



## Large-scale screening and quantitation of pesticide residues in milk using GC-(EI)-MS/MS

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### Keywords

TraceFinder, pesticide residues, milk, QuEChERS, GC-MS/MS, TSQ 9000, quantitation, ExtractaBrite

### Goal

The objective of the experiment described here was to set up a complete analytical solution to enable commercial food testing laboratories to analyze 155 pesticide residues in milk using gas chromatography-tandem mass spectrometry. The optimized method was validated per SANTE validation guidelines and assessed for MRL compliance per the Food Safety and Standards Authority of India (FSSAI) as well as the European Commission (EC).

### Introduction

In agriculture, crops like fruits, vegetables, and cereals are treated with different types of pesticides including insecticides, herbicides, rodenticides, and fungicides. These pesticides can be transferred from plants to animals through the food chain and can accumulate in higher organisms.<sup>1</sup> Sometimes pesticides are sprayed directly on animal housing for insect pest management.<sup>2</sup> Both sources lead to the bioaccumulation of pesticides in animal products like milk and meat. Pesticide residues have a more significant impact on human health through chronic effects.<sup>3</sup> Applications of pesticides cause acute as well as chronic effects and may also lead to death in extreme cases.<sup>4</sup> Currently, there are 288 chemicals registered under the Central Insecticide Board and Registration Committee (CIBRC), Government of India.<sup>5</sup> Controlling the presence of pesticide residues in fresh milk and milk

products is a big concern for the producer, consumer, and government due to the potential health risks. Therefore, monitoring pesticide residues in milk is becoming more critical. A citrate buffered QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was used followed by gas chromatography-tandem mass spectrometry with a Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system.<sup>6</sup> The data acquisition and processing were carried out using Thermo Scientific™ TraceFinder™ software. The optimized method was validated per the SANTE/11813/2017 validation guidelines.<sup>7</sup>

## Experimental

### GC-MS/MS analysis

A Thermo Scientific™ TRACE 1310 gas chromatograph was coupled with a TSQ 9000 triple quadrupole mass spectrometry equipped with Thermo Scientific™ ExtractaBrite™ electron ionization (EI) source and vacuum probe interlock (VPI) technology. The optimized GC-MS/MS conditions are given in Table 1.

**Table 1A. GC instrument conditions**

<b>Gas chromatography method</b>	
Instrumentation:	TRACE 1310 GC with Thermo Scientific™ TriPlus™ RSH™ autosampler
Column:	Thermo Scientific™ TraceGOLD™ TG-5SIL MS, 30 m × 0.25 mm ID × 0.25 μm (P/N 26096-1420)
Injector:	Spit/Spitless (SSL)
Liner:	SSL spitless liner, single taper, deactivated (P/N 453A1925)
Injector mode:	Spitless
Spitless time:	2 min
Injection volume:	1 μL
Injector temp.:	280 °C
Column flow:	1.20 mL/min
Carrier gas and purity:	Helium (99.999%)
Purge flow:	5 mL/min
Split flow:	50 mL/min
Total run time:	32 min
GC oven program:	90 °C, 5 min 25 °C/min to 180 °C 5 °C/min to 280 °C 10 °C/min to 300 °C, 2 min

**Table 1B. MS/MS instrument conditions**

### Mass spectrometry method

Instrumentation:	TSQ 9000 triple quadrupole mass spectrometer with ExtractaBrite ion source and VPI
Method type:	Acquisition-Timed (t-SRM mode)
MS transfer line temperature:	310 °C
Ion source temperature:	280 °C
Ionization:	Electron Ionization (EI)

### Sample preparation

#### Reagents and chemicals

- Acetonitrile, Optima™ LC/MS Grade, Fisher Scientific™ [P/N 514 L-16923 U]
- Anhydrous Magnesium Sulfate, Thermo Scientific™ [P/N 80020-415-500]
- EN 15662 QuEChERS Extraction kit, Thermo Scientific™ [P/N 60105-216]
- C18 Octadecyl Endcapped, Thermo Scientific™ [P/N 80020-413-100]
- PSA (Primary Secondary Amine), Thermo Scientific™ [80020-416-100]

The EN 15662 buffered QuEChERS method<sup>6</sup> was used for extraction, as described below.

#### Sample extraction and cleanup

- Weigh 10 g homogenized sample into a 50 mL extraction tube.
- Prepare recovery spike samples (n=5 for each level) by spiking blank samples with a target list of pesticides at 0.005, 0.010, and 0.025 mg/kg.
- Add 10 mL of HPLC grade water.
- Add 10 mL acetonitrile.
- Mix vigorously for 1 minute on a vortex mixer at 2500 rpm.
- Add EN 15662 QuEChERS Extraction kit (4 g anhydrous MgSO<sub>4</sub>, 1 g sodium chloride, 1 g trisodium citrate, and 500 mg disodium citrate) to the tube and again mix vigorously for 1 minute on a vortex mixer at 2500 rpm.

- Centrifuge at 5000 rpm for 5 min.
- Transfer supernatant (1 mL) into the 2 mL microcentrifuge tube containing 150 mg MgSO<sub>4</sub>, 25 mg PSA, and 50 mg C18.
- Vortex for 1 min and centrifuge samples with 10,000 rpm for 5 min.
- Collect supernatant and transfer into a GC vial for instrumental analysis.
- Matrix-matched calibration standards:
  - Prepare blank (control) extract by following the above protocol.
  - Prepare the matrix-matched calibration standards by post-extraction spiking (Table 2) of the working standard at various concentration levels.
- Inject the final extract, as well as the matrix-matched calibration standards, into the GC-MS/MS.

### Data acquisition and processing

The data acquisition and processing were carried out by using the TraceFinder 4.1 software utilizing the instrument method conditions detailed in Table 1. The data were acquired in t-SRM mode, with two or more transitions per analyte obtained from the compound database (CDB). The target list of analytes is given in Table 3 (Appendix) with quantitative and qualitative ions, collision energies, and expected retention times (min). For data processing, the ion ratio ( $\pm 30\%$ ), retention time ( $\pm 0.1$  min), linearity ( $>0.99$  with residuals  $\pm 20$ ), recovery (70–120%) and precision ( $\pm 20\%$ ) were set as criteria with user filters per the SANTE guidelines.

## Results and discussion

### Sample preparation

Milk is a high-water matrix containing 80–90% water. The determination of pesticide residues in milk is a difficult task due to the complexity of the matrix because of high fat content (1–9%), protein levels (4–5%) and carbohydrates (4–5%), which may interfere with the analyte signals. Hence 25 mg/mL PSA and 50 mg/mL C<sub>18</sub> were used for cleanup to remove the interferences from protein and fat, which offered excellent performance of the method in terms of recovery and precision at 0.005 mg/kg.

### GC-MS/MS analysis

The gas chromatographic method is taken from Thermo Scientific™ Pesticide Analyzer Rev. 2, which offered excellent separation for the target analytes and absence of isobaric interferences from the matrix. The total ion chromatogram (TIC) is shown in Figure 1 for 155 compounds without the internal standards (Figure 1).

The number of scans across a chromatographic peak depends on the dwell time required to monitor a specific SRM transition. In general, for accurate peak integration and, in turn, for reliable quantification of a target compound, a minimum of 10 scans/peak is recommended. In this method, the automatically optimized dwell (2–10 ms) time per transitions offered at minimum 12–15 points per peak. Early eluting compounds like trifluralin have more than 15 points per peak as shown in Figure 2.

User-defined parameters for data processing include two SRM transitions per analyte, retention time, correlation coefficient, and residuals ion ratio set in the data processing method of TraceFinder software.

**Table 2. Matrix-matched calibration standards preparation**

Working standard ( $\mu\text{g/mL}$ )	Volume taken from working standard ( $\mu\text{L}$ )	Extracted matrix ( $\mu\text{L}$ )	Final concentration ( $\mu\text{g/mL}$ )	Total volume (mL)
2.000	50	950	0.100	1.0
1.000	50	950	0.050	1.0
0.500	50	950	0.025	1.0
0.200	50	950	0.010	1.0
0.100	50	950	0.005	1.0
0.050	50	950	0.0025	1.0
0.020	50	950	0.001	1.0

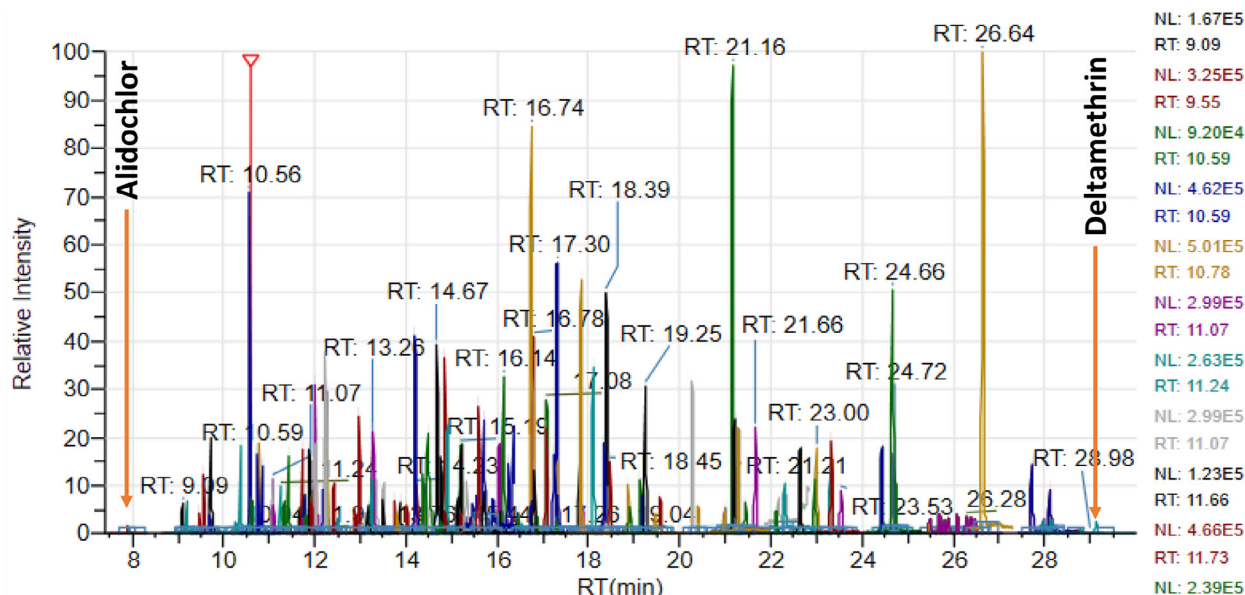


Figure 1. Overlay of extracted ion chromatograms for 155 compounds in a single window

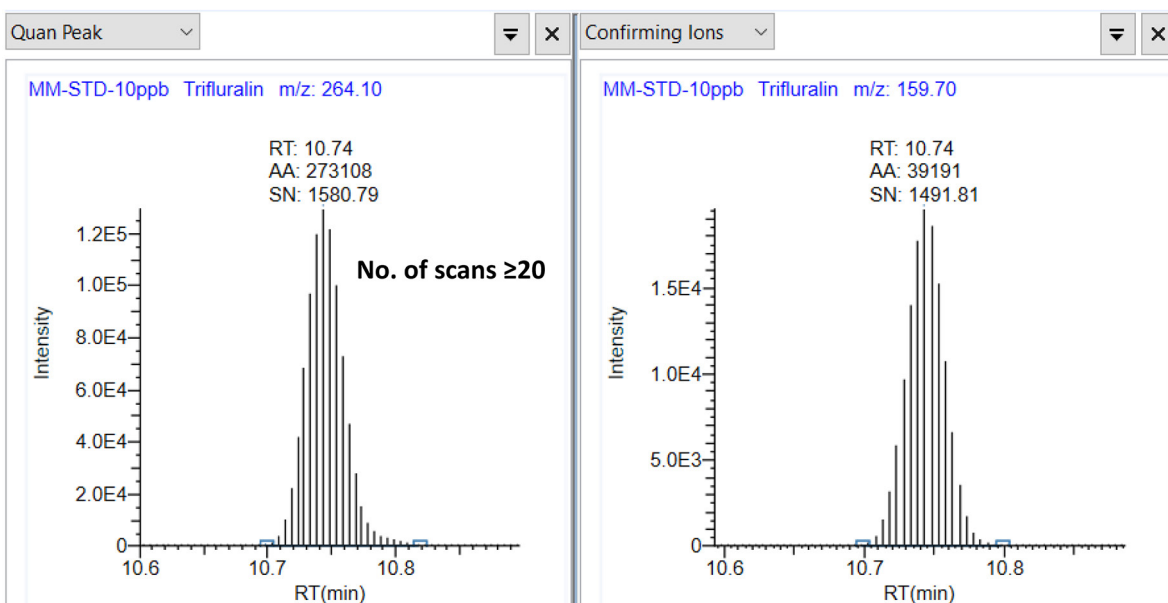


Figure 2. Impact of automatically optimized dwell time on the number of scans per peak for trifluralin

Based on these parameters, the data was processed automatically with flagging. The green flags indicated the fulfillment of user-defined criteria based on the SANTE guidelines, i.e., for ion ratio,  $\pm 30\%$ , and  $RT \pm 0.1$  min, given in the processing method (Figure 3); whereas the red flags indicated that the data must be reviewed. Overall, this flagging system minimized the data review time and improved the reporting output of the lab.

### Identification and quantitation

An excellent isomeric base to the base separation of tetramethrin isomers is offered by the optimized

chromatographic system in standards as well as spiked samples (Figure 4). Apart from this, the identification of tetramethrin isomers in milk was demonstrated with two transitions 164.0 $\rightarrow$ 107.1 (quantitative) and 164.0 $\rightarrow$ 77.1 (confirmatory) at the same retention with 91.89% (64.67–97.00%) for peak 1 and 86.65% (67.27–100.90%) of peak 2 observed ion ratio in milk against the matrix-matched standard ion ratio. The linearity for both the isomers of tetramethrin provided a correlation coefficient  $>0.999$  with  $<20\%$  RSD residuals. This approach meets the requirement of SANTE guidelines for identification and quantitation.

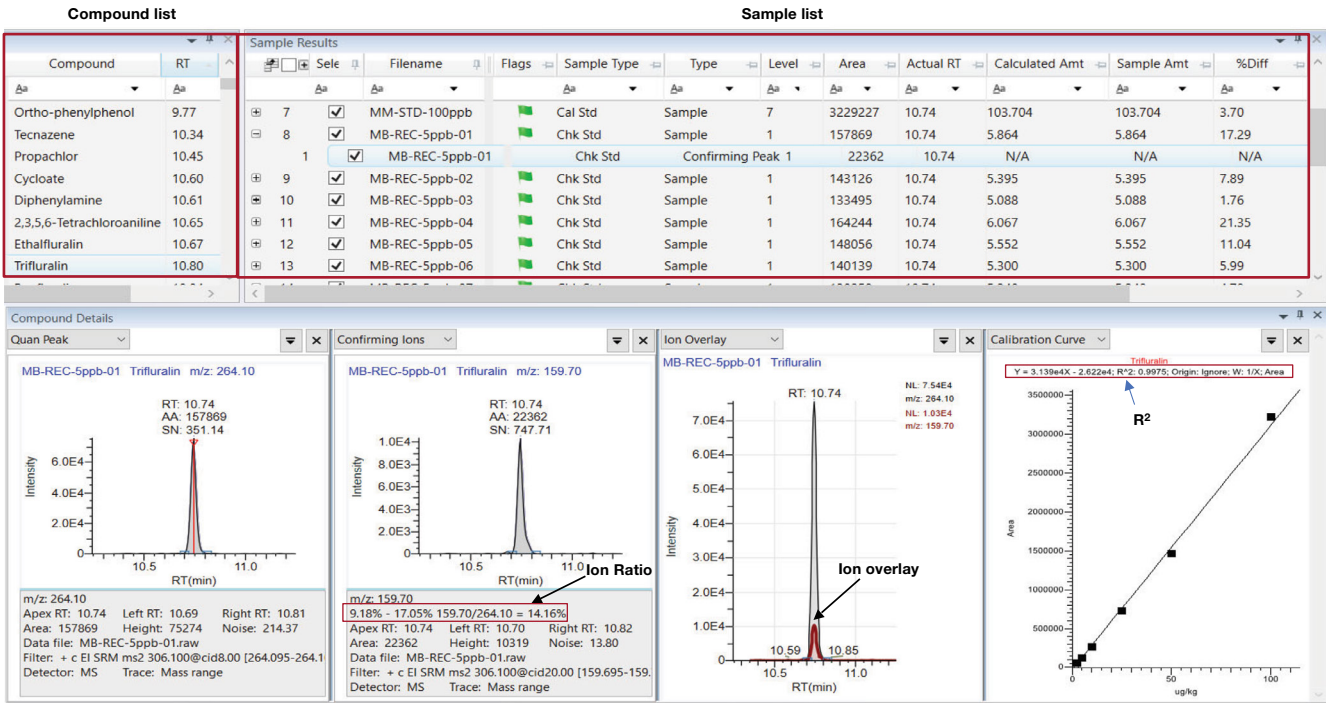


Figure 3. Identification and confirmation of the compounds based on quantitative and confirmatory ions at the same RT, ion ratio, ion overlay, and linearity

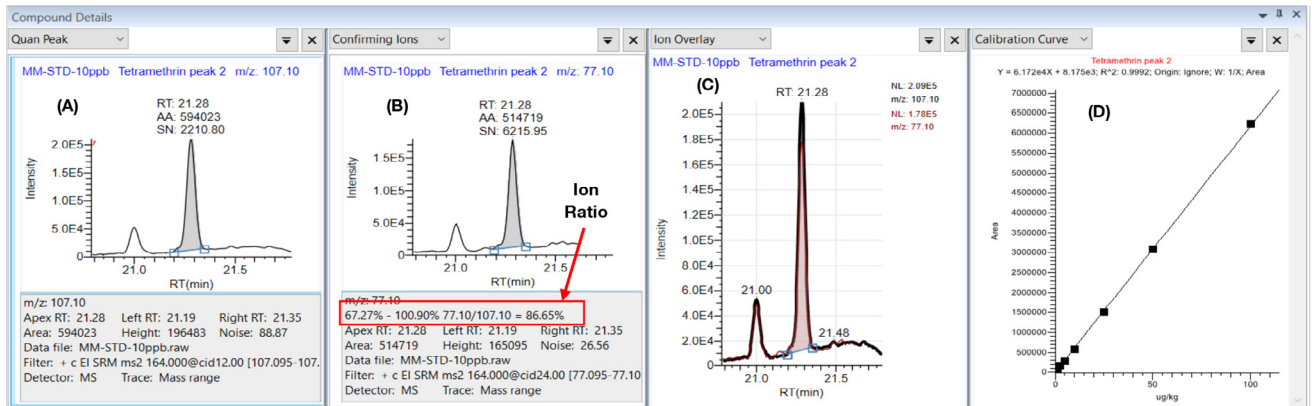
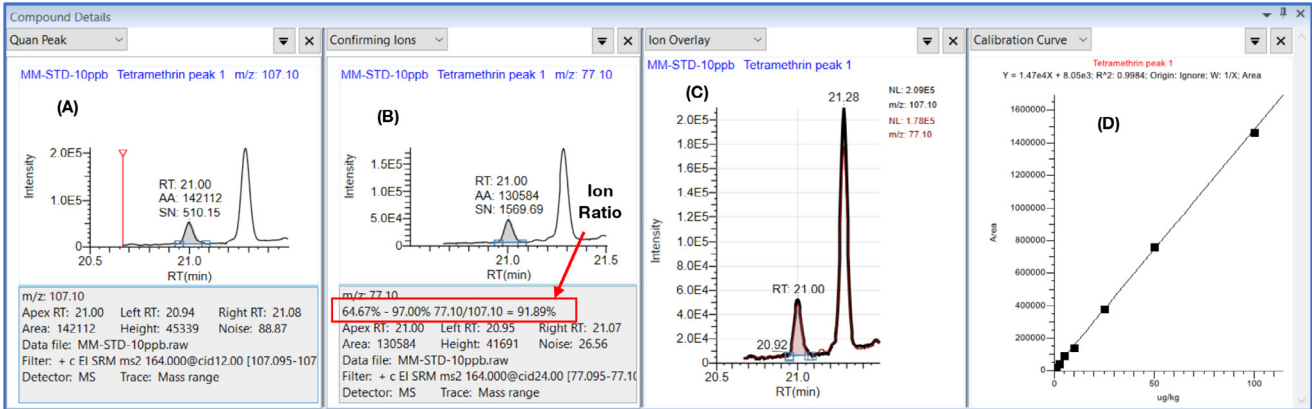


Figure 4. Effect of gradient oven program on chromatographic separation or extracted ion chromatogram for two isomers of tetramethrin. (A) Extracted ion chromatogram for quantifier ion of both the isomers of tetramethrin, (B) extracted ion chromatogram for confirming ion of both the isomers of tetramethrin, (C) ion overlay for both the isomers, (D) linearity for tetramethrin peak 1 and peak 2.

## Method performance

The linearity was plotted in the range of 0.001 to 0.10 mg/kg and offered an excellent correlation coefficient (>0.99) with <20% residuals for all the target analytes in both solvents as well as in the milk matrix. The lower calibration level (0.001 mg/kg) showed good sensitivity with  $\geq 15$ –20 signal-to-noise ratio. The solvent standards against matrix-matched calibration were compared for assessment of the matrix effect, presented in Figure 5. Matrix enhancement was observed for almost all target analytes. Hence the matrix-matched calibration standard was used for the concentration measurement in spiked samples (recovery).

The limit of quantification (LOQ) values observed in the milk matrix were in the range of 0.001 to 0.005 mg/kg. Out of 155 compounds, 134 compounds (87%) were detected in the milk matrix (post spike) at 0.001 mg/kg, 17 (11%) were detected at 0.0025 mg/kg, and only 4 (2%) at the 5.0 ng/mL level. Here, a default reporting limit for all target analytes was considered as 0.01 mg/kg. The recovery experiment was carried out at 0.005 (1/2 X reporting limit), 0.010 (1 X reporting limit)

and 0.025 (2.5 X reporting limit) mg/kg to demonstrate the recovery and precision (n=6). The average recoveries were observed in the range of 72–117% with <15 % RSD (Table 3, Appendix), which were within acceptance criteria (recovery 70–120% and precision <20%) of the SANTE guidelines.<sup>7</sup>

The optimized method was tested for repeatability of results obtained through large batch injections (n=88) by considering the commercial food testing lab schedule. The area of all injections was compared with the first injection and calculated % difference for all the compounds. The % difference observed was <8%. This reveals that the optimized method offered excellent repeatability in results. Similarly, the observed retention time repeatability for all the components between each injection is also passing the criteria, i.e., < 0.1 min. Area % difference and retention time repeatability for several compounds are shown in Figures 6 and 7, respectively. The targeted ion ratio repeatability was  $18 \pm 30\%$  (12.6–23.4) for ions 306.1→264.1 and 306.1→206. In Figure 8, the ion ratio repeatability for trifluralin was demonstrated as per the SANTE guidelines.

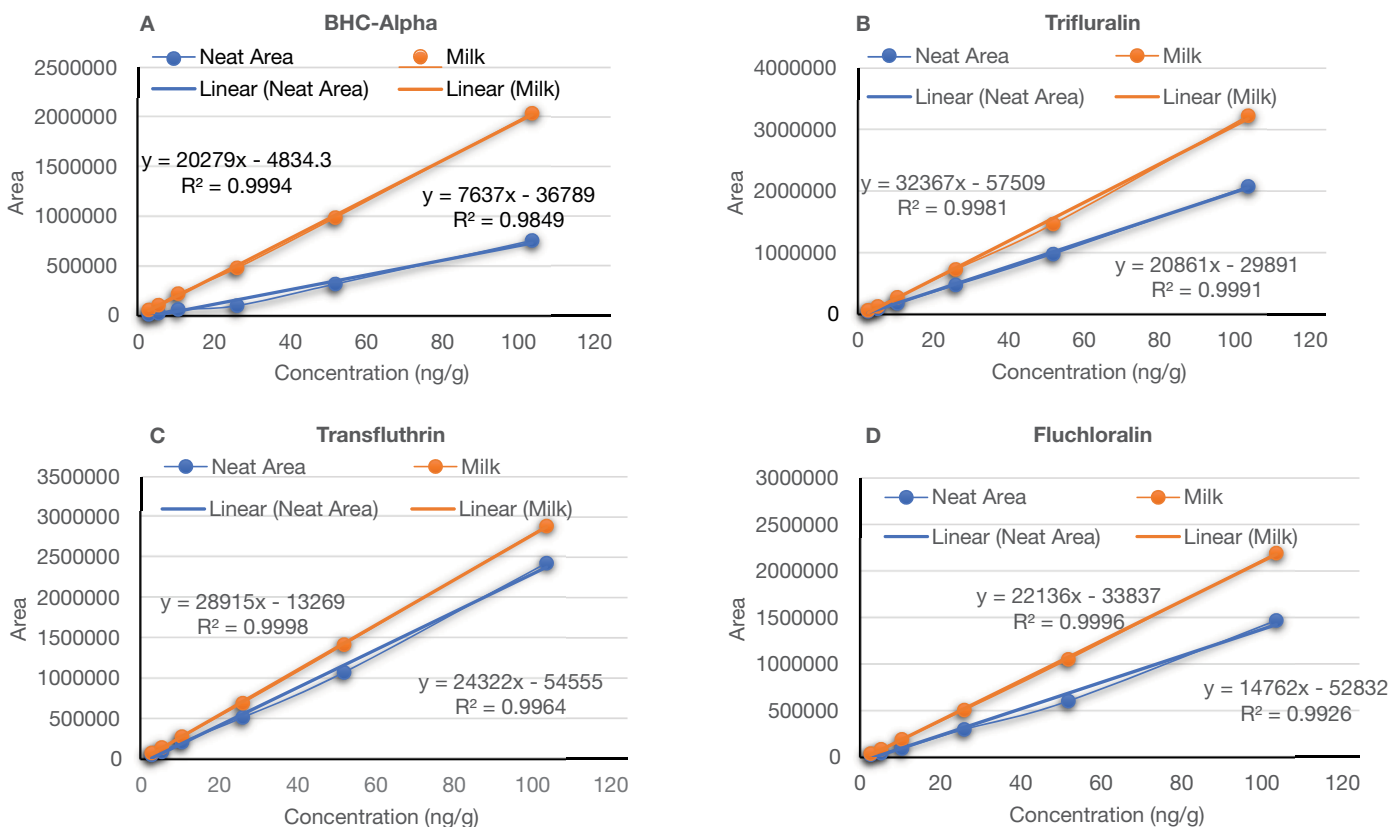


Figure 5. Comparison of neat solvent standards against matrix-matched calibration standards to estimate the matrix effect for (A) BHC-alpha, (B) trifluralin, (C) transfluthrin, and (D) fluchloralin

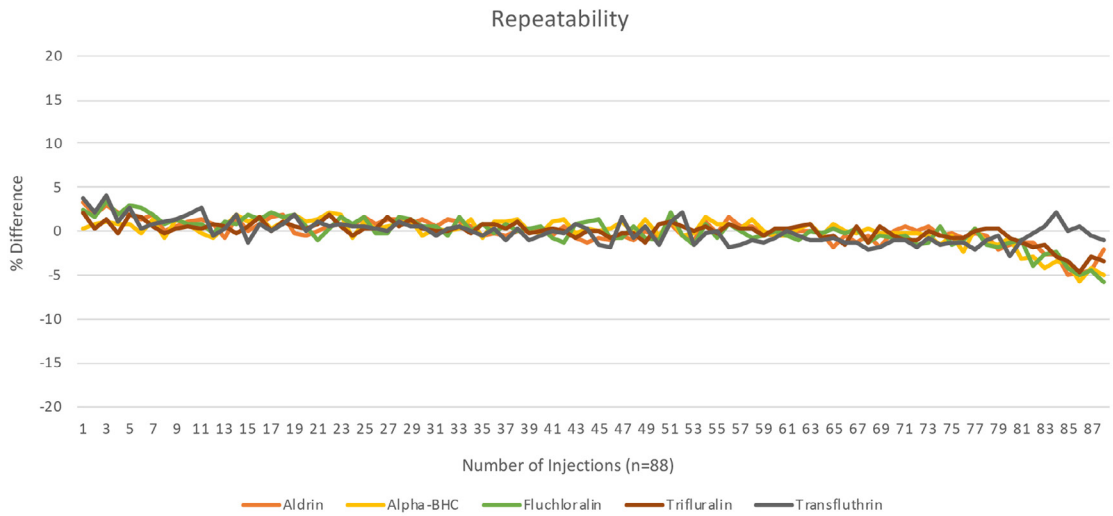


Figure 6. % difference repeatability for aldrin, BHC-alpha, fluchloralin, trifluralin, and transfluthrin (n=88)

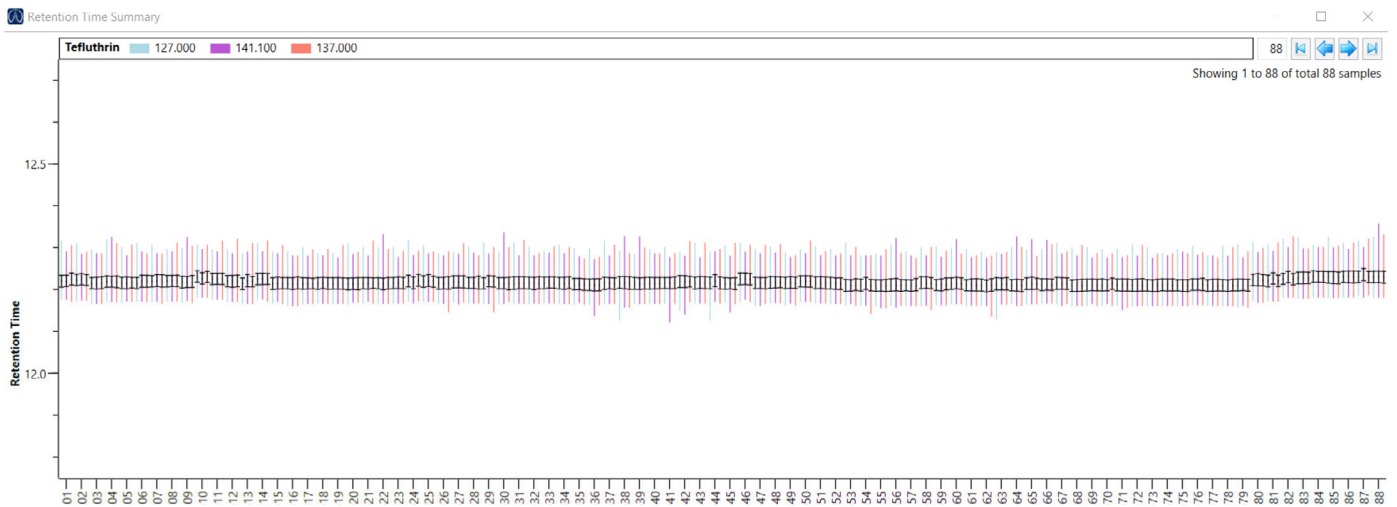


Figure 7. Retention time repeatability for trifluralin (n=88)

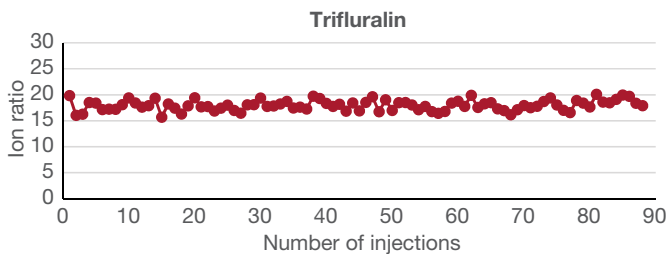


Figure 8. Ion ratio repeatability for trifluralin (n=88)

### Conclusion

This application note offered a total solution for the trace-level quantification of 155 pesticide residues in milk by using a Thermo Scientific GC-EI-MS/MS system. The use of a citrate buffered QuEChERS method for extraction and cleanup followed by analysis

using GC-MS/MS decreased downtime and increased productivity for commercial food testing laboratories. Using this approach, at least 40 injections (standards, samples, blank) could be completed in a day (24 hr cycle). Other features such as the VPI NeverVent™ technology, which allows changing of the ion source and column without venting the system, and the robustness of the ionization source enhance productivity due to the extended uptime. Features such as auto-SRM and automatic dwell time assignment reduce the time required for method development and improve the accuracy and precision of the determination. This validated method data meets the requirements of the SANTE guidelines. Also, this method complies with the EU and FSSAI MRL requirements by achieving an excellent lower limit of quantification (LOQ).<sup>8,9</sup>

## References

- Jones K. C. and De Voogt, P. *Environ. Pollut.*, **1999**, *100*, 209. [https://doi.org/10.1016/S0269-7491\(99\)00098-6](https://doi.org/10.1016/S0269-7491(99)00098-6).
- Stefanelli, P.; Santilio, A.; Cataldi L.; Dommarco, R. *J. Environ. Sci. Health B*, **2009**, *44*, 350. <https://doi.org/10.1080/03601230902801000> (accessed June 4, 2019).
- Tao, S.; Liu, W. X.; Li, X. Q.; Zhou, D. X.; Li, X.; Yang Y. F.; Coveney, R. M. *Environ. Pollut.*, **2009**, *157*, 497. <https://doi.org/10.1016/j.envpol.2008.09.005> (accessed June 4, 2019).
- Organochlorine and Organophosphorus Pesticide Residues analysis by GC-MS/MS in Raw Cow Milk. Available from: [https://www.researchgate.net/publication/303304980\\_Organochlorine\\_and\\_Organophosphorus\\_Pesticide\\_Residues\\_analysis\\_by\\_GC-MSMS\\_in\\_Raw\\_Cow\\_Milk](https://www.researchgate.net/publication/303304980_Organochlorine_and_Organophosphorus_Pesticide_Residues_analysis_by_GC-MSMS_in_Raw_Cow_Milk) (accessed June 4, 2019).
- Insecticides / Pesticides Registered under section 9(3) of the Insecticides Act, 1968 for use in the Country:(As on 15/05/2019) <http://ppqs.gov.in/insecticides-pesticides-registered-under-section-93-insecticides-act-1968-use-country-15052019> (accessed June 27, 2019).
- Citrate buffered QuEChERS method EN 15662:2008 (BS EN 15662:2008).
- SANTE guidelines, Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed (2017) SANTE/11813/2017, 21 –22 November 2017 rev.0. [https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides\\_mrl\\_guidelines\\_wrkdoc\\_2017-11813.pdf](https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_2017-11813.pdf) (accessed June 4, 2019).
- FSSAI Manual for food safety, 17th Edition-2017 (THE FOOD SAFETY AND STANDARDS ACT, 2006).
- EU MRL Database: <http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=product.resultat&language=EN&selectedID=363> (accessed June 4, 2019).

## Appendix

**Table 3 (part 1). List of pesticides with SRM transitions used and validation data (linearity, recovery, and precision)**

Compound	RT min	Quantifier ion			Confirmatory ion			R <sup>2</sup>	LOQ (mg/kg)	0.005 (mg/kg)		0.01 (mg/kg)		0.025 (mg/kg)	
		Q1	Q3	CE (V)	Q1	Q3	CE (V)			% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
2,3,5,6-Tetrachloroaniline	10.6	231	158	20	231	160	22	0.9995	0.005	86.0	6.2	90.5	4.7	86.6	2.3
3,4-Dichloroaniline	9.1	160.9	126	10	160.9	99	20	0.9995	0.005	103.8	7.0	104.4	1.8	103.0	1.4
4,4'-Methoxychlor olefin	19.26	238.1	223.1	10	308	238.2	12	0.9993	0.005	96.7	2.0	101.2	1.7	98.6	1.7
Alachlor	13.27	188.1	130	32	188.1	160.1	8	0.9988	0.005	99.0	7.8	104.9	2.6	103.5	2.1
Aldrin	14.41	330	298.9	10	262.7	192.9	28	0.9995	0.005	95.0	8.5	102.9	4.7	102.1	2.3
Allidochlor	7.9	132	56.1	8	132	49	24	0.9990	0.005	97.4	6.0	101.0	4.2	102.0	2.2
Anthraquinone	14.49	208	151.7	22	208	180	10	0.9972	0.005	97.9	3.1	101.0	2.7	96.7	1.3
Atrazine	11.67	200	122.1	8	215.1	173	8	0.9989	0.005	93.7	11.0	101.0	4.4	99.5	4.4
Azinphos-ethyl	23.54	160	77	16	132	77	12	0.9985	0.005	97.7	6.9	94.8	4.6	91.3	10.6
Benfluralin	10.79	292	264	8	292	206.1	10	0.9974	0.005	99.3	4.1	98.0	3.5	99.9	1.5
BHC, Alpha	11.26	218.8	183	8	182.8	146.7	12	0.9990	0.005	91.5	6.8	95.8	5.2	96.4	2.1
BHC, Beta	11.78	218.7	183	8	180.9	145	14	0.9983	0.005	94.1	5.4	92.3	3.5	95.6	4.9
BHC, delta	12.52	218.8	182.9	8	182.8	146.7	14	0.9985	0.005	84.5	2.5	91.8	6.6	93.3	8.2
BHC, gamma	11.9	218.7	183	8	180.9	145	14	0.9978	0.005	95.9	3.3	99.8	8.5	97.5	2.2
Bifenthrin	21.16	181	165.9	10	181	179	12	0.9997	0.005	90.1	2.2	95.6	2.4	93.3	0.9
Bromophos-ethyl	15.98	302.7	284.8	14	96.9	65	16	0.9987	0.005	92.7	11.3	96.2	4.3	97.9	4.3
Bromophos-methyl	14.85	330.8	315.8	14	328.9	313.8	14	0.9990	0.005	90.4	6.3	94.3	4.7	94.2	3.5
Bromopropylate	21.21	340.8	185	14	184.9	156.9	12	0.9992	0.005	98.5	1.8	103.4	3.7	100.0	1.1
Bupirimate	17.32	208.1	140.1	12	273.1	193.2	8	0.9993	0.005	97.2	4.9	103.9	4.5	101.9	2.9
Carbophenothion	19.2	342	157	10	157	45	12	0.9988	0.005	102.6	4.5	102.4	1.5	99.8	1.5
Carfentrazon-ethyl	19.14	311.9	150.7	18	340.1	312.1	10	0.9996	0.005	102.3	6.3	104.5	4.1	106.4	2.4
Chlorbenside	16.05	125	89	16	125	99	16	0.9997	0.005	91.1	3.5	95.2	3.5	92.2	1.9
Chlorfenapyr	17.61	248.9	112	24	248.9	137.1	18	0.9994	0.005	99.8	10.7	98.0	7.8	96.7	8.1
Chlorfenoson	16.79	174.9	111	10	111	75	14	0.9996	0.005	98.7	4.7	104.9	2.0	102.0	2.3
Chlorobenzilate	18.11	139	111	12	139	74.9	26	0.9993	0.005	98.8	3.0	102.3	3.3	100.1	0.9
Chloroneb	9.56	190.9	141	10	190.9	113	14	0.9990	0.005	90.0	5.8	96.8	4.1	97.1	1.7
Chlorpyrifos-ethyl	14.24	313.9	257.9	12	196.7	168.9	12	0.9991	0.005	98.1	3.9	102.3	1.5	100.3	3.6
Chlorpyrifos-methyl	13.11	285.9	93	20	125	47	12	0.9995	0.005	100.5	10.0	99.6	6.2	98.8	4.3
Chlorthal-dimethyl (Dacthal)	14.41	300.7	222.9	22	300.7	272.9	12	0.9983	0.005	99.0	3.3	104.4	3.2	100.2	1.3
Chlorthiophos	18.47	268.9	205	14	324.9	269	12	0.9997	0.005	96.4	3.8	101.7	3.7	99.7	1.8
Chlozolinate	15.34	331	259	8	259	187.9	12	0.9993	0.005	94.1	6.8	98.6	10.1	99.8	5.1
Clomazone	11.74	204	107	18	125	89	13	0.9989	0.005	98.5	6.9	97.8	3.8	99.8	2.4

Q1 = Precursor ion, Q3 = Product ion, CE = Collision energy



**Table 3 (part 2). List of pesticides with SRM transitions used and validation data (linearity, recovery, and precision)**

Compound	RT min	Quantifier ion			Confirmatory ion			R <sup>2</sup>	LOQ (mg/kg)	0.005 (mg/kg)		0.01 (mg/kg)		0.025 (mg/kg)	
		Q1	Q3	CE (V)	Q1	Q3	CE (V)			% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
Cycloate	10.6	154.1	83.1	8	154.1	55.1	18	0.9986	0.005	92.4	5.9	95.5	2.3	94.6	2.1
Cyfluthrin peak 1	25.49	163	127.1	6	163	65.1	26	0.9943	0.005	98.3	8.1	98.4	3.4	93.4	8.9
Cyfluthrin peak 2	25.69	163	127	6	163	91.1	12	0.9947	0.005	91.1	10.7	96.1	5.7	92.7	9.2
Cyfluthrin peak 3	25.8	163	127	6	226	206.1	163	0.9947	0.005	94.6	6.6	96.2	4.5	92.1	8.9
Cyfluthrin peak 4	25.89	163	127	6	226	206.1	12	0.9940	0.005	90.0	7.2	96.2	1.9	91.9	9.1
Cyhalothrin I (lambda)	23.01	207.9	180.9	8	197.1	141.1	10	0.9983	0.005	95.7	8.2	102.4	3.4	101.8	2.7
Cypermethrin peak 1	26.09	163	127.1	6	163	91.1	12	0.9948	0.005	97.5	6.2	99.3	2.3	93.3	9.9
Cypermethrin peak 2	26.29	163	127	6	163	91.1	12	0.9931	0.005	90.3	9.7	96.5	6.8	91.0	9.9
Cypermethrin peak 3	26.39	180.9	152.2	20	163	127	6	0.9930	0.005	86.8	7.7	95.5	2.7	92.8	8.2
Cypermethrin peak 4	26.47	163	127.1	6	180.9	152.2	20	0.9960	0.005	87.8	5.9	96.1	4.9	90.5	7.9
Cyprodinil	15.19	224.1	196.9	20	224.1	208	18	0.9984	0.005	87.3	3.8	94.6	1.3	90.1	1.8
DDD p,p	18.4	235	165.1	20	236.8	165	20	0.9993	0.005	92.2	2.1	95.3	2.5	94.2	1.7
DDD, o, p	17.31	235	199	14	235	165.1	20	0.9999	0.005	89.6	2.1	96.6	2.9	94.7	1.7
DDE o,p	16.15	246	176.1	28	317.8	248	18	0.9997	0.005	87.0	4.0	91.1	2.6	88.1	2.9
DDE p, p	17.09	246	176.1	28	317.8	246	20	0.9995	0.005	82.8	7.1	84.7	4.4	82.2	3.3
DDT o,p	18.47	235	165.1	20	236.8	165	20	0.9902	0.005	84.9	7.7	83.1	10.0	81.3	5.8
DDT p,p	19.58	235	165.1	22	236.8	165	22	0.9991	0.005	85.8	9.6	85.8	5.5	89.5	13.0
Deltamethrin	28.95	252.8	172	8	252.8	92.9	16	0.9962	0.005	106.6	7.9	101.0	2.7	92.1	9.3
Diallate-cis	11.09	234.1	150	18	234	192	12	0.9991	0.005	91.3	4.2	98.9	7.7	99.3	2.7
Diallate-trans	11.26	234.1	150	18	234.1	192	12	0.9960	0.005	101.9	3.9	97.9	7.5	97.7	4.2
Diazinon	11.99	137.1	84.1	12	137.1	54.1	20	0.9992	0.005	96.3	6.3	101.4	3.8	101.9	3.5
Dichlorobenzophenone, 4, 4	14.68	139	111	12	139	74.9	26	0.9990	0.005	95.0	3.6	99.2	2.5	95.6	1.7
Dieldrin	17.27	262.8	227.8	16	262.8	190.9	30	0.9944	0.005	110.9	10.7	105.2	6.9	103.4	9.0
Dimethachlor	12.98	197	148.1	10	134	105.1	12	0.9988	0.005	99.0	3.3	104.6	3.3	103.9	1.9
Diphenamid	14.88	239.1	167.1	8	166.8	152	16	0.9998	0.005	99.7	6.3	105.6	5.7	104.4	3.1
Diphenylamine	10.57	169	168	12	169	167	25	0.9998	0.005	95.1	3.5	100.8	3.1	99.0	1.8
Disulfoton	12.26	185.9	96.9	16	88	59.8	6	0.9980	0.005	97.1	4.0	100.0	4.2	100.1	2.7
Endosulfan ether	12.89	240.9	206	14	238.9	204	12	0.9995	0.005	90.6	7.2	95.1	6.6	97.8	2.2
Endosulfan peak 1	16.47	240.6	205.9	14	194.7	125	22	0.9982	0.005	88.8	4.6	93.3	8.0	89.5	2.7
Endosulfan peak 2	18.26	240.6	205.8	12	194.7	159	8	0.9958	0.005	87.6	11.3	99.8	9.2	96.0	4.1
Endosulfan sulfate	19.47	271.7	236.8	12	238.7	203.9	12	0.9991	0.005	97.6	5.5	99.3	4.8	98.3	6.4
Endrin-Ketone	20.99	249.8	214.9	24	173	138.1	16	0.9987	0.005	100.8	10.4	94.4	5.8	93.2	5.4
EPN	21.2	169	141	8	169	77	22	0.9977	0.005	107.2	3.4	103.4	3.6	100.3	4.5
Esfenvalerate	28.12	167	125	10	125	89.3	18	0.9991	0.005	91.3	6.4	94.3	1.7	90.0	6.4
Ethalfuralin	10.62	315.9	276.1	8	276	202	14	0.9973	0.005	101.2	3.4	104.5	5.6	100.9	3.0
Ethion	18.35	230.9	174.9	12	230.9	128.9	22	0.9985	0.005	102.0	4.9	106.8	2.8	104.3	1.1
Etofenprox	26.65	163.1	135.1	10	163.1	107.1	16	0.9998	0.005	92.3	2.4	96.5	1.4	93.0	2.1
Etridiazole (Terrazole)	9.16	211	139.9	20	211	182.9	10	0.9855	0.005	105.8	9.9	100.9	10.1	97.7	5.1
Fenarimol	23.31	139	111	14	219	107	10	0.9996	0.005	99.3	4.6	100.0	4.1	98.3	1.9
Fenchlorfos	13.52	285	270	11	287	272	11	0.9992	0.005	93.5	6.2	96.9	5.4	95.7	2.5
Fenitrothion	13.88	277	260	6	277	109	16	0.9979	0.005	100.9	5.0	105.3	4.1	105.4	3.3
Fenson	14.85	141	77	8	77	51	14	0.9998	0.005	97.6	3.6	105.8	1.2	103.5	1.2
Fenthion	14.37	278	169	14	278	109	18	0.9991	0.005	99.6	4.4	103.1	3.0	102.0	3.4
Fenvalerate	27.72	167	125	10	125	89	18	0.9964	0.005	97.4	10.3	99.6	4.2	92.0	11.9
Fluazifop-P-butyl	17.81	383.1	282.1	14	282	91.1	18	0.9986	0.005	103.3	5.1	107.3	2.4	103.9	1.5
Fluchloralin	12.03	306	264	8	264	206.1	8	0.9993	0.005	107.1	3.2	106.1	4.9	104.3	3.8
Fluquinconazole	24.73	340	298	16	340	108.1	36	0.9994	0.005	99.2	4.5	103.2	2.0	98.4	4.3
Flusilazole	17.31	233	164.9	16	233	151.9	14	0.9993	0.005	97.9	7.9	104.4	3.7	99.2	2.6

Q1 = Precursor ion, Q3 = Product ion, CE = Collision energy

**Table 3 (part 3). List of pesticides with SRM transitions used and validation data (linearity, recovery, and precision)**

Compound	RT min	Quantifier ion			Confirmatory ion			R <sup>2</sup>	LOQ (mg/kg)	0.005 (mg/kg)		0.01 (mg/kg)		0.025 (mg/kg)	
		Q1	Q3	CE (V)	Q1	Q3	CE (V)			% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
Flutolanil	16.75	281	173	10	173	145	14	0.9996	0.005	101.7	3.2	108.7	1.8	106.1	1.5
Fluvalinate peak 1	27.98	250	55.1	16	250	199.9	18	0.9988	0.005	96.9	9.4	107.6	8.3	110.4	7.7
Fluvalinate peak 2	28.13	250	55.1	16	250	200	18	0.9936	0.005	114.6	6.7	109.7	9.1	98.6	7.8
Fonofos	12.03	246	137	6	137	109	6	0.9972	0.005	97.9	7.4	105.7	4.3	100.1	3.6
Hexachlorobenzene	11.33	283.8	248.8	18	283.8	213.8	30	0.9993	0.005	72.1	2.4	73.8	4.6	71.4	1.5
Iodofenfos	16.76	376.8	361.8	16	125	79	6	0.9987	0.005	91.8	9.6	93.1	4.4	96.1	3.5
Isazophos	12.27	161	119	8	161	146	6	0.9998	0.005	101.3	4.9	106.0	5.2	104.0	2.3
Isodrin	15.16	192.9	123	28	192.9	157.2	20	0.9975	0.005	88.7	6.6	90.8	5.8	86.1	6.0
Isopropalin	14.92	280.1	238.2	8	280.1	180.2	10	0.9980	0.005	109.0	2.0	105.1	2.3	101.5	2.4
Leptophos	22.34	171	124.3	10	171	77.1	18	0.9995	0.005	83.7	4.3	85.2	3.5	83.2	4.4
Metazachlor	15.22	209	132.1	16	133.1	132.1	12	0.9993	0.005	100.9	3.2	104.2	3.5	102.2	0.8
Methacrifos	9.47	240	180	10	180	93	10	0.9983	0.005	98.7	7.0	100.7	4.3	104.6	3.9
Methoxychlor	21.44	227.1	169.1	22	227.1	141.1	32	0.9994	0.005	103.3	5.9	97.5	7.1	98.5	11.2
Metolachlor	14.21	238.1	162.2	10	162.1	132.9	14	0.9998	0.005	102.2	3.7	107.9	1.9	107.7	2.4
MGK-264 A	14.86	164	93.1	10	164	98.1	10	0.9999	0.005	92.8	8.4	99.1	4.3	97.8	5.2
MGK-264 B	15.21	164	98	10	164	67.1	8	0.9997	0.005	99.1	7.5	101.3	4.1	102.4	2.5
Myclobutanil	22.97	179	125	14	179	151.7	8	0.9992	0.005	103.3	4.6	105.2	3.8	102.6	3.1
Nitralin	17.24	316.2	274	8	274	216	8	0.9923	0.005	117.6	1.7	114.4	3.1	115.0	2.6
Nitrofen	17.87	202	139	24	283	202	10	0.9985	0.005	100.7	4.4	102.4	5.3	101.2	2.5
Nonachlor-cis	16.55	408.6	300	18	262.8	192.8	28	0.9976	0.005	86.9	14.7	93.4	8.1	88.5	4.4
Nonachlor-trans	18.4	408.7	300	18	236.8	142.9	24	0.9983	0.005	83.1	4.6	95.6	7.7	92.1	4.4
Ortho-phenylphenol	9.72	170.1	141.1	22	170.1	115	34	0.9993	0.005	95.9	1.6	98.0	3.5	99.5	2.6
Oxadiazon	17.08	174.9	112	12	174.9	76	28	0.9991	0.005	94.5	2.7	100.6	3.8	98.3	2.7
Oxyfluorfen	17.29	252	146	30	252	169.8	28	0.9993	0.005	92.3	9.1	106.6	7.1	102.4	3.3
Paclobutrazol	16.26	236	125	12	236	167	10	0.9991	0.005	107.2	7.4	117.0	2.1	110.5	2.6
Parathion (ethyl)	14.46	291	109	12	109	81	10	0.9976	0.005	102.4	7.2	110.6	4.7	111.3	2.5
Parathion-methyl	13.28	263	109	12	124.9	79	6	0.9978	0.005	103.1	8.9	103.9	6.9	103.6	3.6
Pebulate	9.19	128	57	8	203	128	8	0.9993	0.005	94.4	3.0	95.7	4.4	96.2	5.5
Penconazole	15.33	248	192	12	248	157	22	0.9982	0.005	96.1	7.6	103.6	3.6	99.5	3.4
Pendimethalin	15.14	252.1	162	8	252.1	161	14	0.9962	0.005	100.8	7.9	105.4	3.2	100.1	1.5
Pentachloroaniline	12.89	264.8	193.6	18	264.8	202.8	20	0.9989	0.005	88.3	4.3	88.4	3.9	87.4	4.0
Pentachloroanisole	11.43	279.9	236.8	22	264.8	236.9	10	0.9997	0.005	77.1	4.5	84.7	4.1	83.7	1.7
Pentachlorobenzene	9.7	249.8	214.8	16	249.8	143.6	38	0.9992	0.005	74.1	2.1	76.0	3.9	79.1	2.9
Pentachlorobenzonitrile	11.9	274.8	239.9	18	272.9	237.9	16	0.9986	0.005	86.1	7.4	91.4	7.5	96.8	2.1
Pentachlorothioanisole	14.03	295.7	262.9	12	295.7	245.9	30	0.9990	0.005	77.0	4.4	79.2	3.1	76.6	2.2
Permethrin peak 1	24.44	183.1	153	12	183.1	168	12	0.9998	0.005	89.5	2.0	93.8	2.1	91.1	1.1
Permethrin peak 2	24.68	183	165.1	10	183	168.1	10	0.9996	0.005	91.9	4.1	97.0	2.8	95.2	1.6
Perthane (Ethylan)	17.84	223.1	167	12	223.1	179	20	0.9994	0.005	96.2	1.3	99.6	1.8	96.9	1.1
Phorate	11.1	260	75	8	121	65	8	0.9979	0.005	101.0	10.4	101.2	4.1	100.7	2.6
Phosalone	22.3	182	74.8	30	182	111	14	0.9986	0.005	99.1	3.9	97.7	5.8	93.4	7.1
Piperonyl butoxide	20.28	176.1	131.1	12	176.1	103.1	22	0.9992	0.005	100.9	2.9	106.4	2.5	104.3	1.8
Pirimiphos-ethyl	14.77	304	168.1	12	318.1	166.1	12	0.9996	0.005	93.8	0.9	100.5	1.9	98.0	2.6
Pirimiphos-methyl	13.75	290.1	233	8	305.1	180.1	8	0.9982	0.005	94.9	6.6	101.2	2.9	101.7	3.1
Pretilachlor	16.87	238.1	146.1	10	202.1	174.2	8	0.9972	0.005	103.8	12.6	111.7	4.5	108.7	5.0
Procymidone	15.72	283	96.1	8	95.9	53	16	0.9989	0.005	105.8	9.1	110.4	4.3	106.6	2.6
Prodiamine	13.8	321.1	279.1	6	275.1	255.1	8	0.9974	0.005	101.0	11.9	103.9	6.4	107.8	4.6
Profuralin	11.76	318.1	199	15	330.2	69.1	20	0.9982	0.005	92.7	7.7	100.8	4.0	99.6	6.1
Propachlor	10.38	176	57	8	120	77	19	0.9993	0.005	94.3	4.0	99.0	3.9	100.9	3.1

Q1 = Precursor ion, Q3 = Product ion, CE = Collision energy

Table 3 (part 4). List of pesticides with SRM transitions used and validation data (linearity, recovery, and precision)

Compound	RT min	Quantifier ion			Confirmatory ion			R <sup>2</sup>	LOQ (mg/kg)	0.005 (mg/kg)		0.01 (mg/kg)		0.025 (mg/kg)	
		Q1	Q3	CE (V)	Q1	Q3	CE (V)			% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
Propisochlor	13.36	162.1	144.1	8	162.1	120.1	12	0.9991	0.005	104.1	5.5	106.5	2.8	101.9	2.1
Propyzamide	12	172.9	109	26	172.9	145	14	0.9980	0.005	100.5	4.8	103.3	2.4	100.1	2.1
Prothiofos	16.81	266.7	220.9	18	266.7	238.9	8	0.9992	0.005	88.8	6.1	94.6	2.4	92.7	3.0
Pyrazophos	23.32	221	193.1	8	231.9	204.1	10	0.9990	0.005	100.4	2.3	99.0	3.4	96.4	4.7
Pyridaben	24.67	147.1	117.1	20	147.1	119.1	8	0.9998	0.005	95.8	4.2	101.8	3.6	97.6	6.5
Pyrimethanil	12.18	198.1	117.9	30	198.1	182.9	14	0.9991	0.005	94.7	7.4	99.4	4.1	94.3	3.5
Pyriproxyfen	22.64	136.1	96	10	136.1	78	20	0.9995	0.005	95.4	2.3	99.7	1.9	97.4	2.2
Quinalphos	15.6	146	118.1	10	157.1	102	22	0.9994	0.005	99.4	6.0	104.7	2.2	102.5	2.3
Quintozene	11.81	294.8	236.9	14	213.8	178.9	14	0.9989	0.005	96.0	6.4	93.9	4.9	94.9	3.2
Sulfotep	10.86	322	202	10	202	145.9	10	0.9996	0.005	102.4	5.5	100.0	4.4	101.6	3.2
Sulprofos	18.87	322	156.1	10	156	141	14	0.9992	0.005	99.6	2.8	105.0	4.1	103.0	1.8
Tebufenpyrad	21.66	276.1	171	10	318.1	131.1	14	0.9996	0.005	94.5	3.0	100.1	2.5	96.7	1.9
Tecnazene	10.27	261	203	13	215	179	8	0.9997	0.005	92.6	7.5	98.4	8.0	98.0	3.0
Tefluthrin	12.24	177	127	14	197	141.1	10	0.9996	0.005	93.2	4.0	96.1	4.5	95.6	1.8
Terbufos	11.89	230.9	128.9	22	230.9	174.9	12	0.9995	0.005	97.6	5.1	99.8	3.8	98.1	3.5
Terbuthylazine	11.93	214.1	132	10	214.1	104	16	0.9987	0.005	97.5	7.7	103.3	6.4	101.5	4.7
Tetradifon	22.12	159	111	20	159	131	10	0.9994	0.005	97.1	7.0	99.8	2.7	96.4	1.0
Tetramethrin peak 1	21	164	107.1	12	164	77.1	24	0.9984	0.005	94.7	10.8	104.2	2.4	102.5	3.3
Tetramethrin peak 2	21.28	164	107.1	12	164	77.1	22	0.9992	0.005	100.9	4.7	99.6	3.1	99.3	2.9
Tolclofos-methyl	13.29	265	250	12	266.8	252	12	0.9994	0.005	95.5	4.3	99.2	2.8	100.9	1.8
Transfluthrin	13.26	163	143	14	163	91.1	12	0.9995	0.005	98.9	5.4	98.8	4.0	96.1	3.4
Triadimefon	14.54	208	111	20	208	180.8	8	0.9985	0.005	100.2	7.5	105.2	3.8	104.0	2.1
Triadimenol	15.72	128	65	18	168.2	70	10	0.9965	0.005	102.0	4.7	110.7	6.1	107.4	5.2
Triallate	12.42	268	226	12	86.1	43.3	6	0.9987	0.005	89.5	7.3	95.3	3.0	93.7	2.9
Triazophos	18.9	161	106.1	12	161	134.1	8	0.9984	0.005	99.5	5.9	101.3	4.1	101.1	5.3
Trifluralin	10.74	306.1	264.1	8	306.1	206	10	0.9975	0.005	109.4	5.5	102.4	3.5	103.3	4.6
Vinclozolin	13.18	198	145	14	186.8	124	18	0.9994	0.005	99.4	3.7	104.8	5.5	101.9	2.7

Q1 = Precursor ion, Q3 = Product ion, CE = Collision energy

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