Validation of the Method for Determination of Pesticide Residues by Gas Chromatography – Triple-Stage Quadrupole Mass Spectrometry

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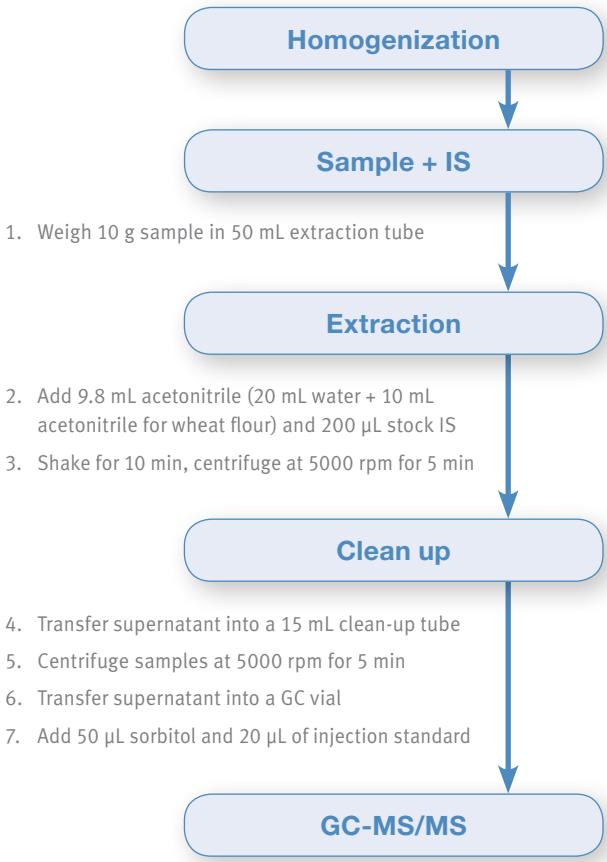
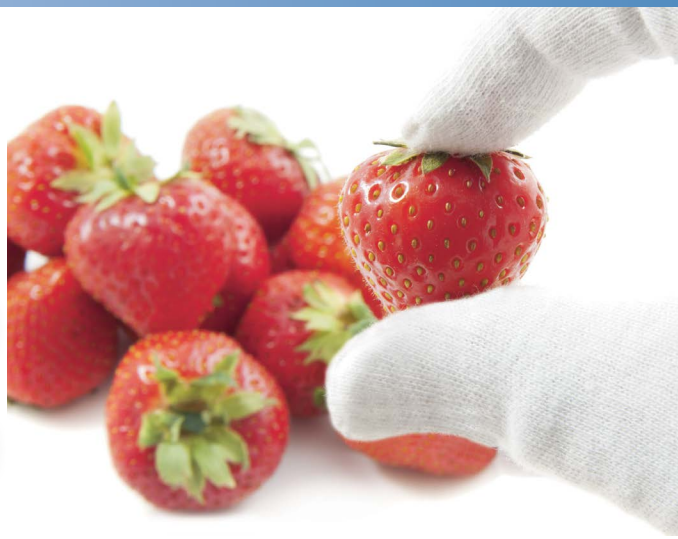
Method 63899

Key Words
TraceFinder, TSQ, Chromatography, GC, GC-MS, Pesticide Residues, QuEChERS, Triple Quadrupole

1. Schematic of Method





2. Introduction

Pesticide residue analysis in food is one of the most important and challenging tasks in routine laboratory practice. The European legislation, which is currently the most strict legislation (European Regulation 396/2005 and Commission Directive 2006/125/EC), sets maximum residue limits (MRL) of pesticides in different products of plant and animal origin. This presents a significant analytical challenge with respect to the low limits of quantification (LOQ) required for some specified food matrices. A variety of GC and HPLC methods have been developed for multi-residue determination of pesticides employing a variety of sample preparation and cleanup techniques. In recent years the QuEChERS method has become widely adopted for preparing samples of fruit and vegetables, but the continuous need for more sensitive and accurate measurements requires new developments from the instrument producers as well.

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This method reports on in-house validation results and assessment of performance parameters of a complete multi-residue pesticide analysis method employing QuEChERS sample preparation kits, sample measurement by the newly developed Thermo Scientific™ TSQ™ 8000 Pesticide Analyzer system and rapid data analysis by Thermo Scientific™ TraceFinder™ software.

3. Scope

The objective of this validation study was to prove a complete workflow solution (delivered by Thermo Scientific chemicals, consumables and instrumentation) that can be implemented for routine multi-residue pesticide analysis (approximately 140 priority pesticides) in representative matrices (strawberry, wheat flour and leek). This was achieved in accordance with current legislation requirements, demonstrating that sensitivity of the assay conforms with the MRL values at the limits of detection (LOQ).[1-4]

4. Principle

Sub-portions of previously homogenized (for some instable compound cryogenic milling is recommended) samples were treated according to a standard QuEChERS method protocol (extraction and clean-up) prior to injection in the TSQ 8000 Triple-Stage Quadrupole GC-MS system.[5, 6]

Ready to use QuEChERS kit containing both extraction and clean-up tubes and associated protocol were used for sample preparation (Thermo Fisher Scientific, Runcorn UK). Identification of pesticide residues was based on retention time and ion-ratio confirmation using selective reaction monitoring (SRM) of characteristic transition ions, while quantification was calculated on matrix matched calibration and internal standardization. All method performance criteria were established according to the relevant guidelines.[1-4, 7]

5. Reagent List

		Part Number
5.1	Acetone, HPLC Grade	A/0606/17
5.2	Acetonitrile, LC-MS Grade	A/0638/17
5.3	Methanol, Optima LC-MS grade	A456-212
5.4	Toluene, HPLC grade	T/2200/08
5.5	Water, LC-MS grade	W/0112/17
5.6	Sorbitol, 500 g	10396733

6. Standard List

6.1 Pesticides

All individual pesticide compounds – Acephate, Acrinathrin, Amitraz, Azinphos-methyl, Azoxystrobin, Bifenthrin, Bitertanol, Boscalid, Bromopropylate, Bromuconazole, Bupirimate, Buprofezin, Cadusafos, Captan, Carbaryl, Carbofuran, Carboxin, Chlorfenapyr, Chlorfenvinphos, Chlorobenzilate, Chlorothalonil, Chlorpropham, Chlorpyrifos-ethyl, Chlorpyrifos-methyl, Cyfluthrin, Cyhalothrin, Cypermethrin, Cyproconazole, Cyprodinil, DDD, DDE,DDT, Deltamethrin, Demeton-S-methyl, Diazinon, Dichlofluanid, Dichloran, Dichlorbenzophenon, Dichlorvos, Dicofol, Difenoconazole, Dimethoate, Dimethomorph, Diphenylamine, Endosulfan, Endosulfan sulfate, EPN, Epoxiconazole, Ethion, Ethoprop (Ethoprophos), Etofenprox, Fenamiphos, Fenamiphos sulfone, Fenamiphos-sulfoxid, Fenarimol, Fenbuconazol, Fenitrothion, Fenoxycarb, Fenpropathrin, Fenpropidin, Fenpropimorph, Fenthion, Fenvalerate, Fipronil, Fludioxonil, Fluquinconazole, Flusilazole, Flutolanil, Flutriafol, Fluvalinate, Folpet, HCH alpha, HCH beta, HCH gamma Lindane, Hexaconazole, Imazalil, Iprodione, Isofenphos-methyl, Kresoxim-methyl, Linuron, Malathion, Mepanipyrim, Metalaxyl, Methacrifos, Methamidophos, Methidathion, Methiocarb, Metribuzin, Monocrotophos, Myclobutanil, Ortho-phenylphenol, Oxadiazon, Oxadixyl, Paclobutrazol, Paraoxon-methyl, Parathion (ethyl), Parathion-methyl, Pendimethalin, Permethrin, Phenthoate, Phosalone, Phosmet, Phosphamidon, Pirimicarb, Pirimicarb-p-desmetyl, Pirimiphos methyl, Prochloraz, Procymidone, Profenofos, Propargite, Propiconazole, Propyzamide, Prothiofos, Pyraclostrobin, Pyridaben, Pyrimethanil, Pyriproxyfen, Quinoxyfen, Spirodiclofen, Tebuconazole, Tebufenocide, Tebufenpyrad, Tefluthrin, Tetraconazole, Tetradifon, Tetrahydrophthalimide, Thiabendazole, Tolclofos-methyl, Tolyfluanid, Triadimefon, Triadimenol, Trifloxystrobin, Trifluralin, Triticonazole, Vinclozolin) were obtained from Sigma-Aldrich® (Germany) and Laboratory Instruments Srl (CASTELLANA GROTTE, Italy).

6.2 Internal standards

1-bromo-4-fluorobenzene (BFB), triphenylphosphate (TPP) (both from Sigma-Aldrich, Germany)

6.3 Quality Control Materials

FAPAS #19140QC (lettuce), FAPAS #19141QC (green bean) and FAPAS #19142QC (melon puree)

Note: FAPAS samples were selected primarily on content of target pesticides. However, due to limited availability, matrices are slightly different from the validated matrices.

7. Standards and Reagent Preparation

7.1 Individual Pesticide Standard Stock Solutions

Prepared gravimetrically in ~1000 mg/L concentration by weighing 10 mg from each analyte into a 20 mL amber screw cap vial on a five digit analytical balance and dissolving in 10 mL of appropriate solvent (acetone, toluene or acetonitrile depending on the individual compound). Concentrations of each individual standard stock solutions were calculated gravimetrically using weight of added compounds and solvents. All individual standard stocks were stored in a freezer at -20 °C. Validity of individual standard stock solutions was 6 months.

7.2 Intermediate Standard Stock and Working Standard Solutions

Prepared by pipetting the appropriate amount of each individual standard stock and diluting it with acetonitrile. The concentration of intermediate standard stock solutions was 5000 ng/mL. Working standards were prepared by diluting intermediate standard stock solution accordingly. Intermediate standard stock solutions were stored in a freezer at -20 °C, and the working solutions in a fridge at 4 °C. Validity of intermediate stock solutions was 3 months.

7.3 Individual Internal Standard Stock Solutions

Prepared gravimetrically in ~1000 mg/L concentration by weighing 10 mg from each analyte into a 20 mL amber screw cap vial on a five digit analytical balance and dissolving in 10 mL of acetone for TPP and 10 mL toluene for BFB. Exact concentration values were determined based on the gravimetrical values of both weighed compound and added solvent. Individual internal standard stock solutions were stored in a freezer at -20 °C. Validity of individual internal standard stock solutions was 6 months.

7.4 Working Internal Standard Stock Solutions

Prepared individually by pipetting the appropriate amount of each individual standard stock solution and diluting it with acetonitrile. The concentration of working internal standard stock solutions was 5000 ng/mL and was used for direct spiking of the samples. Validity of working stock solutions was 3 months.

7.5 1% Sorbitol Solution (Analyte Protectant)

Prepared in 70/30 v/v% ACN/H_2O and used for adding prior to injection. Protectant solution was added to the sample prior to injection in order to prevent undesired analyte interaction and consequent losses during the injection.[8]

8. Apparatus

		Part Number
8.1	Fisher precision balance	XP-1500FR
8.2	Sartorius analytical balance	ME235S
8.3	Thermo Barnstead EASYpure®II water	3125753
8.4	ULTRA-TURRAX® – G25 dispergation tool	1713300
8.5	ULTRA-TURRAX	3565000
8.6	Vortex shaker	3205025
8.7	Vortex universal cap	3205029
8.8	Horizontal shaker	1069-3391
8.9	Horizontal shaker plate	1053-0102
8.10	Thermo Heraeus Freco 17 micro centrifuge	3208590
8.11	Pesticide Analyzer (TSQ 8000 Triple Stage Quadrupole GC-MS with Thermo Scientific™ TRACE™ 1310)	

9. Consumables

		Part Number
9.1	GC vial kit	60180-599
9.2	Pipette Finnpipette 100–1000 µL	3214535
9.3	Pipette Finnpipette 10–100 µL	3166472
9.4	Pipette Finnpipette 500–5000 µL	3166473
9.5	Pipette holder	3651211
9.6	Pipette tips 0.5–250 µL, 500/box	3270399
9.7	Pipette tips 1–5 mL, 75/box	3270420
9.8	Pipette tips 100–1000 µL, 200/box	3270410
9.9	Spatula, 18/10 steel	3458179
9.10	Spatula, nylon	3047217
9.11	Centrifuge tube rack	1066-3721
9.12	QuEChERS extraction tube, 50 mL, 250 pack	60105-216
9.13	QuEChERS clean-up tube, 15 mL, 50 pack	60105-225
9.14	GC column Thermo Scientific™ TraceGOLD™ TG-5SilMS, 30 m × 0.25 × 0.25 mm	10177894
9.15	PTV Baffle Liner (Siltek), Deactivated, 2 mm ID × 2.75 mm OD × 120 mm Length	453T2120
9.16	2 mL vial rack	12211001

10. Glassware

		Part Number
10.1	Volumetric flask, 10 mL	FB50143
10.2	Volumetric flask, 25 mL	FB50147
10.3	40 mL screw cap vial	1054-1593
10.4	Caps for 40 mL screw cap vial	1009-0962
10.5	500 mL bottle	9653640
10.6	100 mL bottle	1006-8060

11. Procedure

11.1 Sample Preparation

Blank matrix samples (strawberry (SB), wheat flour (WF) and leek (LK)) used for validation experiments were purchased in local retail stores and were homogenized with an Ultra-Turrax homogenizer, extracted and cleaned-up prior to sample preparation. Matrix extracts were used as matrix blank samples and dilution solvents for matrix-matched calibration. Ready to use Thermo Scientific QuEChERS extraction kits were used for sample preparation, and contained 4 g $MgSO_4$, 1 g NaCl, 1 g trisodiumcitrate dehydrate and 0.5 g disodiumcitrate sesquihydrate for buffered extraction of target compounds. Pre-prepared clean-up tubes contained 1200 mg $MgSO_4$, 400 mg PSA and 400 mg C18 for increased clean-up efficiency for more complex matrices such as leek. The same QuEChERS protocol was applied for all of the matrices.

11.1.1 Homogenization of Matrices

11.1.1.1 Select larger amount of strawberry (~500 g) and bunch of leek matrices and put into an appropriate size beaker and label it.

11.1.1.2 Attach the G25 dispergation tool to the Ultra-Turrax homogenizer. (For better recovery for some unstable compounds cryogenic homogenization is advised).

11.1.1.3 Start homogenization at middle rotation speed (speed level 2–3) and continue to form a smooth homogenate.

11.1.2 Sample Extraction and Clean-up

11.1.2.1 Weigh 10 g sample into a 50 mL QuEChERS extraction tube containing 4 g $MgSO_4$, 1 g NaCl, 1 g trisodiumcitrate dehydrate and 0.5 g disodiumcitrate sesquihydrate.

11.1.2.2 Add 200 µL 5000 ng/mL internal standard #141 to the samples.

11.1.2.3 Add 10 mL ACN to SB and LK samples. For WF, first add 20 mL H_2O to the samples, let it completely wet the sample and then add 10 mL ACN to it.

11.1.2.4 Shake samples for 10 min on a horizontal shaker and centrifuge with 5000 rpm for 5 min. Transfer supernatant (~8 mL) into the 15 mL QuEChERS clean-up tubes containing 1200 mg $MgSO_4$, 400 mg PSA and 400 mg C18.

11.1.2.5 Vortex for 1 min and centrifuge samples with 5000 rpm for 5 min.

11.1.2.6 Collect supernatant and transfer 1 mL into a GC vial for instrumental analysis.

11.1.2.7 Add 50 µL sorbitol solution (protectant) and 20 µL 5000 ng/mL injection standard (BFB) to the GC vials prior to injection.

11.2 GC-MS/MS Analysis

Sample measurements were carried out using the TRACE 1310 gas chromatograph coupled to the TSQ 8000 Triple Stage Quadrupole Mass Spectrometer (Pesticide Analyzer). For instrument control, analysis, data review and reporting TraceFinder 3.1 software was used.

11.2.1 GC method settings

The injector settings were as follows:

Injector:	Thermo Scientific™ TriPlus RSH Autosampler with 10 µL injection syringe
Liner:	PTV Baffle Liner (Siltek), Deactivated, 2 mm ID × 2.75 mm OD × 120 mm Length (recommended to be changed after 40 injections of matrix samples)
Injection mode:	splitless PTV, basic mode
Carrier mode:	constant flow
Inlet temp:	75 °C
Split flow:	50 mL/min
Splitless time:	1 min
Injection volume:	1 µL
Plunger strokes:	3
Air filling mode:	auto
Carrier flow:	1.2 mL/min
PTV injection time:	0.1 min
PTV transfer rate:	2.5 °C/s
PTV transfer temp:	300 °C
PTV transfer time:	3 min
PTV cleaning rate:	14.5 °C
PTV cleaning temp:	330 °C
PTV cleaning time:	20 min
PTV cleaning flow:	75 mL/min
PTV cleaning phase:	post cycle temperature cool down

The GC oven settings were as follows:

Carrier gas:	1.2 mL/min Helium (constant flow)
PTV cleaning phase:	post cycle temperature cool down

Table 1. GC temperature programming

#	Rate [°C/min]	Temperature [°C]	Hold Time [min]
Initial		40	1.5
1	25	90	1.5
2	25	180	0
3	5	280	0
4	10	300	5

11.2.2 Triple Quadrupole MS Settings

Mass spectrometric detection was carried out using the TSQ 8000 triple-quadrupole mass spectrometer in timed-SRM mode. All method and SRM settings were taken from the Thermo Scientific TSQ 8000 Pesticide Analyzer system method.[6] Ion ratio values were revised and adapted for each investigated matrices.

The settings were as follows:

Scan type:	timed-SRM (details in Table 2)
Ionization:	EI +
MS transfer line temp:	250 °C
Ion source temp:	300 °C
Cycle time:	0.3 s
Minimum baseline peak width:	3 s
Desired scans per peak:	10
Minimum dwell time:	0.001 s
Q1 resolution:	normal (0.7 Da)

11.3 Calculation of Results

Internal standardization was applied for quantification of target pesticides. The relevant response factors (R_f) were defined by the equation below. Calculation of final result was performed using the following equations.

11.3.1 Equations

Calculation of the response factor:

$$R_f = \frac{A_{St} \times c_{[IS]}}{A_{[IS]} \times c_{St}}$$

R_f – the response factor

A_{St} – the area of the pesticide peak in the calibration standard

$A_{[IS]}$ – the area of the internal standard peak of the calibration standard

c_{St} – pesticide concentration of the calibration standard solution

$c_{[IS]}$ – the internal standard concentration of the calibration standard solution

Calculations of sample amount in each sample (the absolute amount of pesticide extracted from the sample):

$$X_{analyte} = \frac{A_{analyte} \times X_{IS}}{A_{IS} \times R_f}$$

$X_{analyte}$ – the absolute amount of pesticide that was extracted from the sample

$A_{analyte}$ – the area of pesticide peak in the sample

$A_{[IS]}$ – the area of the internal standard peak in the sample

$X_{[IS]}$ – the absolute amount of internal standard added to the sample

Calculations of sample amount in each sample (the absolute amount of pesticide extracted from the sample):

$$C = \frac{X_{analyte}}{m}$$

m – the weight of sample [g]

$X_{analyte}$ – absolute analyte amount [ng]

12. Method Performance Characteristics

In-house validation of the method was carried out on all matrices and target pesticides. European guidelines for single laboratory validation and pesticide residue analysis were used for establishing method performance criteria.[1, 2] All method performance parameters were compared to the relevant legislative requirements and maximum residue limit (MRLs).[2-4, 7] For compounds containing more isoforms, only one performance criteria was established.

12.1 Selectivity

Method (SRM) selectivity was assessed based on the presence of specific ion transitions (quantifier ion and two transitions for compound confirmation) at the corresponding retention time (Table 2), as well as the observed ion ratio values corresponding to those of the standards. Acceptance criteria for retention time and ion ratios were set according to current quality control criteria.[1, 3] Matrix blank samples were also inspected for the presence of interfering peaks in close vicinity of the target retention times for which (according to SANCO guideline definitions) <30% of LOQ acceptance criteria was applied.[3] Additional peaks in close vicinity of target peaks in blank samples were observed for chlorpropham (LK), demethon-s-methyl (SB), fenhexamide (WF, LK), fenitrothion (WF, LK), procymidon (WF), phosphalone (SB), permethrin (WF, LK), fenpropathrin (LK), o-phenylphenol (WF) and carbofuran (SB, WF). However, they were all clearly resolved by retention time from the target peaks (Rs>1.5) except carbofuran in SB and WF and propargite in WF and LK matrices.

12.2 Linearity, Response Factor, Matrix Effect

The calibration curves were created at six levels (matrix-matched) and injected in duplicate. R_f values for internal standardization were determined from the calibration curves for all matrices and internal standards by calculating cumulative average response factor over the whole calibration range. The linearity of calibration curves was assessed in three groups of compounds (depending on the relevant MRL values) in calibration ranges of 0–200, 0–1000 and 0–2000 ng/g, respectively, (details and results in Table 3). Calibration levels were equidistantly distributed over the calibration range. Linear function was evaluated according to Mandel's fitting test and plotting of residuals for which <20% acceptance limit was set.[3] Correlation coefficient values were additionally established for which an artificial 0.985 was set as an acceptance limit, as no legislative limits are defined for them. The set value wasn't met for fenpropathrin and dichlofluanid (LK) and propargite (WF) based on the high LOQ values related to the calibration levels. No weighted function was applied.

Matrix effects were evaluated by (Youden-) plotting of measured relative peak areas of calibration standards in solvent against the areas in the relevant matrix. No matrix effect is observed if the difference of the slope (dif%) of the fitted line is less than 20% from the ideal (y=x) curve, while matrix effects are observed when the difference is between 20–50% (minor matrix effect) or exceeds 50% (major matrix effect). Matrix effect results are listed in Table 3. For the compounds with demonstrated matrix effect application of matrix matched calibration is required.

12.3 Accuracy

Method trueness was assessed by recovery studies using blank matrices spiked at three concentration levels (L1, L2 and L3) and injected in six individually prepared replicates. (Table 4). Spiking of samples occurred prior to sample preparation. Found concentrations, recovery and relative standard deviation (% RSD) were calculated (Table 5). According to SANCO requirements recovery values are deemed acceptable if between 70–120%.[3] Values were calculated only for those cases in which spiking levels were higher than the compound LOQ in the particular matrix. Recovery values could not been established for amitraz in WF and captan, chlorthalonil and tolyfluanid in LK matrices due to the high LOQ values measured relative to the spiked levels. Strong influence of matrix on the results were observed in several cases and results could not been established at one or two spiking levels based on the measured different LOD/LOQ values in the different matrices (details in Table 4). For routine measurement these compounds in these matrices have to be measured with separate, specially optimized analytical methods. Method bias was established by means of external quality control materials obtained from FAPAS (York, UK). Available FAPAS materials were #19140QC (lettuce puree), #19141QC (green bean puree) and #19142QC (melon puree). The available Fapas samples represented only a limited number of the target compounds and different matrices from those targeted. However, measured values showed good agreement with the assigned values in all cases except carbofuran, in which the measured value was slightly below the acceptance range. This could be due to differences between the two different matrix characteristics. Details on the measured FAPAS values are listed in Table 7.

12.4 (Intermediate) Precision

Instrument injection precision was tested for both retention time and peak area for all target compounds by subsequent injections (n=6) of low concentration level (L1) standard solutions. Instrument injection precision for retention time was below 0.5% for all compounds and between 1.2–18.04% (fipronil and fenamiphos-sulfoxide) for peak area without internal standard compensation indicating reliable instrument performance. Method within-day and between-day precision values were determined for each matrix at middle spiking level (L2) and expressed as %RSD over 3 days with individually prepared samples (n=6). Mean within-day precision values were determined as an average of the 3 individual days' mean precision, while between-day precision was expressed as mean of the overall precision data. According to SANCO requirements <20% was set as acceptance criteria for the target compounds and matrices.[3] Measured values are shown in Table 5.

12.5 Limit of Detection, Limit of Quantification

Limits of detection and quantification were estimated following the IUPAC. Measured method LOD, LOQ and the relevant legislative limits (MRLs) are listed in Table 6.[7] An artificial MRL=10 ng/g was set as target value for compounds, for which no MRL values are legislatively defined. The expectation of the method was to meet MRL values at least at LOQ level which was achieved for the vast majority of target compounds. For methiocarb (WF, LK), carbofuran (SW), oxadyxil (WF) and propargite (WF, LK) the established LOQ values were below the targeted MRLs' value. However, with exchanging of quantifier and qualifier ions the target values can be reached. For fenpropathrin (WF, LK), amitraz (WF) and tebufenocid (all matrices), the target values could not be reached even when exchanging the quantifier and qualifier ions.

12.6 Robustness

A robustness study was performed by varying parameters like laboratory personnel, extraction and clean-up batches. Results were compared to the original method and significant differences were sought based on ANOVA analysis. None of the parameters which were varied led to significant differences in measured values, consequently indicating that the method was robust.

13. Conclusion

Full in-house validation of a complete method intended for routine pesticide residue measurements was carried out. The goal of the study was to obtain an objective and realistic overview of the analytical performance of a widely used and accepted sample preparation method combined with state of the art analytical instrumentation. The method performance parameters indicate that the performance for the majority of target compounds complies with current regulatory requirements. Independent, external quality control materials were additionally applied to improve confidence in the measurement results. In some cases method performance parameters could not be established or measured values fell outside of the targeted range due to individual properties of compounds or strong matrix influences on the analytical results. For those compounds (in the relevant matrix), individually optimized sample preparation (additional or special clean-up) and instrumental methods have to be applied. From a practical point of view (especially for instable or active compounds) the best performance can be achieved by replacing the liner (and septum) after 40–50 injections. Overall it can be concluded that the complete workflow solution offered by Thermo Fisher Scientific in conjunction with the newly developed TSQ 8000 GC-MS system delivers the required system performance for the target compounds especially regarding sensitivity, selectivity and recovery.

14. References

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2. European Commission 2006/125/EC
3. European Commission SANCO/12495/2011
4. European Commission 788/2012/EC
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6. Thermo Scientific TSQ 8000 Pesticide Analyzer Brochure, https://static.thermoscientific.com/images/D22018~.pdf
7. EU Pesticides Database, http://ec.europa.eu/sanco_pesticides/public/index.cfm
8. Anastassiades et al. (2003) *J. Chromatogr A*, 1015:163-184

15. Annex

Tables and Figures

Table 2. Selectivity parameters for the target compounds

** retention times for all isomers ** internal standard compound*

Name	RT (min)	Quantifier Ion			Qualifier Ion 1			Qualifier Ion 2			Ion Ratio (for qualifier ion 1/ qualifier ion 2) [% of quant. ion]
		Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	
Acephate	9.36	95.5	65.4	8	136.0	42.1	8	136.0	94.0	12	0.2 / 99
Acrinathrin	24.33	181.0	152.0	22	208.1	180.9	8	289.0	93.1	8	110 / 52
Amitraz	24.03	121.0	106.1	10	131.9	117.1	16	161.9	132.0	8	85 / 78
Azinphos-methyl	23.29	132.0	77.0	12	160.0	50.9	34	160.0	77.0	16	55 / 120
Azoxystrobin	30.33	344.1	156.0	34	344.1	171.9	36	344.1	329.0	14	100 / 250
Bifenthrin	22.08	165.1	163.6	24	181.0	165.9	10	181.0	179.0	12	3800 / 400
Bitertanol	25.25	170.0	115.1	34	170.0	141.1	20	170.0	169.1	16	140 / 40
Boscalid (Nicobifen)	27.09	112.0	76.0	12	139.9	76.0	22	139.9	112.0	10	240 / 350
Bromopropylate	22.09	184.9	75.5	30	184.9	156.9	12	340.8	185.0	14	2500 / 600
Bromuconazole	21.87/ 22.6*	172.9	74.0	38	172.9	109.0	26	172.9	144.9	16	100 / 150
Bupirimate	18.08	208.1	140.1	12	208.1	165.0	12	273.1	193.2	8	260 / 60
Buprofezin	18.08	105.1	50.9	32	105.1	77.0	18	175.0	132.1	12	275 / 75
Cadusafos	11.5	159.0	96.9	16	159.0	130.9	8	213.0	89.1	12	550 / 15
Captan	16.35	149.0	70.0	20	149.0	78.8	14	149.0	105.0	6	120 / 130
Carbaryl	14.13	115.0	89.0	16	144.0	115.1	22	144.0	116.1	10	800 / 400
Carbofuran	11.98	149.1	77.0	24	149.1	121.1	8	164.0	149.1	8	120 / 120
Carboxin	18.11	87.0	43.0	6	143.0	43.0	16	143.0	87.0	8	200 / 100
Chlorfenapyr	18.37	136.9	102.0	12	248.9	112.0	24	248.9	137.1	18	45 / 30
Chlorfenvinphos	16.13	266.9	159.0	16	266.9	203.0	10	323.0	266.9	14	25 / 80
Chlorobenzilate	18.89	111.0	75.1	14	139.0	74.9	26	139.0	111.0	12	215 / 440
Chlorothalonil	12.72	228.8	168.0	8	265.8	133.0	36	265.8	170.0	24	350 / 160
Chlorpropham	11.17	171.0	127.0	8	213.0	127.0	14	213.0	171.0	6	65 / 45
Chlorpyrifos-ethyl	14.88	196.7	107.0	36	196.7	168.9	12	313.9	257.9	12	240 / 135
Chlorpyrifos-methyl	13.67	125.0	47.0	12	125.0	79.0	6	285.9	93.0	20	110 / 55
Cyfluthrin	26.67	163.0	65.1	26	163.0	91.1	12	163.0	127.1	6	100 / 25
Cyhalothrin	23.94	180.9	151.9	22	197.0	141.1	10	208.1	180.9	8	95 / 80
Cypermethrin	27.28/ 27.53/ 27.63/ 27.72*	163.0	91.1	12	163.0	127.1	6	180.9	152.1	20	100 / 50
Cyproconazole	18.53	222.0	82.1	10	222.0	89.3	38	222.0	125.0	20	35 / 210
Cyprodinil	15.85	224.1	196.9	20	224.1	208.0	18	225.1	209.7	16	500 / 40
DDD p,p	19.16	235.0	165.1	20	235.0	199.0	14	236.8	165.0	20	21 / 48
DDE p, p	17.85	246.0	176.1	28	317.8	246.0	20	317.8	248.0	18	28 / 30
DDT p,p	20.39	235.0	165.1	22	235.0	199.5	10	236.8	165.0	22	1.5 / 48
Deltamethrin	30.04	181.0	152.1	22	252.8	92.9	16	252.8	172.0	8	40 / 35
Demeton-S-methyl	10.91	88.0	59.8	6	109.0	79.0	6	141.9	79.0	12	10.1 / 25
Diazinon	12.51	137.1	54.1	20	137.1	84.1	12	179.1	121.5	26	170 / 10

Table 2 continued

** retention times for all isomers ** internal standard compound*

Name	RT (min)	Quantifier Ion			Qualifier Ion 1			Qualifier Ion 2			Ion Ratio (for qualifier ion 1/ qualifier ion 2) [% of quant. ion]
		Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	
Dichlofluanid	14.69	123.0	51.0	32	123.0	77.0	18	223.9	123.0	10	210 / 120
Dichloran	12.03	175.9	148.0	10	205.9	147.9	20	205.9	176.0	10	50 / 160
Dichlorbenzophe-non, p,p'-	16.61	139.0	110.9	15	249.9	139.0	10				0.3
Dichlorvos	8.10	109.0	79.0	6	185.0	93.0	12	186.9	93.0	12	60 / 16
Dicofol	24.18	111.0	74.9	12	139.0	111.0	12	251.0	139.0	15	460 / 160
Difenoconazole	29.51/ 29.62*	265.0	139.0	36	265.0	202.1	16	323.0	265.0	14	90 / 220
Dimethoate	11.92	87.0	42.1	10	93.0	63.0	8	125.0	79.0	8	70 / 55
Dimethomorph	30.51/ 31.00*	165.0	77.0	18	165.0	137.0	10	301.0	165.1	12	390 / 130
Diphenylamine	10.96	167.1	139.4	26	167.1	140.1	18	167.1	166.1	16	130 / 550
Endosulfan	17.19/ 19	194.7	125.0	22	194.7	159.4	8	240.6	205.9	14	140 / 120
Endosulfan sulfate	20.23	238.7	203.9	12	271.7	234.9	12	271.7	236.8	12	47 / 550
EPN	22.04	157.0	77.0	22	169.0	77.0	22	169.0	141.0	8	120 / 210
Epoxiconazole	21.34	165.0	138.0	8	192.0	111.0	22	192.0	138.0	12	150 / 300
Ethion	19.17	153.0	97.0	10	230.9	128.9	22				90
Ethoprop (Ethoprophos)	11.02	157.9	96.9	16	157.9	113.9	6	200.0	158.0	6	75 / 70
Etofenprox	27.66	163.1	77.1	32	163.1	107.1	16	163.1	135.1	10	300 / 350
Fenamiphos	17.39	154.0	139.0	10	216.9	202.0	12	303.1	195.2	8	85 / 50
Fenamiphos sulfone	21.74	320.0	213.9	14	320.0	249.1	18	320.0	292.1	8	95 / 420
Fenamiphos-sulfoxid	21.59	304.0	196.0	10	304.0	234.0	10				35
Fenarimol	24.16	139.0	74.9	26	139.0	111.0	14	219.0	107.0	10	185 / 80
Fenbuconazol	26.31	129.0	77.8	18	129.0	102.0	14	198.1	129.1	8	230 / /370
Fenitrothion	14.44	125.0	79.0	8	277.0	109.0	16	277.0	260.0	6	45 / 48
Fenoxycarb	22.19	116.0	44.1	16	116.0	88.0	8	255.1	186.1	10	460 / 60
Fenpropathrin	22.39	97.1	55.1	6	181.0	126.8	28	181.0	151.9	22	22 / 92
Fenpropidin	14.38	98.2	41.5	18	98.2	55.1	14	98.2	70.0	10	1650 / 1850
Fenpropimorph	15.06	128.1	41.7	24	128.1	70.1	12	128.1	110.1	8	400 / 300
Fenthion	14.98	245.3	125.0	12	278.0	109.0	18	278.0	169.0	14	1300 / 500
Fenvalerate	28.73	125.0	89.0	18	167.0	89.0	32	167.0	125.0	10	45 / 300
Fipronil	15.96	366.9	212.9	28	366.9	244.9	20	368.8	214.9	30	30 / 65
Fludioxonil	17.61	153.7	127.0	8	248.0	127.0	26	248.0	153.8	18	290 / 160
Fluquinconazole	25.61	340.0	108.1	36	340.0	298.0	16	340.0	313.0	14	160 / 65
Flusilazole	18.05	206.0	151.3	14	233.0	151.9	14	233.0	164.9	16	230 / 350
Flutolanil	17.47	173.0	95.0	28	173.0	145.0	14	281.0	173.0	10	350 / 56
Flutriafol	17.31	123.0	75.0	24	123.0	95.0	12	219.0	123.0	12	180 / 72

Table 2 continued

** retention times for all isomers ** internal standard compound*

Name	RT (min)	Quantifier Ion			Qualifier Ion 1			Qualifier Ion 2			Ion Ratio (for qualifier ion 1/ qualifier ion 2) [% of quant. ion]
		Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	
Fluvalinate	29.03/ 29.16*	180.8	152.1	22	250.0	55.1	16	250.0	199.9	18	45 / 35
Folpet	16.54	104.0	76.0	10	130.0	102.0	12	259.9	130.1	14	92 / 62
HCH alpha	11.71	216.9	180.9	8	218.8	182.9	8				95
HCH beta	12.19	216.9	180.9	8	218.8	182.9	8				90
HCH gamma_ Lindane	12.39	216.9	180.9	8	218.8	182.9	8				100
Hexaconazole	17.54	213.9	123.5	28	213.9	159.0	18	231.0	175.0	10	950 / 1100
Imazalil	17.58	172.8	109.0	26	174.7	147.0	16	215.0	173.0	8	90 / 130
Iprodione	21.77	314.0	245.0	10	315.7	247.0	10	315.7	273.0	8	50 / 22
Isofenphos-methyl	15.65	199.0	65.0	34	199.0	121.0	10	241.1	121.1	20	395 / 70
Kresoxim-methyl	18.12	116.0	62.9	24	116.0	89.0	14	130.9	130.1	10	324 / 102
Linuron	14.63	159.8	133.0	12	187.0	124.0	20	248.0	61.1	8	70 / 120
Malathion	14.68	92.8	63.0	8	125.0	79.0	8	173.1	99.0	12	110 / 300
Mepanipyrim	17.21	222.0	206.0	26	222.0	207.1	14	223.1	207.4	24	220 / 41
Metalaxyl	14.01	131.9	117.0	12	160.1	130.0	18	160.1	144.8	10	100 / 80
Methacrifos	9.8	125.0	79.0	8	180.0	93.0	10	240.0	180.0	10	55 / 40
Methamidophos	8.03	141.0	64.0	18	141.0	79.0	20	141.0	94.8	8	420 / 520
Methidathion	16.7	145.0	58.0	14	145.0	85.0	6	302.6	284.9	14	370
Methiocarb	14.98	153.0	45.0	12	153.0	109.1	6	168.1	153.0	10	225 / 554
Metribuzin	13.67	198.0	55.0	26	198.0	82.1	16	198.0	110.0	10	300 / 100
Monocrotophos	11.4	96.9	82.0	10	127.0	95.0	16	127.0	109.0	10	105 / 350
Myclobutanil	17.98	179.0	90.0	28	179.0	125.0	14	179.0	151.7	8	320 / 60
Ortho-phenyl-phenol	10.09	141.1	115.1	14	170.1	115.0	34	170.1	141.1	22	91 / 100
Oxadiazon	17.87	174.9	76.0	28	174.9	112.0	12	174.9	147.2	6	226 / 52
Oxadixyl	19.12	131.9	117.0	16	163.1	117.0	24	163.1	132.1	8	110 / 260
Paclobutrazol	16.97	125.0	89.0	18	236.0	125.0	12	236.0	167.0	10	290 / 90
Paraoxon-methyl	12.83	95.9	65.0	12	109.0	79.0	6	230.0	105.9	16	140 / 110
Parathion (ethyl)	15.07	109.0	81.0	10	124.9	97.0	6	291.0	109.0	12	75 / 48
Parathion-methyl	13.85	124.9	47.0	12	124.9	79.0	6	263.0	109.0	12	105 / 60
Pendimethalin	15.81	252.1	161.0	14	252.1	162.0	8	252.1	191.3	8	130 / 85
Permethrin	25.38/ 25.64*	163.0	91.1	12	183.1	153.0	12	183.1	168.0	12	100 / 105
Phenthoate	16.25	121.0	77.0	22	246.0	121.0	8	274.0	121.0	10	100 / 120
Phosalone	23.15	121.1	65.0	10	182.0	74.8	30	182.0	111.0	14	105 / 190
Phosmet	21.89	160.0	50.9	38	160.0	76.9	22	160.0	133.0	10	170 / 110
Phosphamidon	13.47	127.0	94.9	16	127.0	109.0	12	264.1	127.0	12	380 / 100
Pirimicarb	13.08	166.1	55.0	18	166.1	96.0	12	238.1	166.1	10	120 / 230
Pirimicarb-p-desmetyl	13.36	152.1	42.0	25	152.1	96.0	10	224.1	152.1	10	230 / 120
Pirimiphos methyl	14.37	290.1	125.0	20	290.1	233.0	8	305.1	180.1	8	60 / 70
Prochloraz	25.74	69.9	42.0	8	180.1	138.1	12	308.0	147.1	12	160 / 10
Procymidone	16.4	95.9	53.0	16	95.9	67.1	8	283.0	96.1	8	400 / 65

Table 2 continued

** retention times for all isomers ** internal standard compound*

Name	RT (min)	Quantifier Ion			Qualifier Ion 1			Qualifier Ion 2			Ion Ratio (for qualifier ion 1/ qualifier ion 2) [% of quant. ion]
		Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	Precursor Mass [m/z]	Product Mass [m/z]	Collision Energy [V]	
Profenofos	17.73	296.7	268.9	10	336.9	266.9	12	336.9	308.9	8	190 / 35
Propargite	20.97	135.1	77.1	26	135.1	107.1	12	150.1	135.1	8	310 / 110
Propiconazole	20.19/ 20.39*	172.9	74.0	38	172.9	109.0	26	172.9	145.0	16	110 / 155
Propyzamide	12.5	172.9	74.0	38	172.9	109.0	26	172.9	145.0	14	105 / 190
Prothiofos	17.57	266.7	220.9	18	266.7	238.9	8	308.9	239.0	14	142 / 160
Pyraclostrobin	28.89	132.0	51.1	35	132.0	77.0	20	164.0	132.1	10	230 / 220
Pyridaben	25.62	147.1	117.1	20	147.1	119.1	8	147.1	132.1	12	55 / 58
Pyrimethanil	12.66	198.1	117.9	30	198.1	157.6	18	198.1	182.9	14	10 / 120
Pyriproxyfen	23.54	136.1	78.0	20	136.1	96.0	10	226.1	186.1	12	90 / 10
Quinoxyfen	20.18	237.0	208.0	26	271.8	237.1	12	307.0	237.0	18	55 / 33
Spirodiclofen	25.09	156.9	73.0	20	156.9	86.7	32	312.2	259.0	8	60 / 105
Tebuconazole	20.85	125.0	89.0	16	125.0	99.0	16	250.0	125.0	20	50 / 110
Tebufenocide	22.58	145.1	117.0	10	160.1	145.1	12				8
Tebufenpyrad	22.58	276.1	171.0	10	318.1	131.1	14	318.1	145.1	14	43 / 31
Tefluthrin	12.79	177.0	127.0	14	177.0	137.0	16	197.0	141.1	10	34 / 40
Tetraconazole	15.18	100.9	51.0	10	159.0	123.4	16	336.0	204.0	28	8 / 100
Tetradifon	22.97	159.0	74.8	32	159.0	111.0	20	159.0	131.0	10	125 / 252
Tetrahydroph-thalimide (THPI)	9.96	151.0	77.1	30	151.0	79.9	6	151.0	122.1	8	140 / 80
Thiabendazole	16.36	174.0	103.0	18	174.0	130.1	10	201.0	174.0	14	110 / 700
Tolclofos-methyl	13.86	265.0	219.9	20	265.0	250.0	12	266.8	252.0	12	285 / 80
Tolyfluanid	16.1	137.0	65.1	28	137.0	91.1	18	238.0	137.0	10	150 / 110
Triadimefon	15.17	208.0	111.0	20	208.0	126.7	12	208.0	180.8	8	65 / 120
Triadimenol	16.39	112.0	57.6	8	128.0	65.0	18	168.2	70.0	10	
Trifloxystrobin	20.16	116.1	63.0	24	116.1	89.0	14	145.0	95.0	14	295 / 40
Trifluralin	11.17	306.1	159.7	20	306.1	206.0	10	306.1	264.1	8	150 / 900
Triphenylphos-phate (TPP)**	21.01	215.0	168.1	16	326.1	168.6	28	326.1	325.3	10	6 / 62
Triticonazole	23.17	217.0	167.0	18	235.1	181.9	12	235.1	217.1	8	92 / 120
Vinclozolin	13.73	241.1	58.1	12	241.1	184.1	10	284.9	269.9	12	160

Table 3. Linearity and matrix effect results *(see text 12.2 for details on Youden plot slope results).* – *residue plot RSD% <20%* – *residue plot RSD% >20%*

Compound	Calibration Range [ng/g]	Strawberry			Wheat Flour			Leek		
		r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]
Acephate	0-200	0.9998		12	0.9995		9	0.9998		35
Acrinathrin	0-200	0.9976		9	0.9985		270	0.9976		61
Amitraz	0-2000	0.9884		39	n.d.	n.d.	n.d.	0.9920		38
Azinphos-methyl	0-1000	0.9885		20	0.9956		0	0.9890		52
Azoxystrobin	0-1000	0.9911		24	0.9979		130	0.9918		63
Bifenthrin	0-200	0.9997		10	0.9939		12	0.9947		24
Bitertanol	0-200	0.9993		24	0.9956		67	0.9986		18
Boscalid (Nicobifen)	0-200	0.9983		16	0.9946		61	0.9976		8
Bromopropylate	0-200	0.9986		9	0.9908		2	0.9988		19
Bromuconazole	0-200	0.9989		6	0.9965		7	0.9994		17
Bupirimate	0-1000	0.9970		5	0.9981		3	0.9995		21
Buprofezin	0-1000	0.9993		16	0.9984		13	0.9961		31
Cadusafos	0-200	1.0000		3	0.9997		14	0.9970		27
Captan	0-200	0.9963		63	0.9967		56	n.d.	n.d.	n.d.
Carbaryl	0-1000	0.9995		54	0.9991		50	0.9833		68
Carbofuran	0-200	0.9987		11	0.9907		31	0.9816		64
Carboxin	0-200	0.9989		6	0.9988		16	0.9998		18
Chlorfenapyr	0-1000	0.9991		16	0.9971		18	0.9994		35
Chlorfenvinphos	0-200	0.9996		9	0.9958		97	0.9982		10
Chlorobenzilate	0-200	0.9999		2	0.9971		5	0.9991		17
Chlorothalonil	0-200	0.9952		77	0.9991		25	n.d.	n.d.	n.d.
Chlorpropham	0-200	0.9999		1	0.9997		11	0.9971		18
Chlorpyrifos-ethyl	0-200	0.9998		11	0.9995		6	0.9994		22
Chlorpyrifos-methyl	0-200	0.9998		25	0.9995		32	0.9991		39
Cyfluthrin	0-200	0.9995		4	0.9918		130	0.9899		5
Cyhalothrin	0-200	0.9979		15	0.9972		39	0.9973		16
Cypermethrin	0-200	0.9993		10	0.9947		105	0.9900		15
Cyproconazole	0-200	0.9994		17	0.9975		29	0.9997		2
Cyprodinil	0-200	0.9594		5	0.9970		5	0.9993		10
DDD p,p	0-200	0.9984		4	0.9982		20	0.9987		7
DDE p, p	0-200	0.9999		11	0.9985		21	0.9983		9
DDT p,p	0-200	0.9974		21	0.9963		26	0.9926		18
Deltamethrin	0-200	0.9994		7	0.9935		149	0.9911		40
Demeton-S-methyl	0-1000	0.9997		0	0.9994		2	0.9995		6
Diazinon	0-200	0.9998		18	0.9996		23	0.9928		36
Dichlofluanid	0-1000	0.9962		6	0.9997		10	0.7016		99
Dichloran	0-200	0.9996		7	0.9993		21	0.9994		25
Dichlorbenzophenon, p,p'-	0-200	0.9976		24	0.9988		65	0.9904		99
Dichlorvos	0-200	0.9996		15	0.9992		37	0.9993		20
Dicofol	0-200	0.9989		2	0.9952		11	0.9991		20
Difenoconazole	0-200	0.9989		13	0.9965		225	0.9995		51
Dimethoate	0-200	0.9996		17	0.9997		4	0.9996		20

Table 3 continued

– residue plot RSD% <20% *– residue plot RSD% >20%*

Compound	Calibration Range [ng/g]	Strawberry			Wheat Flour			Leek		
		r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]
Dimethomorph	0-200	0.9995		37	0.9996		181	0.9984		42
Diphenylamine	0-200	0.9999		12	0.9994		24	0.9969		22
Endosulfan	0-1000	0.9994		7	0.9961		4	0.9969		17
Endosulfan sulfate	0-200	0.9988		4	0.9920		2	0.9980		20
EPN	0-200	0.9960		2	0.9947		56	0.9926		0
Epoxiconazole	0-200	0.9992		5	0.9966		14	0.9994		8
Ethion	0-200	0.9977		11	0.9967		21	0.9995		3
Ethoprop (Ethoprophos)	0-200	0.9998		7	0.9997		16	0.9978		17
Etofenprox	0-200	0.9985		15	0.9939		60	0.9986		3
Fenamiphos	0-200	0.9996		2	0.9992		40	0.9999		41
Fenamiphos sulfone	0-200	0.9968		16	0.9981		74	0.9933		25
Fenamiphos-sulfoxid	0-2000	0.9907		10	0.9940		101	0.8709		44
Fenarimol	0-200	0.9979		2	0.9958		8	0.9987		22
Fenbuconazol	0-200	0.9990		7	0.9949		33	0.9991		6
Fenitrothion	0-200	0.9994		15	0.9993		15	0.9992		23
Fenoxycarb	0-200	0.9990		9	0.9970		52	0.9989		4
Fenpropathrin	0-200	0.9981		7	0.9972		45	0.9146		6
Fenpropidin	0-1000	0.9998		18	0.9997		7	0.9962		17
Fenpropimorph	0-200	0.9998		10	0.9997		5	0.9943		27
Fenthion	0-200	0.9987		17	0.9998		21	0.9997		5
Fenvalerate	0-200	0.9999		10	0.9949		84	0.9973		19
Fipronil	0-200	0.9998		8	0.9984		26	0.9991		29
Fludioxonil	0-200	0.9800		1	0.9979		11	0.9992		23
Fluquinconazole	0-200	0.9976		22	0.9990		153	0.9995		39
Flusilazole	0-200	0.9984		2	0.9953		13	0.9977		11
Flutolanil	0-200	0.9989		15	0.9996		38	0.9997		7
Flutriafol	0-200	0.9996		1	0.9991		14	0.9996		23
Fluvalinate	0-200	0.9995		20	0.9956		131	0.9938		1
Folpet	0-2000	0.9959		76	0.9984		48	n.d.	n.d.	n.d.
HCH alpha	0-200	0.9999		8	0.9951		8	0.9977		15
HCH beta	0-200	0.9999		14	0.9993		16	0.9981		29
HCH gamma_Lindane	0-200	0.9999		12	0.9945		17	0.9961		21
Hexaconazole	0-1000	0.9938		8	0.9995		11	0.9999		11
Imazalil	0-1000	0.9987		14	0.9985		14	0.9998		26
Iprodione	0-200	0.9981		5	0.9984		34	0.9917		13
Isofenphos-methyl	0-200	0.9996		6	0.9996		54	0.9992		6
Kresoxim-methyl	0-200	0.9990		15	0.9974		15	0.9992		35
Linuron	0-1000	0.9986		50	0.9967		55	0.9996		42
Malathion	0-200	0.9985		14	0.9995		11	0.9816		30
Mepanipyrim	0-200	0.9993		24	0.9928		38	0.9995		11
Metalaxyl	0-1000	0.9999		20	0.9996		30	0.9980		37
Methacrifos	0-200	0.9994		3	0.9983		16	0.9951		19

Table 3 continued

– residue plot RSD% <20% *– residue plot RSD% >20%*

Compound	Calibration Range [ng/g]	Strawberry			Wheat Flour			Leek		
		r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]
Methamidophos	0-200	0.9995		0	0.9995		9	0.9967		33
Methidathion	0-200	0.9984		13	0.9997		14	0.9988		32
Methiocarb	0-2000	0.9988		2	0.9963		20	0.9876		33
Metribuzin	0-1000	0.9997		21	0.9996		22	0.9995		28
Monocrotophos	0-1000	0.9997		36	0.9990		11	0.9982		45
Myclobutanil	0-200	0.9994		2	0.9979		8	0.9991		20
Ortho-phenylphenol	0-200	0.9999		4	0.9995		18	0.9945		24
Oxadiazon	0-200	0.9999		8	0.9968		11	0.9956		28
Oxadixyl	0-200	0.9997		5	0.9969		4	0.9989		25
Paclobutrazol	0-200	0.9996		4	0.9997		1	0.9988		15
Paraoxon-methyl	0-1000	0.9957		40	0.9964		27	0.9875		43
Parathion (ethyl)	0-1000	0.9968		7	0.9956		4	0.9964		20
Parathion-methyl	0-200	0.9996		24	0.9985		30	0.9997		35
Pendimethalin	0-200	0.9950		15	0.9910		121	0.9937		75
Permethrin	0-200	0.9951		27	0.9961		70	0.9970		13
Phenthoate	0-1000	0.9991		18	0.9989		25	0.9996		32
Phosalone	0-200	0.9976		2	0.9921		33	0.9939		12
Phosmet	0-200	0.9972		28	0.9961		34	0.9922		61
Phosphamidon	0-200	0.9989		42	0.9997		37	0.9961		70
Pirimicarb	0-200	0.9998		16	0.9997		22	0.9990		32
Pirimicarb-p-desmetyl	0-1000	0.9999		26	0.9998		28	0.9994		36
Pirimiphos methyl	0-200	0.9987		15	0.9980		4	0.9986		25
Prochloraz	0-1000	0.9924		9	0.9974		37	0.9925		12
Procymidone	0-200	0.9999		17	0.9996		6	0.9969		26
Profenofos	0-200	0.9988		2	0.9992		>200	0.9940		34
Propargite	0-200	0.9991		9	0.8967		17	0.9997		51
Propiconazole	0-200	0.9986		13	0.9976		15	0.9877		10
Propyzamide	0-200	0.9999		9	0.9995		14	0.9946		25
Prothiofos	0-200	0.9993		20	0.9987		80	0.9986		4
Pyraclostrobin	0-200	0.9997		6	0.9954		56	0.9964		1
Pyridaben	0-200	0.9961		29	0.9967		79	0.9953		14
Pyrimethanil	0-200	0.9999		13	0.9997		13	0.9963		20
Pyriproxyfen	0-200	0.9982		1	0.9964		12	0.9996		17
Quinoxyfen	0-200	0.9977		15	0.9979		28	0.9998		2
Spirodiclofen	0-200	0.9995		7	0.9974		8	0.9950		34
Tebuconazole	0-200	0.9995		17	0.9969		22	0.9986		3
Tebufenocide	0-1000	0.9980		11	0.9975		34	0.9984		12
Tebufenpyrad	0-200	0.9987		8	0.9996		126	0.9996		4
Tefluthrin	0-200	1.0000		14	0.9994		20	0.9929		31
Tetraconazole	0-1000	0.9997		17	0.9997		13	0.9975		33
Tetradifon	0-200	0.9998		10	0.9959		11	0.9989		30
Tetrahydrophthalimide	0-200	0.9645		106	0.9638		51	0.8388		93

Table 3 continued

– residue plot RSD% <20% *– residue plot RSD% >20%*

Compound	Calibration Range [ng/g]	Strawberry			Wheat Flour			Leek		
		r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]	r2	Residue Plot Deviation [%RSD]	Youden Plot Slope [diff%]
Thiabendazole	0-1000	0.9987		9	0.9996		8	0.9998		28
Tolclofos-methyl	0-200	0.9998		27	0.9990		57	0.9987		6
Tolyfluanid	0-1000	0.9970		6	0.9989		47	n.d.	n.d.	n.d.
Triadimefon	0-1000	0.9987		7	0.9996		8	0.9995		22
Triadimenol	0-1000	0.9993		2	0.9991		8	0.9992		26
Trifloxystrobin	0-200	0.9985		17	0.9978		61	0.9994		3
Trifluralin	0-200	0.9913		311	0.9973		62	0.9821		30
Triticonazole	0-200	0.9977		27	0.9975		70	0.9983		20
Vinclozolin	0-200	0.9996		18	0.9983		22	0.9973		27

Table 4: Recovery values [%] at 10 ng/g (level 1), 20 ng/g (level 2) and 100 ng/g (level 3) spike levels.

** spiking levels are 50, 100 & 500 ng/g* *** spiking levels are 100, 200 & 1000 ng/g* *<LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry			Wheat Flour			Leek		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
Acephate	84	88	63	68	75	60	68	72	56
Acrinathrin	100	79	67	121	118	85	129	69	24
Amitraz**	98	79	57	n.d.	n.d.	n.d.	126	95	69
Azinphos-methyl*	127	102	79	101	128	99	126	88	68
Azoxystrobin*	101	87	67	111	123	95	78	88	82
Bifenthrin	101	104	73	94	117	76	94	108	84
Bitertanol	101	109	82	116	118	81	82	109	88
Boscalid (Nicobifen)	93	101	81	111	116	83	111	111	86
Bromopropylate	92	109	90	117	114	82	97	111	89
Bromuconazole	87	106	90	108	114	79	88	106	88
Bupirimate*	83	111	101	105	113	83	93	120	99
Buprofezin*	82	112	97	100	112	80	100	125	97
Cadusafos	78	109	88	96	111	85	68	111	95
Captan	74	42	71	42	32	66	n.d.	n.d.	n.d.
Carbaryl*	106	81	65	110	100	71	83	76	72
Carbofuran	87	99	85	106	133	107	<LOQ	54	43
Carboxin	96	107	94	99	100	80	83	107	89
Chlorfenapyr*	86	112	100	104	118	83	84	118	99
Chlorfenvinphos	101	110	89	105	119	91	84	98	79
Chlorobenzilate	87	114	94	115	123	73	85	123	97
Chlorothalonil	133	73	36	76	56	62	n.d.	n.d.	n.d.
Chlorpropham	84	113	94	87	109	86	73	118	100
Chlorpyrifos-ethyl	86	110	87	95	113	88	91	132	100
Chlorpyrifos-methyl	114	112	80	100	121	95	93	135	103
Cyfluthrin	102	103	77	127	114	73	119	98	67
Cyhalothrin	103	85	79	117	118	86	104	77	65

Table 4 continued

** spiking levels are 50, 100 & 500 ng/g ** spiking levels are 100, 200 & 1000 ng/g <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry			Wheat Flour			Leek		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
Cypermethrin	84	86	73	181	136	84	112	112	80
Cyproconazole	83	103	88	111	112	80	73	107	89
Cyprodinil	21	30	24	106	109	81	84	120	92
DDD p,p	96	105	86	88	108	85	79	120	100
DDE p, p	76	104	85	89	100	75	80	121	96
DDT p,p	97	94	68	124	141	120	82	118	90
Deltamethrin	100	77	56	114	107	70	93	84	58
Demeton-S-methyl*	93	106	84	97	111	93	96	122	92
Diazinon	87	113	91	95	110	86	77	125	101
Dichlofluanid*	110	72	62	37	48	73	<LOD	<LOD	55
Dichloran	83	109	95	106	120	92	78	116	90
Dichlorbenzophenon, p,p'-	77	104	86	<LOD	<LOQ	84	<LOQ	105	103
Dichlorvos	89	122	92	98	118	112	98	112	85
Dicofol	86	98	85	114	114	80	83	103	85
Difenoconazole	93	104	80	101	113	90	66	87	69
Dimethoate	86	95	82	79	113	95	94	117	86
Dimethomorph	92	99	73	90	124	114	86	102	81
Diphenylamine	102	107	74	56	70	79	75	122	95
Endosulfan*	86	101	78	114	121	67	76	118	97
Endosulfan sulfate	102	109	87	126	129	86	114	122	95
EPN	121	113	84	134	123	96	122	122	85
Epoxiconazole	103	116	88	109	119	86	89	116	95
Ethion	112	110	84	116	120	86	77	116	97
Ethoprop (Ethoprophos)	91	99	73	99	111	89	72	114	97
Etofenprox	91	101	79	119	114	78	89	103	82
Fenamiphos	90	103	92	68	84	71	75	103	87
Fenamiphos sulfone	106	95	66	119	117	92	63	51	57
Fenamiphos-sulfoxid**	144	150	117	119	137	131	65	89	91
Fenarimol	95	100	79	111	115	79	85	101	83
Fenbuconazol	100	110	85	123	123	85	92	113	92
Fenitrothion	105	102	83	107	123	94	111	129	96
Fenoxycarb	98	103	85	114	120	89	97	112	91
Fenpropathrin	86	105	91	<LOD	<LOD	82	<LOD	<LOD	77
Fenpropidin*	35	36	23	43	29	26	n.d.	9	20
Fenpropimorph	59	79	65	68	79	62	40	80	73
Fenthion	87	100	108	61	84	77	108	122	102
Fenvalerate	82	93	79	111	118	85	99	109	81
Fipronil	89	110	92	119	119	96	74	104	83
Fludioxonil	<LOD	<LOD	55	104	117	68	87	117	98
Fluquinconazole	99	102	82	96	108	84	92	110	91
Flusilazole	90	119	99	123	112	85	75	99	101
Flutolanil	88	116	100	93	114	86	87	122	99
Flutriafol	85	108	91	77	114	66	81	114	92
Fluvalinate	35	97	77	121	122	91	98	101	76
Folpet**	133	34	45	66	36	29	<LOD	<LOD	<LOQ

Table 4 continued

** spiking levels are 50, 100 & 500 ng/g ** spiking levels are 100, 200 & 1000 ng/g <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry			Wheat Flour			Leek		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
HCH alpha	79	109	87	113	121	88	84	135	108
HCH beta	85	111	90	109	110	85	87	138	109
HCH gamma_Lindane	87	110	89	115	123	88	81	132	106
Hexaconazole*	95	97	84	95	103	75	90	111	88
Imazalil*	72	97	84	87	102	67	69	96	78
Iprodione	109	111	86	120	124	94	109	102	84
Isofenphos-methyl	85	111	92	99	112	89	94	128	103
Kresoxim-methyl	86	111	96	114	119	85	86	120	101
Linuron*	126	118	95	95	100	63	126	133	98
Malathion	108	106	90	83	122	101	150	121	88
Mepanipyrim	82	111	96	123	138	72	93	121	95
Metalaxyl*	84	111	91	97	115	90	75	115	95
Methacrifos	89	108	78	82	109	96	66	130	103
Methamidophos	56	60	63	59	61	50	97	73	51
Methidathion	110	106	84	99	118	94	106	125	98
Methiocarb**	85	98	81	<LOD	<LOD	75	<LOD	<LOQ	78
Metribuzin*	87	111	98	89	117	84	94	129	99
Monocrotophos*	90	92	74	110	99	60	107	87	63
Myclobutanil	91	115	96	104	109	83	77	116	94
Ortho-phenylphenol	95	102	74	63	75	78	61	120	99
Oxadiazon	84	115	95	111	117	81	69	117	100
Oxadixyl	89	108	87	116	118	84	76	108	93
Paclobutrazol	81	106	91	95	109	85	90	111	91
Paraoxon-methyl*	102	108	109	137	146	111	132	117	73
Parathion (ethyl)*	69	98	101	54	95	95	120	132	100
Parathion-methyl	83	107	98	108	129	95	101	138	105
Pendimethalin	45	81	118	51	73	85	117	132	96
Permethrin	109	107	83	109	115	81	91	112	94
Phenthoate*	83	111	105	124	124	95	99	125	97
Phosalone	115	106	82	97	87	83	103	108	86
Phosmet	114	87	71	104	115	88	107	85	63
Phosphamidon	109	112	95	115	131	98	53	64	120
Pirimicarb	85	110	87	90	113	90	77	118	94
Pirimicarb-p-desmetyl*	79	99	81	85	106	82	82	122	89
Pirimiphos methyl	90	109	93	116	113	93	71	111	92
Prochloraz*	117	94	72	112	124	87	76	86	71
Procymidone	85	107	87	84	115	86	82	119	98
Profenofos	112	107	89	112	108	90	119	89	77
Propargite	104	104	90	<LOD	<LOD	58	62	89	88
Propiconazole	89	95	74	102	110	77	79	107	90
Propyzamide	84	110	89	100	116	88	90	133	103
Prothiofos	73	96	92	95	99	82	89	104	81
Pyraclostrobin	100	116	90	128	139	97	101	123	92
Pyridaben	111	110	86	108	114	81	92	108	87
Pyrimethanil	78	103	84	84	103	84	70	118	95

Table 4 continued ** spiking levels are 50, 100 & 500 ng/g ** spiking levels are 100, 200 & 1000 ng/g <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry			Wheat Flour			Leek		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
Pyriproxyfen	101	107	84	106	113	81	90	112	92
Quinoxyfen	89	97	79	95	100	75	81	105	85
Spirodiclofen	91	88	78	132	113	75	<LOQ	96	71
Tebuconazole	80	95	75	100	111	79	89	110	91
Tebufenocide*	86	101	43	<LOD	<LOQ	84	<LOQ	106	87
Tebufenpyrad	80	102	89	101	104	89	70	91	78
Tefluthrin	85	109	87	86	109	86	72	126	102
Tetraconazole*	84	108	93	98	115	89	79	118	101
Tetradifon	77	119	106	104	112	78	75	116	95
Tetrahydrophthalimide (THPI)	<LOQ	<LOQ	90	<LOQ	117	115	<LOQ	111	95
Thiabendazole*	77	96	82	83	88	67	75	97	79
Tolclofos-methyl	81	108	89	102	110	84	91	119	83
Tolyfluanid*	111	71	67	87	79	77	n.d.	n.d.	n.d.
Triadimefon*	76	106	98	95	111	88	91	121	100
Triadimenol*	79	106	87	96	110	82	77	103	90
Trifloxystrobin	103	111	87	103	112	87	94	123	97
Trifluralin	121	84	59	54	39	50	77	50	87
Triticonazole	101	105	82	106	112	81	88	106	86
Vinclozolin	89	114	94	130	107	75	67	111	90

Table 5. Method precision and intermediate precision values [RSD %] at 10 ng/g (level 1), 20 ng/g (level 2) and 100 ng/g (level3). ** spiking levels are 50, 100 & 500 ** spiking levels are 100, 200 & 1000 <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry				Wheat Flour				Leek			
	Precision			Intermediate Precision	Precision			Intermediate Precision	Precision			Intermediate Precision
	Level 1	Level 2	Level 3		Level 1	Level 2	Level 3		Level 1	Level 2	Level 3	
Acephate	7	7	12	15	29	4	27	9	12	18	8	22
Acrinathrin	32	51	18	37	9	3	7	5	4	20	17	22
Amitraz**	5	11	11	14	n.d.	n.d.	n.d.	n.d.	3	7	15	27
Azinphos-methyl*	2	4	7	5	6	1	6	3	6	10	7	23
Azoxystrobin*	3	6	2	7	12	4	4	12	5	6	10	11
Bifenthrin	6	10	3	9	13	6	5	9	15	12	8	13
Bitertanol	2	3	2	4	4	2	4	2	2	6	11	10
Boscalid (Nicobifen)	3	3	2	3	3	2	3	2	6	2	11	7
Bromopropylate	7	8	4	10	10	5	6	8	5	13	7	13
Bromuconazole	2	4	2	4	7	3	4	3	2	6	9	11
Bupirimate*	6	3	3	4	3	3	3	3	6	5	9	6
Buprofezin*	6	4	3	5	4	3	3	4	2	4	8	4
Cadusafos	7	9	3	8	15	3	12	5	2	7	6	6
Captan	31	64	15	75	28	21	52	66	n.d.	n.d.	n.d.	n.d.
Carbaryl*	10	13	8	25	18	3	20	9	<LOQ	22	15	29
Carbofuran	18	5	4	16	27	5	17	11	11	40	20	50
Carboxin	7	4	2	7	6	4	3	6	4	5	7	7

Table 5 continued

** spiking levels are 50, 100 & 500 ** spiking levels are 100, 200 & 1000 <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry				Wheat Flour				Leek			
	Precision			Intermediate Precision	Precision			Intermediate Precision	Precision			Intermediate Precision
	Level 1	Level 2	Level 3		Level 1	Level 2	Level 3		Level 1	Level 2	Level 3	
Chlorfenapyr*	5	7	5	6	11	5	6	6	4	5	6	8
Chlorfenvinphos	4	5	4	7	33	5	15	37	3	4	8	10
Chlorobenzilate	3	7	4	6	5	3	38	4	3	5	8	6
Chlorothalonil	4	18	18	16	38	9	27	11	n.d.	n.d.	n.d.	n.d.
Chlorpropham	4	5	3	4	20	4	12	6	4	8	5	5
Chlorpyrifos-ethyl	5	7	2	6	11	7	10	8	13	7	7	6
Chlorpyrifos-methyl	5	3	5	6	17	3	12	6	8	5	6	5
Cyfluthrin	6	7	3	7	4	2	5	3	9	19	13	19
Cyhalothrin	8	25	9	19	3	3	3	3	3	20	15	18
Cypermethrin	6	12	5	9	11	2	3	3	17	9	12	13
Cyproconazole	5	4	3	4	4	2	2	3	5	6	7	4
Cyprodinil	3	8	3	6	7	5	8	7	8	6	6	8
DDD p,p	2	3	2	5	2	4	3	4	4	5	6	7
DDE p, p	7	7	4	6	6	4	2	5	4	6	5	16
DDT p,p	4	9	4	18	10	3	7	6	3	4	9	9
Deltamethrin	9	32	11	23	15	2	4	6	5	18	13	19
Demeton-S-methyl*	1	6	4	5	12	4	13	9	5	4	7	11
Diazinon	7	9	3	6	14	4	13	6	12	8	6	6
Dichlofluanid*	8	25	12	20	56	20	17	17	<LOD	<LOD	90	n.d.
Dichloran	11	10	4	8	11	5	16	6	10	8	5	8
Dichlorbenzophenon, p,p'-	14	18	5	14	<LOD	<LOQ	11	n.d.	<LOQ	16	7	18
Dichlorvos	5	7	8	13	28	5	19	9	8	7	10	9
Dicofol	9	4	2	5	5	1	4	4	5	2	10	8
Difenoconazole	7	4	3	10	19	5	5	14	10	5	3	12
Dimethoate	10	10	6	12	17	3	11	10	5	5	6	8
Dimethomorph	5	3	3	11	18	7	9	13	5	7	9	6
Diphenylamine	7	7	3	6	33	12	19	21	8	12	7	8
Endosulfan*	9	10	5	8	6	7	46	21	17	8	6	6
Endosulfan sulfate	9	3	4	5	4	3	4	3	4	6	9	6
EPN	4	3	3	11	8	4	4	11	4	6	9	6
Epoxiconazole	4	5	2	4	6	3	6	2	5	4	7	5
Ethion	1	3	2	3	4	2	3	2	8	7	9	5
Ethoprop (Ethoprophos)	2	7	2	5	16	4	13	12	4	6	6	5
Etofenprox	3	5	2	6	4	2	2	2	3	3	9	6
Fenamiphos	9	7	3	8	10	4	7	6	5	9	12	10
Fenamiphos sulfone	11	30	10	27	12	2	5	11	15	19	17	16
Fenamiphos-sulfoxid**	8	22	7	28	26	3	12	17	9	5	21	9
Fenarimol	3	3	1	3	7	2	3	3	3	5	9	9
Fenbuconazol	3	5	3	4	3	3	3	2	1	6	10	5
Fenitrothion	9	7	4	8	16	4	11	8	5	5	7	7
Fenoxycarb	3	3	2	3	6	5	5	7	2	7	8	8
Fenpropathrin	9	4	2	4	<LOD	<LOD	8	n.d.	<LOD	<LOD	13	n.d.
Fenpropidin*	27	26	11	21	29	12	61	15	n.d.	37	17	42

Table 5 continued

** spiking levels are 50, 100 & 500 ** spiking levels are 100, 200 & 1000 <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry				Wheat Flour				Leek			
	Precision			Intermediate Precision	Precision			Intermediate Precision	Precision			Intermediate Precision
	Level 1	Level 2	Level 3		Level 1	Level 2	Level 3		Level 1	Level 2	Level 3	
Fenpropimorph	7	11	3	7	14	6	8	8	18	10	9	9
Fenthion	16	5	6	13	30	12	9	48	12	13	5	10
Fenvalerate	5	8	3	7	7	2	3	2	3	4	12	9
Fipronil	8	5	3	7	24	4	18	17	11	4	4	17
Fludioxonil	<LOD	<LOD	6	n.d.	7	5	46	5	6	9	5	8
Fluquinconazole	7	7	5	7	13	4	4	11	3	6	10	16
Flusilazole	12	14	3	9	7	7	4	7	14	15	6	15
Flutolanil	5	2	2	5	8	4	6	5	4	8	8	8
Flutriafol	6	1	2	5	23	2	40	5	6	6	7	8
Fluvalinate	8	12	5	9	6	5	4	4	9	14	14	14
Folpet**	30	71	21	74	27	12	43	22	<LOD	<LOD	<LOQ	n.d.
HCH alpha	7	9	3	6	9	4	11	5	3	8	5	13
HCH beta	7	8	3	7	18	4	10	7	7	8	7	12
HCH gamma_Lindane	10	9	1	7	12	4	11	4	10	9	6	10
Hexaconazole*	14	12	3	9	11	6	4	7	13	4	10	8
Imazalil*	7	4	3	4	9	5	10	4	6	4	10	8
Iprodione	12	4	4	5	6	5	8	7	7	7	11	10
Isofenphos-methyl	3	3	3	3	13	4	9	6	4	4	7	7
Kresoxim-methyl	1	6	4	5	5	2	5	3	8	4	6	5
Linuron*	5	5	7	18	18	6	20	12	5	4	10	9
Malathion	3	8	4	8	14	4	14	10	10	11	10	12
Mepanipyrim	10	4	3	6	13	4	22	8	4	7	9	5
Metalaxyl*	5	5	5	5	17	5	12	6	2	7	4	6
Methacrifos	11	11	3	7	75	3	17	8	7	11	6	11
Methamidophos	15	12	14	31	23	7	25	8	7	14	9	22
Methidathion	6	7	5	7	14	3	13	5	5	4	8	6
Methiocarb**	15	15	5	17	<LOD	<LOD	11*	n.d.	<LOD	<LOQ	11	n.d.
Metribuzin*	8	7	6	9	15	5	11	6	5	7	7	7
Monocrotophos*	13	13	11	20	9	2	13	6	6	15	10	18
Myclobutanil	5	3	3	6	1	5	3	4	6	9	5	7
Ortho-phenylphenol	4	7	3	6	31	12	15	20	4	8	6	6
Oxadiazon	3	9	4	7	5	4	6	4	9	8	6	8
Oxadixyl	4	4	4	5	8	2	4	3	7	5	8	8
Paclobutrazol	3	6	5	4	16	4	10	7	4	4	8	6
Paraoxon-methyl*	7	10	12	17	12	4	17	10	4	16	16	16
Parathion (ethyl)*	8	10	3	12	25	8	11	17	4	5	7	5
Parathion-methyl	13	11	6	9	8	7	12	8	4	5	7	4
Pendimethalin	22	20	5	25	17	13	11	32	8	9	6	14
Permethrin	3	4	3	4	2	3	4	3	4	10	11	8
Phenthoate*	5	7	4	6	5	3	13	23	3	5	8	4
Phosalone	2	5	2	4	42	3	3	22	4	10	8	10
Phosmet	7	10	9	14	6	1	8	4	6	23	13	26
Phosphamidon	7	9	10	21	20	2	15	8	76	42	24	62

Table 5 continued

** spiking levels are 50, 100 & 500 ** spiking levels are 100, 200 & 1000 <LOD/LOQ – spiking value below LOD/LOQ value*

Compound	Strawberry				Wheat Flour				Leek			
	Precision			Intermediate Precision	Precision			Intermediate Precision	Precision			Intermediate Precision
	Level 1	Level 2	Level 3		Level 1	Level 2	Level 3		Level 1	Level 2	Level 3	
Pirimicarb	9	7	5	6	13	5	12	6	7	9	6	7
Pirimicarb-p-desmetyl*	12	16	8	11	13	3	12	5	4	8	9	5
Pirimiphos methyl	6	6	4	5	10	4	11	22	6	7	6	5
Prochloraz*	4	3	4	7	9	5	7	10	5	6	14	6
Procymidone	8	6	4	7	16	2	8	10	8	6	7	9
Profenofos	19	12	7	13	14	8	12	12	13	27	12	31
Propargite	5	4	4	11	<LOD	<LOD	56	n.d.	10	9	8	16
Propiconazole	2	2	3	4	8	4	11	3	3	6	8	6
Propyzamide	4	6	3	5	11	3	11	5	2	7	5	5
Prothiofos	9	3	4	6	17	5	8	17	8	10	6	11
Pyraclostrobin	5	3	3	8	2	2	3	2	2	3	11	5
Pyridaben	3	2	3	4	3	2	2	3	6	8	12	9
Pyrimethanil	4	7	2	6	13	3	8	5	3	9	7	6
Pyriproxyfen	3	4	2	4	4	1	3	1	2	4	8	6
Quinoxyfen	2	4	2	3	4	2	2	5	5	3	8	3
Spirodiclofen	10	6	5	13	14	5	10	10	<LOQ	11	12	17
Tebuconazole	3	2	1	3	6	3	7	2	3	3	9	7
Tebufenocide*	6	5	2	6	<LOD	<LOQ	6	7	<LOQ	6	9	7
Tebufenpyrad	3	6	3	5	18	7	10	16	3	8	8	6
Tefluthrin	7	7	4	5	16	5	11	6	4	8	6	6
Tetraconazole*	4	6	4	4	13	4	11	6	4	4	6	4
Tetradifon	11	7	4	5	7	2	6	4	7	6	7	7
Tetrahydrophthalimide (THPI)	<LOQ	<LOQ	8	n.d.	<LOQ	27	11	23	<LOQ	9	6	8
Thiabendazole*	5	3	4	3	16	3	14	6	4	5	9	7
Tolclofos-methyl	4	6	6	9	15	6	15	18	5	8	5	20
Tolyfluanid*	9	22	10	20	21	8	17	10	n.d.	n.d.	n.d.	n.d.
Triadimefon*	4	4	2	5	12	3	9	6	1	6	6	7
Triadimenol*	9	7	3	7	10	3	9	10	9	7	7	5
Trifloxystrobin	4	4	2	3	6	4	3	3	4	8	8	6
Trifluralin	3	16	8	17	1	12	13	20	2	12	8	32
Triticonazole	7	3	3	3	4	3	2	3	5	6	9	6
Vinclozolin	15	4	6	8	16	6	14	14	23	9	7	10

Table 6: Method LOD, LOQ and current legislative residue level values *(all values in ng/g).*

** default value of 10 ng/g set as no MRL values defined*

Compound	Strawberry			Wheat Flour			Leek		
	LOD	LOQ	MRL	LOD	LOQ	MRL	LOD	LOQ	MRL
Acephate	0.3	1	20	0.6	2	20	1.5	5	20
Acrinathrin	6	20	200	2.7	9	50	6	20	50
Amitraz	6	20	50	300	1000	50	12	40	50
Azinphos-methyl	3	10	50	0.9	3	50	2.4	8	50
Azoxystrobin	0.9	3	1000	0.3	1	300	1.5	5	1000
Bifenthrin	6	20	500	4.8	16	500	7.5	25	50
Bitertanol	0.9	3	50	0.6	2	50	0.6	2	50
Boscalid (Nicobifen)	0.3	1	1000	0.15	0.5	500	0.6	2	5000
Bromopropylate	3	10	10	2.1	7	10	1.5	5	10
Bromuconazole	2.4	8	50	0.27	0.9	200	1.2	4	50
Bupirimate	3	10	1000	3	10	50	4.5	15	50
Buprofezin	6	20	3000	15	50	50	4.5	15	50
Cadusafos	1.5	5	10	0.3	1	10	1.5	5	10
Captan	3	10	3000	3	10	20	1000	1500	2000
Carbaryl	4.5	15	50	4.5	15	500	4.5	15	50
Carbofuran	9	30	20	3	10	20	4.5	15	20
Carboxin	1.8	6	20	6	20	20	0.6	2	20
Chlorfenapyr	4.5	15	10*	1.5	5	10*	3	10	10*
Chlorfenvinphos	1.5	5	10*	0.3	1	10*	1.2	4	10*
Chlorobenzilate	0.9	3	20	0.3	1	20	1.2	4	20
Chlorothalonil	12	40	5000	0.3	1	100	1500	2500	40000
Chlorpropham	1.5	5	50	0.6	2	20	1.2	4	50
Chlorpyrifos-ethyl	1.5	5	10*	0.3	1	10*	1.5	5	10*
Chlorpyrifos-methyl	1.5	5	500	0.3	1	3000	0.75	2.5	50
Cyfluthrin	4.5	15	20	3.6	12	20	2.4	8	20
Cyhalothrin	1.8	6	10*	0.9	3	10*	1.5	5	10*
Cypermethrin	4.5	15	70	15	50	2000	4.5	15	500
Cyproconazole	1.5	5	50	1.8	6	100	1.5	5	50
Cyprodinil	1.2	4	5000	0.3	1	500	1.5	5	50
DDD p,p	0.3	1	50	0.21	0.7	50	0.75	2.5	50
DDE p,p	0.3	1	10*	0.24	0.8	10*	1.2	4	10*
DDT o,p	0.6	2	10*	0.9	3	10*	0.6	2	10*
Deltamethrin	4.5	15	200	2.4	8	2000	7.5	25	200
Demeton-S-methyl	1.5	5	10*	1.5	5	10*	1.2	4	10*
Diazinon	0.3	1	10	0.3	1	20	0.3	1	10
Dichlofluanid	13.5	45	10*	3	10	10*	150	500	10*
Dichloran	4.5	15	300	3	10	10	2.4	8	100
Dichlorbenzophenon, p,p'-	3	10	10*	15	50	10*	4.5	15	10*
Dichlorvos	3	10	10	3	10	10	2.7	9	10
Dicofol	2.4	8	20	1.5	5	20	1.5	5	20
Difenoconazole	1.5	5	400	1.2	4	100	0.9	3	500
Dimethoate	1.2	4	20	0.6	2	50	0.6	2	20
Dimethomorph	1.5	5	10*	1.5	5	10*	0.6	2	10*

Table 6 continued

** default value of 10 ng/g set as no MRL values defined*

Compound	Strawberry			Wheat Flour			Leek		
	LOD	LOQ	MRL	LOD	LOQ	MRL	LOD	LOQ	MRL
Diphenylamine	0.3	1	50	0.3	1	50	0.6	2	50
Endosulfan	1.5	5	50	6	20	50	1.2	4	50
Endosulfan sulfate	0.6	2	10*	1.5	5	10*	0.9	3	10*
EPN	2.1	7	10*	2.1	7	10*	0.9	3	10*
Epoxiconazole	1.2	4	50	0.6	2	600	0.6	2	50
Ethion	1.2	4	10	0.9	3	10	0.6	2	10
Ethoprop (Ethoprophos)	0.3	1	20	0.6	2	20	0.9	3	20
Etofenprox	0.9	3	1000	0.9	3	500	0.6	2	10
Fenamiphos	1.2	4	20	1.2	4	20	0.9	3	20
Fenamiphos sulfone	3.6	12	10*	0.9	3	10*	1.5	5	10*
Fenamiphos-sulfoxid	0.9	3	10*	10.5	35	10*	7.5	25	10*
Fenarimol	0.9	3	300	0.3	1	20	0.3	1	20
Fenbuconazol	0.6	2	50	0.6	2	100	0.75	2.5	50
Fenitrothion	3	10	10	1.5	5	50	2.4	8	10
Fenoxycarb	0.9	3	50	1.2	4	50	0.75	2.5	50
Fenpropathrin	7.5	25	2000	30	100	10	30	100	10
Fenpropidin	4.5	15	50	12	40	500	7.8	26	50
Fenpropimorph	0.15	0.5	1000	0.3	1	500	1.2	4	1000
Fenthion	1.5	5	10	1.8	6	10	1.5	5	10
Fenvalerate	2.25	7.5	20	1.5	5	50	0.9	3	20
Fipronil	0.3	1	5	1.5	5	5	0.9	3	10
Fludioxonil	30	100	3000	1.2	4	200	1.2	4	50
Fluquinconazole	0.6	2	50	0.3	1	100	0.6	2	50
Flusilazole	4.5	15	20	2.4	8	100	1.5	5	20
Flutolanil	0.6	2	50	0.3	1	50	0.6	2	50
Flutriafol	0.3	1	500	0.9	3	500	0.45	1.5	50
Fluvalinate	6	20	10*	3.6	12	10*	4.5	15	10*
Folpet	75	250	3000	450	1500	2000	600	2000	20
HCH alpha	0.3	1	10	0.3	1	20	0.3	1	10
HCH beta	0.3	1	10	0.3	1	20	0.3	1	10
HCH gamma_Lindane	0.15	0.5	10	0.3	1	10	0.6	2	10
Hexaconazole	9	0	200	4.5	15	100	4.5	15	20
Imazalil	1.5	0	50	6	20	50	1.8	6	50
Iprodione	1.5	5	1000	1.5	5	500	1.2	4	20
Isofenphos-methyl	0.3	1	10*	0.3	1	10*	1.2	4	10*
Kresoxim-methyl	1.5	5	1000	1.8	6	50	1.5	5	5000
Linuron	3	10	50	1.8	6	50	1.5	5	50
Malathion	3	10	20	10.5	35	8000	3.6	12	20
Mepanipyrim	1.8	6	2000	2.4	8	10	1.2	4	10
Metalaxyl	9	30	500	10.5	35	50	7.5	25	200
Methacrifos	0.9	3	50	1.8	6	50	0.9	3	50
Methamidophos	0.75	2.5	10	0.9	3	10	1.5	5	10
Methidathion	0.6	2	20	0.9	3	20	1.5	5	20

Table 6 continued

** default value of 10 ng/g set as no MRL values defined*

Compound	Strawberry			Wheat Flour			Leek		
	LOD	LOQ	MRL	LOD	LOQ	MRL	LOD	LOQ	MRL
Methiocarb	150	500	1000	300	1000	100	135	450	200
Metribuzin	0.6	2	100	1.8	6	100	2.1	7	100
Monocrotophos	3	10	10*	4.5	15	10*	3	10	10*
Myclobutanil	0.3	1	1000	1.2	4	20	1.2	4	20
Ortho-phenylphenol	1.5	5	10*	1.5	5	10*	1.5	5	10*
Oxadiazon	0.3	1	50	0.9	3	50	0.6	2	50
Oxadixyl	3	10	10	5.4	18	10	3	10	70
Paclobutrazol	0.9	3	500	0.3	1	20	1.2	4	20
Paraoxon-methyl	6	20	20	6	20	20	3	10	20
Parathion (ethyl)	12	40	10*	37.5	125	10*	12	40	10*
Parathion-methyl	0.6	2	10*	1.2	4	10*	1.5	5	10*
Pendimethalin	1.5	5	50	1.2	4	50	2.1	7	50
Permethrin	2.4	8	50	1.8	6	50	4.5	15	50
Phenthoate	12	40	10*	1.8	6	10*	7.5	25	10*
Phosalone	1.8	6	50	1.2	4	50	1.5	5	50
Phosmet	0.24	0.8	50	0.3	1	50	0.6	2	50
Phosphamidon	0.3	1	10	3	10	10	3	10	10
Pirimicarb	0.9	3	3000	0.9	3	500	0.6	2	1000
Pirimicarb-p-desmetyl	0.9	3	10*	1.2	4	10*	1.5	5	10*
Pirimiphos methyl	0.27	0.9	50	0.6	2	5000	3	10	50
Prochloraz	15.6	52	50	30	100	500	15	50	50
Procymidone	3	10	20	3.9	13	20	1.8	6	20
Profenofos	3	10	50	2.1	7	50	2.1	7	50
Propargite	3	10	10	30	100	10	7.5	25	10
Propiconazole	1.8	6	50	1.2	4	50	0.6	2	100
Propyzamide	0.21	0.7	20	0.9	3	20	0.6	2	20
Prothiofos	2.4	8	10*	0.9	3	10*	1.5	5	10*
Pyraclostrobin	0.75	2.5	1000	0.3	1	100	0.3	1	500
Pyridaben	0.9	3	1000	1.8	6	50	1.5	5	50
Pyrimethanil	0.9	3	5000	1.5	5	50	1.2	4	1000
Pyriproxyfen	0.3	1	50	1.2	4	50	0.6	2	50
Quinoxyfen	0.15	0.5	300	0.24	0.8	20	0.6	2	20
Spirodiclofen	6	20	2000	6	20	20	6	20	20
Tebuconazole	1.5	5	50	0.24	0.8	200	0.3	1	1000
Tebufenocide	30	100	50	60	200	50	30	100	50
Tebufenpyrad	0.3	1	500	0.6	2	50	0.6	2	50
Tefluthrin	0.15	0.5	50	0.3	1	50	1.5	5	50
Tetraconazole	2.4	8	200	1.5	5	100	1.2	4	20
Tetradifon	1.2	4	10	1.8	6	10	0.9	3	10
Tetrahydrophthalimide (THPI)	7.5	25	10*	4.5	15	10*	4.5	15	10*
Thiabendazole	4.5	15	50	1.5	5	50	2.7	9	50
Tolclofos-methyl	0.3	1	50	0.6	2	50	2.1	7	50
Tolyfluanid	7.5	25	5000	1.8	6	50	1000	3000	10*

Table 6 continued

** default value of 10 ng/g set as no MRL values defined*

Compound	Strawberry			Wheat Flour			Leek		
	LOD	LOQ	MRL	LOD	LOQ	MRL	LOD	LOQ	MRL
Triadimefon	0.6	2	500	2.1	7	200	1.2	4	100
Triadimenol	7.5	25	500	2.1	7	200	2.7	9	100
Trifloxystrobin	1.5	5	500	1.2	4	50	1.2	4	200
Trifluralin	15	50	100	4.5	15	100	3	10	500
Triticonazole	1.5	5	10	0.6	2	10	1.5	5	10
Vinclozolin	2.4	8	50	0.9	3	50	2.7	9	50

Table 7: External quality control (FAPAS) results for the relevant compounds.

Compound	Fapas Sample Number	Assigned Value [µg/kg]	Acceptance Range [µg/kg]	Measured Value [µg/kg] (RSD%)
Carbaryl	T19142	89	49.9-128.2	51.2 (22)
beta Endosulfan	T19140	93.6	52.4-134.9	91.3 (7)
Chlorpyrifos-methyl	T19141	86.0	48.2-123.9	88.8 (8)
Cypermethrin	T19141	128.8	72.3-184.1	111.9 (8)
Cypermethrin	T19142	140.4	80.0-200.7	120.2 (17)
DDT, o,p	T19141	67.4	37.8-97.1	38.7 (16)
Dicloran	T19142	66.3	37.1-95.5	63.1 (15)
Dimethoate	T19141	69.0	38.6-99.4	62.3 (15)
Ethoprophos	T19142	29.3	16.4-42.4	25.7 (10)
Methidathion	T19141	29.0	16.3-41.8	29.1 (19)
Monocrotophos	T19141	26.4	14.8-38.0	36.8 (13)
Phosalone	T19140	70.4	39.4-101.4	68.3 (9)
Propyzamide	T19140	89.9	50.4-129.5	94.7 (4)

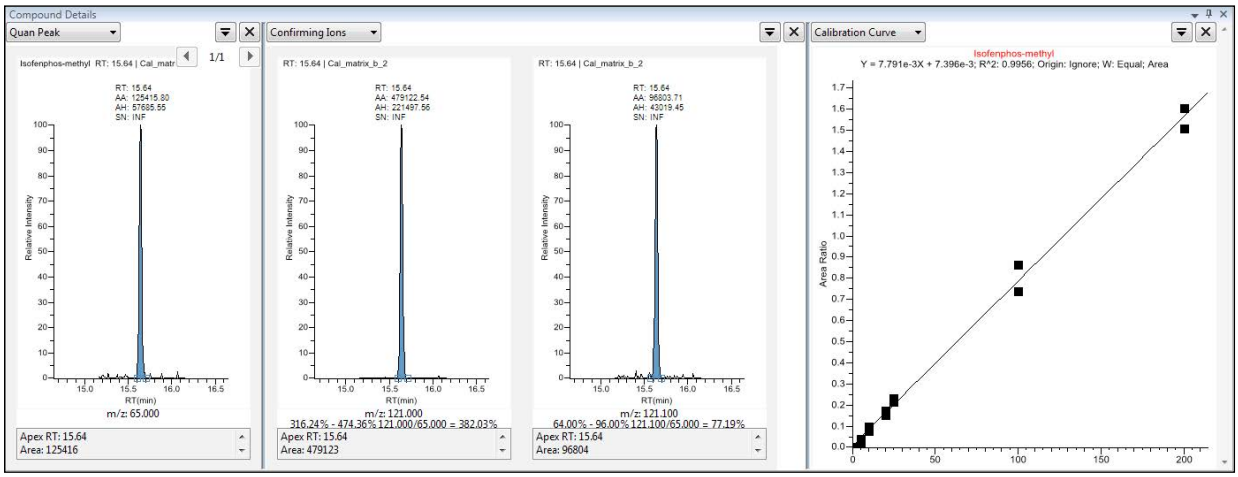

Figure 1. Chromatogram of isofenphos-methyl in leek at at calibration level 2 [5ng/g].

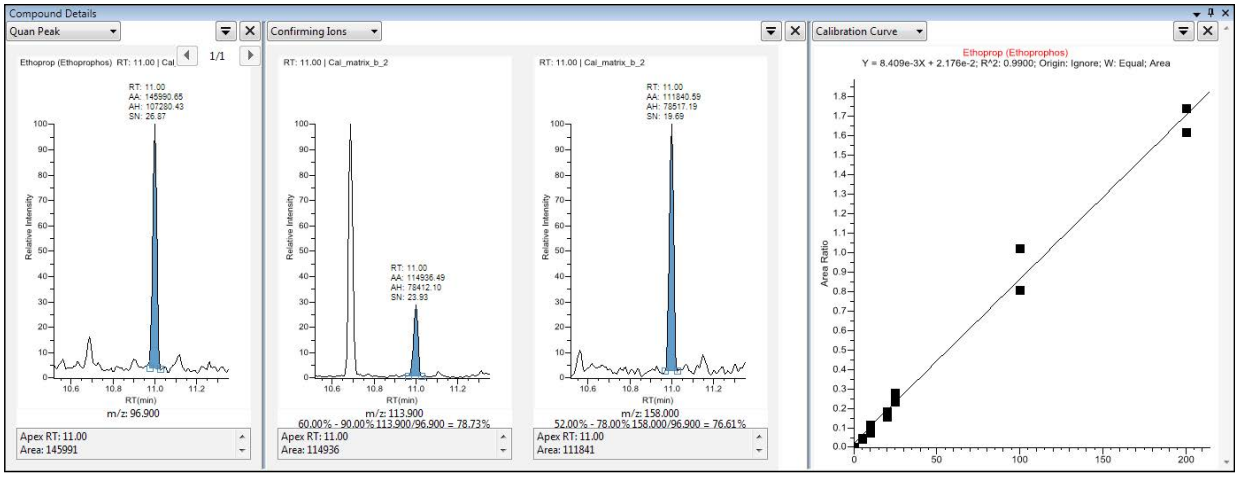

Figure 2. Chromatogram of ethoprop in leek at calibration level2 [5ng/g].

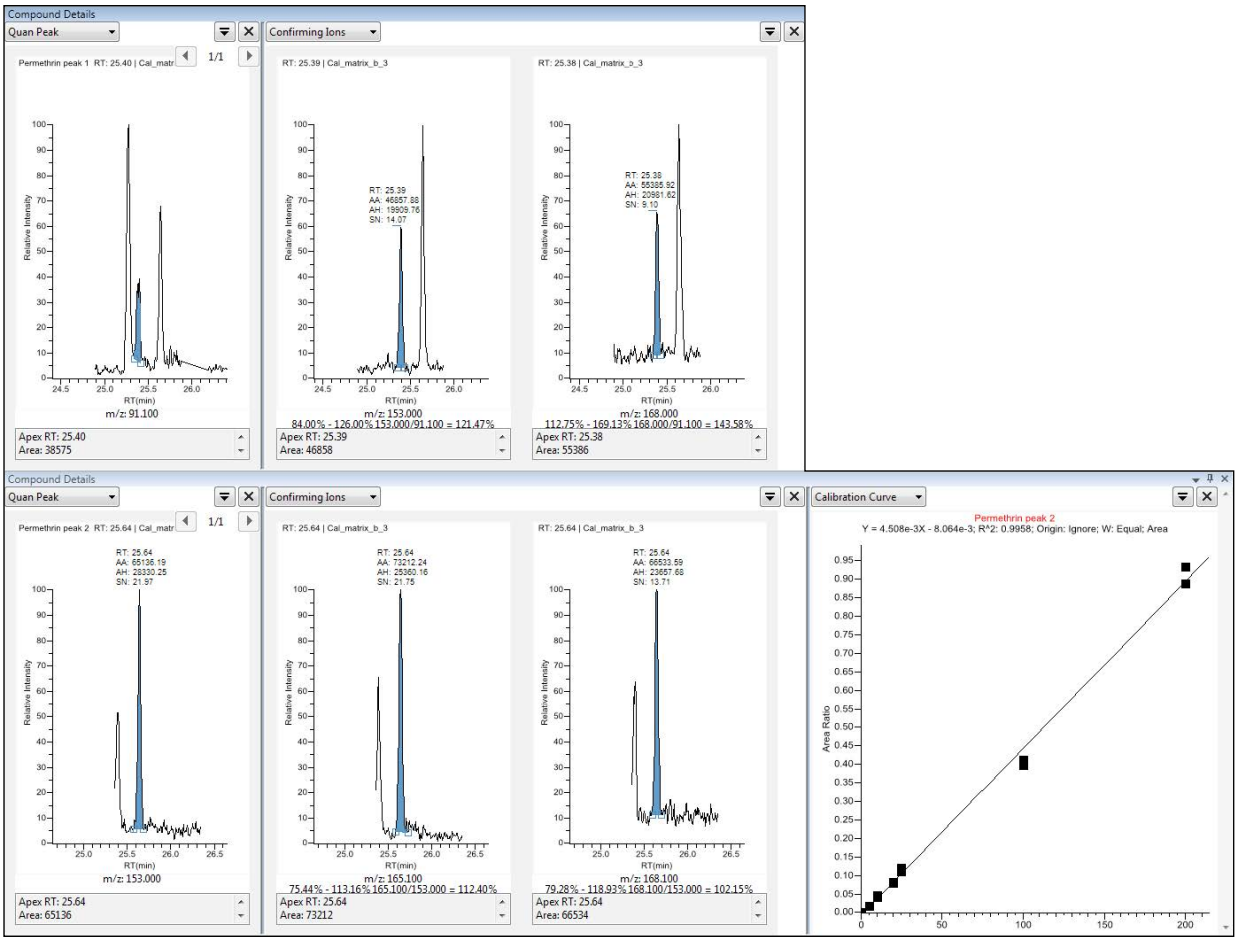

Figure 3. Chromatogram of both permethrine peaks in leek at calibration level3 [10ng/g].

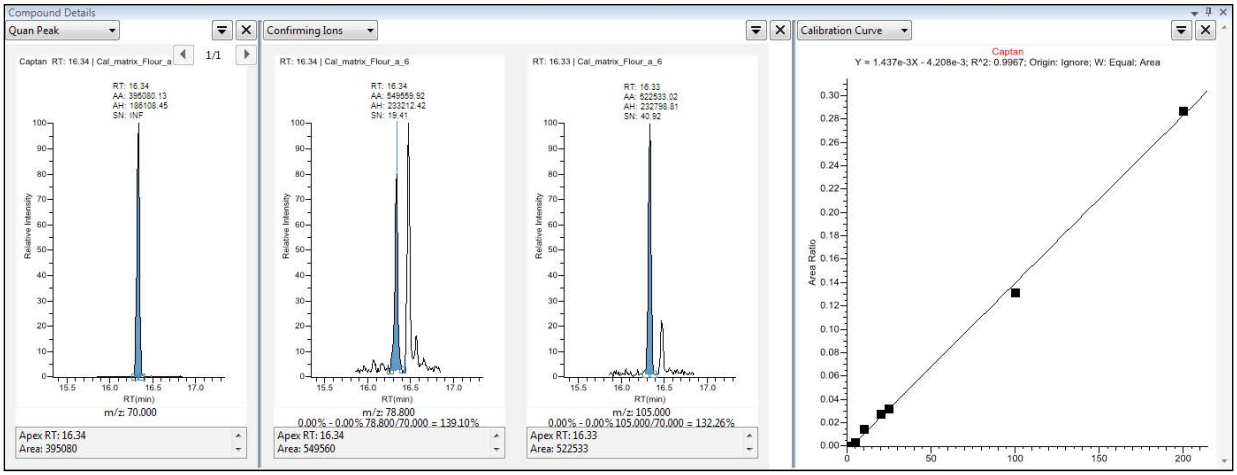

Figure 4. Chromatogram of captan in wheat flour at calibration level6 [100 ng/g].

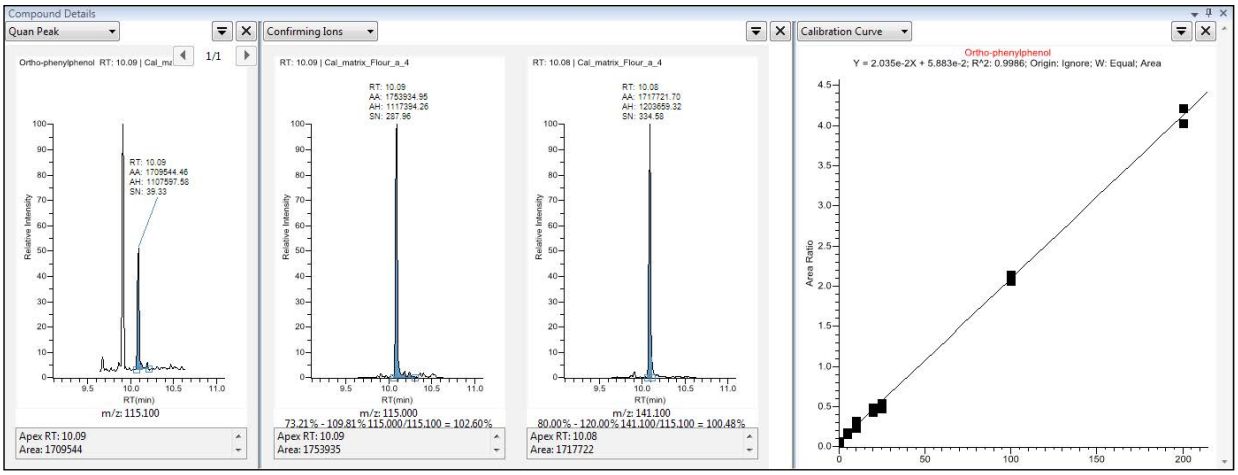

Figure 5. Chromatogram of o-phenylphenol wheat flour at calibration level4 [25ng/g].

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