# 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™ Finnpipette™ 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: $MgSO_4$-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 note[6].

**Table 1a. LC instrument conditions**

| Liquid chromatography method | |
|---|---|
| Instrumentation | Thermo Scientific™ Vanquish™ Flex Binary UHPLC system, consisting of:<br>• Vanquish Split Sampler FT, P/N VF-A10-A<br>• Vanquish Column Compartment, P/N VH-C10-A<br>• Binary Pump F, P/N VF-P10-A<br>• 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)<br>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 | *Time (min) / Flow rate (mL/min) / %B / Curve*<br>0.0 / 0.3 / 0 / 5<br>0.5 / 0.3 / 0 / 5<br>7.0 / 0.3 / 70 / 5<br>9.0 / 0.3 / 100 / 5<br>12.0 / 0.3 / 100 / 5<br>12.1 / 0.3 / 0 / 5<br>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<br>Positive: 3,700 V<br>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 method[5] 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 $MgSO_4$ and 1.5 g Na-acetate, to the tube.
- Mix vigorously for 1 min on a vortex mixer at 2,500 rpm.
- Centrifuge 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 $MgSO_4$ 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 (±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 the SANTE guideline[7].

## 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.

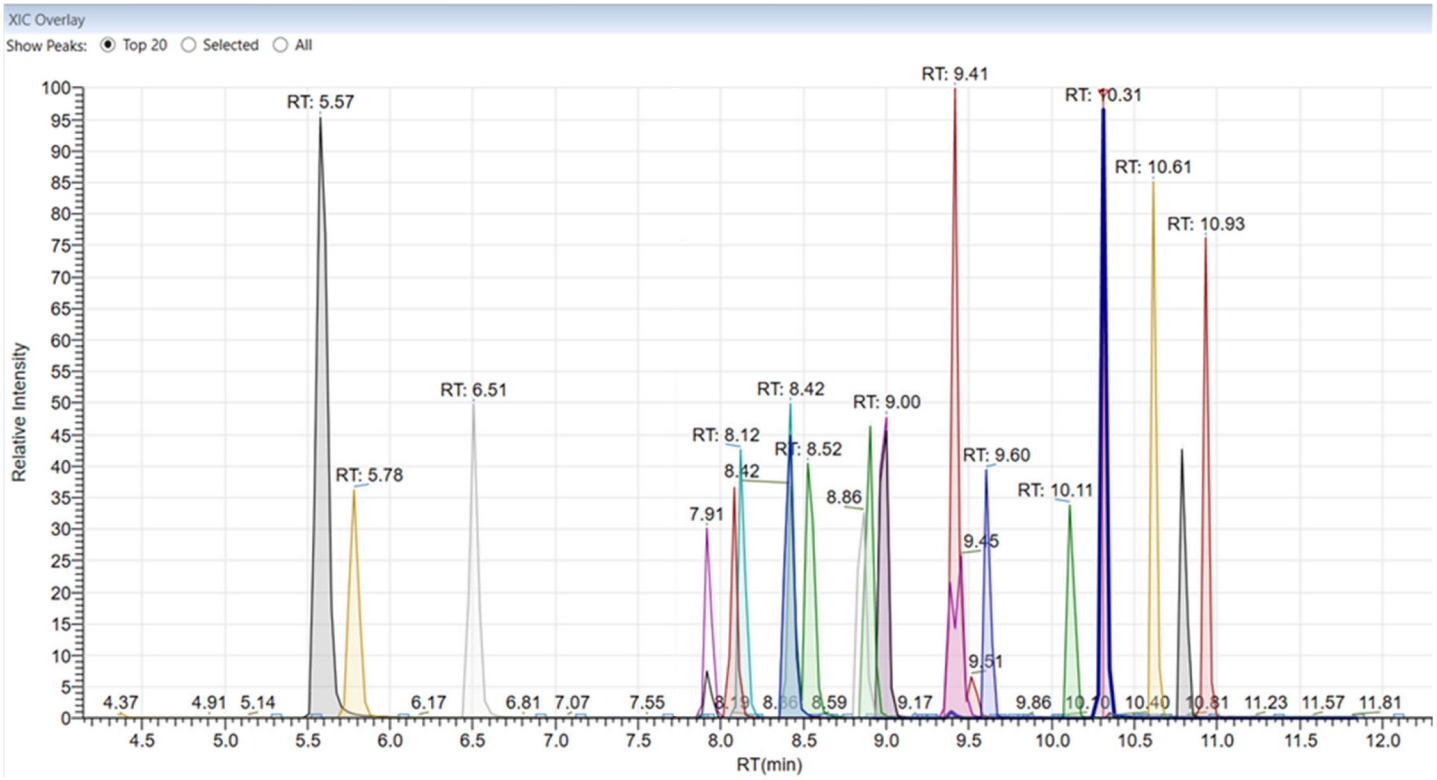



Figure 1. Extracted ion chromatogram for the top twenty most intense analytes at 5 ng/mL matrix-matched standard (MMS) in spinach

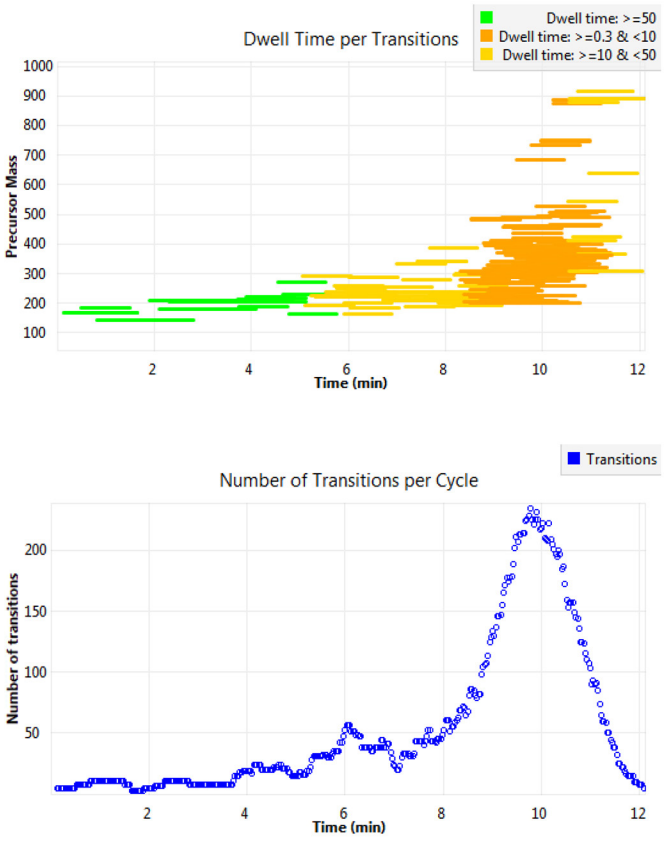



Figure 2. Representation of SRM transitions with auto-optimized dwell time

## 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→198.815, quantifier ion and *m/z* 229.82→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 ±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/× weighting faction and linear equation (Figure 3C).

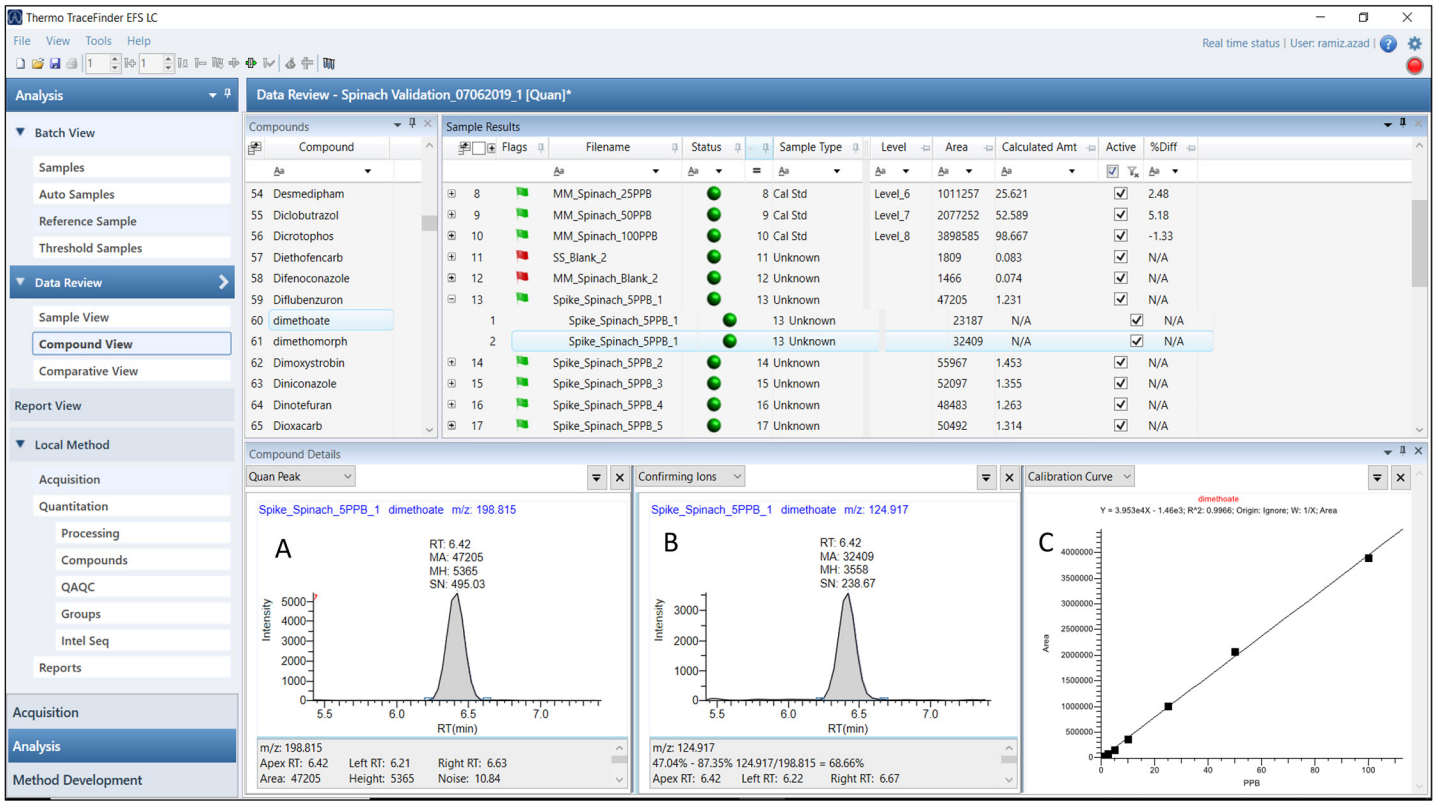



**Figure 3. (A) Extracted ion chromatogram for quantifier ion of dimethoate, (B) identification based on confirmatory ion with ion ratio, and (C) calibration curve**

## 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/× 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, bifenazate, 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 ±20% was considered here as low matrix effect within acceptance criteria of the SANTE guideline. ME values from ±20% to ±50% were considered medium, and those with ME greater than ±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 are in Table 3.

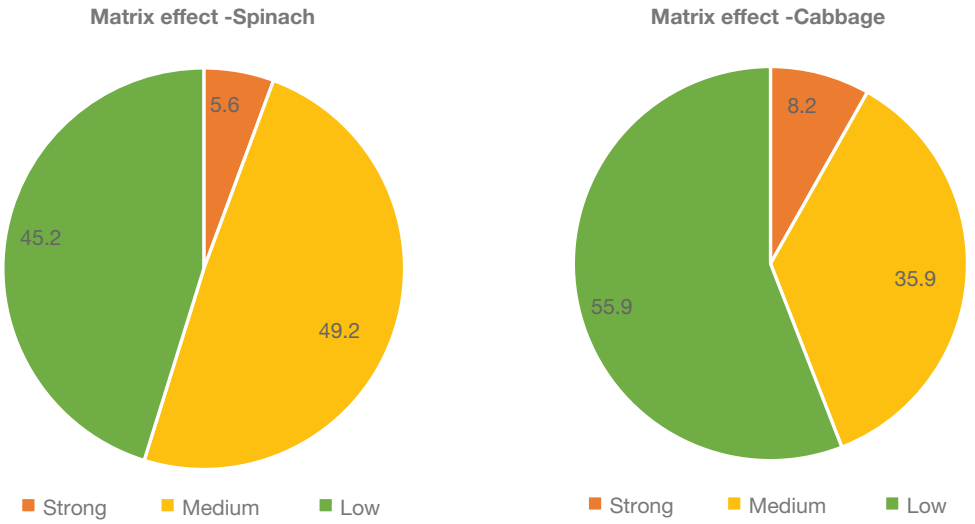



**Figure 4. Matrix effect observed in spinach and cabbage (Low: <±20%; Medium: ±20%–±50%; High: >±50%)**

## 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×2), and 0.025 (LOQ×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).

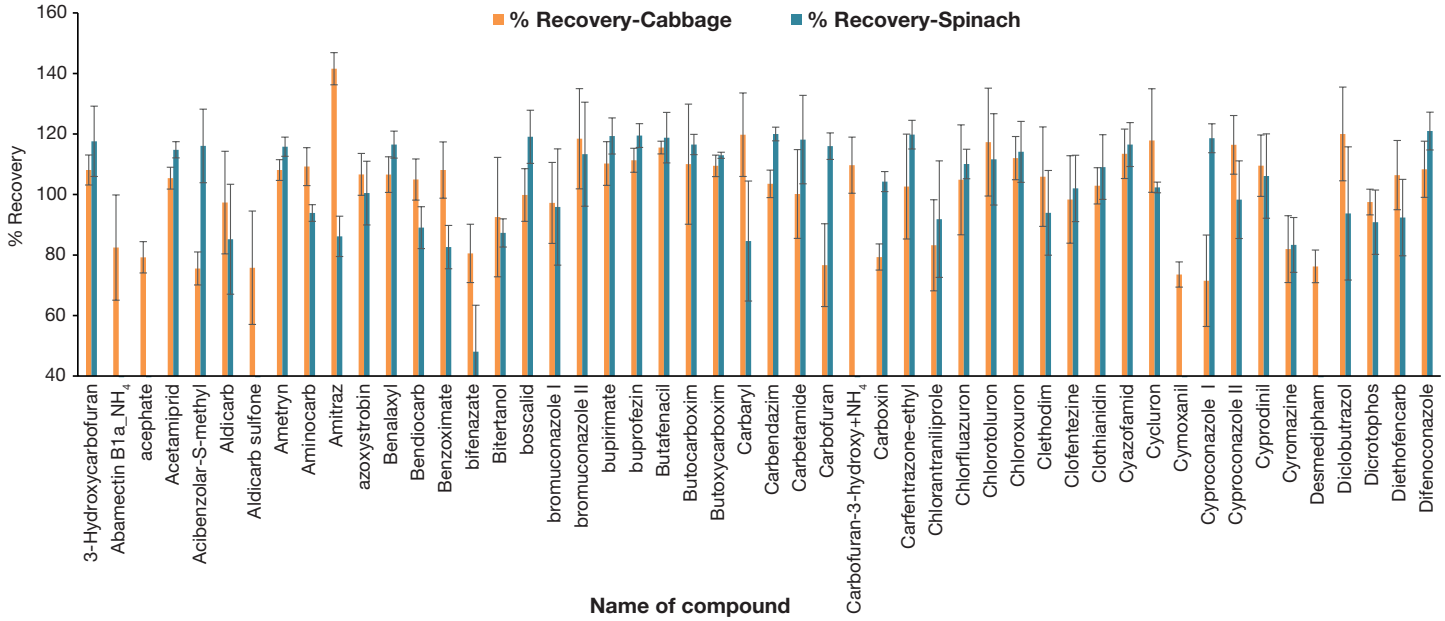



**Figure 5 (part 1). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg**

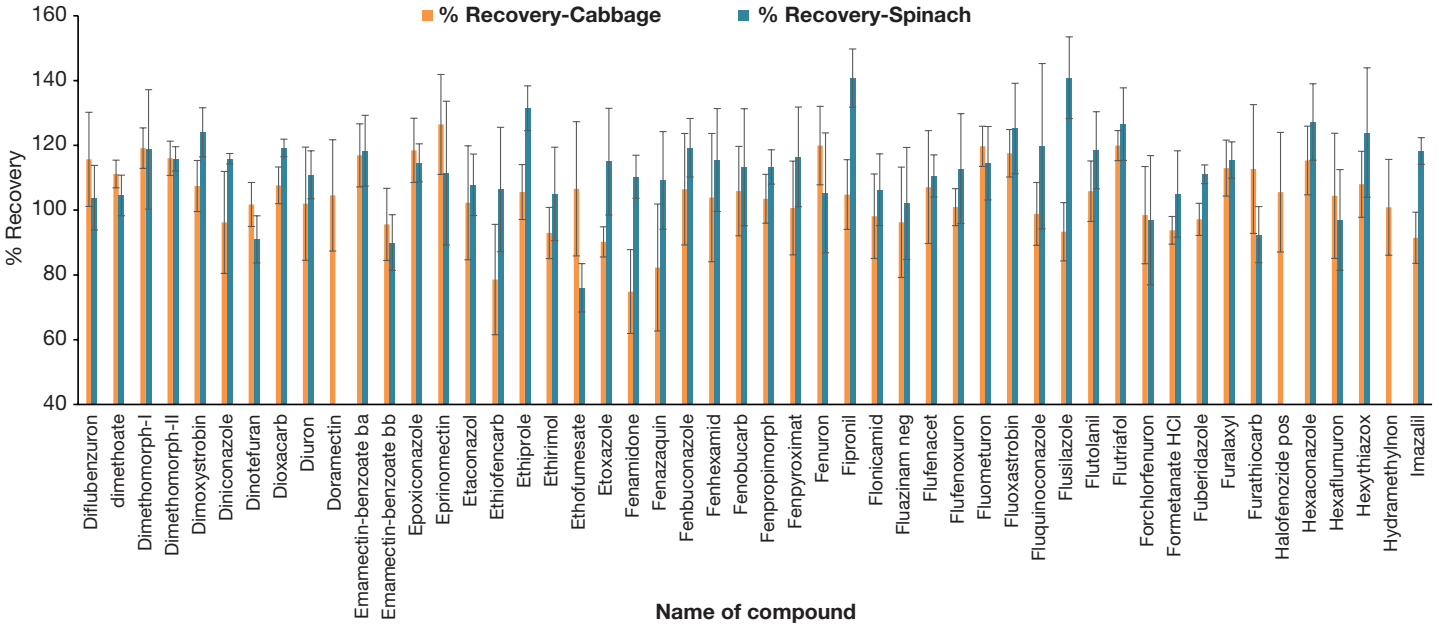



Figure 5 (part 2). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

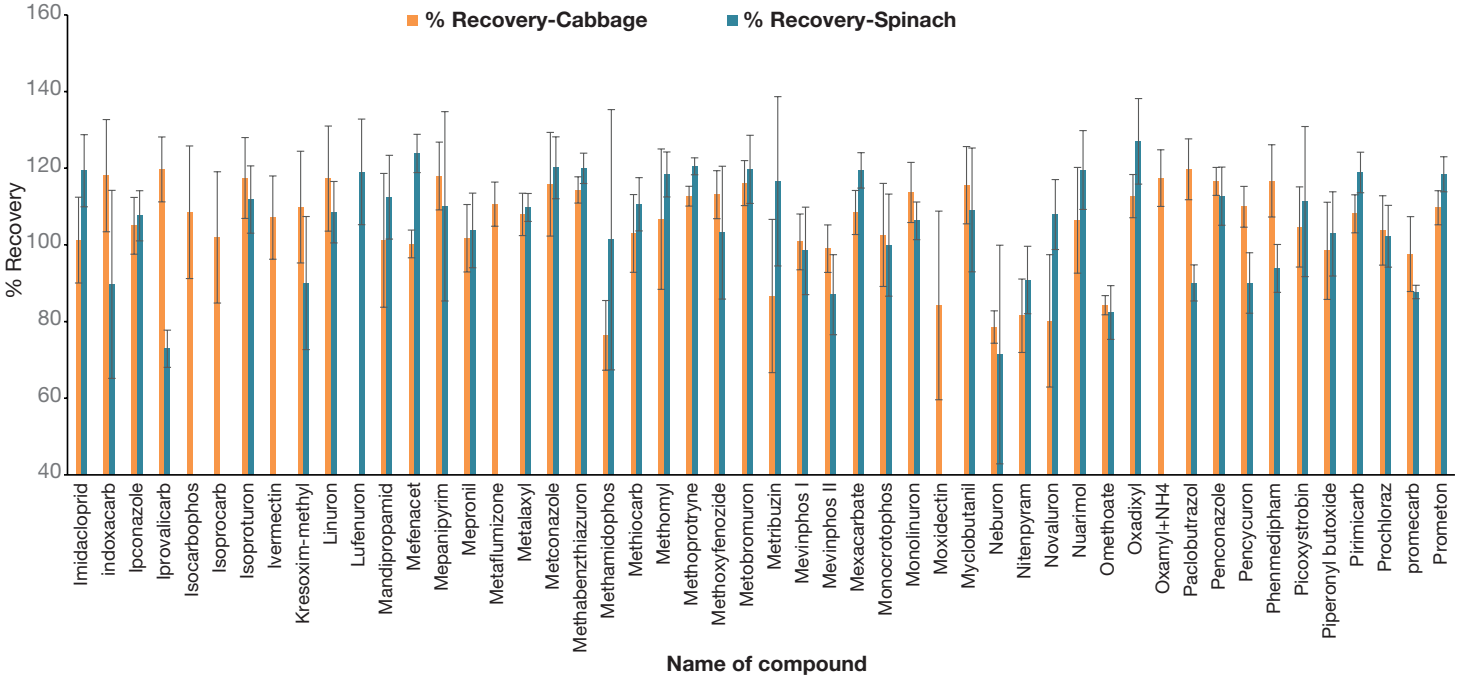



Figure 5 (part 3). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg

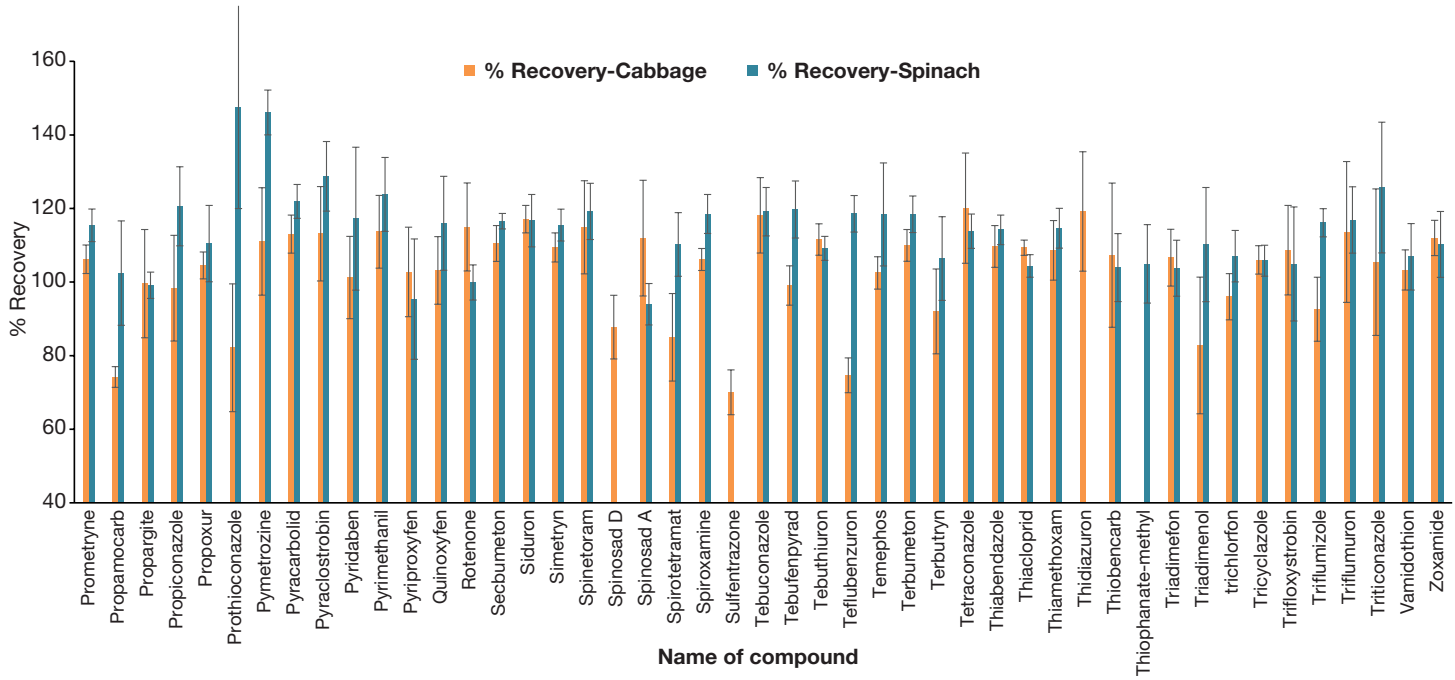



**Figure 5 (part 4). % Recoveries observed in cabbage and spinach spiked samples at 0.005 mg/kg**

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).

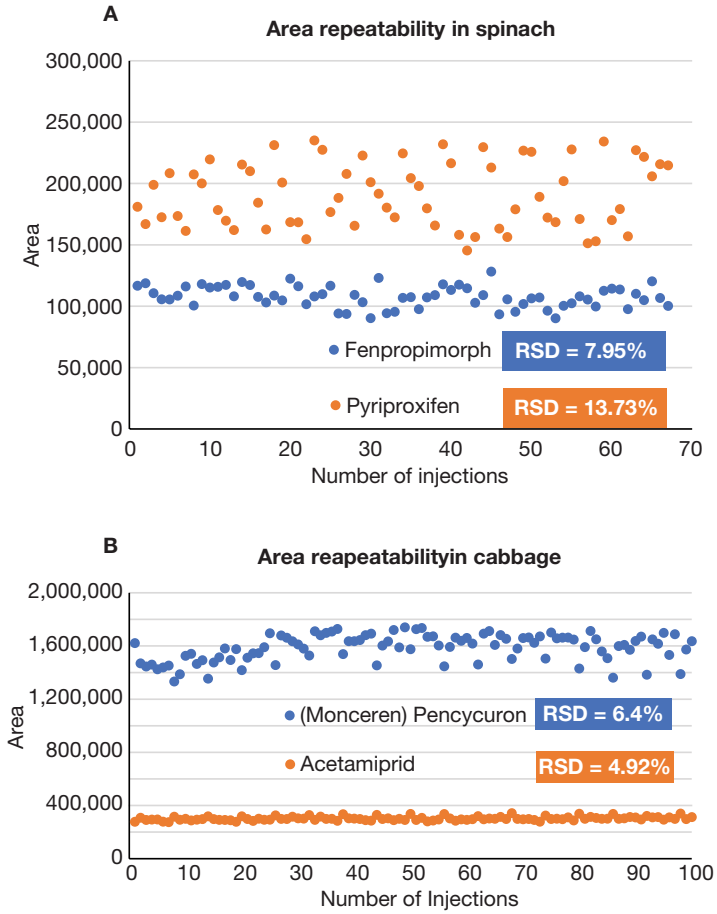
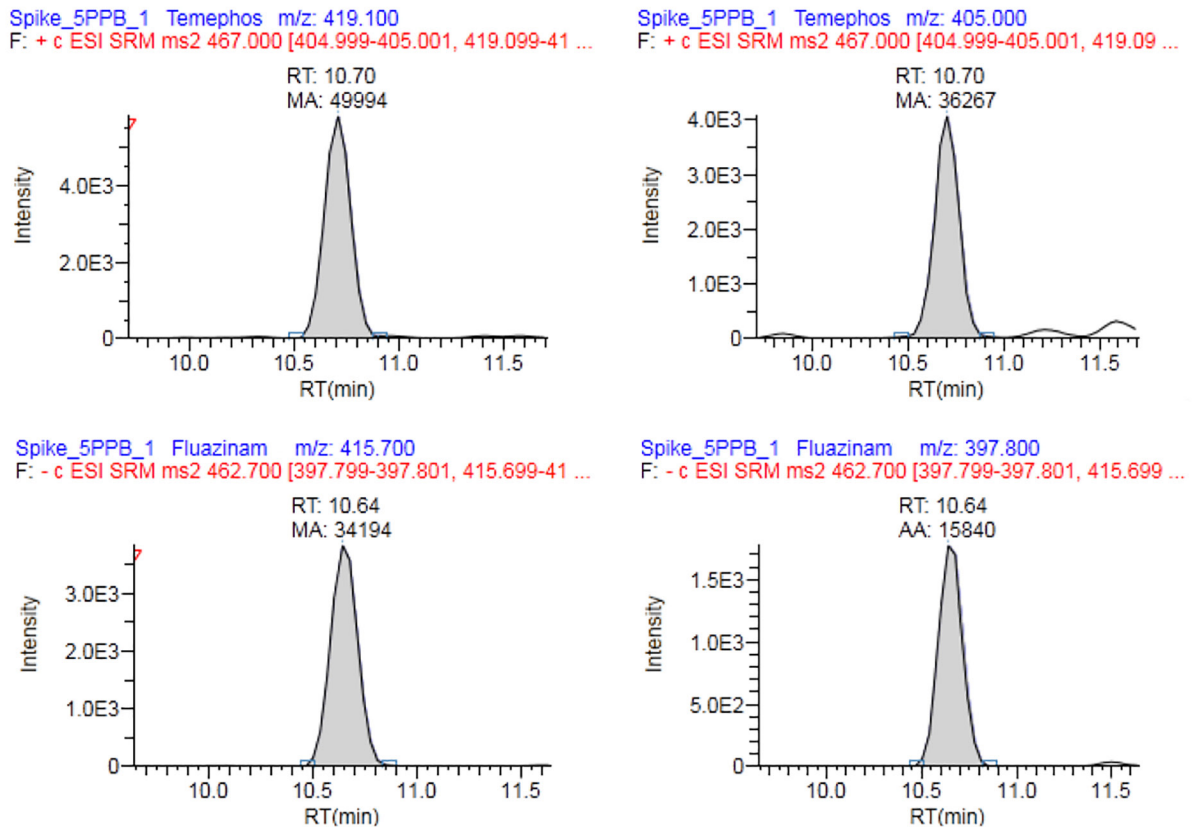



**Figure 6. (A) Area repeatability shown for fenpropimorph and pyriproxyfen in spinach (n=67) at 0.005 mg/kg (spiked sample); (B) Area repeatability shown for (monceren) pencycuron and acetamiprid in cabbage (n=100) at 0.005 mg/kg (spiked sample)**

(A) Spinach




(B Cabbage)

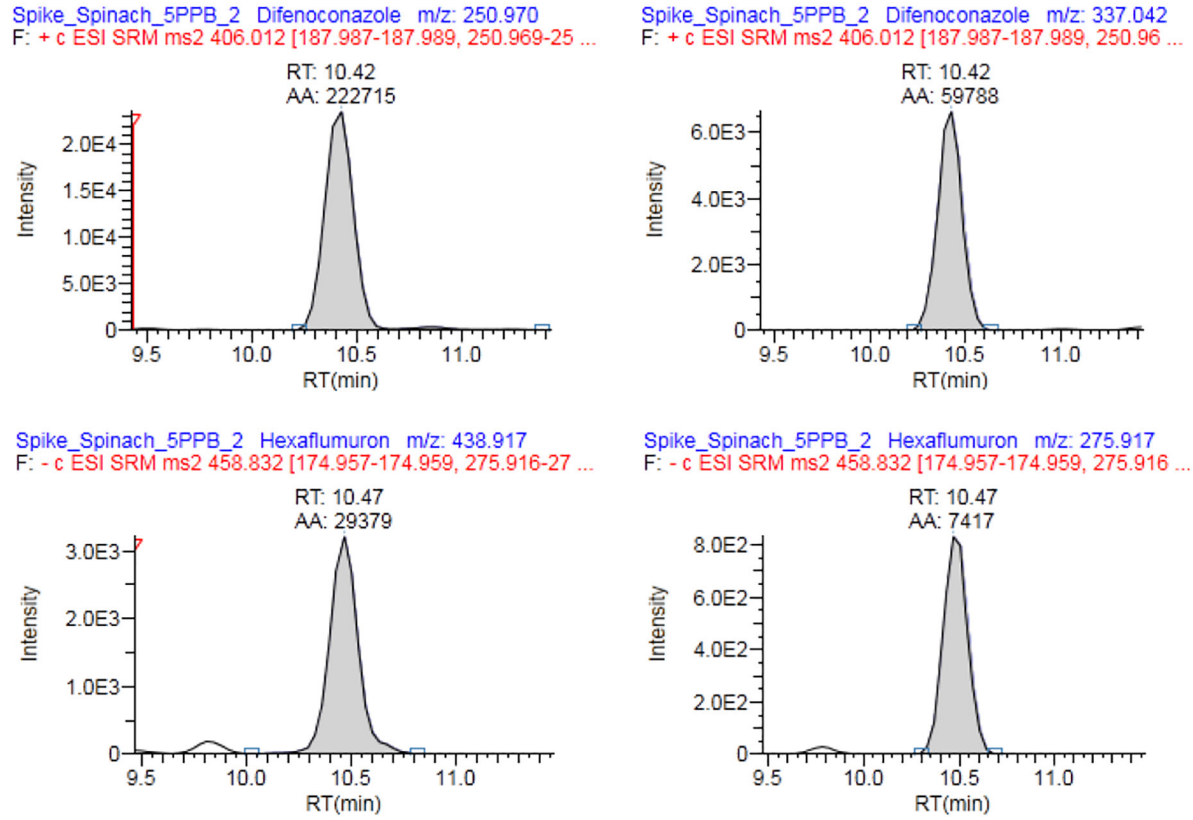



Figure 7. The sensitivity observed for temephos, fluazinam, difenoconazole, and hexaflumuron at 0.005 mg/kg in spinach (A) and cabbage (B)

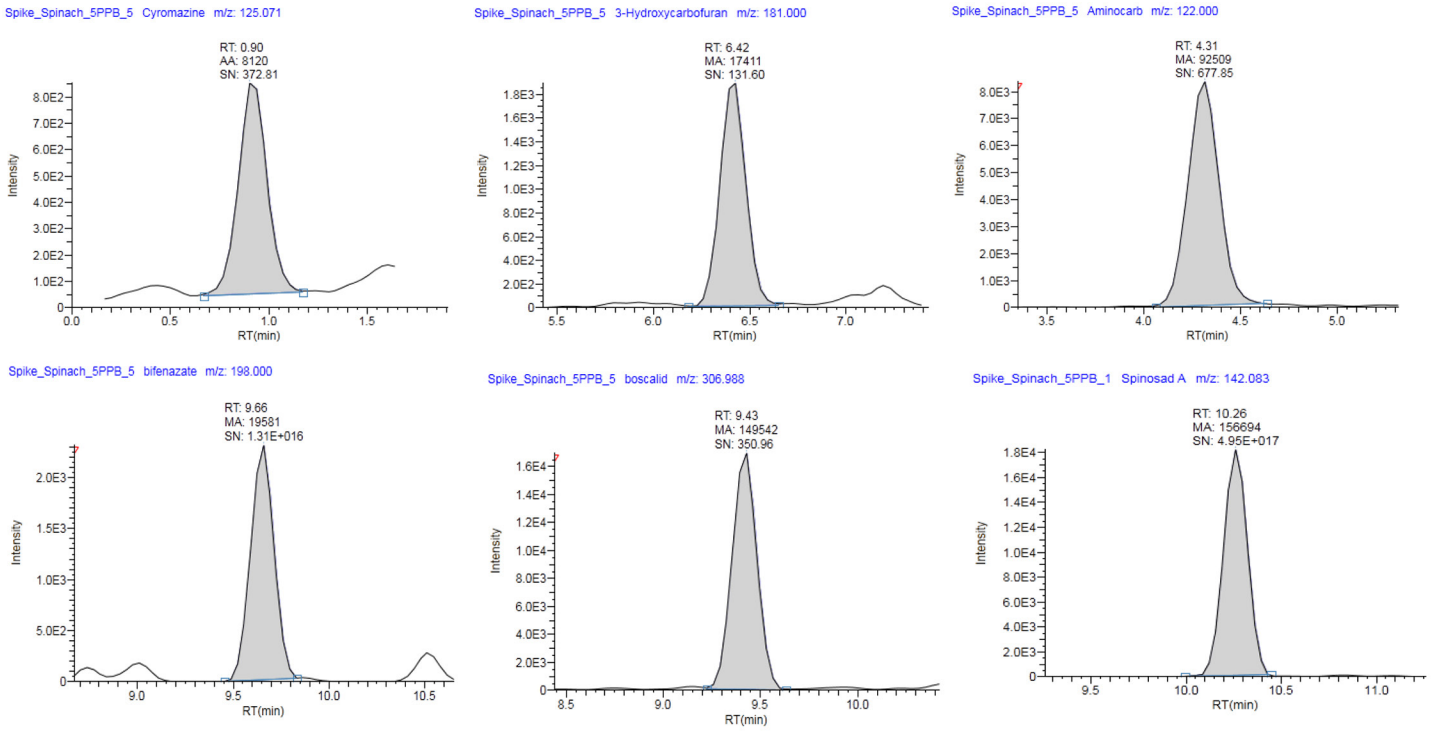



**Figure 8. Extracted ion chromatogram for the selected compounds at LOQ level with the signal-to-noise ratio**

## 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).

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## Appendix

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

| | | Spinach | | | | | | | | Cabbage | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | |
| Sr. No. | Analyte | $R^2$ | LOQ (mg/kg) | % Rec. | % RSD | % Rec. | % RSD | % Rec. | % RSD | $R^2$ | LOQ (mg/kg) | % 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 | Bromucanozole-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 | Bromucanozole-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 | Chlorfluazuron | 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

| | | Spinach | | | | | | | | Cabbage | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | |
| Sr. No. | Analyte | $R^2$ | LOQ (mg/kg) | % Rec. | % RSD | % Rec. | % RSD | % Rec. | % RSD | $R^2$ | 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 | Dioxacarb | 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 | Fluquinoconazole | 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

| | | Spinach | | | | | | | | Cabbage | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | |
| Sr. No. | Analyte | $R^2$ | LOQ (mg/kg) | % Rec. | % RSD | % Rec. | % RSD | % Rec. | % RSD | $R^2$ | LOQ (mg/kg) | % 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 | Isocarbophos | 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

| | | Spinach | | | | | | | | Cabbage | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | | | | 0.005 mg/kg | | 0.01 mg/kg | | 0.025 mg/kg | |
| Sr. No. | Analyte | $R^2$ | LOQ (mg/kg) | % Rec. | % RSD | % Rec. | % RSD | % Rec. | % RSD | $R^2$ | LOQ (mg/kg) | % 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 | Quinoxyfen | 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 |