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Application News

Gas Chromatograph Mass Spectrometer

Simultaneous Analysis of Pesticide Residues in Food Using Triple Quadrupole GC-MS/MS with SPL Mode of a Multimode injection Unit (MMI)

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User Benefits

- The MMI's rapid heating and cooling technology significantly reduces waiting time during inlet maintenance, improving instrument uptime.
- The Smart Pesticides Database™ enables automatic creation of analytical methods without the need for pesticide standards.
- Peakintelligence™ for GCMS uses AI-based peak processing to deliver highly accurate analysis with no parameter settings required.

■ Introduction

GC-MS/MS is an indispensable tool for the simultaneous analysis of pesticide residues in food. However, improving productivity in high-throughput workflows remains a persistent challenge. With the increasing use of simplified sample preparation methods such as QuEChERS, contamination of the inlet by matrix components is unavoidable, and frequent inlet maintenance, including liner replacement, is often required. Because this maintenance involves both cooling the inlet and waiting for temperature re-stabilization afterward, it can become a major source of instrument downtime.

The newly developed Multi-Mode Inlet (MMI) incorporates Shimadzu's proprietary thermal insulation technology, providing excellent temperature stability together with rapid heating and cooling performance. While maintaining high data compatibility with conventional split/splitless inlets, the MMI significantly reduces the waiting time associated with inlet maintenance.

In this Application News, simultaneous multiresidue analysis in SPL mode is demonstrated for four food matrices with different characteristics - spinach, orange, avocado, and ginger - using the GCMS-TQ™8040 RX triple quadrupole GC-MS/MS equipped with the MMI.

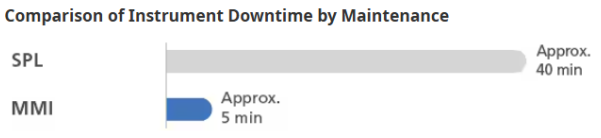

Fig. 1 Comparison of Maintenance-Related Instrument Downtime Between SPL and MMI

Fig. 2 GCMS-TQ™8040 RX

■ Automated Development of a Multiresidue Analysis Method Using the Smart Pesticides Database

The simultaneous MRM acquisition method for pesticide residue analysis was developed using the Smart Pesticides Database. The database contains retention indices and MRM transitions for 530 pesticide compounds regulated in various countries (Fig. 3). By simply measuring *n*-alkanes, a multiresidue analytical method can be generated automatically, without using pesticide standard solutions, based on retention indices and the AART function. Because up to six transitions are registered for each pesticide, transitions that avoid matrix interference can be selectively used (Fig. 4).

Compound Name (E)	Ret. Index 1	Ret. Index 2	Ret. Index 3	Cas#	Ion1				Ion2			
	Method1	Method2	Method3		Type	m/z	CE	Ratio	Type	m/z	CE	Ratio
Clothianidin	1502	1496	1488	210880 - 92 - 5	T	132.0>71.0	14	100.00	Ref.1	132.0>45.0	22	78.58
Thiocyclam	1509	1505	1490	31895 - 21 - 3	T	135.0>71.0	8	100.00	Ref.1	135.0>56.0	24	33.28
Chloroneb	1510	1508	1502	2675 - 77 - 6	T	206.0>191.0	12	100.00	Ref.1	206.0>141.0	20	26.60
Cymoxanil	1514	1509	1501	535 - 89 - 7	T	171.1>142.1	8	100.00	Ref.1	156.1>128.1	8	30.27
2-Phenylphenol	1525	1521	1511	90 - 43 - 7	T	170.1>141.1	24	100.00	Ref.1	141.1>115.1	18	73.17
Pentachlorobenzene	1528	1525	1511	608 - 93 - 5	T	249.9>214.9	18	100.00	Ref.1	249.9>178.9	28	65.84
Tebuthiuron	1530	1520	1514	34014 - 18 - 1	T	171.1>156.1	10	100.00	Ref.1	156.1>74.0	18	83.85
Isoprocarb	1539	1535	1531	2631 - 40 - 5	T	136.0>121.0	10	100.00	Ref.1	121.0>77.0	22	85.79
Molinate	1548	1543	1532	2212 - 67 - 1	T	126.1>55.0	14	100.00	Ref.1	187.1>126.1	6	38.33
XMC	1565	1559	1555	2655 - 14 - 9	T	122.1>107.1	14	100.00	Ref.1	107.1>77.0	18	44.38

Fig. 3 Registered Information in the Smart Pesticides Database

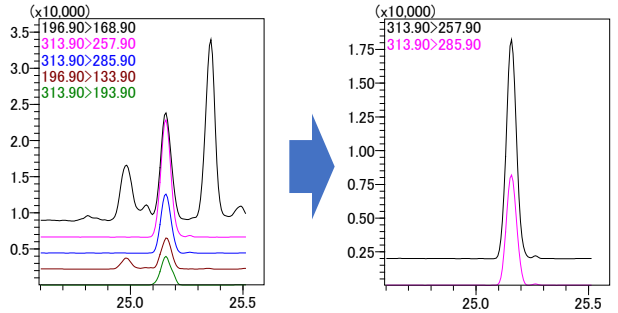

Fig. 4 Example of MRM Transition Selection for Chlorpyrifos in Spinach Extract at an Equivalent Concentration of 10 ppb

■ Sample Preparation and Pretreatment

Spinach, orange, avocado, and ginger, which contain a variety of matrix interferences, were selected as representative food matrices. Each sample was homogenized using a pre-cooled dry ice cryogenic grinding method, and 15 g of sample (1.5 g for ginger) was weighed out. Extraction and cleanup were then performed using the QuEChERS method based on AOAC Official Method 2007.01.

The sample preparation workflow is shown in Fig. 5. For extraction, a Q-sep QuEChERS extraction salt kit (Restek, AOAC 2007.01 compliant, P/N: 25852) was used. For cleanup, Q-sep QuEChERS dSPE tubes (Restek, AOAC 2007.01 compliant) were used: P/N: 26219 for spinach and ginger, and P/N: 26222 for orange and avocado.

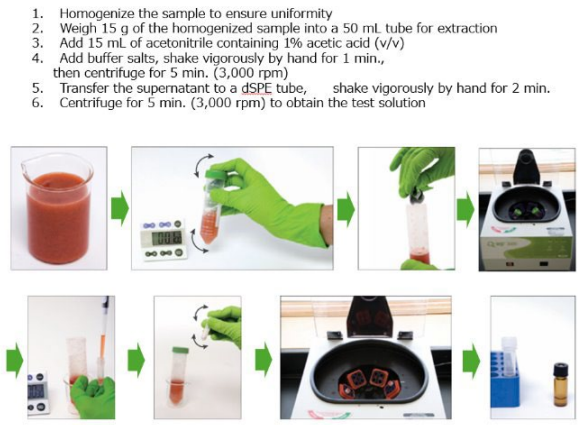

Fig. 5 Example of Sample Preparation Using QuEChERS

Calibration curves were prepared using pesticide standards diluted with acetonitrile. Standard solutions were prepared at concentrations of 0.1, 0.5, 1, 5, 10, 20, 50, 100, 200, and 400 ppb, and Analyte Protectants (APs) were added as a pseudo-matrix.

The AP mixture consisted of 3-ethoxy-1,2-propanediol, D-sorbitol, and L-gulonic acid γ-lactone. An AP solution was prepared by dissolving 500 mg of 3-ethoxy-1,2-propanediol, 50 mg of D-sorbitol, and 50 mg of L-gulonic acid γ-lactone, and making the total volume up to 50 mL with a solution of 1 % acetic acid and 12 % water in acetonitrile. This AP solution was added to the sample solutions at 10 % (v/v).

■ Analytical Conditions

The instrument configuration and analytical conditions are summarized in Table 1. Method 3 in the Smart Pesticides Database was used as the basis for the analytical method. To improve the peak shapes of low-boiling pesticides in acetonitrile, the initial GC oven temperature was changed to 70 ˚C.

■ Data Analysis

LabSolutions Insight™, a quantitative data processing software package designed for high-throughput sample analysis, was used for data analysis, with Peakintelligence for GCMS applied as the peak integration algorithm (Fig. 6). Peakintelligence is an AI-based waveform processing algorithm that uses machine learning to emulate the peak processing performed by experienced analysts. It requires no operator-defined parameter settings and provides peak integration performance comparable to that of skilled users.

For more information on improving the efficiency of pesticide data analysis using Peakintelligence for GCMS, please refer to Application News 01-00585-EN, "Time-Saving Data Processing for Pesticide Residues with Peakintelligence for GCMS."

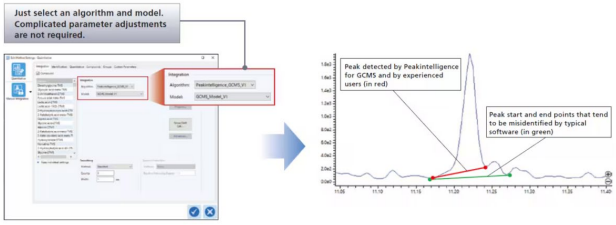

Fig. 6 Peakintelligence for GCMS

Table 1 Instrument Configuration and Analytical Conditions

Configuration		
GC-MS	:	GCMS-TQ™8040 RX
Injection Unit	:	MMI-U
Column	:	SH-I-5Sil MS (30 m × 0.25 mm I.D., 0.25 µm) (P/N: 221-75954-30)
Guard Column	:	SH-I Guard / Retention Gap Column (5 m × 0.25 mm I.D.) (P/N: 227-36303-01)
Liner	:	Xtra Inert Splitless Liner (P/N: 227-36701-01)

GC		
MMI Mode	:	Split / Splitless injection
Injection Mode	:	Pulsed Splitless
MMI Program	:	250 ˚C
Sampling Time	:	1 min
Carrier Gas Control	:	Linear Velocity (44.1 cm/s) (He)
Pulsed Injection	:	250 kPa (1.5 min)
Injection Volume	:	2 µL
Oven Program	:	70 ˚C (3 min) - (10 ˚C/min) - 130 ˚C - (4 ˚C/min) - 200 ˚C - (8 ˚C/min) - 290 ˚C (12.25 min)

MS		
Ion Source Temp.	:	230 ˚C
IF Temp.	:	280 ˚C
Acquisition Mode	:	MRM
Loop Time	:	0.4 sec

■ Matrix Evaluation by Scan Analysis

Fig. 7 shows the total ion current chromatograms (TICCs) obtained by scan analysis of blank extracts from the four food matrices evaluated in this study: spinach, orange, avocado, and ginger. In all matrices, a large number of peaks derived from matrix components were detected. These coextractives may interfere with the MRM transitions of the target pesticides, potentially leading to reduced quantitative accuracy and false identification. These results suggest that, for such complex matrix samples, appropriate selection of MRM transitions and advanced peak processing technology are essential.

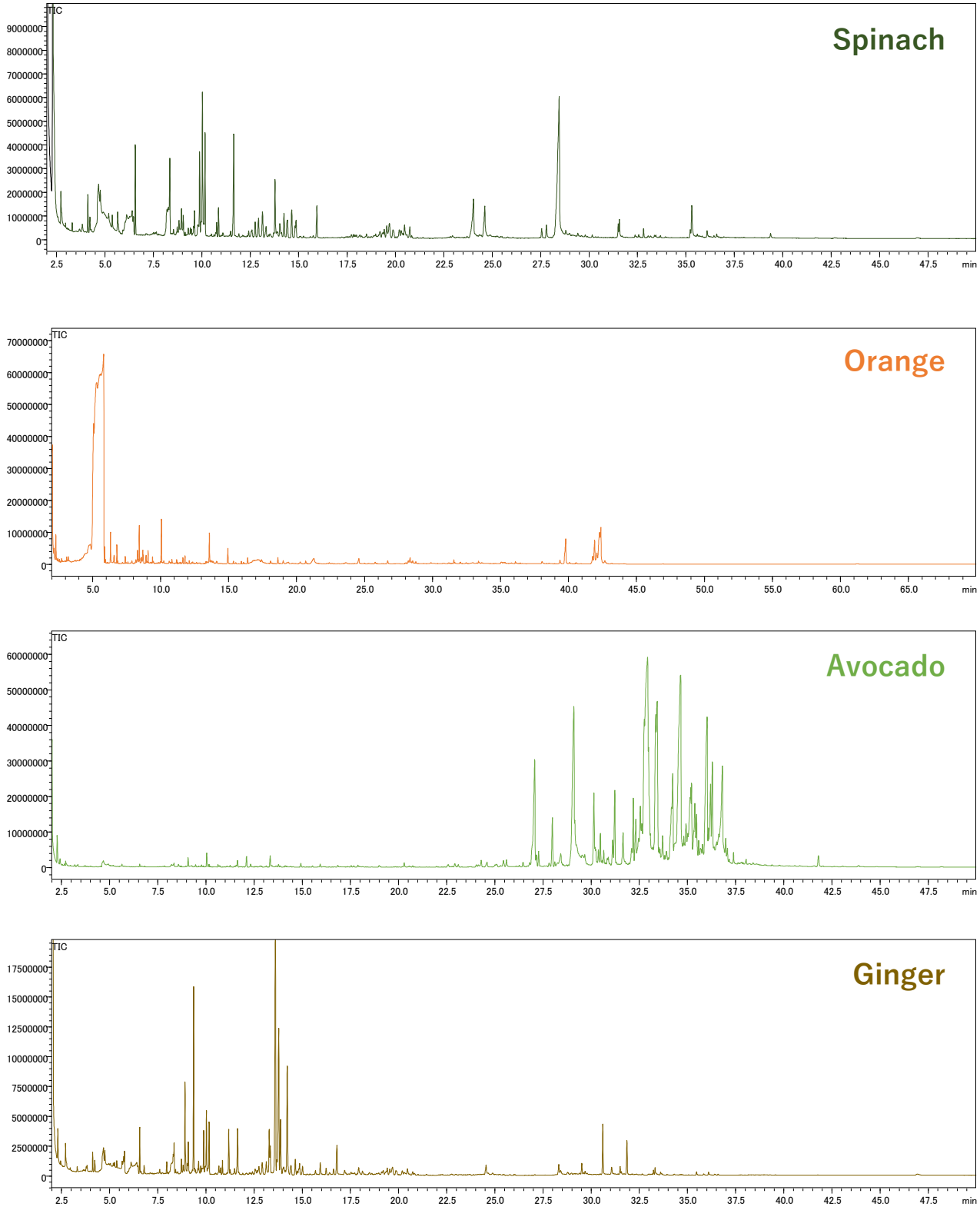

Fig. 7 Scan Analysis of Actual Samples (Total Ion Current Chromatograms, TICCs)

■ Results for Standard Solutions

The linearity of the calibration curves and the repeatability of peak areas were evaluated. Calibration curves were prepared using standard solutions containing AP over the range of 0.1 to 400 ppb (up to 200 ppb for some compounds). Of the 386 pesticides evaluated, 362 compounds (approximately 94 %) showed good linearity with correlation coefficients (R^2) of 0.99 or higher (Fig. 8). Among these, 142 compounds (approximately 39 %) were detectable at 0.1 ppb (Fig. 9). Repeatability at 10 ppb was assessed by repeated analysis (n = 6), and stable results were obtained for 344 of the 362 compounds (approximately 95 %), with %RSD values below 10 % (Fig. 10). Fig. 11 shows representative calibration curves and chromatograms obtained near the LOQ for selected pesticides.

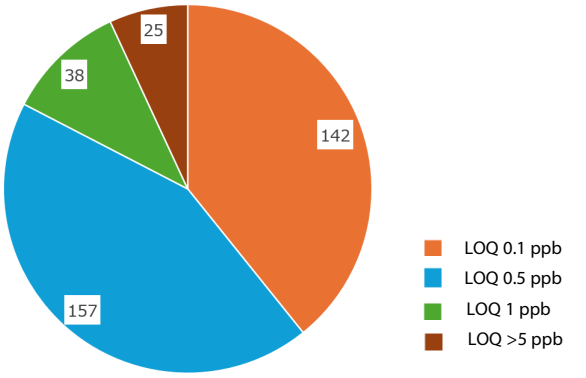

Fig. 9 Distribution of LOQs for 362 Compounds, with numbers indicating the number of compounds

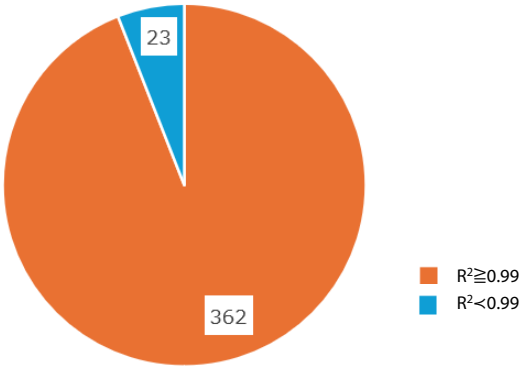

Fig. 8 Distribution of Calibration Curve Linearity ($R^2 \geq 0.99$), with numbers indicating the number of compounds

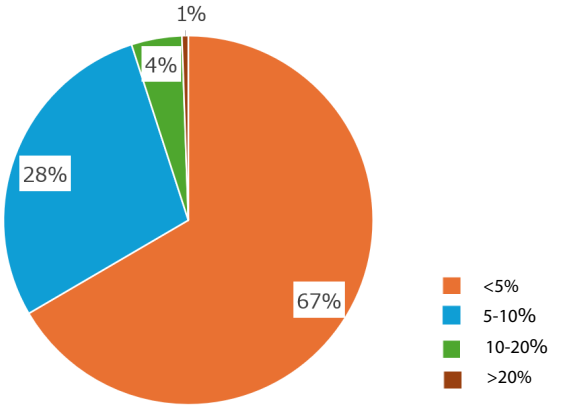

Fig. 10 Distribution of peak area repeatability (%RSD) at 10 ppb for standard solutions (362 compounds)

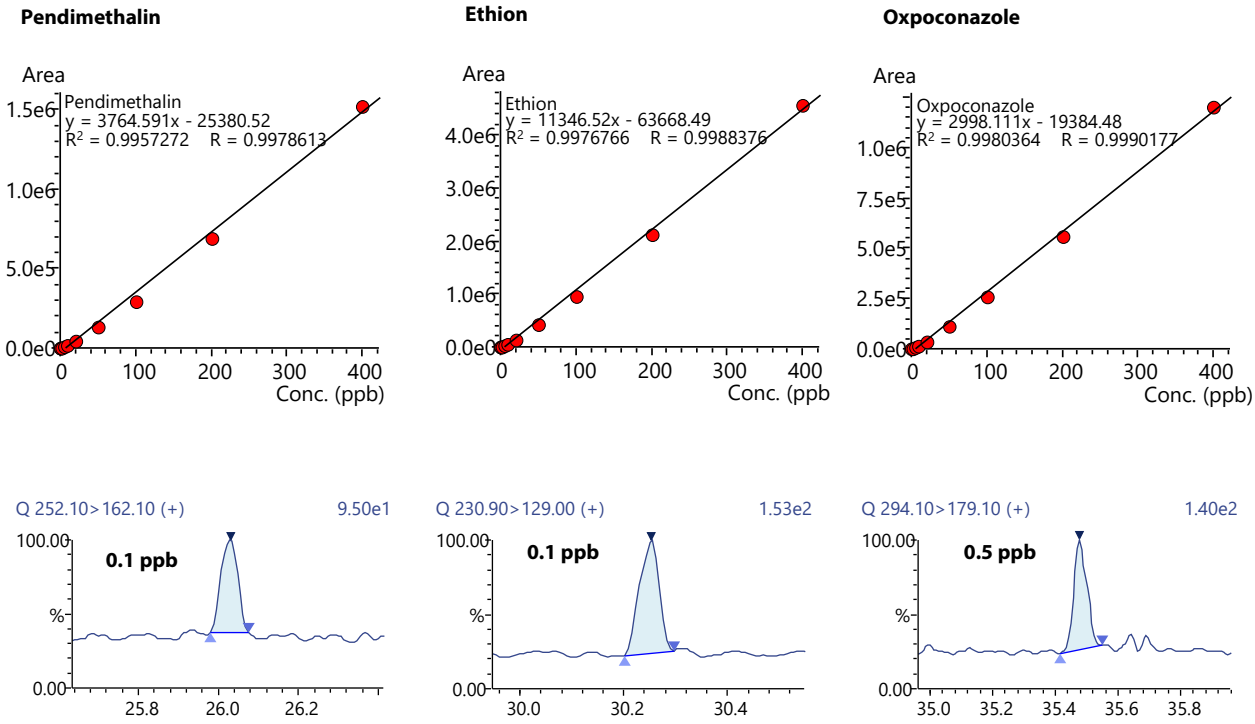

Fig. 11 Calibration Curves and Chromatograms at the Limit of Quantification (LOQ)

■ Results for Standard Solutions

Pesticides equivalent to 10 ppb were spiked into extracts of four food matrices—spinach, orange, avocado, and ginger—and peak area repeatability (%RSD) was evaluated by six replicate analyses.

The repeatability results for the matrix-spiked samples are shown in Fig. 12 and Table 2 (partial excerpt). The samples analyzed in this study contained large amounts of pigments, acids, lipids, and other matrix components, representing challenging matrices for GC-MS/MS analysis. Nevertheless, good repeatability was achieved, with %RSD values below 10 % for more than 80 % of the pesticides evaluated.

■ Conclusion

In this Application News, an example of simultaneous multiresidue pesticide analysis in food using a triple quadrupole GC-MS/MS equipped with a Multi-Mode Inlet (MMI) was presented. By adopting the MMI, instrument downtime associated with inlet maintenance can be significantly reduced while maintaining high quantitative performance. In addition, by combining automated method creation with the Smart Pesticides Database and efficient data analysis using the AI-based waveform processing algorithm Peakintelligence for GCMS, highly accurate results were obtained even for complex food matrices. This system optimizes the overall analytical workflow, from method development and maintenance to data analysis, and can make a substantial contribution to improving productivity in high-throughput pesticide residue analysis.

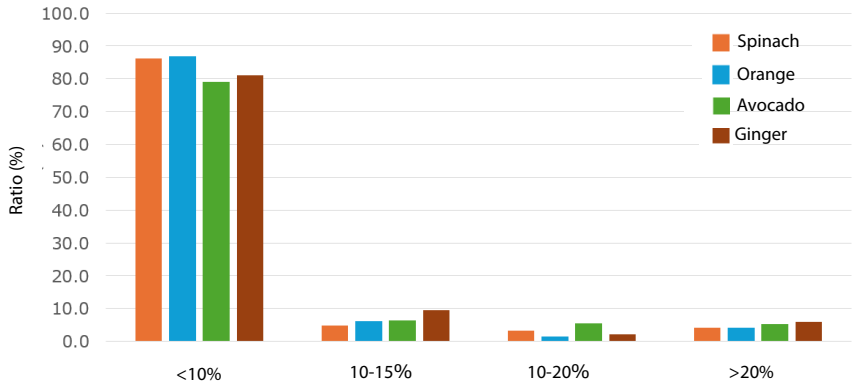

Fig. 12 Distribution of Peak Area Repeatability (%RSD) for Each Matrix

Table 2 Peak Area Repeatability (%RSD) for Pesticide-Spiked Samples at an Equivalent Concentration of 10 ppb (Excerpt)

Compound Name	Spinach	Orange	Avocado	Ginger
Dichlorvos	3.4	4.5	2.6	3.1
Nereistoxin	4.2	1.8	3.0	2.6
Allidochlor	4.9	2.2	2.4	2.5
Dichlobenil	2.9	2.4	0.8	1.8
EPTC	3.8	2.4	1.0	1.6
Biphenyl	3.3	2.7	1.4	1.1
Mevinphos-1	5.5	2.6	11.9	4.2
Mevinphos-2	3.5	3.6	3.3	3.4
Butylate	4.4	3.3	1.8	2.7
Chlormephos	3.3	3.2	1.7	1.8
Etridiazole	4.2	3.7	2.1	2.5
Thiocyclam	4.7	3.2	2.1	2.2
Methacrifos	3.4	3.7	1.5	2.4
Crimidine	2.5	2.8	1.5	2.1
Chloroneb	4.0	3.8	2.4	5.3
2-Phenylphenol	5.7	2.8	3.0	2.0
Isoprocarb	2.6	3.3	3.3	2.1
Molinate	3.8	3.9	2.3	2.1
XMC	2.1	3.5	3.9	3.2
Omethoate	14.5	10.8	14.4	10.5
Tecnazene	4.1	4.2	2.0	1.9
Xylylcarb	9.3	4.8	4.8	14.8
Propachlor	2.5	3.5	2.4	1.9
Propoxur	3.0	3.5	5.1	4.6
Chlorethoxyfos	4.9	2.3	5.9	1.7
Demeton-S-methyl (Methyl demeton)	2.6	4.9	4.1	3.6
Diphenylamine	1.8	3.5	1.6	2.9
Ethoprophos	3.8	4.1	4.4	3.4
Dichlofluanid metabolite	14.6	11.7	8.3	10.7
Ethalfluralin	6.5	3.3	4.7	2.5
Chlorpropham	3.0	3.5	2.8	2.0
2,6-Dichlorobenzamide	4.0	8.1	3.1	3.8
Dioxabenzofos (Salithion)	3.2	2.9	4.2	1.4
Dicrotophos	4.0	5.2	10.3	3.1

Compound Name	Spinach	Orange	Avocado	Ginger
Trifluralin	5.0	5.4	6.3	1.8
Sulfotep	5.3	4.0	2.4	1.6
Benfluralin	7.5	4.2	5.6	4.3
Cadusafos	4.9	3.8	1.7	2.4
Di-allate-1	5.2	5.3	4.3	2.7
Phorate	2.2	4.7	2.6	3.0
alpha-BHC	2.8	3.0	1.7	3.6
Di-allate-2	4.6	3.2	3.6	3.5
Thiometon	6.4	3.1	6.3	4.0
Dicloran	8.0	8.0	7.3	5.5
Dimethoate	6.5	8.7	8.0	11.0
Furilazole	4.3	2.6	3.1	3.7
Carbofuran	7.8	5.0	13.2	6.3
beta-BHC	6.0	4.9	2.4	3.1
Simazine	5.2	4.0	2.4	3.1
Dimethipin	7.9	9.2	19.1	10.0
Quintozene	9.2	7.7	2.7	2.7
Swep	4.6	3.8	2.7	7.4
Atrazine	5.8	4.4	2.1	3.2
Clomazone	2.9	2.5	2.2	2.0
Chlorbufam	5.5	7.9	5.0	6.3
gamma-BHC (Lindane)	3.9	6.8	3.6	5.2
Propazine	2.6	5.1	3.0	2.5
Tolylfluanid metabolite	15.2	13.6	19.0	3.8
Dioxathion deg.	6.9	6.0	8.5	6.4
Cyanophos	3.6	5.8	2.3	2.4
Terbufos	4.8	2.9	3.5	1.5
Pyroquilon	3.4	4.2	3.7	2.5
Fonofos	5.2	4.2	2.9	4.0
Propyzamide	3.8	4.0	2.1	1.7
Chlorothalonil	8.9	8.2	14.3	6.7
Phosphamidon-1	6.1	5.8	19.7	6.4
Pyrimethanil	3.3	2.9	1.3	2.6
Diazinon	3.2	2.4	2.3	1.2

Table 2 Peak Area Repeatability (%RSD) for Pesticide-Spiked Samples at an Equivalent Concentration of 10 ppb (Continued)

Compound Name	Spinach	Orange	Avocado	Ginger
Disulfoton	4.0	7.3	5.4	5.6
delta-BHC	2.9	2.6	9.0	7.2
Terbacil	4.2	7.3	6.2	8.4
Isazofos	4.1	2.9	2.4	5.5
Prohydrojasmon-1	2.6	5.4	4.9	2.9
Tri-allate	1.9	3.4	1.1	2.3
MCPA-thioethyl	5.4	4.6	2.8	3.1
Etrimfos	4.8	6.7	2.6	3.6
Tefluthrin	2.7	4.2	0.5	1.9
Iprobenfos	2.7	2.7	1.9	2.0
Oxabetrinil	4.4	10.4	17.7	3.1
Tebupirimfos	3.9	3.9	2.1	4.9
Benoxacor	4.9	6.6	3.0	2.1
Prohydrojasmon-2	7.2	9.5	6.6	5.0
Formothion	3.6	5.6	5.2	7.6
MCPB-ethyl	2.5	2.9	1.6	1.2
Benfuresate	3.3	2.6	2.9	3.1
Phosphamidon-2	2.9	7.1	14.4	6.9
Dimethenamid (Dimethenamid-P)	3.6	3.4	2.4	2.3
Dichlofenthion	1.8	4.3	3.0	2.0
Propanil	2.5	1.8	5.8	5.2
Bromobutide	3.3	7.3	4.9	4.7
Terbucarb	3.2	3.4	1.1	1.0
Chlorpyrifos-methyl	3.0	7.7	3.2	3.9
Metribuzin	5.2	2.7	3.2	3.7
Acetochlor	2.8	3.8	2.3	2.5
Oxpoconazole-formyl deg.	2.5	4.3	6.3	3.4
Vinclozolin	6.3	5.3	3.5	6.9
Parathion-methyl	6.0	6.9	3.0	5.5
Tolclofos-methyl	3.1	3.9	1.7	2.5
Simeconazole	4.8	6.2	4.7	3.0
Alachlor	3.3	3.4	1.2	3.4
Spiroxamine-1	3.4	3.8	0.7	2.1
Simetryn	3.2	5.1	4.7	4.5
Metalaxyl (Mefenoxam)	2.3	5.9	3.8	2.2
Fenchlorphos	2.7	2.7	2.9	2.5
Ametryn	5.6	3.0	1.9	2.5
Cinmethylin	4.6	7.0	3.1	2.8
Prometryn	4.0	1.4	2.0	3.4
2-(1-Naphthyl)acetamide	4.1	6.4	2.3	4.6
Dithiopyr	4.4	4.2	2.0	2.6
Fenitrothion	5.9	4.7	2.6	2.6
Pirimiphos-methyl	5.7	2.6	1.6	3.2
Terbutryn	5.7	4.1	2.2	2.8
Spiroxamine-2	2.9	4.8	7.0	3.5
Ethofumesate	4.4	4.4	2.8	2.0
Dichlofluanid	4.0	7.3	7.2	5.0
(E)-Dimethylvinphos	2.8	5.5	8.5	3.6
Bromacil	10.6	11.1	6.7	15.0
Esprocarb	3.0	4.0	0.8	2.1
Malathion	3.9	5.5	6.2	3.6
Metolachlor (S-Metolachlor)	3.6	3.5	1.3	1.9
Chlorpyrifos	4.1	5.1	3.5	2.0
Thiobencarb	2.3	4.8	3.8	4.0
(Z)-Dimethylvinphos	4.5	4.7	11.1	5.7
Fenthion	2.0	5.0	1.9	3.9
Chlorthal-dimethyl	4.8	4.2	1.4	1.1
Cyanazine	7.0	6.6	11.0	9.9
Diethofencarb	5.0	3.7	2.7	3.2
Parathion	7.8	5.3	7.8	4.2
Fenpropimorph	2.6	3.4	1.3	2.0
Phthalide	2.8	5.8	2.8	2.1
Triadimefon	4.1	4.7	1.4	3.9
Imibenconazole-debenzyl	3.5	9.0	5.2	14.1
Diclobutrazol	2.4	3.1	3.9	4.4
Flusilazole	6.2	5.6	4.0	2.7
Buprofezin	6.1	4.2	3.0	2.7
Azaconazole	3.4	2.5	2.0	2.4

Compound Name	Spinach	Orange	Avocado	Ginger
Isocarbophos	3.8	4.7	6.5	5.2
Isofenphos oxon	2.9	4.0	4.6	3.1
Tetraconazole	3.8	5.9	3.1	4.6
Bromophos	2.8	5.1	5.2	4.1
Fosthiazate-1	6.0	10.9	19.1	6.5
Diphenamid	2.4	3.0	2.1	1.5
Fosthiazate-2	4.0	8.3	19.3	13.0
Thiamethoxam deg.	27.2	2.1	2.4	8.4
Cyprodinil	3.6	4.6	2.5	2.9
Pendimethalin	6.3	3.0	3.5	6.6
(E)-Chlorfenvinphos	4.6	5.9	7.2	3.1
Penconazole	5.8	2.6	1.6	3.6
Tolylfluanid	2.0	1.2	5.7	3.4
Dimethametryn	3.4	3.5	2.1	1.4
(Z)-Pyrifenox	7.0	10.3	8.6	10.1
Chlozolinate	4.6	5.6	6.6	3.8
Ethychlozate	10.2	5.4	2.4	7.5
Thiabendazole	3.0	3.3	21.2	6.8
Isofenphos	4.5	4.2	2.2	1.2
(Z)-Chlorfenvinphos	3.7	4.8	3.7	4.2
Mecarbam	4.6	7.2	5.6	11.2
Phenthoate	3.9	5.0	3.2	3.9
Diclocymet-1	4.2	2.9	4.2	3.1
Quinalphos	4.1	8.3	12.5	3.5
Dimepiperate	3.4	2.4	1.9	2.0
Folpet	11.2	10.0	19.8	10.2
Procymidone	2.2	2.9	2.5	4.0
Triadimenol-1	7.1	6.9	11.3	6.1
Zoxamide deg.	17.7	5.2	2.3	3.3
Chinomethionat	3.3	1.8	4.2	7.9
Chlorbenside	2.8	5.9	2.8	4.3
Triadimenol-2	3.6	6.8	3.0	4.1
Bromophos-ethyl	5.6	5.5	2.4	2.8
Diclocymet-2	3.8	2.1	2.8	2.2
(E)-Pyrifenox	6.1	6.0	3.3	2.8
Propaphos	2.4	3.7	1.2	3.0
Paclobutrazol	4.2	2.7	1.9	2.2
Tetrachlorvinphos	3.0	4.9	16.2	9.6
Trichlamide	2.7	4.3	3.0	2.4
alpha-Endosulfan	10.0	5.1	11.7	7.1
Disulfoton sulfone	2.3	3.4	10.6	7.2
Fenothiocarb	2.9	3.0	1.4	2.0
Butachlor	3.5	6.0	1.5	2.8
Ditalimfos	7.3	7.1	6.0	4.2
Flutriafol	1.2	5.9	2.3	4.5
Butamifos	7.7	7.2	4.2	7.1
Napropamide	3.0	5.0	2.0	8.3
Chlorfenson	2.5	3.7	5.5	1.4
Fenamiphos	6.6	6.0	3.1	4.3
Hexaconazole	4.1	13.1	6.9	11.3
Flutolanil	1.7	2.0	3.3	2.5
Prothiofos	4.6	5.6	2.4	3.3
(E)-Metominostrobin	3.2	5.0	0.9	3.1
Isoprothiolane	7.0	2.5	2.1	5.2
Pretilachlor	3.0	7.6	4.1	4.7
Profenofos	6.1	9.2	8.0	7.4
Uniconazole (Uniconazole-P)	5.8	4.7	8.3	4.7
Tribufos	5.7	6.4	7.3	4.3
Myclobutanil	1.3	4.4	3.9	1.2
Oxadiazon	4.6	5.7	4.7	4.0
Flamprop-methyl	2.9	3.8	4.3	2.3
Thifluzamide	3.3	5.5	3.3	3.3
Carboxin	2.1	2.4	0.7	3.8
Bromopropylate	0.8	1.1	1.9	2.4
Piperophos	3.6	5.3	6.0	4.6
Bifenthrin	2.9	3.1	2.3	3.2
Tetramethrin-2	5.9	3.4	n.d.	7.9
Fenoxycarb	2.0	6.6	5.5	4.9

Table 2 Peak Area Repeatability (%RSD) for Pesticide-Spiked Samples at an Equivalent Concentration of 10 ppb (Continued)

Compound Name	Spinach	Orange	Avocado	Ginger
Bupirimate	2.9	4.8	3.3	5.0
Oxyfluorfen	10.5	7.8	5.2	11.7
(Z)-Metominostrobin	2.7	3.5	4.0	4.2
Kresoxim-methyl	3.6	3.4	3.3	1.8
Chlorfenapyr	22.7	12.8	14.9	11.2
Isoxathion	11.1	6.5	5.4	10.4
Cyflufenamid	7.3	6.6	10.1	7.1
Nitrofen	3.4	7.8	4.2	5.4
Chlorthiophos-1	17.2	16.0	10.3	11.0
Fenoxanil	2.7	4.6	4.0	2.8
1,1-Dichloro-2,2-bis(4-ethylphenyl)ethane	4.4	4.1	1.6	3.7
beta-Endosulfan	6.4	5.7	8.5	10.1
Chlorthiophos-2	5.9	4.2	6.1	9.9
Chlorobenzilate	2.1	3.7	1.2	1.6
Chloropropylate	3.8	4.5	1.2	2.6
Fensulfothion	6.2	7.6	5.5	6.8
Diniconazole	5.1	4.1	3.2	1.0
(Z)-Pyriminobac-methyl	3.2	4.3	1.1	2.3
Flufenpyr-ethyl	5.2	4.6	3.5	4.8
Ethion	4.5	4.5	1.7	4.5
Chlorthiophos-3	3.3	4.4	2.6	3.2
Mepronil	3.1	2.7	3.1	4.2
Fluacrypyrim	5.1	6.0	3.6	3.0
Sulprofos	6.4	3.6	2.8	4.7
Triazophos	2.3	4.0	4.0	2.8
Chlornitrofen	5.8	7.2	5.7	8.2
Benalaxyl	4.7	4.7	5.7	3.3
Isoxadifen-ethyl	4.2	2.4	4.7	4.8
Carbophenothion	5.0	5.8	5.0	5.1
Edifenphos	6.5	7.4	16.9	9.7
Carfentrazone-ethyl	4.7	3.6	2.3	4.6
Cyanofenphos	3.4	5.0	3.5	5.8
Endosulfan sulfate	8.7	21.1	29.3	27.8
Norflurazon	4.2	4.2	1.3	3.6
Quinoxyfen	1.8	4.9	1.6	1.9
Propiconazole-1	7.7	6.8	4.9	4.7
Lenacil	2.2	5.6	3.2	4.5
Trifloxystrobin	3.0	9.2	3.4	5.7
Propiconazole-2	3.7	3.6	4.8	3.4
(E)-Pyriminobac-methyl	4.0	3.1	1.5	2.9
Pyraflufen-ethyl	2.9	3.8	4.4	2.5
Hexazinone	3.0	4.6	2.2	2.6
Thenylchlor	3.2	5.9	4.1	5.5
Tebuconazole	4.7	4.7	2.8	3.3
Diclofop-methyl	3.1	3.8	3.7	2.9
Diflufenican	3.1	3.4	2.7	1.6
Piperonyl butoxide	3.3	1.8	15.1	2.4
Epoxiconazole	2.6	2.7	1.8	3.2
Resmethrin-2 (Bioresmethrin)	3.7	2.5	17.6	3.0
Zoxamide	10.5	8.8	17.1	12.6
Mefenpyr-diethyl	3.6	3.7	1.9	1.5
Pyributicarb	3.4	4.3	1.7	3.0
Chlomethoxyfen (Chlormethoxynil)	6.9	12.5	6.4	8.8
Iprodione	9.3	6.1	n.d.	11.0
Bromuconazole-1	3.2	7.6	4.5	4.6
Phosmet	17.0	17.7	53.4	15.1
Tetramethrin-1	6.6	7.2	n.d.	7.3
EPN	4.5	5.6	n.d.	4.7

Compound Name	Spinach	Orange	Avocado	Ginger
Etoxazole	17.0	9.7	11.4	7.8
Fenamidone	3.6	6.9	3.8	5.6
Fenpropathrin	3.0	6.1	3.9	3.2
Indanofan	11.7	6.4	n.d.	5.6
Anilofos	9.8	8.7	15.5	9.5
Tebufenpyrad	5.9	3.9	2.3	3.6
Bifenox	10.2	23.0	13.6	14.6
Clomeprop	3.0	4.4	4.7	2.0
Furametpyr	5.6	3.5	5.8	4.9
Phenothrin-1	9.7	12.8	n.d.	4.8
Tetradifon	3.5	4.6	5.7	5.1
Phosalone	3.4	5.2	7.8	5.5
Phenothrin-2	4.8	7.1	9.7	4.7
Leptophos	3.0	5.0	8.1	6.2
Pentoxazone	2.9	2.5	1.8	1.4
Azinphos-methyl	18.8	14.6	28.1	13.3
Pyriproxyfen	5.2	8.7	7.3	7.1
Mefenacet	1.9	5.5	2.8	5.1
Cyhalothrin-1	3.9	4.9	1.4	7.9
Cyhalofop-butyl	3.1	4.9	2.3	4.5
Furametpyr metabolite	4.2	7.2	n.d.	7.1
Cyhalothrin-2	5.7	4.8	3.3	4.7
Fenarimol	2.4	4.1	2.6	3.6
Pyrazophos	2.5	5.3	3.6	3.5
Acrinathrin-2	7.8	8.3	13.0	4.2
Azinphos-ethyl	3.9	6.3	8.3	6.7
Dialifos	4.8	5.5	2.7	5.4
Pyraclofos	7.4	11.3	16.5	10.5
Fenoxaprop-ethyl (Fenoxaprop-P-ethyl)	2.1	4.0	2.9	4.8
Spirodiclofen	9.6	n.d.	19.8	18.6
Bitertanol-1	3.1	4.3	17.6	8.5
Permethrin-1	3.9	5.9	2.1	3.1
Fluquinconazole	2.3	2.8	3.0	3.7
Pyridaben	4.4	7.3	4.7	9.6
Permethrin-2	3.1	3.3	3.9	2.4
Dioxathion	7.2	9.7	4.0	9.1
Oxpoconazole	4.1	5.3	3.4	12.1
Butafenacil	2.7	5.0	1.6	11.7
Etobenzanid	4.3	4.5	n.d.	4.3
Fenbuconazole	1.3	4.6	2.1	8.9
Cyfluthrin-1	3.1	9.0	9.7	3.5
Cyfluthrin-2	13.7	9.5	5.1	4.7
Cyfluthrin-3	11.6	7.9	4.6	5.5
Cyfluthrin-4	6.1	11.5	10.5	9.6
Cypermethrin-1	2.0	4.0	7.9	4.5
Cypermethrin-2	1.9	6.8	3.9	2.4
Quizalofop-ethyl (Quizalofop-P-ethyl)	5.2	2.7	2.3	5.2
Cypermethrin-3	2.4	7.5	5.0	7.2
Flucythrinate-1	3.5	4.3	2.3	7.9
Cypermethrin-4	4.1	6.2	7.5	6.2
Etofenprox	2.3	3.1	2.0	2.2
Flucythrinate-2	5.6	3.3	3.1	8.9
Silafluofen	2.6	2.5	1.8	3.8
Pyrimidifen	5.6	4.6	1.2	7.3
Flumioxazin	9.9	11.6	7.4	23.9
Fenvalerate-1	8.3	6.1	3.6	12.2
Pyraclostrobin	7.2	8.3	5.4	17.8
Fenvalerate-2 (Esfenvalerate)	6.9	4.6	7.1	5.6

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