

# **Validation of an automated pressurized liquid extraction method for the analysis of pesticide residues in complex matrices (black tea and green coffee)**

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## 1. Aim and scope

This study reports the validation data for 233 LC-amenable pesticides, most of them included in the European Union Multi Annual Control Program (EU-MACP) and the Working Document SANCO/ 12745/2013, using a multiresidue method by liquid chromatography coupled to triple quadrupole mass spectrometry (LC-MS/MS). An automatic extraction based on automated pressurized liquid extraction employing the EXTREVA® instrument has been developed for the extraction of these residues in complex matrices like tea and green coffee.

## 2. Short description

A new automated extraction method based on the use of an automated pressurised liquid extraction instrument (Extreva®) has been validated for 228 pesticides in black tea and 233 pesticides in green coffee using an LC-MS/MS instrument. With this purpose, blank samples were spiked at concentrations levels of 0.01, 0.02 and 0.05 mg/kg and extracted automatically with an EXTREVA instrument for pressurised liquid extraction (PLE). In the case of tea, no clean-up step was applied. For green coffee, freezing-out of the extracts was used before its analysis by LC-MS/MS.

The validation of the extraction method has been performed in terms of accuracy (spiking concentrations 0.01, 0.02 and 0.05 mg/kg) and repeatability (n=5). Matrix effects have also been assessed.

## 3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes from 1 µL to 5000 µL
- Graduated 10 mL pipette
- 15 mL PTFE centrifuge tubes
- Vortex Shaker IKATM 4 Basic
- Centrifuge Orto Alresa Consul 21, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 4000 rpm
- Injection vials, 2 mL, suitable for LC auto-sampler
- Amber vials, 4 mL
- EXTREVA® instrument supplied by ThermoFisher Scientific (Waltham, Massachusetts, United States of America)
- Extraction cells type SST 22 mL supplied by ThermoFisher Scientific (Waltham, Massachusetts, United States of America)
- Collection bottle of 60 mL
- ASE extraction filters cellulose

- Diatomaceous Earth (DE)(ASE)

#### 4. Chemicals

- Methanol ultra-gradient grade (MeOH)
- Acetonitrile ultra-gradient grade (AcN)
- Anhydrous magnesium sulphate
- Ammonium formate
- Ultra-pure water
- Formic acid
- Pesticide analytical standards
- Dry ice
- Nitrogen 5.0

#### 5. Procedure

##### 5.1. Sample preparation

The validation has been made in green coffee and black tea. All parts of the sample are taken as specified in Annex I to COMMISSION Regulation (EU) No 752/2014 of 24 June 2014 (replacing Annex I to Regulation (EC) No 396/2005). In both cases after crushing, a completely homogeneous powder with a particle size  $\leq 1$  mm must be obtained.

##### 5.2. Pesticide stock solutions and working mix solutions.

Individual pesticide stock solutions (1000–2000 mg/L) were prepared in acetonitrile and were stored in screw-capped glass vials in the dark at -20 °C.

For spiking, representative portions of the previously homogenized samples were spiked homogeneously with the appropriate amount of the working standard solution in acetonitrile. The validation methods were performed at spiking levels of 0.01, 0.02 and 0.05 mg/kg. Five replicates were analysed at each spiking level using procedural-standards for the calibration curve. Matrix effects have been assessed by matrix-matched calibration.

##### 5.3. Automated sample extraction using PLE

The efficiency of PLE <sup>[1]</sup> depends mainly on three factors which are temperature, extraction time and pressure. The extraction parameters of the method developed in this study are shown in **Table 1**.

To prepare the extraction cell, 3 grams of the sample are weighed and hydrated with 3 mL of water, followed by the addition of 3 grams of diatomaceous earth (DE). The extraction cell is assembled by placing a cellulose filter at the base and adding 225 milligrams of magnesium sulphate. The hydrated sample-DE mixture is then introduced into the cell, which is securely sealed and inserted into the pressurized liquid extraction (PLE) equipment.

**Table 1.** Extraction parameters

<b>Oven temperature</b>	45°C
<b>Purge time</b>	30 sec
<b>Gas Flowrate</b>	10 mL/min
<b>Cell type</b>	SST 22 mL
<b>Flowrate</b>	0.5 mL/Min
<b>Extraction time</b>	8 min
<b>Estimated volumen</b>	20 mL
<b>Pressure</b>	203 psi
<b>Solvent</b>	AcN/MeOH 1:1
<b>Rinse</b>	Pre-run 5 mL

After obtaining the extract (10 mL) from the automated extraction process, it is transferred from the collection tube to a 15 mL Falcon tube. For tea, the extract undergoes centrifugation for one minute before being transferred to a 4 mL vial, preparing it for analysis. For coffee, after transferring the extract to the 15 mL Falcon tube, a freezing-out step is performed using dry ice to precipitate lipids present in the matrix.

#### 5.4. Measurement

All samples were analysed by LC-MS/M system operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. Two SRM transitions and a correct ratio between the abundance of the two optimised SRM transitions (SRM2/SRM1) were used for confirmation of the studied compounds, along with retention time matching. The mass transitions used are summarized in **Appendix I (Table A1)**.

#### 5.5. Instrumentation and analytical conditions for the LC- MS/MS system

##### 5.5.1. 1290 UHPLC (Agilent)

- Column: Zorbax Eclipse Plus C8 2.1x100 mm and 1.8 µm particle size (Agilent)
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)

- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)
- Column temperature: 35 °C
- Flow rate: 0.3 ml/min
- Injection volume: 5 µL (10 µL in the case of rice)
- Autosampler temperature: 12 °C

Mobile phase gradient for pesticides analysis:

Time [min]	Mobile phase A%	Mobile phase B %
0	100	0
2	80	20
15	0	100
18	0	100

Re-equilibration with initial mobile phase: 2.5 minutes.

#### 5.5.2. 6490A triple quadrupole system (Agilent)

- Ionisation mode : positive mode and negative mode
- Capillary (positive and negative): 3000 V
- Nebulizer: 45 psi
- Nozzle: 400 V
- Drying gas Flow: 13 L/min
- Drying gas temperature: 120°C
- Sheath gas Flow: 10 L/min
- Sheath gas temperature: 375 °C
- High Pressure RF (positive): 150 V
- High Pressure RF (negative): 110 V
- Low Pressure RF (positive): 60 V
- Low Pressure RF (negative): 60 V

## 6. Results

### 6.1 Green coffee:

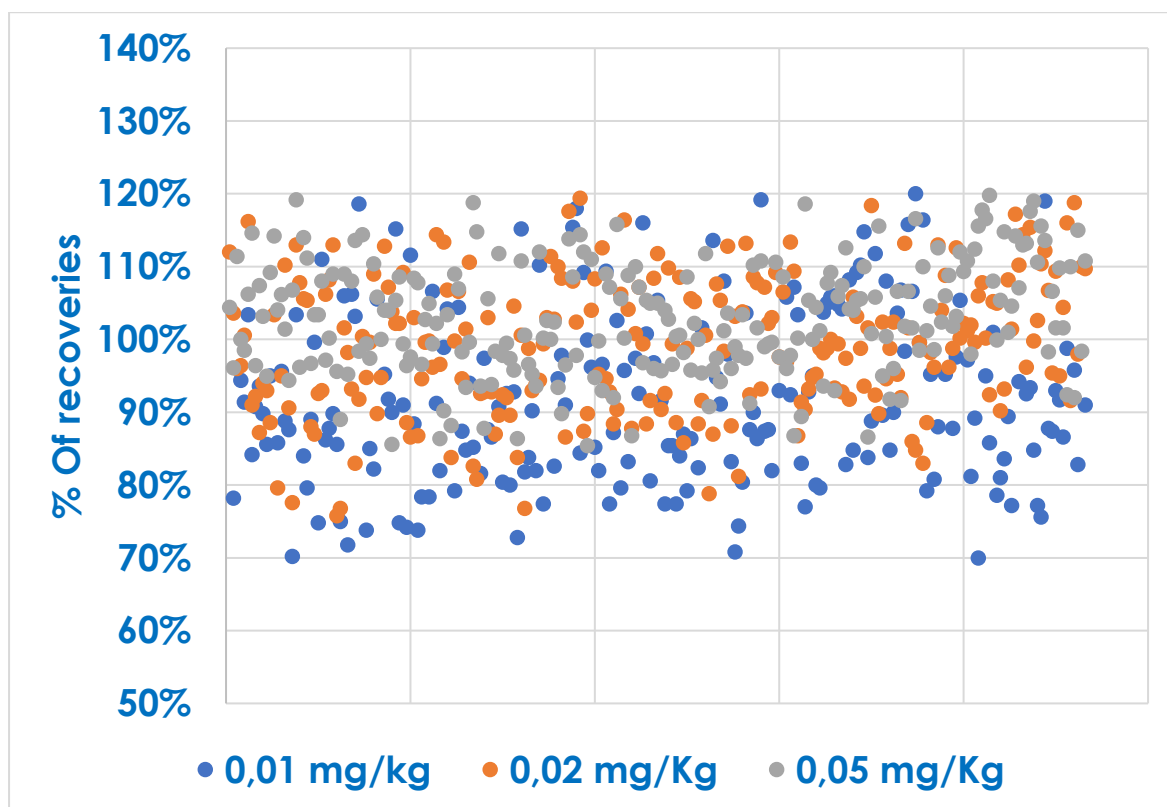
Procedural calibration was used to perform the validation in this study for both matrices (calibration points: 0.005, 0.010, 0.020, 0.050, and 0.100 mg/kg. The coefficient of determination ( $R^2$ ) was higher than 0.99 for all compounds). Prior to this, an experiment to determine absolute recovery was conducted during the initial validation, as it is a necessary step when employing a procedural standard.

In this experiment all recoveries exceeded 40%, allowing the standard procedure to be performed without any issues.

-Validation:

In the case of coffee, 233 compounds were validated. Five replicates were evaluated at three fortification levels: 0.01, 0.02, and 0.05 mg/kg, and quantified using procedural calibration, resulting in %RSD values below 20%. The range of %RSD values obtained was from 1 to 20%, yet for each fortification level, the mean values were found to be 7% (0.01 mg/kg), 7% (0.02 mg/kg) and 5% (0.05 mg/kg). This finding suggests that the automation process exhibits a high degree of reproducibility.

As demonstrated in **Figure 1**, the observed recoveries ranged from 70% to 120%.

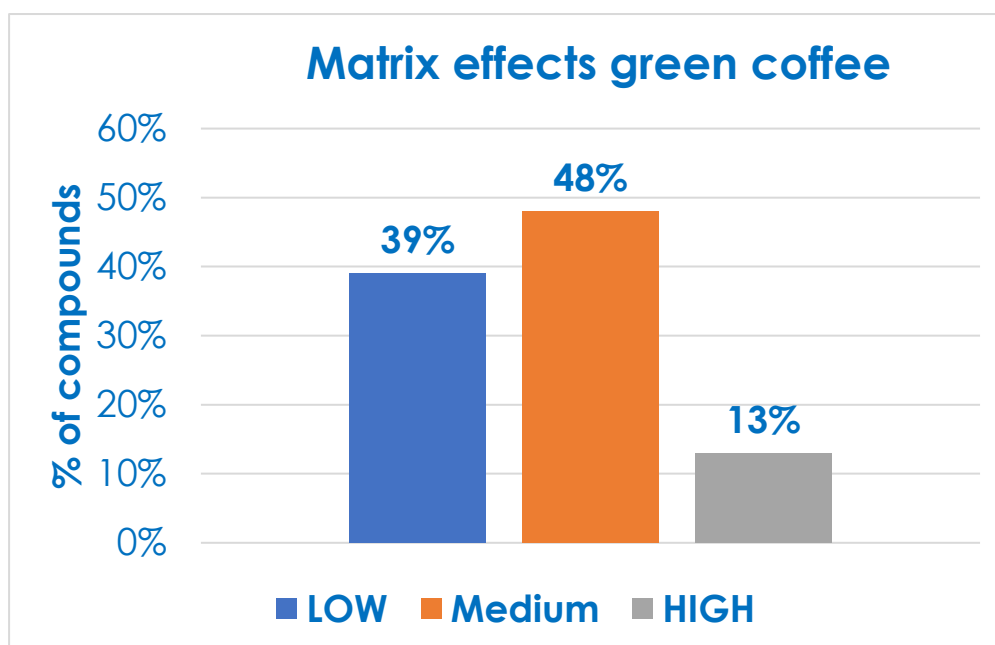


**Figure 1.** Scatter plot illustrates the percentage of recovery obtained at varying fortification levels in green coffee.

A significant proportion of the compounds analysed (89%) had an LOQ of 0.01 mg/kg, with only a small percentage having an LOQ of 0.02 mg/kg (11%). Individual results are shown in **Appendix I, Table (A2)**. The majority of the MRLs established for these matrices are established at 0.05 mg/kg.

-Matrix effect:

The assessment of matrix effects was conducted through a comparison of the slopes of five-point matrix-matched calibration curves with the slopes of the calibration curves in solvent. The calibration points were 0.005, 0.010, 0.020, 0.050, and 0.100 mg/kg. The coefficient of determination ( $R^2$ ) was higher than 0.99 for all compounds. The following classification system was employed: low matrix effect was assigned to values between 0 and 20%, moderate matrix effect was assigned to values between 20 and 50%, and strong matrix effect was assigned to values over 50%. The matrix effects are summarised in **Appendix I, Table (A2)**, and visualised in **Figure 2**.



**Figure 2.** Matrix effects for the target analytes in green coffee.

It has been observed that the compounds demonstrating the most significant matrix effect, or more precisely, the greatest suppression, are those that elute around minute 4 (flonicamid, thiamethoxan, demeton-s-methyl-sulfone), coinciding with the elution of caffeine. However, it can be stated that the matrix effects in coffee are predominantly medium to low.

6.2 Black tea:

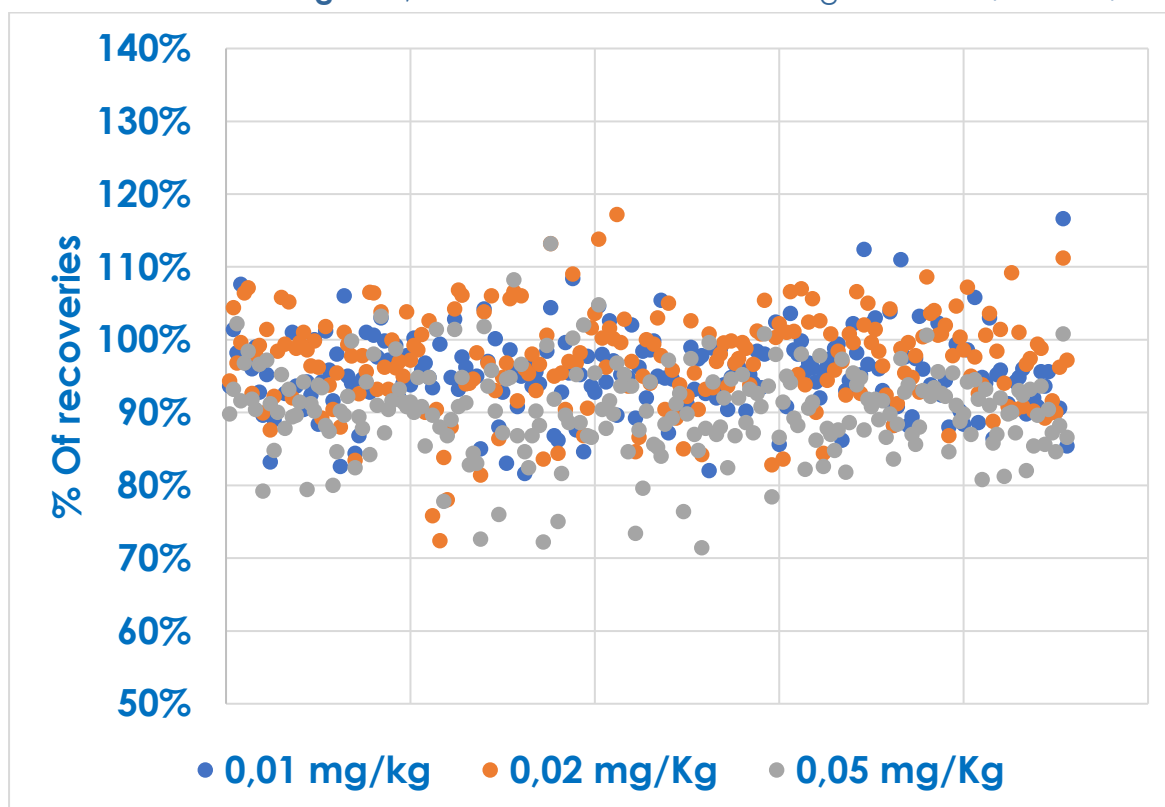
The results of the absolute-recovery experiment demonstrated that all recoveries achieved a success rate exceeding 40%, thereby enabling the standard procedure to be conducted without encountering any difficulties.



-Validation:

In the case of black tea, 228 compounds were validated. Five replicates were evaluated at three fortification levels: 0.01, 0.02, and 0.05 mg/kg, and quantified using procedural calibration, resulting in %RSD values below 20%. The range of %RSD values obtained was from 1 to 19%; however, for each fortification level, the mean values were found to be 6% (0.01 mg/kg), 6% (0.02 mg/kg) and 6% (0.05 mg/kg). This finding suggests that the automation process exhibits a high degree of reproducibility.

As demonstrated in **Figure 3**, the observed recoveries ranged from 70% to 120%.



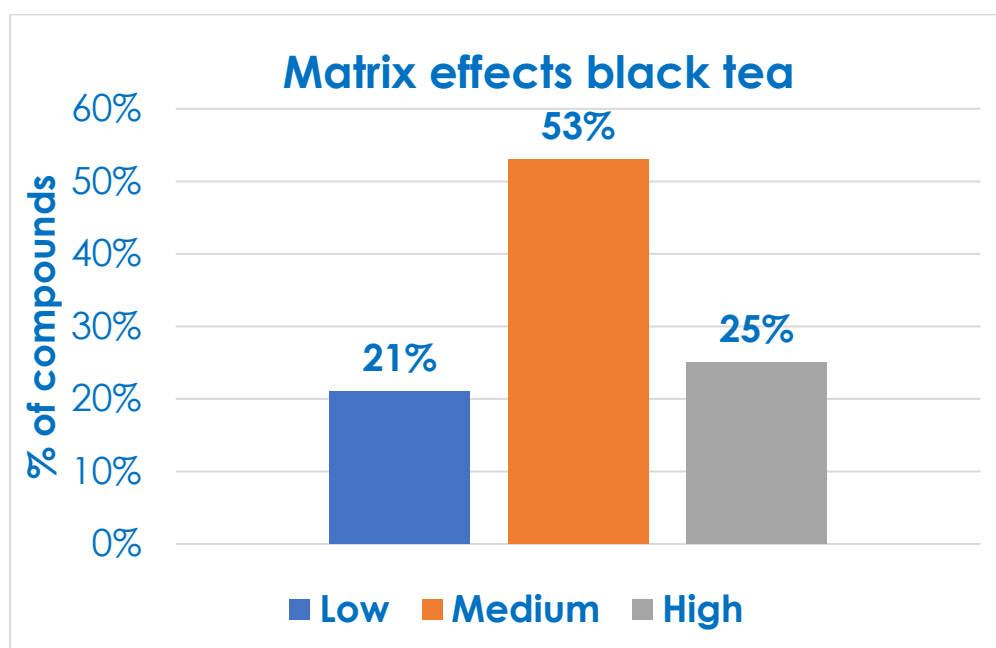
**Figure 3.** Scatter plot illustrates the percentage of recovery obtained at varying fortification levels in black tea.

A significant proportion of the compounds analysed have an LOQ of 0.01 mg/kg (90%), with only a small percentage having an LOQ of 0.02 mg/kg (10%). Individual results are shown in **Appendix I, Table (A3)**. The majority of the MRLs established for these matrices are established at 0.05 mg/kg.

-Matrix effect:

The assessment of matrix effects was conducted through a comparison of the slopes of five-point matrix-matched calibration curves with the slopes of the

calibration curves in solvent. The calibration points were 0.005, 0.010, 0.020, 0.050, and 0.100 mg/kg. The coefficient of determination ( $R^2$ ) was higher than 0.99 for all compounds. The following classification system was employed: low matrix effect was assigned to values between 0 and 20%, moderate matrix effect was assigned to values between 20 and 50%, and strong matrix effect was assigned to values over 50%. The matrix effects are summarised in **Appendix I, Table (A3)**, and visualised in **Figure 4**.



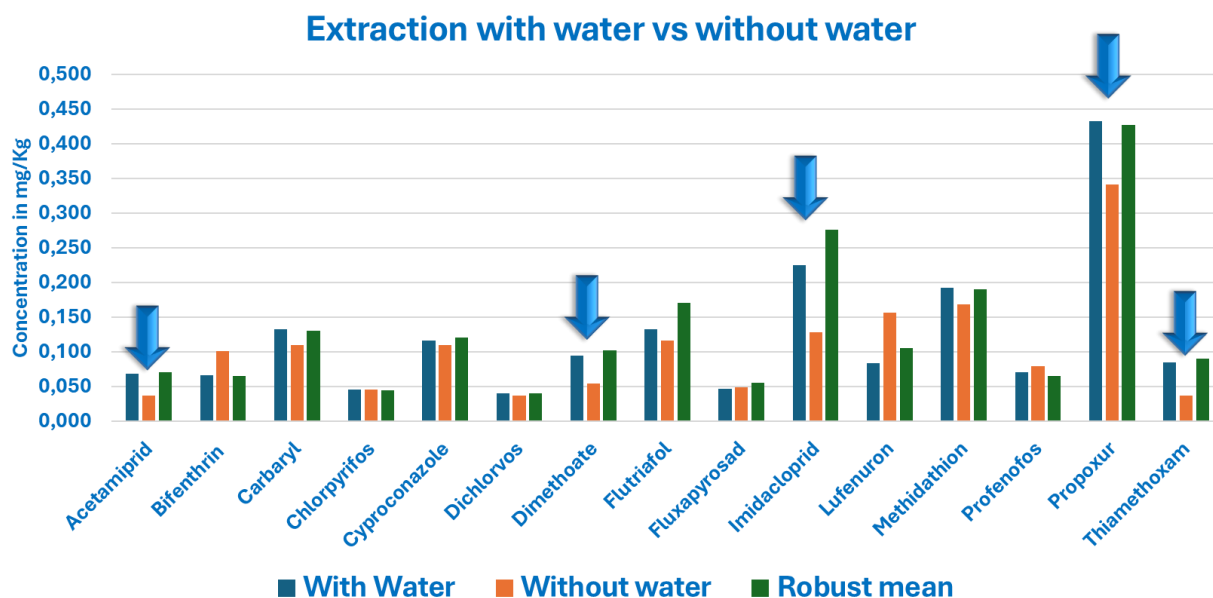
**Figure 4.** Matrix effects for the target analytes in black tea.

As with green coffee, it was observed that the compounds demonstrating the most significant matrix effect, the greatest suppression, were those that eluted around minute 4 (flonicamid, thiamethoxan, demeton-s-methyl-sulfone), coinciding with the elution of caffeine. Additionally, those compounds eluting around minute 2 also had a strong suppression, probably due to the elution of theobromine at a similar retention time. In the case of black tea, matrix effects were predominantly medium to high.

### 6.3 Extraction with water vs without water:

The addition of water has been demonstrated to enhance the extraction of caffeine and thus, to increase signal suppression. However, it has also been demonstrated that the addition of water is essential in this type of matrices to facilitate the extraction of more polar pesticides. To ascertain the relevance of water addition during extraction, an EUPT-FV-SC07 sample (green coffee) was

analysed with and without the addition of water prior to extraction. As shown in **Figure 5**, the addition of water is critical in the case of polar pesticides such as acetamiprid, dimethoate, imidacloprid, propoxur and thiamethoxam.



**Figure 5.** Extraction with water vs without water

Analysing EUPT-FV-SCO7 sample (green coffee) by automated extraction (PLE), acceptable values were obtained, as shown in **Table 2**.

**Table 2.** EUPT-FV-SCO7 results

	With Water	Without water	Robust mean	Zscore(with water)	Zscore(without water)
Acetamiprid	0,069	0,037	0,071	-0,1	-1,9
Bifenthrin	0,067	0,102	0,066	0,1	2,2
Carbaryl	0,133	0,11	0,131	0,1	-0,6
Chlorpyrifos	0,046	0,046	0,045	0,1	0,1
Cyproconazole	0,116	0,11	0,121	-0,2	-0,4
Dichlorvos	0,040	0,037	0,041	-0,1	-0,4
Dimethoate	0,095	0,055	0,103	-0,3	-1,9
Flutriafol	0,133	0,117	0,171	-0,9	-1,3
Fluxapyrosad	0,047	0,049	0,056	-0,6	-0,5
Imidacloprid	0,226	0,129	0,277	-0,7	-2,1
Lufenuron	0,084	0,157	0,106	-0,8	1,9
Methidathion	0,193	0,169	0,191	0,0	-0,5
Profenofos	0,071	0,08	0,066	0,3	0,8
Propoxur	0,433	0,342	0,428	0,0	-0,8
Thiamethoxam	0,086	0,038	0,091	-0,2	-2,3

## 7. Conclusions

An automated approach to sample extraction, such as the PLE, constitutes a favourable alternative to the QuEChERS methodology for this type of samples. A notable advantage of the PLE is that it has been demonstrated to exhibit low scatter of data, with percentage relative standard deviation (RSD) values of less than or equal to 20%.

The present technique has been developed with the purpose of minimising the number of manual manipulation steps in the extraction process, thus reducing the potential for human error. The technique has been designed to be very intuitive to use, with the intention that it will be easy to introduce into the workflow of the laboratory.

Using this technique the clean-up step can be skipped or minimised by using less reagents (no PSA or  $\text{MgSO}_4$ ). The addition of water is imperative for the extraction of more polar pesticides. In the context of green coffee and tea, caffeine has been observed to induce suppression during the elution of compounds exhibiting analogous retention times.

## 8. References

[1] Gerardo Alvarez-Rivera, Monica Bueno, Diego Ballesteros-Vivas, Jose A. Mendiola, Elena Ibañez, Chapter 13 - Pressurized Liquid Extraction, Editor(s): Colin F. Poole, In Handbooks in Separation Science, Liquid-Phase Extraction, Elsevier, 2020, Pages 375-398, ISBN 9780128169117, <https://doi.org/10.1016/B978-0-12-816911-7.00013-X>.

**APPENDIX I: MASS TRANSITIONS AND VALIDATION RESULTS**
**Table A1.** Detection parameters for the selected compounds analysed by LC-MS/MS.

Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Acephate	2.82	380	184.00	143.00	5	184.00	125.00	15	Positive
Acetamiprid	6.04	380	223.00	126.00	20	223.00	56.00	15	Positive
Alachlor	11.87	380	270.10	238.10	10	270.10	162.00	20	Positive
Ametoctradin	12.99	380	276.20	176.10	35	276.20	149.00	35	Positive
Anilofos	12.52	380	368.10	198.70	10	368.10	170.90	20	Positive
Atrazine	9.77	380	216.20	173.80	15	216.20	131.90	20	Positive
Azinphos-ethyl	11.63	380	368.00	160.10	10	368.00	131.90	15	Positive
Azinphos-methyl	10.36	380	318.00	261.00	0	318.00	132.10	8	Positive
Azoxystrobin	10.75	380	404.00	372.00	10	404.00	344.00	20	Positive
Benalaxyl	12.58	380	326.20	208.00	15	326.20	148.00	15	Positive
Bendiocarb	8.72	380	224.10	166.70	5	224.10	109.10	20	Positive
Benzovindiflupyr	12.48	380	398.00	377.90	10	398.00	342.00	15	Positive
Bifenazate	11.57	380	301.10	198.20	10	301.10	169.90	20	Positive
Bifenthrin	15.24	380	440.10	198.20	5	440.10	181.00	20	Positive
Bitertanol	12.71	380	338.20	269.20	5	338.20	99.10	10	Positive
Boscalid	11.06	380	343.00	307.10	16	343.00	272.10	32	Positive
Bromuconazole	11.83	380	378.00	159.00	20	378.00	70.00	20	Positive
Bupirimate	11.74	380	317.00	272.00	20	317.00	166.00	20	Positive
Buprofezin	13.65	380	306.00	201.00	10	306.00	116.00	15	Positive
Butoxycarboxim	3.60	380	240.10	222.70	5	240.10	165.90	5	Positive
Carbaryl	9.03	380	202.00	145.00	10	202.00	127.00	20	Positive
Carbendazim	4.17	380	192.00	160.00	15	192.00	132.00	20	Positive
Carbofuran	8,717	380	222	165	10	222	123	15	Positive
Chlorantraniliprole	10.42	380	483.90	452.90	16	483.90	285.90	8	Positive
Chlorbromuron	11.00	380	292.90	203.90	20	292.90	181.90	15	Positive
Chlorfenvinphos	12.78	380	358.90	155.00	8	358.90	99.20	28	Positive
Chloridazon	5.98	380	222.10	104.10	20	222.10	92.00	20	Positive
Chlorotoluron	9.51	380	213.10	140.00	20	213.10	72.00	20	Positive
Chloroxuron	11.48	380	291.20	217.80	20	291.20	71.90	20	Positive
Chlorpyrifos	13.79	380	352.00	200.00	20	349.93	198.00	20	Positive
Chromafenozide	11.87	380	395.20	339.10	5	395.20	174.90	10	Positive
Clofentezine	12.48	380	303.00	138.00	12	303.00	102.00	40	Positive
Clomazone	10.54	380	240.10	127.80	10	240.10	124.90	20	Positive
Coumaphos	12.37	380	363.00	307.00	20	363.00	227.00	28	Positive
Cyantraniliprole	9,206	380	474,9	285,8	25	474,9	444	15	Positive
Cyflufenamid	12.89	380	413.00	294.90	15	413.00	240.80	15	Positive
Cymoxanil	6.44	380	199.10	128.00	4	199.10	110.90	12	Positive

Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Cyproconazole	11.52	380	292.10	125.00	32	292.10	70.00	16	Positive
Cyprodinil	11.67	380	226.20	92.90	40	226.20	76.90	40	Positive
Cyromazine	2.01	380	167.00	125.00	15	167.00	59.90	20	Positive
Deltamethrin	14,505	380	522,9	280,8	10	522,9	278,7	10	Positive
Demeton-S-methyl	8.76	380	230.90	89.10	5	230.90	61.10	20	Positive
Demeton-S-methylsulfone	4,401	380	230,9	169	12	230,9	109	24	Positive
Demeton-S-methylsulfoxide(Oxydemeton-methyl)	4,131	380	247	169	8	247	109	24	Positive
Desethylterbutylazine	9.06	380	202.10	146.10	15	202.10	110.10	20	Positive
Diazinon	12.60	380	305.00	169.00	15	305.00	153.00	20	Positive
Dichlorvos	8.56	380	220.80	108.80	15	220.80	78.90	30	Positive
Dicrotophos	5.15	380	238.09	112.10	8	238.09	72.10	28	Positive
Diethofencarb	10.70	380	268.00	226.00	5	268.00	180.00	15	Positive
Difenoconazole	12.94	380	406.00	337.00	15	406.00	251.00	20	Positive
Difenoxyuron	9.94	380	287.20	123.10	15	287.20	72.10	15	Positive
Diflubenzuron	11.94	380	311.00	158.00	8	311.00	141.00	32	Positive
Dimethoate	6.07	380	230.00	199.00	5	230.00	171.00	10	Positive
Dimethomorph	11.00	380	388.00	301.00	20	388.00	165.00	20	Positive
Dimethylvinphos	11.56	380	331.00	204.80	10	331.00	127.00	10	Positive
Diniconazole	13.05	380	326.10	159.00	28	326.10	70.00	28	Positive
Dinotefuran	3.28	380	203.10	129.10	9	203.10	114.10	9	Positive
Diuron	10.09	380	233.03	160.00	20	233.03	72.10	20	Positive
Dodine	12.62	380	228.20	60.10	20	228.20	57.20	20	Positive
Edifenphos	12.40	380	311.10	282.80	10	311.10	110.90	20	Positive
EPN	12,967	380	324,1	296	10	324,1	156,99	20	Positive
Epoxiconazole	11.80	380	330.10	121.00	16	330.10	101.20	52	Positive
Ethion	13.80	380	385.10	199.00	5	385.10	171.00	10	Positive
Ethiprole	11.06	380	397.00	351.00	20	397.00	254.80	40	Positive
Ethirimol	7.35	380	210.16	140.10	20	210.16	43.10	52	Positive
Ethoprophos	11.91	380	243.10	130.90	15	243.10	97.00	30	Positive
Etofenprox	14.98	380	394.20	359.10	10	394.20	177.30	8	Positive
Etozazole	14,114	380	360	304	20	360	140,9	30	Positive
Fenamidone	11.06	380	312.00	92.20	28	312.00	65.10	56	Positive
Fenamiphos	12.12	380	304.10	234.00	12	304.10	217.10	20	Positive
Fenamiphos-sulfone	9.03	380	336.10	266.00	16	336.10	188.00	24	Positive
Fenamiphos-sulfoxide	8.81	380	320.11	292.10	8	320.11	108.10	44	Positive
Fenarimol	11.79	380	331.00	268.00	20	331.00	259.00	20	Positive
Fenazaquin	14,419	380	307,3	161,3	15	307,3	147,2	15	Positive
Fenbendazole	11.20	380	300.10	268.00	20	300.10	158.90	35	Positive
Fenbuconazole	11.97	380	337.10	125.10	40	337.10	70.00	33	Positive

Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Fenhexamid	11.70	380	302.00	97.00	25	302.00	55.00	30	Positive
Fenobucarb	10.88	380	208.20	151.90	5	208.20	95.10	20	Positive
Fenoxycarb	12.07	380	302.20	116.20	5	302.20	88.20	20	Positive
Fenpicoxamid	13.35	380	615.30	515.00	13	615.30	238.90	25	Positive
Fenpropathrin	14,257	380	367,2	124,8	15	367,2	350	5	Positive
Fenpropidin	10.38	380	274.30	147.10	30	274.30	85.80	25	Positive
Fenpropimorph	10.66	380	304.30	147.10	30	304.30	130.00	25	Positive
Fenpyrazamine	11.55	380	332.20	272.10	10	332.20	230.20	20	Positive
Fenpyroximate	13.97	380	422.21	366.20	12	422.21	107.00	64	Positive
Fensulfothion	10.01	380	309.00	252.80	17	309.00	157.00	29	Positive
Fenthion	12.33	380	279.00	247.10	8	279.00	169.10	12	Positive
Fenthion-sulfone	9.29	380	310.70	125.00	15	310.70	108.80	15	Positive
Fenthion-sulfoxide	8.99	380	295.02	280.00	16	295.02	109.00	32	Positive
Fenuron	5.67	380	165.20	92.10	20	165.20	71.80	20	Positive
Fipronil	12.28	380	434.90	329.90	12	434.90	249.90	28	Negative
Flazasulfuron	10.46	380	408.00	227.00	20	408.00	182.10	20	Positive
Flonicamid	4.38	380	230.10	202.60	10	230.10	173.90	10	Positive
Florpyrauxifen-benzyl	12,753	380	439,2	91,1	40	439,2	65	75	Positive
Fluacrypyrim	13.12	380	427.10	205.00	10	427.10	145.10	15	Positive
Fluzifop	10.97	380	328.20	282.20	15	328.20	254.20	20	Positive
Flubendiamide	12.46	380	680.90	273.90	15	680.90	254.00	20	Negative
Flufenacet	11.91	380	364.10	194.10	15	364.10	152.00	15	Positive
Flufenoxuron	14.07	380	489.10	158.00	20	489.10	140.90	56	Positive
Fluometuron	9.46	380	233.20	187.90	20	233.20	72.20	20	Positive
Fluopyram	11.77	380	397.10	208.00	20	397.10	173.10	20	Positive
Flupyradifuron	6,077	380	289,2	126	20	289,2	72,9	75	Positive
Fluquinconazole	11.55	380	376.00	307.10	24	376.00	108.00	56	Positive
Flusilazole	12.16	380	316.10	247.10	12	316.10	165.00	24	Positive
Flutriafol	9.90	380	302.10	95.00	56	302.10	70.10	16	Positive
Fluxapyroxad	11.30	380	381.90	362.00	10	381.90	342.00	15	Positive
Forchlorfenuron	9,907	380	248	128,9	20	248	93	30	Positive
Formetanate Hydrochloride	2,89	380	222,13	165	8	222,13	65,1	52	Positive
Fosthiazate	9.52	380	284.00	227.80	10	284.00	103.80	20	Positive
Haloxifop	12.22	380	362.10	316.20	12	362.10	288.10	24	Positive
Haloxifop-methyl	13,019	380	375,9	316	15	375,9	287,9	25	Positive
Hexaconazole	12.78	380	314.10	159.00	30	314.10	70.10	20	Positive
Hexaflumuron	13.12	380	459.00	439.00	5	459.00	276.10	20	Negative
Hexythiazox	13.98	380	353.10	228.20	10	353.10	168.20	20	Positive
Imazalil	9.51	380	297.00	255.00	15	297.00	159.00	20	Positive
Imidacloprid	5.29	380	256.00	209.00	15	256.00	175.00	15	Positive

Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Indoxacarb	13.13	380	528.10	218.00	20	528.10	203.00	45	Positive
Ioxynil	10.10	380	369.80	214.80	30	369.80	126.80	30	Negative
Iprovalicarb	11.88	380	321.20	202.90	0	321.20	119.00	16	Positive
Isofenfos-methyl	12.39	380	231.00	199.00	15	231.00	121.00	15	Positive
Isoprocarb	9.92	380	194.10	152.00	5	194.10	95.10	15	Positive
Isoprothiolane	11.25	380	291.00	230.70	10	291.00	189.10	15	Positive
Isoproturon	9.98	380	207.15	165.10	20	207.15	72.10	10	Positive
Isoxaflutole	10,168	380	360	250,9	15	360	219,7	50	Positive
Kresoxim-methyl	12.26	380	314.10	267.00	0	314.10	222.10	10	Positive
Lenacil	9.96	380	235.10	152.90	10	235.10	136.00	20	Positive
Lufenuron	13,742	380	508,9	339	10	508,9	325,9	10	Negative
Malathion	11.28	380	331.00	285.00	5	331.00	127.10	15	Positive
Mandipropamid	11.15	380	412.13	356.10	4	412.13	328.10	8	Positive
Mebendazole	9.23	380	296.10	263.90	21	296.10	105.00	37	Positive
Mefentrifluconazole	12,56	380	397,8	70	25	397,8	182	35	Positive
Metaflumizone	13.38	380	505.00	328.00	10	505.00	302.00	10	Negative
Metalaxyl	10.10	380	280.30	220.00	5	280.30	192.40	10	Positive
Metamitron	5.66	380	203.20	174.90	15	203.20	104.10	15	Positive
Metconazole	12.73	380	320.10	125.00	48	320.10	70.10	24	Positive
Methamidophos	2.31	380	142.10	125.00	10	142.10	94.10	10	Positive
Methidathion	10.29	380	302.90	145.00	0	302.90	85.10	15	Positive
Methiocarb	10.96	380	226.10	121.10	12	226.00	169.00	5	Positive
Methiocarb-sulfone	6.35	380	275.00	201.10	5	275.00	122.00	15	Positive
Methiocarb-sulfoxide	5.79	380	242.00	185.00	10	242.00	170.00	20	Positive
Methomyl	4.11	380	163.10	106.00	4	163.10	88.00	0	Positive
Methoxyfenozide	11.57	380	369.30	149.00	15	369.30	133.00	20	Positive
Metobromuron	9.58	380	259.00	170.00	15	259.00	148.00	10	Positive
Metolachlor	12.01	380	284.20	252.10	15	284.20	175.90	20	Positive
Metrafenone	12.83	380	409.10	226.90	16	409.10	209.10	8	Positive
Monocrotophos	4.73	380	224.20	193.10	5	224.20	127.00	10	Positive
Monolinuron	9.18	380	215.06	148.10	8	215.06	126.00	16	Positive
Monuron	8.20	380	199.10	125.80	20	199.10	71.90	15	Positive
Myclobutanil	11.52	380	289.20	125.10	20	289.20	70.20	15	Positive
Neburon	12.29	380	275.10	113.90	10	275.07	88.10	12	Positive
Nitfenpyram	3.83	380	271.00	225.00	10	271.00	99.00	10	Positive
Novaluron	13.29	380	490,8	470,7	5	490,8	305,1	15	Negative
Omethoate	3.12	380	214.10	183.00	5	214.10	125.00	20	Positive
Orthosulfamuron	10.03	380	425.00	226.90	15	425.00	199.10	15	Positive
Oxadiazyl	12.74	380	341.05	222.90	13	341.05	150.90	33	Positive
Oxadixyl	7.80	380	279.10	219.20	5	279.10	132.30	32	Positive



Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Oxamyl	3.82	380	237.00	90.00	5	237.00	72.00	10	Positive
Oxasulfuron	8.14	380	407.10	209.70	24	407.10	150.10	16	Positive
Oxathiapipronil	11.22	380	540.20	522.00	29	540.20	500.00	29	Positive
Oxfendazole	7.98	380	316.10	284.10	20	316.10	159.10	35	Positive
Paclobutrazol	11.32	380	294.10	125.20	36	294.10	70.10	16	Positive
Penconazole	12.44	380	284.00	159.00	20	284.00	70.00	15	Positive
Pencycuron	12.97	380	329.10	125.10	24	329.10	89.10	60	Positive
Pendimethalin	13.89	380	282.10	212.10	4	282.10	194.10	16	Positive
Penflufen	12.37	380	318.10	234.00	10	318.10	141.00	20	Positive
Phenthoate	12.29	380	321.00	247.10	4	321.00	79.10	44	Positive
Phosalone	12.74	380	368.00	182.00	8	368.00	110.90	44	Positive
Phosmet	10.46	380	317.99	160.00	8	317.99	133.00	36	Positive
Phoxim	12.67	380	299.00	129.10	4	299.00	77.10	24	Positive
Pirimicarb	7.62	380	239.20	182.10	15	239.20	72.20	20	Positive
Pirimiphos-methyl	12.66	380	306.20	164.20	20	306.20	108.20	20	Positive
Prochloraz	12.49	380	376.00	308.00	10	376.00	266.00	15	Positive
Profenofos	13.42	380	374.90	347.00	5	374.90	304.90	15	Positive
Promecarb	11.25	380	208.20	150.90	5	208.20	108.80	10	Positive
Propamocarb	3.27	380	189.20	144.10	10	189.20	102.10	15	Positive
Propaquizafop	13.45	380	444.10	371.00	15	444.10	99.90	20	Positive
Propargite	14.13	380	368.10	231.20	0	368.10	175.20	8	Positive
Propazine	10.87	380	230.20	187.90	15	230.20	146.00	20	Positive
Propiconazole	12.48	380	342.10	159.00	32	342.10	69.10	16	Positive
Propoxur	8.60	380	210.11	168.10	5	210.11	111.10	10	Positive
Propyzamide	11.31	380	256.00	190.00	10	256.00	173.00	20	Positive
Proquinazid	14.15	380	373.00	331.00	20	373.00	289.10	20	Positive
Prosulfocarb	13.32	380	252.10	128.00	10	252.10	90.90	20	Positive
Pymetrozine	2.81	380	218.11	105.00	20	218.11	51.00	60	Positive
Pyraclostrobin	12.54	380	388.11	193.80	8	388.11	163.10	20	Positive
Pyridaben	14.54	380	365.20	309.20	10	365.20	147.30	20	Positive
Pyridalyl	15.32	380	490.00	203.90	20	490.00	108.80	20	Positive
Pyridaphenthion	11.50	380	341.10	205.00	20	341.10	189.00	15	Positive
Pyridate	14.78	380	379.10	351.10	5	379.10	206.80	10	Positive
Pyrimethanil	10.07	380	200.00	183.00	20	200.00	107.00	20	Positive
Pyriofenone	12.86	380	366.10	209.00	20	366.10	183.90	20	Positive
Pyriproxyfen	13.63	380	322.00	185.00	20	322.00	96.00	10	Positive
Quinalphos	12.12	380	299.10	270.80	10	299.10	242.80	10	Positive
Quinoclamine	7.70	380	208.00	105.10	25	208.00	77.00	40	Positive
Quinoxifen	13.71	380	308.10	271.90	25	308.10	196.90	35	Positive
Quizalofop	11.83	380	345.00	299.00	20	345.00	254.90	35	Positive

Compounds	tR (min)	Cone voltage (V)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)	Polarity
Quizalofop-ethyl	13.25	380	373.09	271.20	24	373.09	255.10	36	Positive
Simazine	8.45	380	202.20	131.80	15	202.20	124.00	15	Positive
SpinosynA	12,589	380	732,5	142,5	35	732,5	98,1	25	Positive
SpinosynD	12,95	380	746,5	142	25	746,5	746,5	40	Positive
Spirodiclofen	14.43	380	411.10	313.00	5	411.10	71.20	15	Positive
Spiromesifen	14.22	380	371.00	273.00	5	371.00	255.00	20	Positive
Spirotetramat	11.72	380	374.20	330.30	15	374.20	270.10	20	Positive
Sulfoxaflor	6.49	380	278.00	153.90	20	278.00	105.10	10	Positive
Tebuconazole	12.45	380	308.00	125.00	20	308.00	70.00	20	Positive
Tebufenozide	12.35	380	353.20	296.90	5	353.20	133.10	15	Positive
Tebufenpyrad	13.58	380	334.20	145.10	20	334.20	117.00	47	Positive
Teflubenzuron	13.57	380	379.00	359.00	0	379.00	339.00	4	Negative
Terbutryn	11.15	380	242.20	186.20	15	242.20	91.00	20	Positive
Tetraconazole	11.92	380	372.00	159.00	36	372.00	70.00	20	Positive
Tetramethrin	13.47	380	332.10	163.90	15	332.10	135.10	15	Positive
Thiabendazole	4.83	380	202.00	175.00	30	202.00	131.00	40	Positive
Thiacloprid	6.75	380	253.00	186.00	10	253.00	126.00	20	Positive
Thiamethoxam	4.38	380	292.00	211.00	10	292.00	181.00	20	Positive
Thiobencarb	12.82	380	258.00	124.70	15	258.00	99.90	10	Positive
Tolclofos-methyl	12.62	380	300.90	269.00	10	300.90	125.00	15	Positive
Tolfenpyrad	13.53	380	384.10	197.00	25	384.10	170.90	20	Positive
Triadimefon	11.48	380	294.20	225.00	10	294.20	197.10	10	Positive
Triallate	13.94	380	306.01	145.00	25	306.01	86.00	15	Positive
Triazophos	11.52	380	314.10	286.20	10	314.10	162.20	20	Positive
Trichlorfon	5.96	380	258.90	222.50	5	258.90	108.80	20	Positive
Triclorcarban	13.10	380	313.00	160.00	20	313.00	126.00	20	Negative
Tricyclazole	7.03	380	190.10	163.00	25	190.10	136.10	35	Positive
Trifloxystrobin	13.20	380	409.20	206.20	10	409.20	186.20	20	Positive
Triflumizole	13.23	380	346.10	277.80	5	346.10	72.90	15	Positive
Triflumuron	12.71	380	359.00	156.00	8	359.00	139.00	32	Positive
Trinexapac-ethyl	10,158	380	253,1	185,1	5	253,1	41,1	45	Positive
Trinexapac-methyl	9,055	380	239,1	69	10	239,1	41,2	40	Positive
Triticonazole	11.79	380	318.10	125.20	20	318.10	70.20	20	Positive
Tritosulfuron	10.61	380	446.00	195.00	20	446.00	145.00	40	Positive
Valifenalate	11.58	380	399.00	313.00	10	399.00	143.70	15	Positive
XMC	9.04	380	180.10	123.10	10	180.10	95.10	20	Positive
Zoxamide	12.59	380	336.00	187.00	16	336.00	159.00	44	Positive

**Table A2.** Results of the validation process in green coffee

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Acephate	-	-	112%	1%	104%	7%	0.02	-32	0.99
Acetamiprid	78%	6%	104%	6%	96%	3%	0.01	-39	0.99
Alachlor	-	-	96%	10%	111%	4%	0.02	-14	0.99
Ametoctradin	94%	8%	96%	10%	100%	6%	0.01	-22	0.99
Anilofos	91%	3%	101%	3%	99%	4%	0.01	-20	0.99
Atrazine	103%	2%	116%	4%	106%	4%	0.01	-34	0.99
Azinphos-ethyl	84%	10%	91%	9%	115%	2%	0.01	-53	0.99
Azinphos-methyl	91%	7%	92%	6%	96%	3%	0.01	-25	0.99
Azoxystrobin	94%	4%	87%	8%	107%	4%	0.01	-13	0.99
Benclaxyl	90%	10%	94%	7%	103%	9%	0.01	-28	0.99
Bendiocarb	86%	8%	93%	7%	95%	3%	0.01	-48	0.99
Benzovindiflupyr	95%	5%	89%	7%	109%	5%	0.01	-22	0.99
Bifenazate	-	-	103%	7%	114%	2%	0.02	-62	0.99
Bifenthrin	86%	12%	80%	20%	104%	5%	0.01	-35	0.99
Bitertanol	96%	11%	95%	11%	106%	4%	0.01	31	0.99
Boscalid	89%	5%	110%	5%	101%	4%	0.01	2	0.99
Bromuconazole	88%	10%	91%	4%	94%	4%	0.01	-11	0.99
Bupirimate	70%	2%	78%	11%	107%	5%	0.01	-11	0.99
Buprofezin	103%	7%	113%	5%	119%	2%	0.01	-28	0.99
Butoxycarboxim	-	-	108%	5%	96%	9%	0.02	-25	0.99
Carbaryl	84%	7%	106%	7%	114%	3%	0.01	-45	0.99
Carbendazim	80%	3%	105%	3%	111%	5%	0.01	-33	0.99
Carbofuran	89%	11%	88%	7%	97%	6%	0.01	-52	0.99
Chlorantraniliprole	100%	4%	87%	7%	103%	5%	0.01	-1	0.99
Chlorbromuron	75%	10%	93%	6%	103%	6%	0.01	-22	0.99
Chlorfenvinphos	111%	3%	93%	11%	108%	6%	0.01	-20	0.99
Chloridazon	86%	7%	106%	4%	97%	2%	0.01	-43	0.99
Chlorotoluron	88%	7%	108%	4%	100%	6%	0.01	-24	0.99
Chloroxuron	90%	6%	113%	3%	109%	5%	0.01	-9	0.99
Chlorpyrifos	86%	8%	76%	5%	96%	5%	0.01	-64	0.99
Chromafenozide	75%	7%	77%	7%	89%	5%	0.01	-6	0.99
Clofentezine	106%	5%	102%	5%	109%	3%	0.01	-18	0.99
Clomazone	72%	6%	98%	4%	95%	4%	0.01	-19	0.99
Coumaphos	106%	6%	93%	6%	108%	5%	0.01	33	0.99
Cyantraniliprole	103%	9%	83%	11%	114%	3%	0.01	-5	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Cyflufenamid	119%	2%	92%	4%	98%	6%	0.01	-37	0.99
Cymoxanil	-	-	100%	7%	114%	4%	0.02	-77	0.99
Cyproconazole	74%	3%	95%	7%	99%	6%	0.01	-27	0.99
Cyprodinil	85%	7%	100%	6%	97%	4%	0.01	-11	0.99
Cyromazine	82%	5%	109%	8%	110%	3%	0.01	87	0.99
Deltamethrin	106%	3%	90%	10%	106%	5%	0.01	-60	0.99
Demeton-S-methyl	-	-	95%	14%	100%	3%	0.02	-55	0.99
Demeton-S-methylsulfone	95%	8%	113%	2%	104%	3%	0.01	-63	0.99
Demeton-S-methylsulfoxide (Oxydemeton-methyl)	92%	2%	107%	2%	104%	5%	0.01	-30	0.99
Desethylterbutylazine	90%	4%	104%	9%	86%	5%	0.01	-56	0.99
Diazinon	115%	1%	102%	9%	105%	7%	0.01	-30	0.99
Dichlorvos	75%	12%	102%	7%	109%	6%	0.01	-25	0.99
Dicrotophos	91%	3%	109%	5%	99%	4%	0.01	-25	0.99
Diethofencarb	74%	5%	89%	6%	96%	7%	0.01	-17	0.99
Difenoconazole	112%	4%	87%	12%	98%	8%	0.01	18	0.99
Difenoxyuron	88%	6%	103%	8%	108%	9%	0.01	-19	0.99
Diflubenzuron	74%	5%	87%	7%	108%	4%	0.01	-14	0.99
Dimethoate	78%	7%	95%	2%	97%	3%	0.01	-36	0.99
Dimethomorph	-	-	100%	6%	103%	3%	0.02	15	0.99
Dimethylvinphos	78%	7%	100%	5%	105%	8%	0.01	-17	0.99
Diniconazole	107%	2%	96%	11%	99%	7%	0.01	-27	0.99
Dinotefuran	91%	3%	114%	5%	102%	3%	0.01	-20	0.99
Diuron	82%	6%	97%	7%	86%	4%	0.01	-31	0.99
Dodine	99%	4%	113%	1%	90%	5%	0.01	42	0.99
Edifenphos	104%	6%	107%	6%	103%	6%	0.01	-17	0.99
EPN	-	-	84%	18%	88%	6%	0.02	-71	0.99
Epoxiconazole	79%	10%	100%	7%	109%	3%	0.01	-2	0.99
Ethion	104%	4%	107%	5%	107%	5%	0.01	-60	0.99
Ethiprole	87%	2%	95%	12%	98%	4%	0.01	22	0.99
Ethirimol	85%	2%	101%	3%	93%	2%	0.01	-28	0.99
Ethoprophos	94%	4%	111%	2%	100%	2%	0.01	-9	0.99
Etofenprox	85%	3%	83%	10%	119%	4%	0.01	-58	0.99
Etoxazole	-	-	81%	11%	115%	6%	0.02	-34	0.99
Fenamidone	82%	7%	93%	9%	94%	7%	0.01	-9	0.99
Fenamiphos	97%	10%	93%	7%	88%	8%	0.01	-13	0.99
Fenamiphos-sulfone	88%	8%	103%	5%	106%	5%	0.01	8	0.99
Fenamiphos-sulfoxide	87%	5%	93%	7%	94%	2%	0.01	11	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Fenarimol	-	-	87%	15%	98%	9%	0.02	-33	0.99
Fenazaquin	91%	5%	90%	10%	112%	6%	0.01	-62	0.99
Fenbendazole	80%	8%	92%	7%	98%	4%	0.01	-41	0.99
Fenbuconazole	93%	4%	92%	8%	100%	3%	0.01	-16	0.99
Fenhexamid	80%	9%	90%	10%	97%	4%	0.01	-17	0.99
Fenobucarb	93%	10%	105%	5%	96%	9%	0.01	-6	0.99
Fenoxycarb	73%	10%	84%	6%	86%	4%	0.01	-10	0.99
Fenpicoxamid	115%	7%	101%	7%	111%	6%	0.01	6	0.99
Fenpropathrin	82%	5%	77%	5%	101%	6%	0.01	-20	0.99
Fenpropidin	84%	6%	99%	6%	97%	3%	0.01	-17	0.99
Fenpropimorph	90%	3%	93%	1%	95%	6%	0.01	-19	0.99
Fenpyrazamine	82%	7%	94%	7%	94%	6%	0.01	-11	0.99
Fenpyroximate	110%	4%	94%	10%	112%	5%	0.01	-30	0.99
Fensulfothion	77%	7%	99%	8%	100%	8%	0.01	-6	0.99
Fenthion	-	-	103%	10%	103%	11%	0.02	-20	0.99
Fenthion-sulfone	-	-	111%	13%	100%	9%	0.02	10	0.99
Fenthion-sulfoxide	83%	7%	103%	6%	102%	5%	0.01	-16	0.99
Fenuron	95%	2%	110%	2%	93%	5%	0.01	-33	0.99
Fipronil	98%	7%	108%	6%	90%	9%	0.01	26	0.99
Flazasulfuron	91%	3%	87%	16%	97%	3%	0.01	69	0.99
Flonicamid	-	-	118%	9%	114%	15%	0.02	-94	0.99
Florpyrauxifen-benzyl	115%	5%	108%	6%	109%	4%	0.01	32	0.99
Fluacrypyrim	118%	5%	102%	5%	98%	5%	0.01	-24	0.99
Fluazifop	84%	20%	119%	20%	114%	4%	0.01	78	0.99
Flubendiamide	109%	16%	87%	6%	112%	7%	0.01	31	0.99
Flufenacet	100%	3%	90%	8%	85%	7%	0.01	-4	0.99
Flufenoxuron	96%	6%	104%	10%	111%	4%	0.01	40	0.99
Fluometuron	85%	6%	108%	4%	95%	6%	0.01	-31	0.99
Fluopyram	82%	6%	95%	9%	100%	7%	0.01	-22	0.99
Flupyradifuron	97%	8%	113%	5%	93%	5%	0.01	-3	0.99
Fluquinconazole	109%	6%	95%	10%	109%	7%	0.01	-20	0.99
Flusilazole	77%	5%	93%	9%	107%	3%	0.01	-29	0.99
Flutriafol	87%	9%	88%	11%	92%	3%	0.01	-4	0.99
Fluxapyroxad	103%	5%	90%	10%	116%	5%	0.01	-19	0.99
Forchlorfenuron	80%	3%	106%	8%	106%	6%	0.01	-22	0.99
Formetanate Hydrochloride	96%	4%	116%	2%	100%	4%	0.01	-20	0.99
Fosthiazate	83%	8%	104%	2%	109%	4%	0.01	-24	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Haloxypop	-	-	88%	10%	87%	10%	0.02	23	0.99
Haloxypop-methyl	97%	5%	101%	10%	110%	5%	0.01	-32	0.99
Hexaconazole	93%	4%	107%	10%	107%	9%	0.01	-22	0.99
Hexaflumuron	116%	9%	99%	6%	97%	7%	0.01	49	0.99
Hexythiazox	101%	2%	88%	12%	105%	6%	0.01	-9	0.99
Imazalil	81%	6%	92%	8%	105%	3%	0.01	-21	0.99
Imidacloprid	97%	3%	108%	2%	96%	1%	0.01	25	0.99
Indoxacarb	105%	6%	112%	4%	105%	6%	0.01	14	0.99
loxynil	92%	5%	90%	6%	96%	4%	0.01	-17	0.99
lprovalicarb	77%	4%	93%	9%	104%	9%	0.01	-25	0.99
Isofenfos-methyl	85%	8%	110%	6%	103%	3%	0.01	-7	0.99
Isoprocarb	85%	8%	99%	6%	97%	6%	0.01	-25	0.99
Isoprothiolane	77%	8%	89%	3%	100%	4%	0.01	-28	0.99
Isoproturon	84%	5%	109%	6%	101%	1%	0.01	-8	0.99
Isoxaflutole	87%	4%	86%	11%	98%	8%	0.01	51	0.99
Kresoxim-methyl	79%	2%	99%	4%	109%	4%	0.01	-23	0.99
Lenacil	86%	5%	106%	4%	96%	3%	0.01	-28	0.99
Lufenuron	-	-	105%	7%	102%	6%	0.02	51	0.99
Malathion	82%	9%	88%	5%	100%	5%	0.01	-15	0.99
Mandipropamid	102%	7%	92%	8%	95%	7%	0.01	0	0.99
Mebendazole	-	-	101%	11%	112%	12%	0.02	17	0.99
Mefentrifluconazole	-	-	79%	12%	91%	7%	0.02	-1	0.99
Metaflumizone	114%	6%	87%	7%	96%	5%	0.01	30	0.99
Metalaxyl	95%	6%	108%	7%	97%	4%	0.01	-22	0.99
Metamitron	91%	10%	105%	8%	94%	5%	0.01	-21	0.99
Metconazole	108%	2%	98%	5%	101%	3%	0.01	-16	0.99
Methamidophos	98%	3%	113%	4%	104%	4%	0.01	-33	0.99
Methidathion	83%	12%	88%	10%	96%	5%	0.01	-25	0.99
Methiocarb	71%	7%	103%	5%	99%	4%	0.01	-16	0.99
Methiocarb-sulfone	74%	2%	81%	6%	98%	3%	0.01	-59	0.99
Methiocarb-sulfoxide	80%	6%	104%	6%	103%	2%	0.01	-32	0.99
Methomyl	104%	11%	113%	15%	97%	6%	0.01	-40	0.99
Methoxyfenozide	88%	6%	92%	7%	91%	3%	0.01	-16	0.99
Metobromuron	90%	8%	109%	5%	110%	5%	0.01	-37	0.99
Metolachlor	86%	7%	108%	6%	102%	6%	0.01	-18	0.99
Metrafenone	119%	1%	93%	10%	111%	6%	0.01	-19	0.99
Monocrotophos	87%	2%	107%	5%	99%	4%	0.01	-41	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Monolinuron	88%	2%	102%	7%	99%	4%	0.01	-36	0.99
Monuron	82%	4%	103%	3%	100%	4%	0.01	-37	0.99
Myclobutanil	-	-	109%	7%	111%	4%	0.02	-8	0.99
Neburon	93%	3%	98%	9%	98%	6%	0.01	-7	0.99
Nitenpyram	-	-	107%	7%	109%	4%	0.02	-67	0.99
Novaluron	106%	5%	97%	7%	96%	10%	0.01	60	0.99
Omethoate	92%	3%	113%	6%	98%	4%	0.01	-24	0.99
Orthosulfamuron	107%	11%	109%	5%	87%	8%	0.01	88	0.99
Oxadargyl	103%	6%	87%	9%	100%	6%	0.01	70	0.99
Oxadixyl	83%	7%	91%	12%	89%	10%	0.01	-33	0.99
Oxamyl	77%	7%	90%	8%	119%	10%	0.01	-89	0.99
Oxasulfuron	93%	3%	93%	6%	105%	4%	0.01	7	0.99
Oxathiapipronil	95%	5%	95%	6%	100%	10%	0.01	20	0.99
Oxfendazole	80%	4%	95%	8%	104%	3%	0.01	53	0.99
Paclobutrazol	80%	3%	99%	6%	101%	2%	0.01	-3	0.99
Penconazole	104%	5%	98%	4%	94%	6%	0.01	-16	0.99
Pencycuron	105%	3%	99%	9%	108%	4%	0.01	-19	0.99
Pendimethalin	106%	4%	100%	10%	109%	5%	0.01	-32	0.99
Penflufen	106%	5%	93%	6%	93%	2%	0.01	-20	0.99
Phenthoate	105%	4%	99%	2%	106%	4%	0.01	-14	0.99
Phosalone	104%	3%	93%	7%	107%	2%	0.01	-7	0.99
Phosmet	83%	3%	97%	11%	113%	7%	0.01	14	0.99
Phoxim	108%	4%	92%	10%	104%	3%	0.01	-33	0.99
Pirimicarb	85%	3%	106%	3%	104%	4%	0.01	-26	0.99
Pirimiphos-methyl	109%	10%	103%	11%	105%	10%	0.01	2	0.99
Prochloraz	110%	3%	99%	6%	106%	4%	0.01	-8	0.99
Profenofos	115%	6%	94%	9%	110%	7%	0.01	-13	0.99
Promecarb	84%	6%	102%	6%	87%	6%	0.01	-30	0.99
Propamocarb	89%	5%	118%	4%	101%	1%	0.01	-6	0.99
Propaquizafop	112%	1%	92%	7%	106%	5%	0.01	-14	0.99
Propargite	-	-	90%	13%	116%	3%	0.02	-58	0.99
Propazine	90%	4%	102%	4%	95%	4%	0.01	-33	0.99
Propiconazole	108%	4%	95%	5%	100%	11%	0.01	-13	0.99
Propoxur	85%	4%	99%	7%	92%	7%	0.01	-44	0.99
Propyzamide	90%	6%	102%	5%	96%	6%	0.01	-27	0.99
Proquinazid	104%	2%	95%	4%	107%	5%	0.01	-61	0.99
Prosulfocarb	107%	4%	92%	3%	92%	5%	0.01	-31	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Pymetrozine	98%	3%	113%	6%	102%	6%	0.01	36	0.99
Pyraclostrobin	116%	2%	102%	5%	107%	10%	0.01	-11	0.99
Pyridaben	107%	2%	86%	8%	102%	4%	0.01	-41	0.99
Pyridalyl	120%	5%	85%	10%	117%	4%	0.01	-42	0.99
Pyridaphenthion	100%	2%	100%	6%	99%	1%	0.01	11	0.99
Pyridate	116%	4%	83%	11%	110%	2%	0.01	24	0.99
Pyrimethanil	79%	8%	89%	7%	101%	5%	0.01	-21	0.99
Pyriofenone	95%	9%	98%	9%	105%	4%	0.01	-18	0.99
Pyriproxyfen	81%	7%	96%	8%	99%	7%	0.01	-18	0.99
Quinalphos	88%	11%	113%	4%	113%	8%	0.01	-9	0.99
Quinoclamine	-	-	104%	2%	102%	4%	0.02	-48	0.99
Quinoxifen	95%	5%	109%	6%	106%	14%	0.01	-35	0.99
Quizalofop	-	-	96%	8%	109%	12%	0.02	-16	0.99
Quizalofop-ethyl	88%	9%	99%	5%	102%	9%	0.01	-20	0.99
Simazine	98%	10%	113%	5%	103%	3%	0.01	-46	0.99
Spinosyn A	105%	6%	100%	8%	112%	2%	0.01	-10	0.99
Spinosyn D	-	-	102%	6%	109%	7%	0.02	-31	0.99
Spirodiclofen	97%	8%	101%	13%	111%	8%	0.01	-47	0.99
Spiromesifen	81%	10%	102%	9%	98%	9%	0.01	-53	0.99
Spirotetramat	89%	8%	100%	11%	112%	4%	0.01	46	0.99
Sulfoxaflor	70%	3%	106%	12%	116%	2%	0.01	-9	0.99
Tebuconazole	-	-	108%	11%	118%	12%	0.02	2	0.99
Tebufenozide	95%	10%	100%	7%	117%	5%	0.01	-12	0.99
Tebufenpyrad	86%	12%	92%	14%	120%	8%	0.01	-16	0.99
Teflubenzuron	101%	15%	105%	12%	108%	2%	0.01	16	0.99
Terbutryn	79%	8%	105%	8%	100%	5%	0.01	-28	0.99
Tetraconazole	81%	10%	90%	9%	105%	4%	0.01	-17	0.99
Tetramethrin	84%	13%	93%	16%	115%	2%	0.01	-16	0.99
Thiabendazole	89%	4%	108%	3%	101%	5%	0.01	-45	0.99
Thiacloprid	77%	8%	101%	4%	105%	3%	0.01	-50	0.99
Thiamethoxam	-	-	117%	8%	114%	8%	0.02	-82	0.99
Thiobencarb	94%	4%	110%	7%	107%	8%	0.01	-17	0.99
Tolclofos-methyl	-	-	114%	17%	113%	11%	0.02	-25	0.99
Tolfenpyrad	93%	4%	96%	13%	113%	9%	0.01	22	0.99
Triadimefon	93%	6%	115%	7%	118%	9%	0.01	-1	0.99
Triallate	85%	17%	100%	14%	119%	4%	0.01	-39	0.99
Triazophos	77%	10%	103%	8%	111%	13%	0.01	-12	0.99



Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Trichlorfon	76%	4%	110%	5%	116%	2%	0.01	-15	0.99
Triclorcarban	119%	13%	112%	3%	114%	12%	0.01	70	0.99
Tricyclazole	88%	4%	107%	4%	98%	2%	0.01	-37	0.99
Trifloxystrobin	87%	9%	95%	7%	107%	3%	0.01	-3	0.99
Triflumizole	93%	3%	109%	6%	102%	10%	0.01	-31	0.99
Triflumuron	92%	5%	95%	13%	110%	13%	0.01	-27	0.99
Trinexapac-ethyl	87%	4%	104%	7%	102%	3%	0.01	-6	0.99
Trinexapac-methyl	99%	4%	116%	7%	92%	5%	0.01	-19	0.99
Triticonazole	-	-	92%	13%	110%	5%	0.02	0	0.99
Tritosulfuron	96%	19%	119%	9%	92%	6%	0.01	100	0.99
Valifenalate	83%	13%	98%	13%	115%	3%	0.01	-2	0.99
XMC	-	-	110%	4%	98%	4%	0.02	-34	0.99
Zoxamide	91%	8%	110%	10%	111%	5%	0.01	-16	0.99

**Table A3.** Results of the validation process in black tea

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Acetamiprid	94%	4%	94%	7%	90%	3%	0.01	-47	0.99
Alachlor	101%	10%	104%	8%	93%	8%	0.01	-25	0.99
Aldicarb-sulfone	98%	16%	97%	5%	102%	5%	0.01	-67	0.99
Ametoctradin	108%	6%	100%	6%	92%	7%	0.01	-51	0.99
Anilofos	97%	5%	106%	8%	97%	4%	0.01	-37	0.99
Atrazine	97%	12%	107%	4%	98%	3%	0.01	-34	0.99
Azinphos-ethyl	96%	13%	93%	10%	92%	5%	0.01	-63	0.99
Azinphos-methyl	99%	8%	98%	10%	90%	4%	0.01	-42	0.99
Azoxystrobin	93%	5%	99%	4%	97%	5%	0.01	-11	0.99
Benalaxyl	90%	4%	90%	6%	79%	7%	0.01	-22	0.99
Bendiocarb	95%	12%	101%	7%	97%	5%	0.01	-44	0.99
Benzovindiflupyr	83%	10%	88%	7%	91%	3%	0.01	-39	0.99
Bifenazate	89%	4%	92%	5%	85%	7%	0.01	-30	0.99
Bifenthrin	-	-	98%	2%	90%	7%	0.02	-51	0.99
Bitertanol	-	-	106%	6%	95%	8%	0.02	48	0.99
Boscalid	93%	5%	99%	7%	88%	4%	0.01	-17	0.99
Bromuconazole	93%	12%	105%	12%	93%	5%	0.01	-8	0.99
Bupirimate	101%	7%	92%	10%	89%	6%	0.01	-31	0.99
Buprofezin	94%	5%	99%	3%	90%	5%	0.01	-41	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/ kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Butoxycarboxim	-	-	100%	9%	91%	7%	0.02	-70	0.99
Carbaryl	90%	3%	101%	4%	94%	5%	0.01	-46	0.99
Carbendazim	94%	7%	99%	3%	79%	5%	0.01	-63	0.99
Carbofuran	92%	7%	96%	6%	91%	6%	0.01	-35	0.99
Chlorantraniliprole	100%	6%	100%	4%	90%	3%	0.01	-16	0.99
Chlorbromuron	88%	5%	96%	4%	94%	5%	0.01	-25	0.99
Chlorfenvinphos	94%	9%	89%	4%	93%	6%	0.01	-33	0.99
Chloridazon	101%	7%	102%	3%	88%	7%	0.01	-61	0.99
Chlorotoluron	96%	6%	94%	4%	87%	3%	0.01	-24	0.99
Chloroxuron	92%	1%	90%	5%	80%	5%	0.01	-16	0.99
Chlorpyrifos	98%	7%	95%	4%	85%	6%	0.01	-59	0.99
Chromafenozide	83%	3%	88%	6%	90%	7%	0.01	-27	0.99
Clofentezine	106%	5%	101%	8%	90%	4%	0.01	-53	0.99
Clomazone	95%	3%	99%	1%	92%	10%	0.01	-27	0.99
Coumaphos	94%	6%	98%	5%	100%	7%	0.01	12	0.99
Cyantraniliprole	84%	7%	83%	4%	82%	7%	0.01	-45	0.99
Cyflufenamid	87%	7%	93%	5%	89%	3%	0.01	-49	0.99
Cyproconazole	95%	3%	98%	5%	88%	4%	0.01	-16	0.99
Cyprodinil	101%	6%	96%	6%	94%	7%	0.01	-38	0.99
Cyromazine	93%	5%	107%	6%	84%	4%	0.01	17	0.99
Deltamethrin	101%	11%	106%	6%	98%	5%	0.01	-44	0.99
Demeton-S-methylsulfone	98%	7%	93%	1%	91%	6%	0.01	-76	0.99
Demeton-S-methylsulfoxide (Oxydemeton-methyl)	103%	4%	104%	2%	103%	4%	0.01	-46	0.99
Desethylterbutylazine	100%	6%	96%	3%	87%	3%	0.01	-49	0.99
Diazinon	97%	6%	93%	9%	90%	6%	0.01	-48	0.99
Dichlorvos	-	-	100%	8%	92%	6%	0.02	-33	0.99
Dicrotophos	99%	3%	96%	2%	99%	3%	0.01	-67	0.99
Diethofencarb	92%	5%	97%	4%	93%	5%	0.01	-31	0.99
Difenoconazole	94%	5%	95%	8%	91%	7%	0.01	-26	0.99
Difloxuron	98%	8%	104%	4%	91%	6%	0.01	-15	0.99
Diflubenzuron	94%	6%	97%	9%	91%	7%	0.01	-13	0.99
Dimethoate	100%	3%	99%	3%	90%	4%	0.01	-54	0.99
Dimethomorph	-	-	99%	4%	95%	4%	0.02	2	0.99
Dimethylvinphos	96%	4%	101%	7%	91%	4%	0.01	-25	0.99
Diniconazole	97%	6%	90%	10%	85%	5%	0.01	-20	0.99
Dinotefuran	95%	6%	103%	10%	95%	5%	0.01	-74	0.99
Diuron	93%	9%	76%	15%	90%	4%	0.01	-21	0.99
Dodine	-	-	90%	5%	101%	12%	0.02	-61	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Edifenphos	99%	6%	72%	7%	88%	5%	0.01	-25	0.99
EPN	-	-	84%	8%	78%	8%	0.02	-62	0.99
Epoxiconazole	-	-	78%	11%	87%	7%	0.02	-13	0.99
Ethion	95%	6%	88%	6%	89%	4%	0.01	-62	0.99
Ethiprole	103%	1%	104%	6%	101%	4%	0.01	0	0.99
Ethirimol	93%	10%	107%	9%	91%	5%	0.01	-42	0.99
Ethoprophos	98%	7%	106%	8%	95%	4%	0.01	-6	0.99
Etofenprox	96%	12%	94%	7%	91%	5%	0.01	-71	0.99
Etoazole	-	-	94%	7%	83%	5%	0.02	-72	0.99
Famoxadone	-	-	95%	14%	84%	9%	0.02	-47	0.99
Fenamidone	95%	4%	98%	7%	83%	4%	0.01	-9	0.99
Fenamiphos	85%	7%	81%	2%	73%	5%	0.01	-36	0.99
Fenamiphos-sulfone	104%	4%	104%	6%	102%	6%	0.01	-4	0.99
Fenamiphos-sulfoxide	97%	4%	97%	5%	94%	5%	0.01	3	0.99
Fenarimol	-	-	106%	8%	96%	10%	0.02	-17	0.99
Fenazaquin	100%	3%	93%	8%	90%	11%	0.01	-69	0.99
Fenbendazole	88%	6%	86%	9%	76%	7%	0.01	-64	0.99
Fenbuconazole	93%	8%	95%	3%	87%	4%	0.01	-26	0.99
Fenhexamid	83%	9%	97%	7%	95%	2%	0.01	7	0.99
Fenobucarb	99%	11%	106%	8%	95%	4%	0.01	-7	0.99
Fenoxycarb	96%	7%	107%	6%	108%	3%	0.01	-27	0.99
Fenpicoxamid	91%	4%	92%	6%	87%	10%	0.01	-32	0.99
Fenpropathrin	95%	12%	106%	8%	97%	6%	0.01	-63	0.99
Fenpropidin	82%	8%	96%	6%	85%	8%	0.01	-46	0.99
Fenpropimorph	96%	4%	95%	5%	82%	8%	0.01	-37	0.99
Fenpyrazamine	94%	4%	98%	4%	87%	3%	0.01	-19	0.99
Fenpyroximate	96%	4%	93%	3%	90%	6%	0.01	-35	0.99
Fensulfothion	94%	7%	97%	2%	88%	3%	0.01	-14	0.99
Fenthion	-	-	84%	15%	72%	5%	0.02	-50	0.99
Fenthion-sulfone	98%	12%	101%	13%	99%	9%	0.01	-25	0.99
Fenthion-sulfoxide	104%	2%	113%	4%	113%	3%	0.01	0	0.99
Fenuron	87%	9%	95%	4%	92%	3%	0.01	-54	0.99
Fipronil	86%	10%	84%	5%	75%	2%	0.01	28	0.99
Flazasulfuron	93%	4%	95%	4%	82%	6%	0.01	78	0.99
Florpyrauxifen-benzyl	100%	6%	90%	9%	90%	7%	0.01	-45	0.99
Fluacrypyrim	95%	2%	97%	3%	89%	3%	0.01	-37	0.99
Fluazifop	108%	9%	109%	4%	100%	8%	0.01	96	0.99
Flubendiamide	88%	4%	97%	11%	95%	6%	0.01	-11	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Flufenacet	95%	5%	98%	7%	89%	7%	0.01	-21	0.99
Flufenoxuron	85%	9%	87%	4%	102%	8%	0.01	-83	0.99
Fluometuron	98%	6%	91%	5%	87%	8%	0.01	-21	0.99
Fluopyram	94%	6%	102%	9%	87%	3%	0.01	-29	0.99
Flupyradifuron	93%	6%	104%	2%	95%	3%	0.01	-26	0.99
Fluquinconazole	105%	9%	114%	3%	105%	8%	0.01	-41	0.99
Flusilazole	98%	7%	100%	7%	90%	8%	0.01	-30	0.99
Flutriafol	94%	1%	96%	3%	88%	5%	0.01	-12	0.99
Fluxapyroxad	103%	4%	102%	2%	92%	6%	0.01	-19	0.99
Forchlorfenuron	97%	3%	100%	4%	90%	3%	0.01	-30	0.99
Formetanate Hydrochloride	90%	10%	117%	3%	97%	4%	0.01	-67	0.99
Fosthiazate	95%	6%	100%	3%	94%	4%	0.01	-23	0.99
Haloxfop	-	-	103%	17%	95%	11%	0.02	99	0.99
Haloxfop-methyl	95%	3%	94%	4%	85%	2%	0.01	-42	0.99
Hexaconazole	102%	8%	97%	7%	94%	3%	0.01	-18	0.99
Hexaflumuron	89%	11%	85%	7%	73%	4%	0.01	-60	0.99
Hexythiazox	96%	6%	87%	6%	88%	5%	0.01	-60	0.99
Imazalil	98%	4%	95%	6%	80%	6%	0.01	-44	0.99
Imidacloprid	92%	7%	100%	6%	90%	4%	0.01	-18	0.99
Indoxacarb	99%	5%	94%	7%	94%	3%	0.01	-2	0.99
Ioxynil	100%	3%	99%	6%	86%	5%	0.01	-23	0.99
Iprovalicarb	95%	6%	103%	6%	85%	13%	0.01	-19	0.99
Isfenfos-methyl	105%	5%	98%	5%	84%	5%	0.01	-26	0.99
Isoprocab	95%	4%	90%	2%	88%	8%	0.01	-28	0.99
Isoprothiolane	87%	13%	105%	6%	97%	8%	0.01	-33	0.99
Isoxaflutole	95%	7%	96%	5%	89%	2%	0.01	33	0.99
Kresoxim-methyl	91%	11%	89%	7%	91%	5%	0.01	-39	0.99
Lenacil	-	-	94%	6%	93%	4%	0.02	-47	0.99
Lufenuron	91%	11%	85%	5%	76%	11%	0.01	-67	0.99
Malathion	91%	11%	92%	9%	90%	10%	0.01	1	0.99
Mandipropamid	99%	7%	103%	6%	97%	8%	0.01	-5	0.99
Mebendazole	93%	7%	95%	8%	87%	4%	0.01	16	0.99
Mefentrifluconazole	97%	9%	90%	7%	85%	8%	0.01	-18	0.99
Metaflumizone	98%	9%	84%	11%	71%	8%	0.01	-45	0.99
Metalaxyl	93%	3%	93%	4%	88%	4%	0.01	-28	0.99
Metamitron	82%	17%	101%	12%	100%	5%	0.01	-26	0.99
Metconazole	99%	7%	93%	3%	94%	4%	0.01	-13	0.99
Methamidophos	92%	6%	97%	5%	87%	2%	0.01	-70	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Methidathion	99%	8%	98%	7%	88%	8%	0.01	-40	0.99
Methiocarb	94%	7%	100%	5%	92%	4%	0.01	-21	0.99
Methiocarb-sulfone	90%	19%	94%	8%	82%	8%	0.01	-77	0.99
Methiocarb-sulfoxide	95%	3%	100%	2%	95%	3%	0.01	-56	0.99
Methomyl	97%	12%	97%	3%	87%	5%	0.01	-83	0.99
Methoxyfenozide	96%	9%	97%	9%	92%	1%	0.01	-34	0.99
Metobromuron	96%	3%	100%	5%	95%	4%	0.01	-29	0.99
Metolachlor	90%	8%	99%	6%	89%	2%	0.01	-31	0.99
Metrafenone	95%	2%	94%	4%	93%	8%	0.01	-32	0.99
Monocrotophos	94%	7%	97%	5%	87%	2%	0.01	-58	0.99
Monolinuron	98%	9%	101%	4%	93%	3%	0.01	-31	0.99
Monuron	93%	7%	101%	3%	91%	3%	0.01	-45	0.99
Neburon	98%	11%	105%	9%	101%	9%	0.01	-26	0.99
Nitenpyram	-	-	-	-	94%	7%	0.02	-44	0.99
Novaluron	-	-	83%	10%	78%	6%	0.02	-49	0.99
Omethoate	102%	5%	100%	3%	98%	4%	0.01	-54	0.99
Orthosulfamuron	86%	5%	102%	7%	87%	4%	0.01	100	0.99
Oxadiazyl	-	-	84%	10%	91%	6%	0.02	0	0.99
Oxadixyl	91%	7%	101%	4%	95%	6%	0.01	-43	0.99
Oxamyl	104%	4%	107%	5%	94%	4%	0.01	-82	0.99
Oxasulfuron	99%	6%	101%	2%	89%	4%	0.01	5	0.99
Oxathiapipronil	98%	8%	95%	5%	88%	5%	0.01	-14	0.99
Oxfendazole	100%	2%	107%	8%	98%	2%	0.01	38	0.99
Paclobutrazol	96%	9%	94%	7%	82%	10%	0.01	-14	0.99
Penconazole	97%	6%	102%	6%	91%	4%	0.01	-27	0.99
Pencycuron	96%	6%	106%	9%	91%	4%	0.01	-39	0.99
Pendimethalin	94%	3%	90%	8%	86%	5%	0.01	-59	0.99
Penflufen	92%	3%	103%	8%	98%	7%	0.01	-33	0.99
Phenthoate	96%	7%	84%	6%	83%	9%	0.01	-28	0.99
Phosalone	96%	6%	94%	7%	88%	7%	0.01	-32	0.99
Phosmet	97%	4%	101%	6%	87%	8%	0.01	-11	0.99
Phoxim	99%	4%	96%	2%	85%	5%	0.01	-47	0.99
Pirimicarb	99%	3%	98%	2%	88%	4%	0.01	-34	0.99
Pirimiphos-methyl	86%	8%	97%	5%	97%	7%	0.01	-31	0.99
Prochloraz	93%	1%	92%	14%	82%	4%	0.01	-45	0.99
Profenofos	94%	3%	101%	5%	89%	10%	0.01	-43	0.99
Promecarb	102%	7%	100%	8%	95%	10%	0.01	-35	0.99
Propamocarb	98%	4%	107%	3%	94%	3%	0.01	-47	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Propaquizafop	95%	5%	93%	5%	95%	6%	0.01	-36	0.99
Propargite	112%	13%	102%	19%	88%	20%	0.01	-74	0.99
Propazine	97%	9%	105%	5%	92%	5%	0.01	-30	0.99
Propiconazole	102%	7%	100%	6%	91%	6%	0.01	-16	0.99
Propoxur	103%	7%	101%	3%	92%	6%	0.01	-48	0.99
Propyzamide	96%	6%	98%	4%	89%	5%	0.01	-19	0.99
Proquinazid	93%	4%	96%	2%	92%	4%	0.01	-48	0.99
Prosulfocarb	92%	6%	92%	7%	87%	5%	0.01	-44	0.99
Pymetrozine	104%	5%	104%	4%	90%	4%	0.01	-43	0.99
Pyraclostrobin	88%	7%	88%	6%	84%	4%	0.01	-42	0.99
Pyridaben	91%	5%	91%	3%	88%	3%	0.01	-66	0.99
Pyridalyl	111%	11%	99%	6%	97%	3%	0.01	-39	0.99
Pyridaphenthion	98%	7%	95%	6%	93%	3%	0.01	1	0.99
Pyridate	88%	8%	100%	5%	94%	5%	0.01	-64	0.99
Pyrimethanil	89%	5%	95%	4%	87%	2%	0.01	-27	0.99
Pyriofenone	97%	5%	98%	6%	86%	9%	0.01	-27	0.99
Pyriproxyfen	103%	3%	93%	5%	88%	5%	0.01	-67	0.99
Quinalphos	96%	5%	100%	5%	93%	6%	0.01	-21	0.99
Quinoclamine	-	-	109%	9%	101%	7%	0.02	-71	0.99
Quinoxifen	94%	4%	104%	4%	92%	5%	0.01	-69	0.99
Quizalofop	-	-	104%	11%	93%	10%	0.02	21	0.99
Quizalofop-ethyl	102%	6%	101%	7%	96%	4%	0.01	-38	0.99
Rotenone	92%	4%	101%	14%	93%	5%	0.01	-1	0.99
Simazine	94%	9%	102%	4%	92%	2%	0.01	-53	0.99
Spinosyn A	88%	10%	87%	8%	85%	7%	0.01	-62	0.99
Spinosyn D	-	-	98%	9%	95%	11%	0.02	-72	0.99
Spirodiclofen	99%	11%	105%	6%	91%	9%	0.01	-59	0.99
Spiromesifen	90%	11%	100%	7%	89%	8%	0.01	-70	0.99
Spirotetramat	88%	5%	99%	5%	90%	4%	0.01	74	0.99
Sulfoxaflor	99%	8%	107%	5%	94%	4%	0.01	-34	0.99
Tebuconazole	-	-	95%	6%	87%	6%	0.02	4	0.99
Tebufenozide	106%	6%	98%	7%	95%	7%	0.01	-50	0.99
Tebufenpyrad	89%	5%	93%	10%	92%	4%	0.01	-35	0.99
Teflubenzuron	95%	7%	94%	9%	81%	10%	0.01	-38	0.99
Terbutryn	94%	6%	101%	6%	93%	7%	0.01	-37	0.99
Tetraconazole	103%	6%	104%	5%	91%	3%	0.01	-30	0.99
Tetramethrin	86%	3%	89%	7%	86%	3%	0.01	-32	0.99
Thiabendazole	95%	3%	98%	3%	87%	4%	0.01	-64	0.99

Compounds	0.01 mg/Kg		0.02 mg/Kg		0.05 mg/Kg		LOQ (mg/kg)	ME (%)	R <sup>2</sup>
	Average % recoveries	%RSD	Average % recoveries	%RSD	Average % recoveries	%RSD			
Thiacloprid	96%	7%	101%	3%	92%	3%	0.01	-57	0.99
Thiamethoxam	-	-	94%	6%	81%	6%	0.02	-85	0.99
Thiobencarb	91%	4%	91%	3%	90%	9%	0.01	-39	0.99
Tolclofos-methyl	-	-	109%	7%	90%	10%	0.02	-44	0.99
Tolfenpyrad	94%	10%	90%	4%	87%	3%	0.01	-43	0.99
Triadimefon	95%	12%	101%	4%	93%	10%	0.01	3	0.99
Triallate	96%	7%	91%	6%	92%	9%	0.01	-44	0.99
Triazophos	90%	6%	97%	7%	82%	4%	0.01	-25	0.99
Trichlorfon	92%	8%	97%	2%	93%	6%	0.01	-41	0.99
Triclorcarban	92%	11%	90%	10%	85%	4%	0.01	-40	0.99
Tricyclazole	91%	4%	99%	4%	90%	2%	0.01	-62	0.99
Trifloxystrobin	96%	5%	99%	5%	94%	7%	0.01	-39	0.99
Triflumizole	94%	8%	89%	4%	86%	3%	0.01	-68	0.99
Triflumuron	96%	6%	90%	7%	90%	7%	0.01	-32	0.99
Trinexapac-ethyl	91%	7%	92%	9%	87%	4%	0.01	-20	0.99
Tritosulfuron	90%	5%	90%	6%	85%	4%	0.01	100	0.99
Valifenalate	91%	7%	96%	5%	88%	5%	0.01	-3	0.99
XMC	117%	8%	111%	6%	101%	5%	0.01	-58	0.99
Zoxamide	85%	7%	97%	6%	87%	3%	0.01	-31	0.99