8	104	4.2	0.9948	0.005	98	12.7	104	11.1	100	1.7
144	Pirimicarb	0.9940	0.005	119	5.3	109	2.1	105	3.3	0.9991	0.005	108	5.0	105	4.0	107	1.5
145	Prochloraz	0.9962	0.005	102	8.1	102	9.5	103	4.0	0.9960	0.005	104	9.0	106	4.8	116	4.1
146	Promecarb	0.9957	0.005	88	1.8	85	15.6	107	13.5	0.9920	0.005	98	9.8	103	16.8	108	12.1
147	Prometon	0.9972	0.005	118	4.6	117	3.7	111	2.7	0.9987	0.005	110	4.4	110	2.7	113	2.9
148	Prometryne	0.9972	0.005	115	4.4	115	2.0	107	2.3	0.9998	0.005	113	6.0	110	4.4	110	2.1
149	Propamocarb	0.9963	0.005	102	14.2	83	3.9	75	6.3	0.9913	0.005	74	2.8	79	13.4	73	9.7
150	Propargite	0.9904	0.005	99	3.6	75	5.8	79	10.6	0.9990	0.005	100	14.7	108	13.8	104	8.5
151	Propiconazole	0.9993	0.005	121	10.7	124	16.6	110	6.0	0.9975	0.005	98	14.4	116	10.2	120	5.0
152	Propoxur	0.9933	0.005	110	10.4	111	3.9	109	3.1	0.9976	0.005	105	3.7	105	4.4	108	4.3

Table 3 (continued). Method validation data includes linearity, LOQ, recovery, and precision (% RSD) for spinach and cabbage matrix

Sr. No.	Analyte	Spinach								Cabbage											
		R ²		LOQ (mg/kg)		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg		R ²		LOQ (mg/kg)		0.005 mg/kg		0.01 mg/kg		0.025 mg/kg	
		% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD	% Rec.	% RSD
153	Prothioconazole	0.9963	0.005	148	27.6	101	4.6	95	8.2	0.9930	0.005	82	17.4	114	17.0	101	6.9				
154	Pymetrozine	0.9935	0.005	146	6.1	108	4.6	93	0.9	0.9916	0.005	111	14.6	101	12.8	99	11.9				
155	Pyracarbolid	0.9974	0.005	122	4.6	126	2.3	124	1.6	0.9990	0.005	113	5.2	113	2.4	118	3.0				
156	Pyraclostrobin	0.9902	0.005	129	9.4	103	19.6	104	8.3	0.9961	0.005	113	12.8	106	15.6	113	4.3				
157	Pyridaben	0.9946	0.005	117	19.4	82	27.2	76	19.5	0.9951	0.005	101	11.2	87	8.2	94	5.0				
158	Pyrimethanil	0.9956	0.005	124	10.0	108	4.6	103	4.7	0.9957	0.005	114	9.9	107	5.7	111	2.2				
159	Pyriproxyfen	0.9924	0.005	95	16.4	101	14.2	84	4.0	0.9983	0.005	103	12.2	106	5.3	105	3.0				
160	Quinoxifen	0.9932	0.005	116	12.8	96	11.7	88	8.4	0.9970	0.005	103	9.2	106	10.5	117	5.9				
161	Rotenone	0.9902	0.005	100	4.8	118	8.8	131	8.9	0.9936	0.005	115	12.0	120	6.3	117	3.4				
162	Secbumeton	0.9958	0.005	117	2.1	113	2.3	110	1.4	0.9977	0.005	110	4.9	108	3.0	110	2.6				
163	Siduron	0.9945	0.005	117	7.1	118	1.5	119	3.8	0.9939	0.005	117	3.7	119	8.5	120	5.6				
164	Simetryn	0.9958	0.005	115	4.3	111	2.4	109	1.3	0.9995	0.005	109	3.9	108	4.1	107	2.0				
165	Spinetoram	0.9909	0.005	119	7.6	106	5.0	99	8.5	0.9991	0.005	115	12.7	107	7.0	108	9.2				
166	Spinosad D	ND	ND	ND	ND	ND	ND	ND	ND	0.9973	0.005	88	8.7	113	10.6	94	12.0				
167	Spinosad A	0.9923	0.005	94	5.6	99	3.5	104	4.4	0.9991	0.005	112	15.7	106	11.8	102	8.1				
168	Spirotetramat	0.9982	0.005	110	8.7	111	7.3	113	7.3	0.9950	0.005	85	11.9	103	11.1	120	3.7				
169	Spiroxamine	0.9944	0.005	119	5.3	103	3.4	107	5.7	0.9994	0.005	106	3.0	102	1.7	104	3.0				
170	Sulfentrazone	ND	ND	ND	ND	ND	ND	ND	ND	0.9911	0.005	70	6.1	113	7.6	115	2.3				
171	Tebuconazole	0.9975	0.005	119	6.6	106	6.9	104	3.4	0.9934	0.005	118	10.3	111	11.5	115	6.2				
172	Tebufenpyrad	0.9984	0.005	120	7.7	114	12.1	115	1.5	0.9946	0.005	99	5.3	101	3.4	108	6.1				
173	Tebuthiuron	0.9977	0.005	109	3.3	114	3.4	114	2.1	0.9969	0.005	112	4.3	111	2.4	110	2.5				
174	Teflubenzuron	0.9969	0.005	119	5.0	103	7.0	85	8.6	0.9915	0.005	75	4.7	97	16.1	79	17.6				
175	Temephos	0.9961	0.005	118	14.0	97	17.0	76	12.3	0.9941	0.005	102	4.4	86	15.9	90	7.8				
176	Terbumeton	0.9962	0.005	118	5.0	116	2.5	113	1.2	0.9979	0.005	110	4.3	111	3.8	111	2.0				
177	Terbutryn	0.9939	0.005	106	11.4	104	8.8	100	4.5	0.9987	0.005	92	11.5	106	3.3	104	3.0				
178	Tetraconazole	0.9901	0.005	114	4.7	118	5.0	117	4.1	0.9936	0.005	120	15.0	108	16.6	106	13.8				
179	Thiabendazole	0.9915	0.005	114	4.0	99	2.6	91	3.1	0.9990	0.005	110	5.7	102	3.7	102	3.1				
180	Thiacloprid	0.9951	0.005	104	3.1	112	0.9	116	1.6	0.9939	0.005	109	2.1	111	2.8	115	4.3				
181	Thiamethoxam	0.9972	0.005	115	5.4	116	4.0	107	4.2	0.9904	0.005	109	8.1	113	4.3	113	3.8				
182	Thidiazuron	0.9936	0.025	ND	ND	ND	ND	119	9.0	0.9921	0.005	119	16.2	120	15.6	93	18.2				
183	Thiobencarb	0.9941	0.005	104	9.2	103	9.4	102	3.0	0.9960	0.005	107	19.6	110	13.0	116	5.3				
184	Thiophanate-methyl	0.9956	0.005	105	10.7	98	4.2	96	4.3	0.9926	0.005	ND	ND	109	10.3	110	5.2				
185	Triadimefon	0.9923	0.005	104	7.6	118	7.4	115	7.5	0.9929	0.005	107	7.7	111	2.2	116	1.4				
186	Triadimenol	0.9948	0.005	110	15.5	95	14.3	118	2.6	0.9929	0.005	83	18.6	108	9.0	116	9.1				
187	Trichlorfon	0.9962	0.005	107	7.0	101	5.1	98	3.9	0.9974	0.005	96	6.3	83	4.2	81	2.6				
188	Tricyclazole	0.9966	0.005	106	4.2	103	2.3	104	1.2	0.9979	0.005	106	3.8	109	4.0	113	2.0				
189	Trifloxystrobin	0.9949	0.005	105	15.5	99	6.5	104	8.4	0.9942	0.005	109	12.2	105	10.4	104	13.5				
190	Triflumizole	0.9900	0.005	116	3.8	111	6.0	116	6.2	0.9961	0.005	93	8.7	78	16.0	79	9.8				
191	Triflumuron	0.9965	0.005	117	9.0	118	18.6	118	11.0	0.9916	0.005	114	19.1	112	10.2	120	2.9				
192	Triticonazole	0.9933	0.005	126	17.8	99	13.2	103	12.4	0.9984	0.005	105	19.9	117	15.0	117	6.4				
193	Vamidothion	0.9960	0.005	107	9.0	102	4.7	101	3.8	0.9970	0.005	103	5.5	103	1.3	102	3.5				
194	Zoxamide	0.9942	0.005	110	8.9	116	9.0	119	7.1	0.9949	0.005	112	4.8	118	9.7	112	6.5				

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