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RESUME EN FRANÇAIS

Le thé est la deuxième boisson la plus consommée dans le monde en raison de ses bienfaits pour la santé, dépassé uniquement par l'eau. Cependant, en raison des pratiques culturales de type monoculture, l'utilisation de pesticides dans la culture du thé est très courante. Au fil du temps, le nombre de pesticides utilisés ayant fortement augmenté, de nombreux pays et régions ont établi des limites maximales de résidus de pesticides pour une variété d'aliments et de boissons, y compris le thé, pour protéger la santé des consommateurs. Ainsi, l'Union européenne (UE) a fixé les limites maximales de résidus (LMR) pour plus de 480 pesticides et leurs métabolites dans les produits à base de thé. Aussi, est-il nécessaire de pouvoir contrôler ces résidus par des analyses régulières des échantillons afin d'évaluer si ces limites sont bien respectées. Le développement de méthodes pour l'analyser ces résidus de multi-pesticides dans le thé constitue donc un défi de taille, car le thé est un produit complexe possédant de nombreux composés qui peuvent interférer avec les résultats, comme les polyphénols, les pigments et la caféine.

L'objectif de cette thèse est de développer des méthodes fiables et robustes avec une sensibilité, une exactitude et une précision élevées pour répondre aux réglementations de l'UE pour déterminer simultanément 400 résidus de pesticides dans les produits de thé. Pour cela, les méthodes d'analyse par chromatographies liquides et gazeuses ultra performantes couplées à la spectroscopie de masse en tandem (UPLC-MS/MS et GC-MS/MS, respectivement) ont été mises en œuvre. La première partie de la thèse a porté sur l'élimination des effets de matrice dans les feuilles de thé vertes en combinant l'extraction QuEChERS (rapide, facile, bon marché, efficace, robuste et sûre) et le nettoyage en mode mixte SPE (extraction en phase solide). Une cartouche SPE C18 couplée à SPE GCB/PSA (noir graphite-carbone/éthylène diamine-n-propyl) s'est avérée être la méthode de nettoyage la plus efficace et a permis de quantifier 225 résidus de pesticides, sur la base de courbes d'étalonnage réalisées dans les solvants (154 résidus utilisant UPLC-MS/MS et 71 résidus utilisant GC-MS/MS). Les

méthodes analytiques ont été entièrement validées conformément aux recommandations du document SANTE/11945/2015 (UE). Les limites de quantification (LOQ) pour la plupart des pesticides (386/400 ou 96,5 %) sont inférieures à 10 µg/kg, c'est-à-dire inférieures à la LMR de l'UE (5-70 mg/kg). Dans la deuxième partie, les effets de matrice de 400 résidus de pesticides ont été étudiés et améliorés pour l'analyse de différents types de thés (blancs, verts, oolongs et noirs). Les résultats ont montré que la combinaison de l'extraction QuEChERS et de la purification SPE en mode mixte et après réduction du volume d'injection s'est avérée être la procédure la plus efficace pour surmonter les effets de matrice. Pour plus de 190 pesticides (> 95 % des 200), l'effet de matrice est compris dans une fourchette de ± 20% pour les analyses par UPLC-MS/MS. De ce fait, ils peuvent être quantifiés à l'aide de courbes d'étalonnage de solvant. Dans le cas des analyses par GC-MS/MS, les courbes d'étalonnage doivent être adaptées à la matrice pour surmonter ces effets de matrice. De plus, nous avons observé que les effets de matrice en GC-MS/MS pouvaient se traduire soit par une augmentation du signal soit par une réduction.

Dans la troisième partie de ces travaux, la méthode a été utilisée avec succès à la détermination de résidus de multi-pesticides dans 106 échantillons de thé. Au total, 26 échantillons de thé (24,5 %) dépassaient les limites autorisées en pesticides, jusqu'à 43 résidus de pesticides. Les pesticides les plus fréquemment détectés ont été les néonicotinoïdes, les pyréthrinoïdes synthétiques et les fongicides triazolés. Par rapport aux origines des thés analysés, les échantillons les plus contaminés par les pesticides avec 83,3 % sont ceux provenant de Taïwan, suivi de ceux de la Chine (73,7 %), du Vietnam (64,7 %) et enfin de l'Inde (Darjeeling) (55,0 %).

Ces travaux ont permis de montrer que les échantillons dépassant les réglementations de l'UE en matière de LMR restent toujours élevés (24,6 %) et qu'il est nécessaire de poursuivre le développement de méthodes pour évaluer de manière fiable les nombreux résidus de pesticides dans le thé.

SUMMARY IN ENGLISH

Tea is the second most-consumed beverage in the world due to its health benefits, surpassed only by water. However, because of monoculture cultivation practices, the use of pesticides during tea cultivation is common. Over time, the number of pesticides used has increased, and, to protect consumers‘ health, many countries and regions have established maximum residue limits of pesticides for a variety of foods and beverages, including tea. For instance, the European Union (EU) has set the maximum residue limits (MRLs) for more than 480 pesticides and their metabolites in tea products. Therefore, the development of analytical methods for multi-pesticide residues in tea is a challenge, because tea is a complex commodity with many compounds that can interfere with results, such as polyphenols, pigments, and caffeine.

The aim of this thesis is to develop rugged and robust methods with high sensitivity, accuracy, and precision to meet the EU regulations for simultaneous determination of 400 pesticide residues in tea products using ultra performance liquid and gas chromatographies coupled to tandem mass spectroscopy (UPLC-MS/MS and GC-MS/MS, respectively). The first part of thesis focused on elimination of matrix effects in green tealeaves by combining QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction and mixed-mode SPE (solid phase extraction) clean-up. A C18 SPE cartridge paired with SPE GCB/PSA proved to be the most effective clean-up method and enabled 225 pesticide residues to be quantified, based on solvent calibration curves (154 residues using UPLC-MS/MS and 71 residues using GC-MS/MS). The analytical methods were validated fully in accordance with the SANTE/11945/2015 (EU). LOQs for most pesticides (386/400 or 96.5%) were below 10 µg/kg, *i.e.*, less than the EU MRL (5-70 mg/kg). In the second part, matrix effects for 400 pesticide residues were investigated and improved for the analysis of different types of teas (white, green, oolong and black ones). Results showed that combining QuEChERS extraction and mixed-mode SPE clean-up, and following the reduction of

the injection volume were found to be the most effective procedure to overcome matrix effects. More than 190 pesticides (> 95% of the 200 ones) had the matrix effect within the range of ± 20% for UPLC-MS/MS. Therefore, they can be quantified using solvent calibration curves. On the other hand, matrix-matched calibration curves should be used to overcome matrix effects for GC-MS/MS. Moreover, we recognized that matrix effects in GC-MS/MS were not only signal enhancement but also suppression.

Finally, in the third part of this work, the established method was successfully applied to the determination of multi-pesticide residues in 106 tea samples. In total, 26 tea samples (24.5%) were containing at least one pesticide noncompliance, with 43 pesticide residue noncompliances. The most frequently detected pesticides were neonicotinoids, synthetic pyrethroids, and triazole fungicides. In terms of origin in this study, Taiwan had the most pesticide-contaminated samples with 83.3%, following by China (73.7%), Vietnam (64.7%), and India (Darjeeling) (55.0%). The results showed that samples exceeding EU MRLs regulations were still high with 24.6%. Therefore, assessments of multi-pesticide residues in tea need to be continued.

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List of abbreviations

Abbreviation	Definition
AA	Acetic acid
ACN	Acetonitrile
ADI	Acceptable daily intake
APCI	Atmospheric-pressure chemical ionization
APPI	Atmospheric pressure photoionization
APs	Analyte protectants
ARfD	Acute reference dose
ASE	Accelerated solvent extraction
C18	Octadecyl
CBs	Carbamate pesticides
DLLME	Dispersive liquid-liquid micro-extraction
d-SPE	Dispersive solid-phase extraction
ECD	Electron capture detector
ESI	Electrospray ionization
EtOAc	Ethylacetate
EU	European Union
FA	Formic acid
FAO	Food and Agriculture Organization
FPD	Flame photometric detector
GC	Gas chromatography
GCB	Graphitized carbon black
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
IS	Internal standard
IT	Ion trap mass spectrometry
IUPAC	The International Union of Pure and Applied Chemistry
LC	Liquid chromatography
LLE	Liquid-liquid extraction
LOD/LODs	Limit(s) of detection
LOQ/LOQs	Limit(s) of quantification
MeOH	Methanol
ME/MEs	Matrix effect(s)
MNPs	Magnetic nanoparticles
MRL/MRLs	Maximum residue limit(s)
MS	Mass spectrometry

Abbreviation	Definition
MS/MS	Tandem mass spectrometry
MSPD	Matrix solid-phase dispersion
MWCNTs	Multi-walled carbon nanotubes
NPD	Nitrogen phosphorus detector
OCPs	Organochlorin pesticides
OPPs	Organophosphorus pesticides
PSA	Primary secondary amines
PYRs	Pyrethroid pesticides
QQQ	Triple quadrupole mass spectrometer
Q-TOF	Quadrupole time-of-flight mass spectrometry
QuEChERS	Quick, easy, cheap, effective, rugged, and safe method
RSD	Relative standard deviation
SE	Solvent extraction
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
SPE	Solid-phase extraction
SPME	Head-space solid-phase micro-extraction
TRZs	Triazine herbicides
TRVs	Toxicological reference values
UPLC	Ultra performance liquid chromatography

INTRODUCTION

Tea is the second most-consumed beverage in the world due to its health benefits, surpassed only by water. However, because of monoculture cultivation practices, the use of pesticides during tea cultivation is common. Over time, the number of pesticides used has increased, and, to protect consumers‘ health, many countries and regions have established maximum residue limits of pesticides for a variety of foods and beverages, including tea. For instance, the European Union (EU) has set the maximum residue limits (MRLs) for more than 480 pesticides and their metabolites in tea products, which range from 0.005 (fipronil) to 70 mg/kg (bromide ion). Therefore, the development of analytical methods that can detect several hundred pesticide residues in tea is a challenge, because tea is a complex commodity with many compounds that can interfere with results, such as polyphenols, pigments, fatty acids, organic acids and caffeine.

For quantitative purpose, the analysis of pesticide residues in tea usually requires extraction, clean-up, and/or enrichment/dilution. Many researchers have focused on QuEChERS (quick, easy, cheap, effective, rugged, and safe method) for sample preparation in combination with dispersive solid-phase extraction (d-SPE) (AOAC 2007.01; Cajka et al., 2012; Chen et al., 2011; Hou et al., 2016; Hou et al., 2014; Lehotay et al., 2010; Lozano et al., 2012; Rajski et al., 2013; Steiniger et al., 2010; J. Wang et al., 2011; Zhao et al., 2012), but QuEChERS extraction and d-SPE clean-up have disadvantages in analysis of tea, including matrix effects and low sensitivity, depending on detection system too (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rajski et al., 2013). Previous studies have shown that it is challenging to eliminate interference using only d-SPE, and this problem is more evident when analyzing residues of several hundred pesticides with very different physical-chemical properties, such as polarization, functional groups, molecular mass, and vapor pressure. So, the thesis focused on elimination of interferences by combining QuEChERS extraction and mixed-mode solid-phase extraction (SPE) clean-up using

different sorbents, such as octadecyl (C18), graphitized carbon black (GCB), and primary secondary amines (PSA), in sample preparation, which allowed for analysis of several hundred pesticides with high sensitivity, accuracy and precision. Subsequently, gas chromatography (GC) or liquid chromatography (LC) coupled with tandem mass spectrometry (GC-MS/MS and LC-MS/MS) are used most to analyse multi-pesticide residues in tea simultaneously

Besides, matrix effect is a common phenomenon in LC-MS/MS and GC-MS/MS, which can cause false-positive and false-negative results. These error problems become more serious if the matrix effects (MEs) are not carefully considered during the development and validation of analytical methods (Rahman, El-Aty, et al., 2013; SANTE/11945/2015; Smeraglia et al., 2002; Taylor, 2005). Removal or reduction of matrix effect is usually conducted by the different ways: (i) improving sample extraction, (ii) changing analyte retention times, (iii) changing ionization source, (iv) using isotope internal standards, (v) adding analyte protectants (for GC only), (vi) dilution, (vii) matrix-matched calibration, and (viii) use of standard addition (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rutkowska et al., 2019; Taylor, 2005). The choice of the appropriate method depends on the amount of analyte, sample matrix, and analytical instrument (GC or LC); for example, adding analyte protectants is only applied for GC but not for LC.

This thesis is organized in 6 chapters, as follow.

Chapter 1 is a state of the art that summaries knowledge related to tea and analytical methods for determination of pesticide residues in tea. It describes in detail about tea, tea processing, pesticide used in tea, pesticides residue in tea, analytical methods and matrix effect.

Chapter 2 introduces the material and methods used in all experiments. It focuses on method development experiments, matrix effects studies, and analytical method validation.

Chapter 3 emphasizes developing analytical methods for 400 pesticide residues in green tea. It involves studies of various sorbents used during the clean-up step, elution volume of the SPE process, as well as evaporation optimization. Subsequently, these methods were validation according to SANTE/11945/2015 requirement. This chapter has published in the journal of Food Chemistry (https://doi.org/10.1016/j.foodchem.2020.126928).

Chapter 4 shows the complexity of matrix effect in multi-pesticide analysis for tea. Then, several methods were investigated to overcome matrix effects such as SPE clean-up, using analyte protectant (for GC only), reduction of injection volume, and dilution. In addition, the comparison of matrix effects in different types of tea was presented.

Chapter 5 presents the result of method validation for both method UPLC-MS/MS and GC-MS/MS in several types of teas. Subsequently, these methods were employed to assess pesticide residue in 106 teas from source (tea gardens) and tea brands.

The last chapter is dedicated to the final conclusions and perspectives of this work.

Chapter 1. State of the art

1.1. Introduction

Tea is the second most-consumed drink in the world, surpassed only by water (Banerjee et al., 2010; Biswas et al., 2007). Different tea styles are produced by altering leaf shape and chemistry, called „processing" or „manufacture", such as black, green, oolong, white, and pu'erh tea. Nevertheless, they originate from the same plant, *Camellia sinensis*. It is a sub-tropical, evergreen plant native to Asia but is now grown around the world. The top 10 tea producing countries in 2017 are presented in Fig. 1-1. Most countries are in Asia, except Kenya, in Africa. The tea plant grows best in loose, deep soil, at high altitudes, and in sub-tropical climates. Therefore, „tea" is anything derived from the *Camellia sinensis* plant. Other beverages that are sometimes called „tea" are more accurately called herbal tea or tisane. Tisanes include chamomile, rooibos and fruit teas (Li et al., 2012).

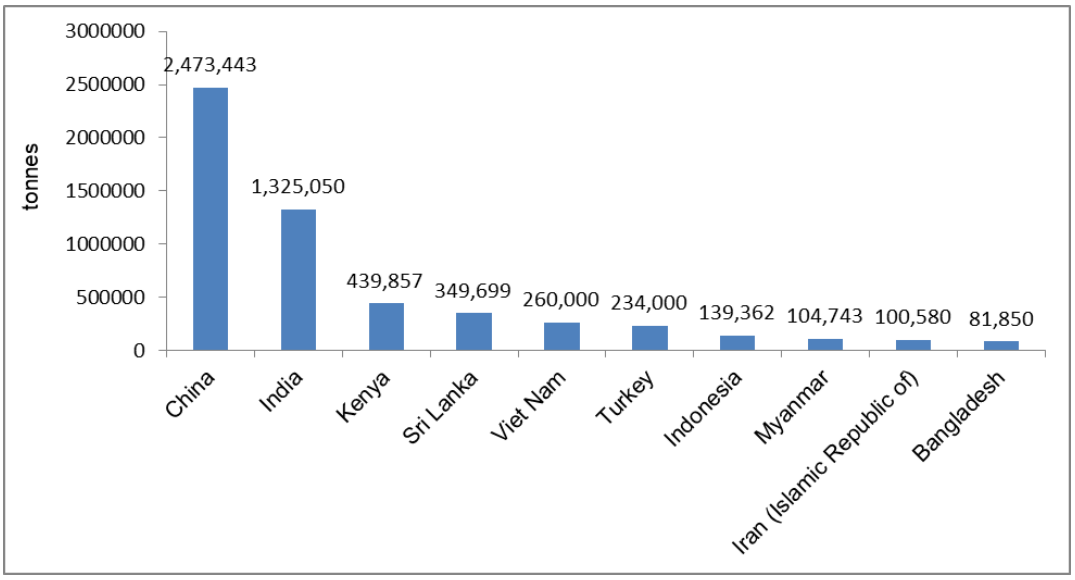

Fig. 1-1. The top 10 tea producing countries in 2017 (FAO, 2017)

Tea has become one of the most popular drinks as some health benefits such as weight control, reducing blood pressure, diabetes, osteoporosis, and risks of cardiovascular disease (Chang et al., 2017; de Amorim et al., 2018). Tea has unique biological activities and consumer health benefits due to its substantial amounts of polyphenols, caffeine (3–5%), and aroma-forming substances (Abd El-Aty et al., 2014). Especially catechins compounds, a form of polyphenols, have potent antioxidant activity that also exists in tea. Catechins in tea include catechin, gallocatechin, catechin gallate, epigallocatechin gallate and gallocatechin gallate (Lee et al., 2010). Depending on oxidation and heat treatment during processing, the content of catechins in teas varies greatly. A review reported the content of six types of catechins in five types of tea, in which the highest and lowest levels were found in green (180 mg/g) and pu-erh tea (4.9 mg/g), respectively (Yashin et al., 2015). In addition to polyphenols, there are other ingredients in tea that have high nutritional value as proteins (15-23% of the dry weight), carbohydrates, lipids, vitamins, and minerals (Stagg & Millin, 1975).

Fresh tea leaves are picked by hand or machine. Usually, only tea buds and from one to two tea leaves are used for processing. The younger tea leaves are used, the more valuable the final product is. Tea‘s quality is mainly reflected in its smell and taste, which are generated by volatile and non-volatile organic compounds present in the tea. Two main factors are affecting the quality of tea: (1) the growing period of the tea plant as well as tea origin and variety; (2) the process stage. The tea processing can be monitored by industrial quality control procedures. However, the biochemical properties of the fresh tea leaves in the growing stage are more difficult to control, though equally important. The concentration of foliar chemical compounds has an essential impact on tea infusion‘s flavor, smell, and other factors that make up the tea‘s quality (Bian).

Until now, teas are classified into five categories comprising six types, namely, non-oxidized (white tea and green tea), lightly oxidized (yellow tea), semi-oxidized (oolong tea), fully oxidized (black tea), and post-oxidized (dark or Pu‘Erh tea)

(Kosińska & Andlauer, 2014; Xu et al., 2018). Tea processing is five main steps; some teas do not utilize all of these steps, while other teas repeat them several times. Primary processing is plucking, withering (allowing the leaves to wilt and soften), rolling (to shape the leaves and wring out the juices), oxidation, and firing (drying). The processing of teas is summarized in Fig. 1-2.

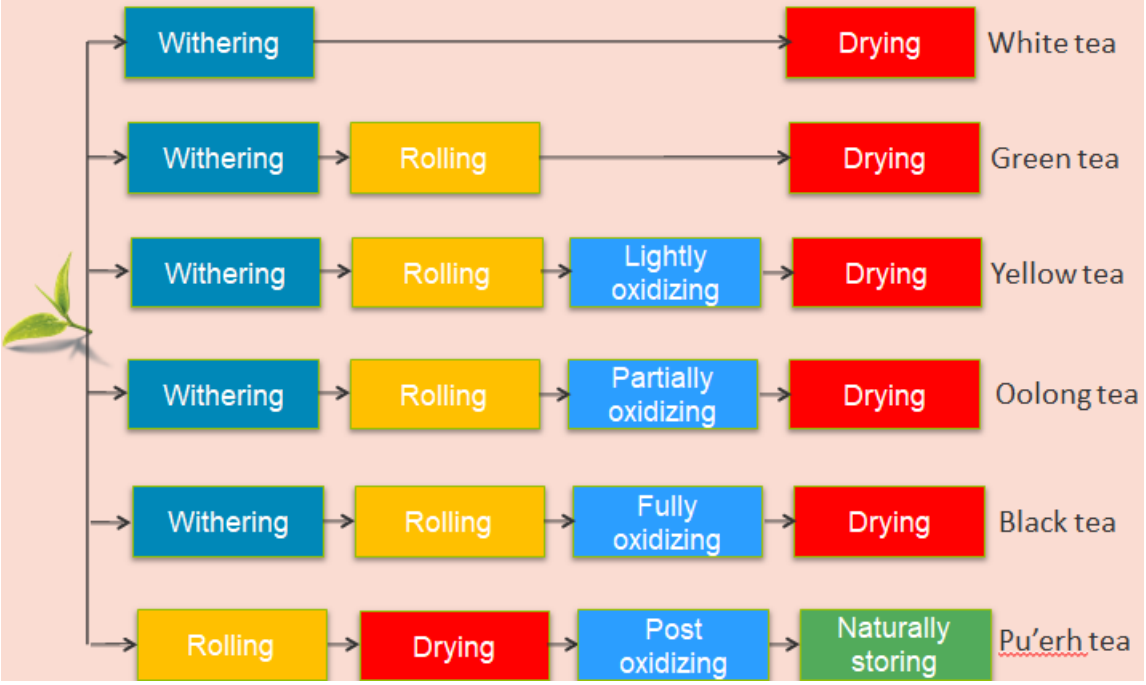

Fig. 1-2. Manufacturing processes of six types of teas

Ideal conditions for proper growth of tea plants are cold temperatures (15-25 °C), high humidity (80-90%), and high annual rainfall. The high humidity helps ensure that leaves grow at a slow rate and remain tender (Fung et al., 1999). Nonetheless, due to monoculture practice and often monoclonal varieties in areas with high moisture and temperature, the tea plant is easily attacked by insects, mites, fungi, viruses, and diseases (Beneta et al., 2018). Over time, the number of pesticides used in agriculture has generally increased. Until now, more than 800 pesticides have been used in agriculture to combat pests, insects, fungi, diseases, and weeds (Zhang et al., 2012). To protect consumers‘ health, many countries and several international

organizations have established maximum residue limits (MRLs) for pesticides in tea. Regulations differ between countries, not only for the number of pesticides but also the MRLs. For instance, while the European Union (EU) has set the list of MRLs for over 480 pesticides and their metabolites in tea products, ranging from 0.005 (fipronil) to 350 mg/kg (fluoride ion) (EU MRLs), Codex only controls 23 compounds, ranging from 0.2 (paraquat) to 70 mg/kg (spiromesifen) (CODEX, 2020). (Table A-1 and Table A-2 in Appendix Table). Therefore, reliable, robust, sensitive analytical methods are needed to determine multi-pesticide residues in tea to meet the strict EU requirements, as well as those of other countries.

1.2. Pesticides use in tea cultivation

Today, there are 5 groups of pesticides commonly used in agriculture, including organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs), carbamate pesticides (CBs), synthetic pyrethroid pesticides (PYRs), neonicotinoids and triazine herbicides (TRZs) (LeDoux, 2011b).

Organochlorine pesticides, effective against a variety of insects, were widely used worldwide in agriculture and animal production until developed countries introduced restrictions in the late 1970s. These pollutants have a highly stable, low volatile, non-polar, and lipophilic nature. Consequently, they exhibit considerable environmental persistence with a tendency to bioaccumulate, leading to the contamination of foodstuffs, especially those with high-fat content. Residue concentrations have decreased in monitored foods since these chemicals were banned in most countries, although trace levels are still detected in many foodstuffs. European regulation establishing pesticide residue levels in food has prompted EU members to monitor OCPs (LeDoux, 2011b).

Organophosphorus pesticides, mainly used as insecticides, are esters of phosphoric acid with different substituents. OPPs have widely varying physicochemical properties such as polarity and water solubility. Since these substances act through inhibition of

acetyl-cholinesterase, they also represent a risk to human health. Maximum residue limits (MRLs) have, therefore, been established for OPPs by the EU authorities (LeDoux, 2011b).

Carbamate pesticides, or N-substituted carbamic acid esters (RO–C(O)–NR‘R‘‘), are used for broad-spectrum insect control around the world. Exposure to carbamate pesticides, acting as acetyl-cholinesterase inhibitors, can lead to reversible neurologic disorders, and some are suspected carcinogens and mutagens. CBs are thermally unstable compounds; their stability has been studied in foodstuffs such as beef and poultry liver. The Canadian authorities recently initiated a re-evaluation of exposure to these substances. In the EU, MRLs have been established for CBs (LeDoux, 2011b).

Synthetic pyrethroid pesticides are effective broad-spectrum insecticides with low mammalian toxicity and short-term environmental persistence. Pyrethroids are non-polar to low-polarity lipophilic compounds. Owing to their metabolism in animals, they tend to bioaccumulate in lipid compartments, becoming a potential source of human exposure through foodstuffs. Maximum residue limits for PYRs have been set by several organizations, including the FAO and the EU Council (LeDoux, 2011b).

Triazines are among the most widely used herbicides in agriculture. Most of them are derived from s-triazine (1,3,5-triazine), but a few are based on 1,2,4-triazine. The triazines are degraded by chemical and biological processes in their respective hydroxytriazines. s-Triazines and their degradation products are weakly basic, poorly water-soluble compounds of low polarity, stable in the environment, and therefore persistent. 1,2,4-Triazines have similar physicochemical properties but are more polar. These herbicides are suspected of causing cancers, congenital disabilities, and disruption of hormone function. The EU Council has also established MRLs for triazines in food-stuffs (LeDoux, 2011b).

In the last ten years, neonicotinoids are a relatively new insecticide, which is increasingly used. Common substances in this group are imidacloprid, dinotefuran,

thiamethoxam, clothianidin, and acetamiprid. Due to the widespread use against a broad spectrum of sucking and certain chewing pests, neonicotinoid insecticides have been the fastest-growing classes of insecticides in the modern crop. Besides, neonicotinoids have many advantages as low risk for non-target organisms and the environment, a high-target specificity to insecticide, and versatility in application methods. However, some reports mention the limitations of the use of neonicotinoids as the Colonial Collapse disorder in bees, affecting the immunocompetence of honey bees, and adverse effects of imidacloprid in birds and aquatic life (Ensley, 2018).

1.3. Pesticide residues in tea

There is a growing number of reports of pesticide contamination in food. A report on pesticide residue in food has shown a significant amount of tea samples contaminated with pesticide residues (EFSA, 2016). Among the unprocessed products, tea is one kind of matrices with the highest MRL exceedance rates (greater than 10%). There are 243 samples of 1016 total samples (accounting 23.9%) of those pesticide residues higher than MRL. For processed food, tea is also in the top 3 matrices with pesticide residues higher than MRL (8/38 samples accounting of 21.1%).

A sample may be contaminated with multiple residues due to various causes: agricultural practices (using of herbicides, fungicides or insecticides against pests or diseases), contaminations during food processing, mixing of several lots, uptake of pesticide residues via soil, or spray drift from nearby fields. According to the current EU regulation, a sample that contaminated multi-pesticide residues is still compliant if each pesticide does not exceed the corresponding MRL. However, the EU 2016 report on pesticides shows that the number of samples contaminated with two or more pesticides is increasing. According to this report, 504 samples (accounting for 49.7%) and 13 samples (accounting for 34.2%) for unprocessed and processed tea, respectively, were contaminated with multiple pesticide residues. A high frequency of

MRL exceedances for anthraquinone in tea was identified; the highest residues amounted to up to 0.37 mg/kg while the MRL is set at the LOQ of 0.02 mg/kg.

Lozano et al. used a modified QuEChERS method for surveying multi-pesticide residues (86 compounds) in teas and chamomile (Lozano et al., 2012). Among 75 samples (green teas, black teas, red teas, white teas, oolong teas, chamomile, hibiscus and melissa), 69 (92%) samples were positive for pesticides. 17% of the samples contained ten or more pesticides. The most frequently detected pesticides were biphenyl (49% of the tested samples), acetamiprid (48%), carbendazim (48%), chlorpyriphos (45%), imidacloprid (41%), bifenthrin (40%), endosulfan (32%), and methomyl (23%). Huang et al. reported a multipesticide residue (102 compounds) method by GC-MS for testing pesticide residues in 3042 real tea samples including 1532 green teas, 620 black teas, 727 oolong teas and 163 flower teas (Z. Huang et al., 2007). Fenvalerate (detected concentration 0.05–0.25 mg/kg), cypermethrin (0.01–0.05), fenpropathrin (0.03–0.30), buprofezin (0.06–0.25) and triazophos (0.02–0.20) were frequently detected. Some pesticides exceeded the EU MRLs, such as fenvalerate (73.4% samples in oolong teas and 52.3% in flower teas), fenpropathrin (57.6%, 30.2%, 22.7% and 16.4% in oolong, flower, black and green teas, respectively). In addition, Huang et al. also used a multipesticide residue method by LC-MS/MS to analyze 3000 tea samples, including 1500 green teas, 650 black teas, and 850 oolong teas (Huang et al., 2009). Among them, acetamiprid (0.01–0.05 mg/kg), imidacloprid (0.01–0.05), paclobutrazol (0.01–0.08) and triazophos (0.06–0.10) were frequently detected. However, these studies show that the number of pesticides surveyed remains low compared to European regulations.

1.4. Analytical methods for determination of multi-pesiticide residues in tea

Determining the pesticide residue in tea is challenging because tea is a complex matrix with many alkaloids, pigments, fats and proteins, polyphenols, amino acids, vitamins, pectin, organic acids, polysaccharides and saccharides (Feng et al., 2013;

Pang et al., 2013; Zhang et al., 2010). In addition, the simultaneous determination of several hundred pesticides with different polarizations and properties at trace levels is difficult. Due to a unique technique of production, the tea cells are usually broken, the components in the sample move outspread over the leaf, so when extracted with an organic solvent, large interference extracted together with the analyte, and therefore, identify pesticides in tea difficult than the vegetables and fruits (Oellig & Schwack, 2012). Although there are many methods of screening, pesticides in tea are published with high recovery. However, those methods are often impractical because the results are based on surveys of spiking samples, pesticides are added to the sample, just over the surface without interacting with the sample structure (Feng et al., 2013). Currently, GC coupled with mass spectrometry (GC-MS) and GC or LC coupled with tandem mass spectrometry (GC-MS/MS and LC-MS/MS) are used most to analyse multi-pesticide residues in tea simultaneously with low limits of detection (LOD), low limits of quantification (LOQ) and good accuracy (Cajka et al., 2012; Fan et al., 2013; Hayward et al., 2015; Hayward et al., 2013; Hou et al., 2016; Z. Huang et al., 2007; Huang et al., 2009; Li et al., 2012; Pang et al., 2011; Y. Wang et al., 2011).

Generally, published analytical methods for one or more groups of pesticides involved the following: (i) use of an extraction procedures, such as accelerated solvent extraction (ASE), head-space solid-phase micro-extraction (SPME), matrix solid-phase dispersion (MSPD) or solvent extraction; (ii) purification procedures, such as gel permeation chromatography (GPC), solid-phase extraction (SPE), dispersive liquid–liquid micro-extraction (DLLME) or dispersive solid-phase extraction (d-SPE); and, finally, (iii) separation and detection on a chromatographic system based on either gas chromatography (GC) or liquid chromatography (LC), coupled to different detectors (Cao et al., 2015; L. Chen et al., 2014; Feng et al., 2013; Hu et al., 2005; Moinfar & Hosseini, 2009; Schurek et al., 2008).

In some cases, the analysis results may be higher or lower than actual samples due to interferences. When analyzing pesticides in tea by GC, a few compounds tend to meet

efficiency and better peak shape when running a standard solution. That is the "ion-enhancement", a type of matrix effect (ME), in the GC technique. Accordingly, the impurities in the extract block the centers operating on the gate and GC column so that the analyte reaches the detector more (Li et al., 2012). ME depends not only on pesticides but also on the type of tea. The pesticides contain carboxyl (-COOH), carbamate (–O–CO–NH–), phosphate (–PO), hydroxyl (–OH), azoles (–N=), amino (–R–NH–), urea (–NH–CO–NH–), imidazole, and benzimidazole are the most susceptible type ofanalytes to matrix effect (Michelangelo Anastassiades et al., 2003; Ying Wang et al., 2011). Whereas, organochlorine compounds, due to the absence of polar groups, are less affected. Black tea is severely affected than green tea because black tea is fully oxidizied and has a more complex matrix than green tea (Li et al., 2012). In addition, a large number of impurities are extracted overwhelming compared to the analyte will cause significant difficulties when analyzing trace pesticides, affect ionization efficiency when analyzed by LC, decreased column life.

Besides the difficulties caused by the complex matrix, screening a large number of pesticides is one of the significant challenges. The simultaneous determination of several hundred pesticides with different polarization and properties at trace levels is not easy. Therefore, the preparation of samples for analysis is a particularly important role. Extraction and clean-up techniques, such as solvent extraction, liquid-liquid extraction (LLE) or solid-phase extraction (SPE), are often used. However, these techniques are often time-consuming, requires a large amount of solvent, consuming cost. Currently, QuEChERS extraction commonly uses for screening pesticides. This technique is fast, easy, but still some disadvantages as high ME and dilution factor. Pesticides are usually acidic or basic, depending on the pH of the extracted solution that may exist in the form of ions or molecules. When in the form of ions, the analyte distribution in the aqueous phase than the organic phase. Therefore, the pH of the extract should be optimized to maximize the extraction of compounds. However, basic

pesticides are less affected by pH extraction than acidic pesticides. In addition to some pesticides unstable in the high pH environment, the acidity extraction is chosen.

Analytical methods of mutipesticide residues analysis in tea in the last decade are presented in Table 1-1

Table 1-1. Summary analytical methods for multipesticide residues analysis in tea

#	Number of pesticides	Extraction procedure	Clean-up procedure	Separation technique	Recovery (%)	LOQ (µg/kg)	Reference
1	102 pesticides	Modified QuEChERS 6 mL H_2O/10 mL ACN (1% AA) 4g $MgSO_4$/1g NaAc	d-SPE PSA/C18/GCB/$MgSO_4$	LC-MS/MS C18 (1.8 µm x 100 mm)	62 – 125	0.1 – 50	(Huang et al., 2019)
2	70 pesticides	Modified QuEChERS 10 mL H_2O/20 mL ACN 5g NaCl/4g $MgSO_4$	d-SPE PSA/C18/GCB/MWCNTs/$MgSO_4$	GC-MS/MS VF-5 30m	70 – 110	5 – 25	(H. Chen et al., 2014)
3	7 benzoylurea pesticides	SE 10 mL ACN	SPE Florisil/activated carbon	LC-MS/MS SB-C18 (3.5 µm x 150 mm)	90.4 – 103	0.1 – 4	(L. Chen et al., 2014)
4	86 pesticides	Modified QuEChERS 4 mL H_2O/10 mL ACN 4 g $MgSO_4$/1 g NaCl/1g trisodium citrate dihydrate/0.5 g disodium hydrogencitrate sesquihydrate	d-SPE $CaCl_2$/PSA	LC-MS/MS C8 (5 µm x 150 mm) GC-MS/MS HP-5ms 15 m	41.7 – 119.6	10 – 100	(Lozano et al., 2012)
5	37 pesticides	Modified QuEChERS 5 mL H_2O/10 mL ACN 1g NaCl/4g $MgSO_4$	d-SPE MWCNTs/ PSA/GCB/$MgSO_4$	LC-MS/MS C18 (3.5 µm x 50 mm)	70 – 111	5 – 20	(Zhao et al., 2012)
6	135 pesticides	QuEChERS 10 mL H_2O/10 mL ACN 1g NaCl/4g $MgSO_4$	LLE 1ml extract/1mL hexan/5mL NaCl (20%)	GC-MS/MS HP-5ms 15 m DB-5ms 0.50	70 - 120	1 – 10	(Cajka et al., 2012)
7	65 pesticides	Modified QuEChERS 10 mL H_2O/10 mL ACN (1% AA) 1.5 g CH_3COONa/4 g MgSO4,	Clean-up with SPE (graphite carbon/aminopropyl silanized silica gel)	LC-MS/MS RP18 (2.1 µm x 150 mm)	70 – 120	10	(Chen et al., 2011)
8	22 pesticides	Modified QuEChERS 15mL ACN (1% AA) 6g $MgSO_4$/1.5g NaAc	d-SPE PSA/$MgSO_4$/$C_{18.}$	GC-MS/MS TR-Pesticide II 30 m	78 – 115	4 – 348	(Steiniger et al., 2010)

#	Number of pesticides	Extraction procedure	Clean-up procedure	Separation technique	Recovery (%)	LOQ (µg/kg)	Reference
9	67 pesticides (CBs, OCPs, OPPs, PYRs,, azole, strobilurin, cyclodiene, dinitroaniline, and nereistoxin)	Modified QuEChERS 10 mL H_2O/10 mL EA-Cyclohexane (9/1) 1g NaCl	d-SPE PSA/GCB/florisil/Na_2SO_4	GC-MS VF-5 30m	70 – 120	2 – 50	(B. Kanrar et al., 2010)
10	42 pesticides	Modified QuEChERS 10 mL H_2O/10 mL EtOAc-Cyclohexane (9/1) 1g NaCl	d-SPE PSA/GCB/florisil/Na_2SO_4	LC-MS/MS C18 (5 µm x 100 mm)	66 – 105	6 – 47	(Bappaditya Kanrar et al., 2010)
11	68 pesticides	Modified QuEChERS 5mL EtOH/Toluene (1/1)	d-SPE MgSO4/PSA/GCB	GC-MS HP-5ms 30m	> 70	< 1	(Zhang et al., 2010)
		Modified QuEChERS 1 mL H_2O/7 mL ACN (1%AA)	d-SPE MgSO4/PSA/GCB	UPLC-MS/MS BEH phenyl (1.7 µm x 50 mm)	> 70	< 10	
12	103 pesticides	SE ACN (2 times with 5 and 2 mL)	SPE Carb-NH_2	LC-MS/MS Eclipse XDB-C18 (5 µm x 150 mm)	65 – 114	10 – 50	(Huang et al., 2009)
13	10 pesticides (OPPs)	SE ACN/Hexane (250/3)	DLLME method. Take 0.5 mL of the mixture of solvent + 5 mL H_2O for DLLME.	GC-FPD BP-5 28.5m	83.3 – 117.4	0.03 – 0.1 (LOD)	(Moinfar et al., 2009)
14	36 pesticides (OPPs and OCPs)	HS-SPME (Fiber: PDMS and PDMS/CX/DVB)		GC x GC/TOF BPX-5 40m		2 – 28	(Schurek et al., 2008)
15	33 pesticides (OPPs, OCPs, and PYRs)	Accelerated solvent extracted	GPC column (neutral, porous polystyrene-diethenyl benzene) SPE Carb-NH_2	GC-MS GC-FPD (OPPs) GC-ECD (OCPs and PYRs)	70 – 120	5 – 50	(Beizhen et al., 2008)
16	102 pesticides	SE Acetone/EtOAc/hexan	GPC system SPE EnviTM-Carb	GC-MS HP-5 30m	60.7 – 136.7	12 – 2450	(Zhiqiang Huang et al., 2007)

#	Number of pesticides	Extraction procedure	Clean-up procedure	Separation technique	Recovery (%)	LOQ (µg/kg)	Reference

Note:
HS: headspace
PDMS: polydimethylsiloxane
CX: carboxen
DVB: divinylbenzene
DLLME: dispersive liquid-liquid microextraction
MWCNTs: multiwalled carbon nanotubes

1.4.1. Sample preparation

1.4.1.1. Solvent extraction (SE)

Solvent extraction (SE) is one of the techniques most commonly used to extract pesticides from the matrix. For pesticide analysis, it is necessary to consider the balance between extraction efficiency and matrix effect. So polarity solvent medium such as acetonitrile (ACN), acetone, and methanol (MeOH) has been used as the extraction solvent because they are easily miscible with the agricultural products and penetrate the tissue of the samples (Picó, 2015). In such solvents, ACN and ethylacetae (EtOAc) are often used not only in tea but also in other matrices. ACN, despite being solvent mixed with water but can be easily separated for a phase when the salt is added in the solution. Moreover, it can extract polarized pesticides, non-polarized pesticides, and a small amount of matrix components (Zhang et al., 2012). EtOAc can reduce the polarization of a polarized solvent so quickly reduce interference for the next stage. However, some polar pesticides do not readily partition into the EtOAc phase. The acetone and methanol are usually less universal solvent because they are difficult for the phase separation with water. Diethyl ether rarely used due to low boiling temperature and easy to form explosive compounds (peroxides). SE extraction techniques usually associated with the ultrasonic to enhance efficiency and reduce processing time, ultrasonic energy to support the process of breaking the cell wall, as well as the penetration of the solvent into the sample (Zhang et al., 2012). Time ultrasound is survey parameters to ensure analytical results. Ultrasound a short time, the extraction process is not entirely. In contrast, ultrasound for a long time can cause decomposition of the labile compounds. The temperature generated during the ultrasound also needs control. Rezaei and colleagues showed that if the process temperature is greater than 40 °C will lead to the breakdown of heat-labile compounds. Also, the pH index is adjusted by formic acid (FA), acetic acid (AA), or sodium hydroxide (NaOH) to achieve the desired performance. This extraction technique is fast, efficient, suitable for the simultaneous extraction of pesticide compounds.

However, the process is extracted in several compounds that cause interference, especially for complex samples such as tea. Frequently solvent extraction techniques usually combined with liquid-liquid extraction (LLE), or solid-phase extraction (SPE), dispersed solid-phase extraction (d-SPE) to remove interferences. In recent decades, SE has been developed to simplify the process, reduce the time, and improve the efficiency of handling as QuEChERS. This method will be described in detail in the following section.

1.4.1.2. Liquid-liquid extraction (LLE)

LLE is one of the techniques used to eliminate interferences in the analysis of pesticides. LLE is based on the principle that a solute or an analyte can distribute itself in a certain ratio between two immiscible solvents, usually water (aqueous phase) and organic solvent (organic phase). LLE is used in the analysis of pesticides to eliminate water, water-soluble compounds, and transfer the analyte into a common polarity solvent, the low boiling point. This method is usually just part of the process of cleaning the complex sample such as tea (Tsipi et al., 2015). Cajka et al. have developed a method for rapid analysis of 135 pesticides in green tea and black tea (Cajka et al., 2012). Samples were processed according to the process QuEChER, then cleaned by LLE extraction LLE with hexane, recovery 70 – 120%, RSD < 20% for all the compounds with three levels 0.001, 0.1, and 1 mg/kg. LLE technique is simple, does not require sophisticated equipment but time-consuming, difficult to automate, use more solvent, so less used.

1.4.1.3. Supercritical fluid extraction (SFE)

In recent years the SFE is applied to extract pesticide compounds in supercritical fluids quickly - a form of matter exists in conditions of pressure and temperature above the critical point. Under these conditions, it can quickly diffuse into the solid form and dissolve analytes. In recent studies, CO_2 supercritical fluid is commonly used in extracting pesticides because of the temperature and pressure for its existence in the

average, low toxicity, non-flammable, and easy drying after extraction. In addition, supercritical CO_2 is effectively extracted the polar or medium polar compounds, should be able to remove the non-polar interference from the sample and leave the polarized pesticides. Arakawa developed a method for the determination of multi-pesticide residues in tea by SFE/GC-MS (Arakawa et al., 2012). It consumed a short period, compared to the total analysis time, and SFE extraction solution contains fewer components than the organic extraction. However, these ingredients interfere with analysis equipment, so the extraction solution is cleanup with SPE column ENVI^{TM}-Carb/NH_2 and InertSep^{TM} SI Cartridge.

In short, compared to the techniques of traditional solvent extraction, SFE technique spends less solvent and time, can extract selectively and efficiently analyze compounds from the sample matrix. Besides, since low-temperature solvent extraction, so it is suitable for heat unstable pesticides. However, due to the low polarity of supercritical CO_2, so only the non-polarized or less polarized pesticides are extracted efficiently (Zhang et al., 2012). For medium polarized or polarized pesticide, need to add organic solvents to improve the efficiency of extraction.

1.4.1.4. Solid-phase extraction (SPE), dispersed solid-phase extraction (d-SPE)

Since mid-1970, SPE, an extractive technique where dissolved or suspended compounds in a liquid mixture are separated with respect to their physical-chemical properties, is considered as one of the techniques commonly used to isolate, enrich pesticide compounds in water, food, or eliminating interference components. By the early 1990s, this technique is used most commonly due to the simplicity and large enrichment factor. First, the sample is extracted by the solvent extraction then isolated, enriched based on SPE. In the loading phase, the sample solution is passed through the SPE column was activated before the analyte, and interferences will be stored in the stationary phase. Then interference substances are removed from the SPE with a suitable solvent. Finally, analytes were eluted and analyzed. With SPE, many of the

problems associated with liquid/liquid extraction can be solved, such as incomplete phase separations, less-than-quantitative recoveries, and disposal of large quantities of organic solvents (Supelco Bulletin 910, 1998). So, SPE is often considered as more efficient than liquid-liquid extraction, yields quantitative extractions that are easy to perform is rapid, and can be automated.

Typically, the selected type of stationary phase must be selectively absorbing analytes to ensure no loss of them. Today there are many different types of stationary phase is produced to allow isolation and enrichment of pesticides from the sample matrix. Lou. Z and his colleagues used SPE extraction combined gas chromatography to identify 92 pesticides in tea (Lou et al., 2008). Samples were extracted with ACN, and then the organophosphorus pesticides were isolated on Envi-Carb SPE cartridge, eluted by 10 mL acetonitrile-toluene (3:1, v/v) and determined by gas chromatography - Flame Photometric Detector (GC-FPD). The organochlorine and pyrethroid pesticides were isolated, enriched with Envi-Carb and NH_2 SPE cartridges, eluted with 5 mL acetonitrile-toluene (3:1, v/v), and determined by gas chromatography - electron capture detector (GC-ECD). Recoveries for all compounds are 80.3% - 117.1%. LODs range 0.0025 - 0.10 mg/Kg. Overall, there are 3 sorbents commonly used in tea pesticide analysis including graphitized carbon black (GCB), primary secondary amine (PSA), and octadecyl (C18) (L. Chen et al., 2014; Hayward et al., 2015; Hayward et al., 2013; Hou et al., 2016). While GCB is suitable for removing coloured compounds, *e.g.*, pigments, and chlorophylls, PSA is used to eliminate sugars, organic acids, caffeine, and fatty acids. In addition, C18 is also used for removal sterols and lipids out of tea extraction solution.

Although SPE gives high yield when processing multiple samples simultaneously, but time-consuming when processing a sample is relatively long, relatively high cost even more, so another form of SPE technique was invented, d-SPE. In this technique, a small amount of adsorbent was put into extract solution; mix well to eliminate interference substances. The solution was centrifuged, and the liquid is taken to

analyze. The d-SPE has many advantages, such as using less static and solvent phases, saving time and labor, without supporting equipment such as vacuum pumps. Compared with SPE, d-SPE is a simpler, faster, and cheaper sample process. The most basic adsorbent in the d-SPE is PSA, a weak anion exchange material that allows the exclusion of compounds such as fatty acids, organic acids, and sugars. The combination of two or more kinds of stationary phase helps achieve maximum efficiency exclusion. Octadecyl (C18) eliminates cholesterol in the fat better than PSA. The new adsorbent as nanocarbon is also recommended to use for the analysis of pesticides in tea. Xue Liu and colleagues developed a method d-SPE with mixed stationary phases include Graphene, PSA, GCB combined LC/MS/MS identified 25 pesticides in green tea, black tea, and white tea with the recovery of 71.1 - 108.3% (Liu et al., 2013).

1.4.1.5. QuEChERS

Today, sample extraction methods developed to identify pesticides simultaneously are simultaneously towards the targets (Wilkowska & Biziuk, 2011): many pesticide detections in one injection, quick analysis, good repeatability, environmentally friendly, and low detection. The traditional methods usually include multi-steps: extract, clean up, change solvent, and using a large sample volume. Therefore it is time-consuming, labor-intensive, and a lot of chemical consumption. On the other hand, the traditional processing technique with complex processes is nowadays considered as leading to poor quantitative results, usually only allows analysis of one or more substances in a group of pesticides. So the traditional methods are no longer appropriate.

QuEChERS method was first published in 2003 (M. Anastassiades et al., 2003), applications to process samples for the analysis of pesticides in fruits and vegetables with high water content. QuEChERS is considered to combine and simplify many different techniques: (i) the extraction process with a mixture of solvent ACN / water;

(ii) ACN-water phase separation by adding anhydrous MgSO4 and NaCl; and (iii) d-SPE solid phase extraction (with a variety of sorbents) to eliminate interfering compounds. The basic stages of the original QuEChERS described, as shown below. The combination of extraction, isolation, and elimination of interference occurs in a process, simplify operations, to avoid the filtering process, thus limiting evaporation and minimize the amount of solvent used. QuEChERS is the acronym of the words: Quick, Cheap, Effective, Rugged, and Safe, which the advantages of this technique. Nowadays, QuEChERS and modified QuEChERS are widely applied in sample handling for the determination of pesticides in food, especially in screening. The basic trends of the future QuEChERS method than the original method is mainly focused on aspects such as the selection of solvent extraction volume, the ratio between the amount of sample and solvent volume, the effect of pH on the performance extraction, the type and concentration of salt, stationary phase used in the extract phase, cleanup in order to improve extract efficiency.

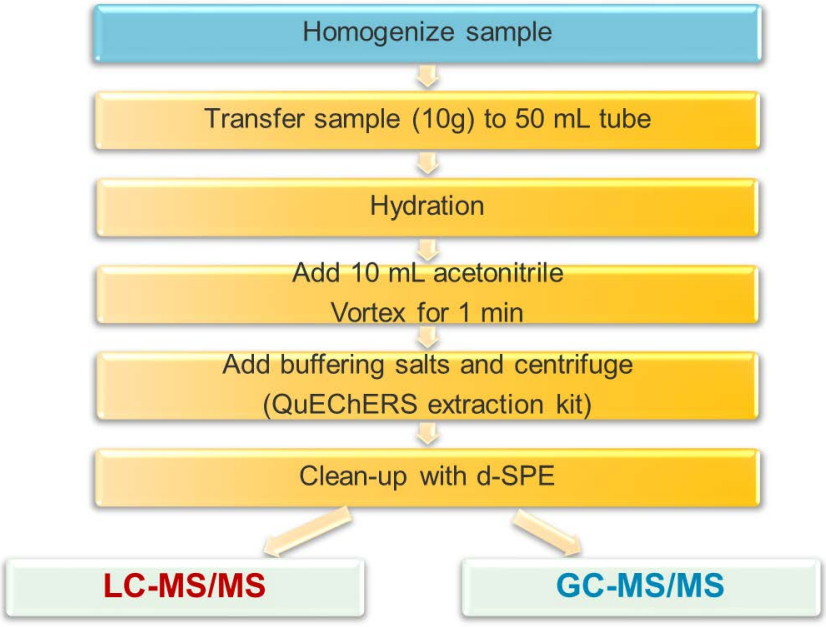

Fig. 1-3. Schematic presentation of the common procedure of QuEChERS

The selection of solvent is essential to achieve the following requirements, including: (i) maximum extraction capacity for a wide polarized range of pesticides; (ii) ability to separate phase with water; (iii) compatibility with many chromatography techniques , and cost, safety; and (iv) environmental concern. Solvents commonly used in the extraction for QuEChERS are ACN, EtOAc, or acetone. Among them, ACN is most widely used due to the selective extraction of analytes, minimizing interfering co-extracts, and suitable for both GC and HPLC (M. Anastassiades et al., 2003). Moreover, due to its higher polarity than acetone and EtOAc, ACN can extract compounds from medium to very polar (Rejczak & Tuzimski, 2015). However, ACN also has some disadvantages: (1) a larger solvent expansion volume during vaporization in GC, (2) ACN‘s detrimental effect on nitrogen phosphorus detector (NPD), and (3) lower volatility (Majors, 2007). Slightly soluble of fat in ACN, so the co-extracted fat is limited; however, this risk is not entirely extracting the non-polar pesticides, particularly when the higher fat content. Ethyl acetate is used less than the ACN because less efficient extraction, waxy and fatty substances easily extracted out with pesticides. Also, if using EtOAc as solvent extraction, the next stage of cleaning by d-SPA ineffective as ACN, recovery of acidic and base pesticides is low.

The homogeneous technique also affects the accuracy of the analysis results. Samples should be pureed to increase the contact area between the solid phase and the organic phase to optimize extraction efficiency. The homogeneous samples should be taken at a low temperature to prevent the loss of non-thermostable substances (M. Anastassiades et al., 2003). Sample and solvent are selected accordingly to minimize the effect of the sample without sacrificing extraction efficiency and meeting of the standing technical sensitivity measurement. Usually, a minimum of 10 g sample is processed to ensure the representativeness. The ratio between the volumes of extraction and sample processing volume is 1:1 (v/m) to effectively extracted analytes without dilution, allowing bypass dried solution stage (M. Anastassiades et al., 2003).

$MgSO_4$ often used in the phase separation stage. $MgSO_4$ not only removes water but also increases the distribution of pesticides into the organic phase. Thereby increasing the extraction efficiency of polar substances such as methamidophos, acephate, or omethoate(Wilkowska et al., 2011). NaCl is often used in combination with $MgSO_4$ at a ratio (1/4) to ensure the selectivity of the extraction process and to limit the interference compounds (*e.g.*, sugar) distributed into the organic phase. $MgSO_4$ quality is also essential. Lehotay suggested using $MgSO_4$ powder, the purity over 98%. Many authors suggested it should be dried at 500 °C before use to eliminate phthalates and humid, but these claims were not strict when chemical quality is good enough (Lehotay, 2006). Recent studies show that ammonium formate is also used effectively in phase separation (González-Curbelo et al., 2014).

The stationary phase type commonly used in the d-SPE stage of the QuEChERS method usually C18, PSA, GCB combined with $MgSO_4$. PSA can eliminate sugar, fatty acids, organic acids, and anthocyanin pigments but can cause loss of potent acidic pesticides. PSA does not remove interferences effectively when the samples contain more carotenoid or chlorophyll. C18 is used to remove the non-polar interferences. GCB has a strong affinity toward planar molecules and thus effectively removes pigments (*e.g.*, chlorophyll, carotenoids) as well as sterols (M. Anastassiades et al., 2003). However, most of the pesticides have an affinity with GCB smaller than chlorophyll pigment, the appropriate amount of GCB should be studied so that the final solution is both light color and no loss of flat structure (Rejczak et al., 2015). ChloroFiltr® was also recently announced as a replacement for GCB. ChloroFiltr® is the material that allows exclusions chlorophyll without losing planar structure compounds. However, it should not be used when analyzing hexachlorobenzene (Rejczak et al., 2015). Wang has reported that the recovery efficiency of substances with a flat structure is significantly higher when using ChloroFiltr® compared to GCB; for example, thiabendazole has recovery of 93.2 and 55.9%, respectively (Rejczak et al., 2015). Recently a multi-walled carbon nanotube (MWCNTs) is used as

a new sorbent. With 6 mg MWCNTs in the d-SPE phase for analysis 78 pesticides, the recoveries of all compounds were in the range of 70-120%, better than using PSA (Hou et al., 2014). Deng et al. used amine-functionalized magnetic nanoparticles and multi-walled carbon nanotubes (MNPs/MWCNTs) as a stationary phase in the d-SPE stage in tea extraction before analysis by GCB (Deng et al., 2014). MNPs interact strongly with polar acids due to its weak anion exchange, while MWCNTs can effectively exclude a large number of pigments and sterols. The author compares three cleaning processes using MNPs/MWCNTs, C18, and PSA/GCB, the performance gain for all three procedures for pesticide compounds over 85%. However, effective cleaning of MNPs/MWCNTs was better C18.

Besides that, the analyte protectants (APs) are also used for GC to minimize peak tailing or degradative effects. According to Anastassiades et al., the best APs are polyhydroxy compounds such as sugars and sugar derivatives (sorbitol, ethylglycerol và δ–gulonolactone) (Michelangelo Anastassiades et al., 2003).

After cleaning with PSA, the pH of the extraction solution is high, typically in the range of 8-9, which reduces the recovery of several pesticides. So many modified QuEChERS used buffer in the extraction step, *e.g.*, Association of Official Agricultural Chemists method (AOAC 2007.01) using acetate buffer (pH 4.7) or the European Standard method (EN 15662:2008) with a citrate buffer (pH 5 - 5.5). The use of buffers to avoid decomposition of sensitive substances at high pH (*e.g.* captan, folpet, dichlofluanid, tolylfluanid, pyridate, methiocarb sulfone and chlorothalonil) (Lehotay et al., 2010; Rejczak et al., 2015). However, interferences are increased when using buffers. Anastassiades et al. have recognized that the procedure used acetate buffer is relatively simple; the buffer is given by adding an acetate salt in the extraction step, and thus retaining the advantages of the original process is ‗fast', simple. A part of acetate can penetrate the organic phase, keeping the pH stable during extraction. However, the intense activity of acetate buffer makes the efficiency of the cleaning phase with d-SPE significantly reduced compared with origin QuEChERS.

Conversely, citrate buffers do not affect the activity of PSA, so Anastassiades et al. have chosen citrate as the most efficient buffer in handling pesticides (Michelangelo Anastassiades et al., 2003).

The traditional pesticide extraction methods in the complicated matrix contained many complicated steps, and required a large sample volume. Therefore, it consumes much time, labor, and large amounts of solvents, chemicals release to the environment. Conversely, the QuEChERS method helps minimize the number of samples as well as analysis tools in sample handling. A simple process is a significant advantage of this method because of the chemical complexity of each stage will increase the risk of systematic and random error (Wilkowska et al., 2011).

1.4.2. Separation and determination

Currently, gas chromatography (GC) coupled with mass spectrometry (GC-MS) and GC or liquid chromatography (LC) coupled with tandem mass spectrometry (GC-MS/MS and LC-MS/MS) are used most to analyze multi-pesticide residues in tea simultaneously with low limits of detection (LOD), low limits of quantification (LOQ) and good accuracy (Cajka et al., 2012; Fan et al., 2013; Hayward et al., 2015; Hayward et al., 2013; Hou et al., 2016; Z. Huang et al., 2007; Huang et al., 2009; Li et al., 2012; Pang et al., 2011; Y. Wang et al., 2011). Tandem mass spectrometry includes triple quadrupole mass spectrometer (QQQ), and quadrupole time-of-flight mass spectrometry (Q-TOF). QTOF has the advantages to increase the sensitivity, mass resolution and mass accuracy of the resulting tandem mass spectrometer in both precursor (MS) and product ion (MS/MS) modes compared to QQQ. Recently, Q-TOF was coupled with liquid chromatography (LC) for screening pesticide residues in food (García-Reyes, Hernando, et al., 2007; García-Reyes, Molina-Díaz, et al., 2007). In contrast, QQQ is used more for the purpose of quantifying pesticide residues in foods because of its high sensitivity, high dynamic range and easier operation than Q-TOF (LeDoux, 2011a). Multiple reaction monitoring (MRM) is the most common mode of

using a QQQ for quantitative analysis. The first quadrupole filters a specific precursor ion of interest. Ions generated in the ion source having a different m/z cannot pass the first quadrupole (Q1). The collision cell is optimized to produce a characteristic product ion by collision of the precursor ion with a neutral collision gas, such as nitrogen, in the second quadrupole (Q2). Generated product ions are transferred into the third quadrupole (Q3) where only a specific m/z is allowed to pass. All other product ions are filtered out in Q3. Thus MRM mode works like a double mass filter which drastically reduces noise and increases selectivity by reducing the noise of eluting background and matrix components.

1.4.2.1. GC-MS/MS

GC is combined with different kinds of detector as electron capture detector (ECD), flame photometric detector (FPD), and nitrogen–phosphorus detector (NPD). These traditional detectors are often selective with some groups of pesticides. Conversely, MS is both a selective and universal detector, depending on the operating mode. This method gives many advantages when screening a large number of pesticide compounds. Nowadays, mass spectrometer detector (such as single quadrupole (Q), ion trap (IT), the time of flight (TOF), and triple quadrupole) have been used for pesticide analysis.

In an identical manner to gas chromatography, samples being analyzed by GC-MS/MS are separated in a gaseous state based on the various physical and chemical properties of analytes of interest and their interaction with the analytical column‘s stationary phase. Upon exiting the analytical column, the analytes enter the tandem mass spectrometer (MS/MS), which consists of two scanning mass analyzers separated by a collision cell. Fragments selected in the first analyzer are reacted with an inert gas in the collision cell, resulting in further fragmentation. These daughter product ions are then resolved in the third quadrupole for analysis (EAG laboratories).

GC-MS/MS was established to allow improved sensitivity compared with a quadrupole system, improve selectivity, precision, detection limit, extending the linear range (Tsipi et al., 2015). In the analysis of screening large numbers of compounds, some of which can be eluted simultaneously or with matrix samples, if using a quadrupole system or IT is difficult to analyze precisely, in the case this GC-MS/MS with MRM mode is considered to be the ideal choice. The ionization technique commonly used in GC-MS/MS is EI because of the availability of quantitative and qualitative peaks from the NIST spectrum library (due to the same 70 eV ionization energy).

1.4.2.2. LC-MS/MS

GC-MS/MS is difficult to analyze non-volatile, thermal unstable, or polarized pesticides. Therefore liquid chromatography with mass spectrometry is the perfect complement. In LC-MS, after leaving the column, the analyte will be ionized at the ionizing source. The ionization interface is often used in this method are electrospray ionization (ESI), atmospheric-pressure chemical ionization (APCI), and atmospheric pressure photoionization (APPI). With ESI sources, the analytes are ionized from the solution as follows: (1) dispersal of a fine spray of charge droplets, followed by (2) solvent evaporation and (3) ion ejection from the highly charged droplets tube (Ho et al., 2003). For APCI, with gas assistance, the solvent and sample flow through the injector. The solvent and sample are vaporized by the heater in the injector and ejected from the injector outlet. At the outlet of the injector, the solvent is ionized by electro-acupuncture corona discharge. The solvent ions react with the sample molecules to ionize the sample (Bruins, 1994). In the case of APPI, UV light photons are used to ionize sample molecules. The technique works well with nonpolar or low-polarity compounds not efficiently ionized by other ionization sources (Kauppila et al., 2002).

ESI is the ionization techniques most commonly used, often used to analyze the compounds polarity medium to high ionic compounds with a molecular weight of

about 100-150000 Da, APCI used for nonpolar compounds, or polarization average with a molecular weight of about 100 - 2000 Da. When the flow rate of HPLC is high (greater than 0.5 mL/min), APCI is more sensitive than ESI. On the other hand, APCI is also less affected by the sample matrix than ESI, since the analyte ionization takes place in the vapor phase (Tsipi et al., 2015). APPI has the same ionization mechanism as APCI, in which a UV source replaces corona discharge. APPI often applies to compounds that ESI and APCI give weak ionization. After the analyte is ionized at the interface, it moves to mass separator before reaching the detector. Like GC, LC can apply different types of mass spectrometry, such as single quadrupole, QQQ, TOF, IT, or a combination of them. However, LC-MS with single quadrupole system, (including ion trap systems operating in selected ion monitoring (SIM) mode) is not commonly used due to: (1) high background signal intensity caused by the sample matrix and solvents, (2) low sensitivity when using full scan mode, and (3) the lack of information about the structure when using SIM mode (Tsipi et al., 2015). This phenomenon can be significantly minimized by using triple quadrupole.

Therefore, LC-QQQ-MS/MS is the device most commonly used because of the simplicity, sensitivity, selectivity, and durability. QQQ system can operate in multiple modes such as parent ion scan, the production scan, and multiple reactions monitoring (MRM). In which MRM mode is used most commonly as quantitative analysis. Typically, the most sensitive MRM transition for each compound is applied for quantification, in which the area of standards using for the calibration curve. The other MRM transitions were applied for confirmation, usually the second most sensitive peak, basing on the ratio between confirmation and quantitation peak. Many studies have been published using LC-QQQ-MS/MS success analysis of screening hundreds of compounds such as pesticides: Huang et al. (2009) apply LC-ESI-Q-MS/MS to analysis of 103 pesticides in tea. Also, QQQ with slow scan speed, so, need to split multiple segments to increase the sensitivity and increase the number of data points obtained for each peak (Tsipi et al., 2015). However, today‘s state-of-the-art QQQ has

supported separate segmentation with dynamic MRM techniques, making it easier to scan spectra according to the compound‘s retention time.

1.5. Matrix effect

The International Union of Pure and Applied Chemistry (IUPAC) defines matrix effects as "the combined effect of all components of the sample other than the analyte on the measurement of the quantity" (Stahnke et al., 2012). It usually occurs in chromatographic analysis, especially with mass spectrometry. The mechanism of this phenomenon is difficult to explain even though it has been studied by many authors (Li et al., 2018). Different matrices will give different ME, even if they belong to the same category type according to the SANTE/11945/2015 guidance document (Gómez-Ramos et al., 2016). There are two ways to estimate ME: (i) comparing compound signal in solvent standard with signal in matrix standard (Gómez-Ramos et al., 2016; Li et al., 2018; Rutkowska et al., 2018; Stahnke et al., 2012); (ii) and using post-column infusion (Kittlaus et al., 2011). The first method estimates ME of each substance with a specific number, while the second method measures ME occurring during the entire chromatographic run (Stahnke et al., 2012). The matrix effects were calculated as (Kittlaus et al., 2011):

Equation 1. Evaluating matrix effect in quantification method

$$Matrix\ effect\ (\%) = \left(\frac{slope\ of\ calibration\ curve\ in\ matrix}{slope\ of\ calibration\ curve\ in\ solvent} - 1\right) * 100$$

Ion suppression (ME < 0) and enhancement (ME > 0) are the two main consequences of the matrix effect (Fig. 1-4) (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Ucles et al., 2017). Ion enhancement usually occurs in GC-MS(/MS), while ion suppression appears in LC-MS(/MS). ME is classified into: soft (< 20%), medium (20 - 50%), and strong (> 50%). ME usually depends not on analyte compounds but mainly on types of the sample matrix, instrument detection, and sample extraction.

Especially in the tea leaves, the complexity of ME increases as ME also depends on the origin, variety, and processing process (Li et al., 2018). For soft ME, it could be used calibration curves in solvent for quantitation. Conversely, it must be minimized or compensated for the matrix effect by different methods.

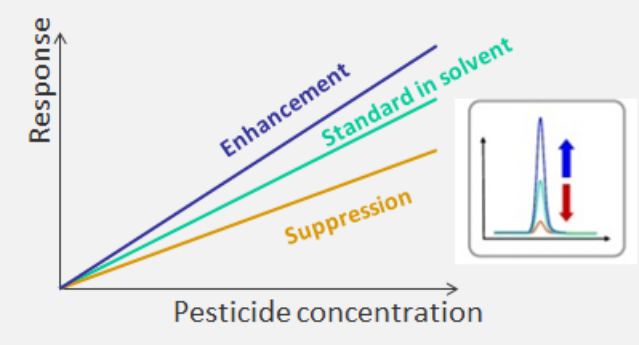

Fig. 1-4. Comparing the slop (left) and the signal (right) of a compound in solvent (cyan) with enhancement (blue), and suppression (orange)

In GC-MS/MS, it was more common to find signal enhancement in tea (Beneta et al., 2018; Li et al., 2012; Li et al., 2018). However, matrix effects also improved peak shapes (less tailing, more symmetric, and higher intensity) compared to those from standard solutions prepared in solvent. The interferences in matrix solutions seem to block active sites of column and injector; thus, more pesticides could quickly reach the MS detector (Lozano et al., 2012). Some pesticide groups often suffer from ME (such as carbamate, phosphate, carboxyl, azole, hydroxyl, amino group, urea, imidazole, and benzimidazole) (Li et al., 2012; Rahman, Abd El-Aty, et al., 2013). These substances often have a high matrix effect because their functional groups interact with silanol or metal ion groups on glass surfaces (lining, glass wool) (M. Anastassiades et al., 2003).

For LC-MS/MS method, ion suppression was more common. That caused by matrix components decreasing the efficiency of the droplet and ion number formation (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Ucles et al., 2017). The matrix effect depends on the commodity type, sample preparation method, mobile

phase composition, and design of the electrospray ionization source (Gómez-Ramos et al., 2016). ME in LC-MS was not affected by the pesticide structure but strongly influenced by its retention time (Kittlaus et al., 2011). In reversed-phase chromatography, strong suppression commonly appears at the beginning of the chromatogram caused by low retained matrix compounds (Kittlaus et al., 2011).

For ME out of range ± 20%, it could be reduced or compensated by (i) diluting; (ii) using of standard addition; (iii) adding isotope internal standards; (iv) adding of analyte protectant (only for GC-MS/MS), and (v) matrix-matched calibration (Kittlaus et al., 2011; Ucles et al., 2017). Dilution is a simple, effective method for reducing ME but requires the high sensitivity of analytical equipment to reach the pesticide MRLs in food. Standard addition is not suitable for routine analysis. Isotope internal standards are costly and usually not available for all substances. For GC-MS/MS, analyte protectants are added to standard and sample solutions to block active sites of column and injector to overcome matrix effect. However, polar solvent as water is used, which is harmful to the GC column and MS detector (Li et al., 2018). Hence, matrix-matched calibration would be one of the best ways to overcome the ME phenomenon and give high accuracy results for multi-pesticide residues analysis. Conversely, it will increase the number of impurities onto the column and detector, leading to increased equipment maintenance.

1.6. Conclusion

The analysis of pesticide residues in tea has the following challenges. Firstly, the tea leaves represent a complex matrix with many organic compounds in high concentrations such as: proteins and amino acids (15 - 23%), carbohydrates (4 – 5%), lipids (2 – 3%), caffeine (1 – 5%), and polyphenol (15%) (Stagg et al., 1975). So it is difficult to extract pesticide residue out of tea matrix. Seconly, matrix effects in teas will affect the qualitative and quantitative of pesticide residues. It requires a sample preparation method that is good enough to reduce matrix effects. Thirdly, there are

now hundreds of pesticides with different physical and chemical properties such as polarization and volatility. It requires an analytical method that detects as many pesticides as possible. Finally, MRL regulations vary widely from country to country, so the detection limit must be as low as possible to accommodate all MRLs.

The QuEChERS extraction and d-SPE clean-up have disadvantages in analysis of pesitcide residue in tea, including matrix effects and low sensitivity. Therefore it needs to be modified to increase the sensitivity, accuracy and precision for simultaneous analysis of hundreds of pesticides in tea.

Various pesticides are frequently detected in tealeaves such as pyrethroid pesticides (cypermethrin, etofenprox, fenpropathrin, and fenvalerate), neonicotinoid insecticides (acetamiprid, imidacloprid), organophosphorus pesticides (triazophos), triazole fungicides (paclobutrazol) and other groups (anthraquinone, buprofezin). These pesticides are sometimes detected at higher levels than EU MRLs. For processed food, tea is also in the top 3 matrices with pesticide residues higher than MRL. Therefore, assessments of multi-pesticide residues in tea need to be continued.

On the other hand, it should be taking into account that the pesticide risk assessment. Assessment of dietary exposure to pesticide residues combines data on level of particular substance in a food and that food‘s consumption rates. Then long- and short-term heathy risk were assessed by comparing the estimated exposure with the health-based toxicological reference values (TRVs), namely, acceptable daily intake (ADI), and acute reference dose (ARfD), respectively (Struciński et al., 2015). Therefore, with an accurate and reliable pesticide residue quantification method, it will contribute to assess the toxic level of each pesticide to consumers.

Chapter 2. Material and methods

2.1. Materials

Glacial acetic acid (AA), HPLC-grade acetonitrile (ACN), methanol (MeOH), hexane, ethyl acetate (EA), and acetone were obtained from Merck (Darmstadt, Germany). The GCB/PSA SPE (500 mg/500 mg/6 mL), PSA SPE (500 mg/6 mL), and C18 SPE (500 mg/6 mL) tubes were obtained from Agilent (Santa Clara, United States). The GCB SPE tube (500 mg/6 mL) was obtained from CNW (Shanghai, China). QuEChERS extraction kits (2 g MgSO4, 0.5 g NaCl, 0.5 g sodium citrate, and 0.25 g disodium citrate sesquihydrate) were prepared by weighing each substance (obtained from Merck, Darmstadt, Germany) into a 15 mL centrifuge tube.

For LC-MS/MS analyses, 204 compounds in pesticide solution kits were obtained from Restek (31971, see Table A-3 of Appendex Tables; Bellefonte, United States) and three other compounds (atrazine, simazine, and phoxim) were obtained from Sigma Aldrich (St. Louis, United States). For the GC-MS/MS analyses, 203 compounds in pesticide kits were purchased from Restek (see Table A-3 of Appendix Tables; Bellefonte, United States). For atrazine, simazine, and phoxim, 100 mg/L stock solutions were prepared for each compound in ACN. For all of the pesticides, intermediate solutions of 10 mg/L were prepared in ACN for LC-MS/MS and toluene for GC-MS/MS and stored in amber screw-capped glass vials in the dark at –20 °C.

Standard mix solutions at concentrations of 1 mg/L were prepared from the stock solutions to optimize and validate each method. Since three of the compounds (alanycarb, benfuracarb, and mesotrione) in the LC-MS/MS standard mix containing 207 pesticides were not stable, 204 pesticides were used for this study.

For the GC-MS/MS method, a surrogate stock solution (a mixture of α-BHC-d6 and parathion-d10 at 40 µg/mL in ACN) obtained from Restek (32571, Bellefonte, United States) was used to monitor validity. A working surrogate solution at 1 mg/L was

prepared in toluene and stored at –20 °C. Trifluralin-d14, purchased from Dr. Ehrenstorfer (Augsburg, Germany), was used as an internal standard (IS) for GC-MS/MS analysis. A stock IS solution was prepared in toluene at 1 mg/L and stored at –20 °C. The working IS solutions (10 µg/L in ACN) was used in the final step of sample extraction, prior to injection into the GC-MS/MS instrument. An analyte protectant (AP) solution was prepared with sorbitol (5 mg/mL), d-(–)gluconic acid-δ-lactone (10 mg/mL), shikimic acid (5 mg/mL) and 3-ethoxy-1,2-propanediol (0.2 g/mL) in ACN/H_2O (6/4, v/v).

2.2. Equipment

A homogeneous machine (IKA, USA), a vortex (Velp, Italy), a multi-vortex (Heidolph, Germany), a 24-port SPE vacuum manifold (Supelco, USA), and a mivac Quattro sample concentrators (Genevac, United Kingdom) were used for preparing the samples.

The UPLC-MS/MS system (Thermo Fisher Scientific, Waltham, United States) was a Vanquish UPLC (equipped with a binary pump, auto-sampler, and column thermostats) linked a TSQ Quantiva triple quadrupole mass spectrometer. An Accucore™ aQ C18 polar end-capped column (100 x 2.1 mm i.d. and 2.6 µm particle size) combined with a 0.5 µm filter cartridge was used (Thermo Fisher Scientific). The mobile phase consisted of MeOH and H_2O in a ratio of 2/98 (v/v) for mobile phase A and 98/2 (v/v) for mobile phase B. Both mobile phases were supplemented with 5mM ammonium formate and 0.1% formic acid to enhance the sensitivity of the signals and stability of retention times. The gradient mobile phase was set up as follows: 0–0.5 min, 0% B; 0.5–2 min, 0–40% B; 2–22 min, 40-100% B; 22–22.1 min, 100–0% B; 22.1–25 min, 0% B (total time of 25 min). The flow rate was fixed at 0.3 mL/min, and the injection volume was 3 µL. The column oven was maintained at constant temperature of 40 °C. This gradient program has been applied according to Center of analytical services and experimentation (CASE) in house method (CASE.SK.0114).

The MS parameters were optimized for each standard in the mass spectrometer by using 1 mg/L solution in both positive and negative MRM mode. The EU 657/2002/EC guidelines for LC-MS/MS analysis were followed with two MRM transitions for each compound (higher intensity for quantification and lower intensity combined with the MRM ratio for confirmation). For the MS detector, N_2 (purity > 99.98%) was used as the sheath gas, ion sweep gas, and auxiliary gas at flow rates of 40, 1, and 12 a.u. (arbitrary units), respectively. The ion transfer tube and vaporizer temperatures were set at 325 °C and 300 °C, respectively; the electrospray voltage was +3.5 kV (positive mode) and –2.5 kV (negative mode). The mass parameters, including the retention time (RT), electrospray ionization (ESI) mode, quantitative peak, confirmation peak, radio frequency (RF), and collision energy (CE), are reported in chapter 3.

The GC-MS/MS system (Thermo Fisher Scientific, Waltham, United States) was a Trace 1300 Thermo Scientific™ gas chromatography coupled with a TSQ 8000 triple quadrupole mass spectrometer. It operated in electron ionization mode (EI, 70 eV). The analytes were separated in a fused silica capillary column DB-5ms (30 m x 0.25 mm i.d., 0.5 µm film thickness) from Agilent. The column oven temperature was programmed as follows: an initial temperature of 90 °C was held for 1 min, then increased by 8.5 °C/min to 320 °C and held for 5 min. The total time was 40 min. The injection volume was 2 µL in splitless mode, held for 1 min at a temperature of 250 °C. The purge N_2 gas flow was set at 50 mL/min. By using the Thermo AutoSRM software, the two most intense transitions and their optimal collision energies were selected. The most intense product was selected as the quantifier ion, and the second most intense was set as the qualifier ion. The settings on the mass spectrometry detector, including the RT, quantitative peak, confirmation peak, and CE, are reported in chapter 3.

2.3. Tea samples

Chapter 3: an organic green tea was obtained from the Fito Pharma pharmaceutical company (Vietnam). This sample was homogenized into a powder using a blender and passed through a 2-mm sieve as a blank sample to optimize and validate the method for green tea.

Chapter 4 and 5: For blank samples, three organic samples (i.e., BT, GT, and WT) were collected from the ancient Shan Tuyet tea garden (Suoi Giang, Yen Bai, Vietnam), and one organic sample (i.e., OT) was collected from Suzuki Company (Lam Dong, Vietnam). The tea leaves were homogenized and kept at 20 °C for method validation. These samples have been analyzed to ensure they are free from pesticide residues.

Chapter 5: for pesticide residue assessment, a total of 106 tea samples were collected from tea stores or tea plantations in Vietnam, China, Taiwan, Singapore, France, and Qatar between October 2017 and May 2019 (Table A-15 of the Appendix Table). The samples included 42 black (BT), 38 green (GT), 17 oolong (OT), 6 white (WT), and 3 Pu-Erh (PT) in various types of packaging.

2.4. Sample preparation

Tea samples were homogenized into a powder using a blender and passed through a 2-mm sieve as subsamples. The subsamples (2 g) were weighed in 50 mL centrifuge tubes, and then 0.02 mL surrogate 1 µg/mL and 10 mL ACN (1% CH_3COOH) were added. The solution was then vortexed for 30 min. QuEChERS extraction kit was added, and the tube was vortexed immediately. After centrifugation, 5 mL of the upper ACN layer was transferred to and purified with mixed-mode SPE as Figure 1. The ACN extract was introduced into the cartridge, and subsequently, 20 mL of ACN-toluene (3/1, v/v) was used as the eluting solvent. All of the extract solution and eluent solvents were collected and concentrated to 1 mL using a concentrator (40 °C, 1000

bar). After drying under N_2 gas, the residue was re-dissolved with 1 mL MeOH and vortexed for 1 min (final solution). For LC-MS/MS solution, 0.4 mL final solution was diluted twice with water. For GC-MS/MS, a 0.4 mL final solution was dried and re-dissolved with 0.8 mL of IS solution, and then a 24 µL analyte protectant (AP) solution was added. The final dilution factor is two for both LC-MS/MS and GC-MS/MS method.

2.5. Experiment procedures

2.5.1. SPE sorbent optimization (chapter 3)

Several types of SPE and d-SPE sorbents were prepared and coded as following: MS-A is an SPE cartridge with only GCB; MS-B is a mixed-mode consisting of one SPE cartridge with a GCB layer on top and PSA on bottom; in MS-C, 250 mg of the C18 sorbent is added into the sample extraction solution (d-SPE) and was vortexed prior loading on a mixed-mode GCB/PSA SPE cartridge; MS-D is similar to MS-C but used 500 mg of the C18 sorbent; in MS-E, 500 mg of the C18 sorbent was added to an SPE cartridge that was connected to the top of a mixed-mode GCB/PSA SPE cartridge by an adaptor. Prior to the SPE procedure, all the targeted pesticides were added at 50 µg/kg into 5 mL of ACN extraction solution (1% AA) from a green tea blank sample.

2.5.2. Elution volume of the SPE process (chapter 3)

Elution volume is also an important factor affecting recovery. If the volume is too low, the analyte would not be released; if the volume is too high, interfering substances would be co-eluted. The experiments were conducted with elution volumes of 10 mL (EV-A), 15 mL (EV-B), 20 mL (EV-C), and 25 mL (EV-D). Solutions were spiked with 50 µg/L of standards prior to loading on mixed-mode SPE.

2.5.3. Evaporation optimization (chapter 3)

Investigations on impact of dryness for 407 pesticides were carried out by adding the standard solution (50 µl, 1 mg/L) to 25 mL of solvent (5 mL ACN containing 1% AA and 20 mL ACN/toluene, 3/1, v/v). The solvent was evaporated until either (i) the remaining volume was 1 mL (EC-A) or (ii) the sample was dry (EC-B). A blank sample was prepared in the same way, up to the concentration step, and a similar standard mix solution was added to obtain 25 mL of the final elution solution (EC-C).

2.5.4. Method validation for green tea (chapter 3)

The method was validated in accordance with the SANTE standard (SANTE/11945/2015), which determined the matrix effects, linearity, repeatability, LOD, and LOQ. Calibration curves were obtained by spiking standards, ranging from 5 to 200 µg/L, into blank matrix extract solutions prior to injection. Recovery and precision were determined based on samples spiked at 10, 50, and 100 µg/kg (6 samples for each level over two days). Matrix effects were assessed by comparing slopes of the matrix-matched calibration curves to the solvent calibration curves. LOQs were evaluated by determining the lowest concentration spike for samples where recovery and repeatability were satisfactory (within 70-120% and less than 20%, respectively) (SANTE/11945/2015). LODs were estimated as one-third of the LOQs.

2.5.5. Matrix effect evaluation (chapter 4)

A total of 200 pesticides in the UPLC-MS/MS and GC-MS/MS standard mix solutions were employed in this study. The post-extraction solutions were prepared through sample preparation sessions for assessing ME. For UPLC-MS/MS, five standard solutions (i.e., 5, 10, 50, and 100 µg/kg) in the solvent and matrix were prepared with MeOH/H_2O (1/1) and post-extraction solution, respectively. Similarly, for GC-MS/MS, five standard solutions (i.e., 5, 10, 50, and 100 µg/kg) were prepared with IS

and post-extraction solution for two types of calibration curves. The MEs were calculated as Equation 1.

First, GT was selected to develop a method combining QuEChERS extraction and mixed-mode SPE cleanup to evaluate MEs. Second, the MEs were overcome by reducing the injection volume from 3 µL to 1 µL for UPLC-MS/MS and from 2 µL to 1 µL for GC-MS/MS. Third, the dilution method was assessed to compensate for the MEs with different dilution factors of 4, 10, and 20. Accordingly, the post-extraction solution was diluted with MeOH/H_2O (1/1, v/v) and IS solution for LC and GC, respectively, before obtaining the matrix-matched calibration curves.

Finally, the MEs of different types of tea (i.e., WT, GT, OT, and BT) were estimated and compared. All samples were organic and tested without pesticides before this study.

2.5.6. Preparation of calibration curves (chapter 5)

The calibration curves were prepared from mixed standards at 0.5, 1, 5, 10, 50, and 100 µg/L in MeOH/H_2O (1/1) solution for the UPLC-MS/MS method. For GC-MS/MS methods, 4 types of organic tea (WT, GT, OT, and BT) were extracted and purified according to Section 2.3. Then, the final extract solutions were mixed before spiking mixed standards at 0.5, 1, 5, 10, 50, and 100 µg/L for performing matrix-matched calibration curves.

2.5.7. Method validation for different types of tea (chapter 5)

The method was validated for four types of tea (i.e., WT, GT, OT, and BT) following the SANTE/11945/2015 standard, which determined the matrix effect (ME), linearity, recovery, precision, and LOQ (SANTE/11945/2015). For blank samples, three organic samples (i.e., BT, GT, and WT) were collected from the ancient Shan Tuyet tea garden

(Suoi Giang, Yen Bai, Vietnam), and one organic sample (i.e., OT) was collected from Suzuki Company (Lam Dong, Vietnam). The tea leaves were homogenized and kept at 20 °C for method validation. These samples have been analyzed to ensure they are free from pesticide residues.

The calibration curves were prepared as previously described. The recovery and precision of the method were determined based on 5 samples spiked at levels of 10, 50, and 100 µg/kg for 4 types of tea. The LOQs were evaluated by determining the lowest concentration spiked for the sample for which the recovery and repeatability were within 70-120% and less than 20%, respectively. In some instances, and typically with multi-residue methods, a mean recovery below 70% and RSD ≤ 20% may be acceptable.

2.5.8. Pesticide residues in teas (chapter 5)

In this survey, a total of 106 tea samples were collected from tea stores or tea plantations from Vietnam, China, Taiwan, Singapore, France, and Qatar between October 2017 and May 2019. Among them, there are 27 organic samples, accounting for 25.5%. In terms of origin, 34 samples came from Vietnam (accounting for 32.1%), followed by India (20 samples), China (19 samples), and Taiwan (12 samples). The rest of the countries like Nepal, Sri Lanka, Japan, and Thailand had less than 10 sample sizes. Besides, 8 samples without origin information were denoted as "unknown".

Chapter 3. Determination of 400 pesticide residues in green tea leaves by UPLC-MS/MS and GC-MS/MS combined with QuEChERS extraction and mixed-mode SPE clean-up method

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3.1. Introduction

Among common beverages, tea is one of the most popular in terms of taste; it also has some health benefits, including weight control, reduction of blood pressure, and reduced risk of diabetes, osteoporosis and cardiovascular disease (Amorim et al., 2018; Chang et al., 2017). Tea is thought to have also some anti-carcinogenic effects (Naveed et al., 2018). However, because of monoculture practices, the use of pesticides during tea cultivation is common. Over time, the number of pesticides used has increased and, to protect consumers‘ health, many countries and regions have established maximum residue limits (MRLs) of pesticides for a variety of foods and beverages, including tea. For instance, the European Union (EU) has set the MRLs for more than 480 pesticides, and their metabolites in tea products, which range from 0.005 (fipronil) to 70 mg/kg (bromide ion) (EU MRL). Therefore, it is necessary to have reliable, robust, and sensitive analytical methods to determine pesticide residues in tea.

The development of analytical methods that can detect several hundred pesticide residues in tea is a challenge, because tea is a complex commodity with many compounds that can interfere with results, such as polyphenols, pigments, fatty acids, organic acids and caffeine (Reto et al., 2007). Generally, published analytical methods for one or more groups of pesticides involved the following: (i) use of an extraction procedures, such as accelerated solvent extraction (ASE), head-space solid-phase micro-extraction (SPME), matrix solid phase dispersion (MSPD) or solvent extraction; (ii) purification procedures, such as gel permeation chromatography (GPC), solid-phase extraction (SPE), dispersive liquid–liquid micro-extraction (DLLME) or dispersive solid-phase extraction (d-SPE); and, finally, (iii) separation and detection on a chromatographic system based on either gas chromatography (GC) or liquid chromatography (LC), coupled to different detectors (Cao et al., 2015; L. Chen et al., 2014; Feng et al., 2013; Hu et al., 2005; Moinfar et al., 2009; Schurek et al., 2008). Currently, GC coupled with mass spectrometry (GC-MS) and GC or LC coupled with

tandem mass spectrometry (GC-MS/MS and LC-MS/MS) are used most to analyse multi-pesticide residues in tea simultaneously with low limits of detection (LOD), low limits of quantification (LOQ) and good accuracy (Cajka et al., 2012; Fan et al., 2013; Hayward et al., 2015; Hayward et al., 2013; Hou et al., 2016; Z. Huang et al., 2007; Huang et al., 2009; Li et al., 2012; Pang et al., 2011; Y. Wang et al., 2011).

For sample extraction, QuEChERS is the most commonly applied method (Liu et al., 2013; Lozano et al., 2012; Pang et al., 2011; Rajski et al., 2013; Steiniger et al., 2010) with or without modifications, *e.g.* Association of Official Agricultural Chemists method using acetate buffer (AOAC 2007.01) or by the European Standard method (EN 15662:2008) with a citrate buffer. For the clean-up step, d-SPE and SPE are used most often. Many kinds of d-SPE sorbents (single or mixed), such as primary secondary amines (PSA), octadecyl (C18) and graphitized carbon black (GCB), have been applied for tea (Lehotay et al., 2010; Liu et al., 2013; Lozano et al., 2012; Steiniger et al., 2010; Zhao et al., 2012). The d-SPE has the advantages of being simple, fast, and inexpensive for most analytical laboratories. It is suitable for screening pesticide residues in several foods and beverages, including tea. However, QuEChERS combined with the d-SPE clean-up has some disadvantages, such as high matrix effects and low sensitivity (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rajski et al., 2013). In particular, in MS methods coupled with GC or LC, matrix effects are an important criterion that can cause false negatives or positives as well as poor quantification (Uclés et al., 2017). As a consequence, frequent maintenance is required, including cleaning the ionization source for LC and exchanging the liner for GC (Rajski et al., 2013). For SPE clean-up, many different kinds of sorbent have been applied to reduce or eliminate matrix effects, such as aminopropylsilanized silica gel (NH_2), PSA, GCB, TPT (including carbon, polyamine silica and amide polystyrene) and/or mixtures of these sorbents (Chen et al., 2011; Hayward et al., 2013; Hou et al., 2016; Huang et al., 2009; Pang et al., 2011). Although SPE clean-up procedures are time-consuming and labour-intensive, they have fewer matrix effects than d-SPE. By

using mix-mode mixed-mode SPE with GCB/PSA cartridges (Hayward et al., 2013) or novel multilayer solid-phase extraction cartridges (*e.g.* Cleanet TPT) (Pang et al., 2011) more 300 pesticides have been detected in tea. However, in the study of Pang et al. (2011), LOD, LOQ, and especially matrix effects were not clearly defined, meaning this method is suitable only for screening purposes.

More generally, analysis of pesticide residues in tea usually requires extraction, clean-up and/or enrichment/dilution. Many researchers have focused on QuEChERS for sample preparation in combination with d-SPE (AOAC 2007.01; Cajka et al., 2012; Chen et al., 2011; Hou et al., 2016; Hou et al., 2014; Lehotay et al., 2010; Lozano et al., 2012; Rajski et al., 2013; Steiniger et al., 2010; J. Wang et al., 2011; Zhao et al., 2012), but QuEChERS extraction and d-SPE clean-up have disadvantages in analysis of tea, including matrix effects and low sensitivity depending on detection system (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rajski et al., 2013). Previous studies have shown that it is difficult to eliminate interference using only d-SPE and this problem is more evident when analysing residues of several hundred pesticides with very different physical-chemical properties, such as polarization, functional groups, molecular mass, and vapour pressure. In this study, we aimed to develop rugged and robust methods with high sensitivity, accuracy, and precision to meet the SANTE/11945/2015 standard for simultaneous determination of 400 pesticide residues in green tea products using ultra performance liquid and gas chromatography coupled to tandem mass spectroscopy (UPLC-MS/MS and GC-MS/MS). The study focused on elimination of matrix effects by combining QuEChERS extraction and mixed-mode SPE clean-up using different sorbents, such as C18, GCB, PSA, in sample preparation, which allowed for analysis of several hundred pesticides with low matrix effects and high recoveries.

3.2. Experimental

3.2.1. Reagents and chemicals

Glacial acetic acid (AA), HPLC-grade acetonitrile (ACN), methanol (MeOH), hexane, ethyl acetate (EA) and acetone were obtained from Merck (Darmstadt, Germany). The GCB/PSA SPE (500 mg/500 mg/6 mL), PSA SPE (500 mg/6 mL) and C18 SPE (500 mg/6 mL) tubes were obtained from Agilent (Santa Clara, United States). The GCB SPE tube (500 mg/6 mL) was obtained from CNW (Shanghai, China). QuEChERS extraction kits (2 g MgSO4, 0.5 g NaCl, 0.5 g sodium citrate and 0.25 g disodium citrate sesquihydrate) were prepared by weighing each substance (obtained from Merck, Darmstadt, Germany) into a 15 mL centrifuge tube.

For LC-MS/MS analyses, 204 compounds in pesticide solution kits were obtained from Restek (31971, see Table A-3 of the Appendix Table; Bellefonte, United States) and three other compounds (atrazine, simazine and phoxim) were obtained from Sigma Aldrich (St. Louis, United States). For the GC-MS/MS analyses, 203 compounds in pesticide kits were purchased from Restek (32562, see Table A-3 of the Appendix Table; Bellefonte, United States). For atrazine, simazine and phoxim, 100 mg/L stock solutions were prepared for each compound in ACN. For all of the pesticides, intermediate solutions of 10 mg/L were prepared in ACN for LC-MS/MS and toluene for GC-MS/MS and stored in amber screw-capped glass vials in the dark at –20 °C.

Standard mix solutions at concentrations of 1 mg/L were prepared from the stock solutions to optimize and validate each method. Since three of the compounds (alanycarb, benfuracarb and mesotrione) in the LC-MS/MS standard mix containing 207 pesticides were not stable, 204 pesticides were used for this study.

For the GC-MS/MS method, a surrogate stock solution (a mixture of α-BHC-d6 and parathion-d10 at 40 µg/mL in ACN) obtained from Restek (32571, Bellefonte, United States) was used to monitor validity. A working surrogate solution at 1 mg/L was prepared in toluene and stored at –20 °C. Trifluralin-d14, purchased from Dr.

Ehrenstorfer (Augsburg, Germany), was used as an internal standard (IS) for GC-MS/MS analysis. A stock IS solution was prepared in toluene at 1 mg/L and stored at –20 °C. The working IS solutions (10 µg/L in ACN) was used in the final step of sample extraction, prior to injection into the GC-MS/MS instrument. An analyte protectant (AP) solution was prepared with sorbitol (5 mg/mL), d-(–)gluconic acid-δ-lactone (10 mg/mL), shikimic acid (5 mg/mL) and 3-ethoxy-1,2-propanediol (0.2 g/mL) in ACN/H_2O (6/4, v/v).

3.2.2. UPLC-MS/MS and GC-MS/MS analysis

The UPLC-MS/MS system (Thermo Fisher Scientific, Waltham, United States) was a Vanquish UPLC (equipped with a binary pump, auto-sampler and column thermostats) linked a TSQ Quantiva triple quadrupole mass spectrometer. An Accucore™ aQ C18 polar end-capped column (100 x 2.1 mm i.d. and 2.6 µm particle size) combined with a 0.5 µm filter cartridge was used (Thermo Fisher Scientific). The mobile phase consisted of MeOH and H_2O in a ratio of 2/98 (v/v) for mobile phase A and 98/2 (v/v) for mobile phase B. Both mobile phases were supplemented with 5mM ammonium formate and 0.1% formic acid to enhance the sensitivity of the signals and stability of retention times. The gradient mobile phase was setup as follows: 0–0.5 min, 0% B; 0.5–2 min, 0–40% B; 2–22 min, 40-100% B; 22–22.1 min, 100–0% B; 22.1–25 min, 0% B (total time of 25 min). The flow rate was fixed at 0.3 mL/min and the injection volume was 3 µL. The column oven was maintained at constant temperature of 40 °C. The MS parameters were optimized for each standard in the mass spectrometer by using 1 mg/L solution in both positive and negative MRM mode. The EU 657/2002/EC guidelines for LC-MS/MS analysis were followed with two MRM transitions for each compound (higher intensity for quantification and lower intensity combined with the MRM ratio for confirmation). For the MS detector, N_2 (purity > 99.98%) was used as the sheath gas, ion sweep gas, and auxiliary gas at flow rates of 40, 1 and 12 a.u. (arbitrary units), respectively. The ion transfer tube and vaporizer temperatures were set at 325 °C and 300 °C, respectively; the electrospray voltage was

+3.5 kV (positive mode) and –2.5 kV (negative mode). The mass parameters, including the retention time (RT), electrospray ionization (ESI) mode, quantitative peak, confirmation peak, radio frequency (RF) and collision energy (CE) are reported in Table A-4 of the Appendix Table.

The GC-MS/MS system (Thermo Fisher Scientific, Waltham, United States) was a Trace 1300 Thermo Scientific^{TM} gas chromatograph coupled with a TSQ 8000 triple quadrupole mass spectrometer and operated in electron ionization mode (EI, 70 eV). The analytes were separated in a fused silica capillary column DB-5ms (30 mx 0.25 mm i.d., 0.5 μm film thickness) from Agilent. The column oven temperature was programmed as follows: an initial temperature of 90 °C was held for 1 min, then increased by 8.5 °C/min to 320 °C and held for 5 min. The total time was 40 min. The injection volume was 2 μL in splitless mode, held for 1 min at a temperature of 250 °C. The purge N_2 gas flow was set at 50 mL/min. By using the Thermo AutoSRM software, the two most intense transitions and their optimal collision energies were selected. The most intense product was selected as the quantifier ion and the second most intense was set as the qualifier ion. The settings on the mass spectrometry detector, including the RT, quantitative peak, confirmation peak and CE are reported in Table A-5 of the Appendix Table.

The chromatograms of LC-MS/MS and GC-MS/MS were shown in Tables A-3 and A-4 of the Appendix Figure.

3.2.3. SPE sorbent optimization

Several types of SPE and d-SPE sorbents were prepared and coded as reported in Table A-6 of the Appendix Table: MS-A is an SPE cartridge with only GCB; MS-B is a mixed-mode consisting of one SPE cartridge with a GCB layer on top and PSA on bottom; in MS-C, 250 mg of the C18 sorbent is added into the sample extraction solution (d-SPE) and was vortexed prior loading on a mixed-mode GCB/PSA SPE cartridge; MS-D is similar to MS-C but used 500 mg of the C18 sorbent; in MS-E, 500

mg of the C18 sorbent was added to an SPE cartridge that was connected to the top of a mixed-mode GCB/PSA SPE cartridge by an adaptor. Prior to the SPE procedure, all the targeted pesticides were added at 50 µg/kg into 5 mL of ACN extraction solution (1% AA) from a green tea blank sample.

3.2.4. Sample preparation

An organic green tea was obtained from the Fito Pharma pharmaceutical company (Vietnam). This sample was homogenized into a powder using a blender and passed through a 2-mm sieve as a blank sample to optimize and validate the method.

Samples (2 g) were weighed into 50 mL PTFE centrifuge tubes and spiked with 0.1 mL of the surrogate solution (1 mg/L). Then, 10 mL ACN (1% CH_3COOH) was added into the tube. Solutions were vortexed for 1 min and shaken for 30 min. The QuEChERS extraction kit was added directly to the tube, which was vortexed immediately for 1 min to prevent coagulation of $MgSO_4$. After centrifugation (4500*g*, 10 min, 10 °C), the upper ACN layer (5 mL) was transferred to and purified in a SPE cartridge.

The GCB/PSA and C18 SPE cartridges were preconditioned with 5 mL ACN (1% CH_3COOH) and coupled together (C18 cartridge on top), using an adapter. The ACN extract obtained was introduced to the cartridge and 20 mL of ACN-toluene (3/1, v/v) used as the eluting solvent. All the extract solutions and eluent solvents were collected and concentrated to 1 mL using a concentrator (40 °C, 1000 Pa, 40 min). The extract was dried under N_2 gas and the residue re-dissolved with 1 mL MeOH and vortexed for 1 min. A 0.4 mL sample of this solution was diluted with 0.4 mL of H_2O for the UPLC-MS/MS analysis. For the GC-MS/MS analysis, 0.4 mL of the solution was dried under N_2 gas and re-dissolved with 0.8 mL of the IS solution; then an AP solution (24 µL) was added before GC injection to obtain good signal and peak shape (Michelangelo Anastassiades et al., 2003; Y. Wang et al., 2011).

3.2.5. Method validation

The method was validated in accordance with the SANTE standard (SANTE/11945/2015),which determined the matrix effects, linearity, repeatability, LOD and LOQ. Calibration curves were obtained by spiking standards, ranging from 5 to 200 µg/L, into blank matrix extract solutions prior to injection. Recovery and precision were determined based on samples spiked at 10, 50 and 100 µg/kg (6 samples for each level over 2 days). Matrix effects were assessed by comparing slopes of the matrix-matched calibration curves to the solvent calibration curves. LOQs were evaluated by determining the lowest concentration spike for samples where recovery and repeatability were satisfactory (within 70-120% and less than 20%, respectively) (SANTE/11945/2015). LODs were estimated as one third of the LOQs.

3.3. Results and Discussion

3.3.1. Extraction and optimization of clean-up

To analyse simultaneously 407 pesticides in green tea using UPLC-MS/MS and GC-MS/MS, QuEChERS was applied and extraction of pesticides investigated with and without hydration. The results showed that QuEChERS extraction using ACN (1% AA) without hydration achieved the maximum pesticide extraction and lowest co-extracting interference, which is consistent with previous work for the analysis of multi-pesticide residues in tea (Hou et al., 2016; Huang et al., 2009). Several SPE sorbents were investigated to reduce the matrix effects during the clean-up step and to achieve low LOQs and high accuracy. Additionally, evaporation conditions and elution volumes were also optimized to achieve maximum recoveries.

3.3.1.1. SPE sorbents

During preliminary investigations on both C18 and PSA sorbents, they showed removal of organic acids, sugars, caffeine, and fatty acids from the tea but not the pesticides. This was probably because interactions of the pesticides with ACN were

stronger than with the solid phases, even C18, which easily absorb organic compounds. GCB removed coloured compounds, *e.g.*, pigments, and chlorophylls, some pesticides with planar structures including aromatic rings or conjugated carbon chains, and substances containing Cl, F, O, and N (Belhamdi et al., 2016). When LC standard mix solution (50 µg/L) was passed through the GCB cartridge (500 mg), 20 compounds interacted strongly, resulting in low recoveries ranging from 1.9% (cyromazine) to 49.1% (bifenazate) (Fig. A-1 of the Appendix Figure). Recoveries of 17 of compounds out of 20 were significantly improved in the presence of tea (standard mix prepared in a blank tea matrix solution). This result can be explained by competitive interaction of pigments, polyphenols, sterols, carotenoids, and chlorophylls in the blank tea solution, which could obstruct the GCB sorbent active centres. However, recoveries of the three remaining compounds (chlorfluazuron, metaflumizone and thiabendazole) were reduced because of ion suppression. Therefore, by combining several types of SPE sorbents, we assumed it would be possible to eliminate interferences in tea extract analysis.

In this study, recoveries were calculated based on solvent calibration curves for UPLC-MS/MS and on the matrix-matched calibration curves for GC-MS/MS (Fig. 3-1). When comparing GCB-only sorbents (MS-A) with PSA in the mixed-mode GCB/PSA cartridge (MS-B), the numbers of pesticides with recoveries of 70–120% increased to 161 for UPLC-MS/MS (78.9%) and 177 pesticides for GC-MS/MS (87.2%). Thus, PSA appeared to be able to remove organic acids, fatty acids, and sugars in the matrix, reducing ion suppression and increasing recoveries. However, eight compounds with acidic properties were adsorbed, reducing their recoveries (Table A-7 of the Appendix Table).

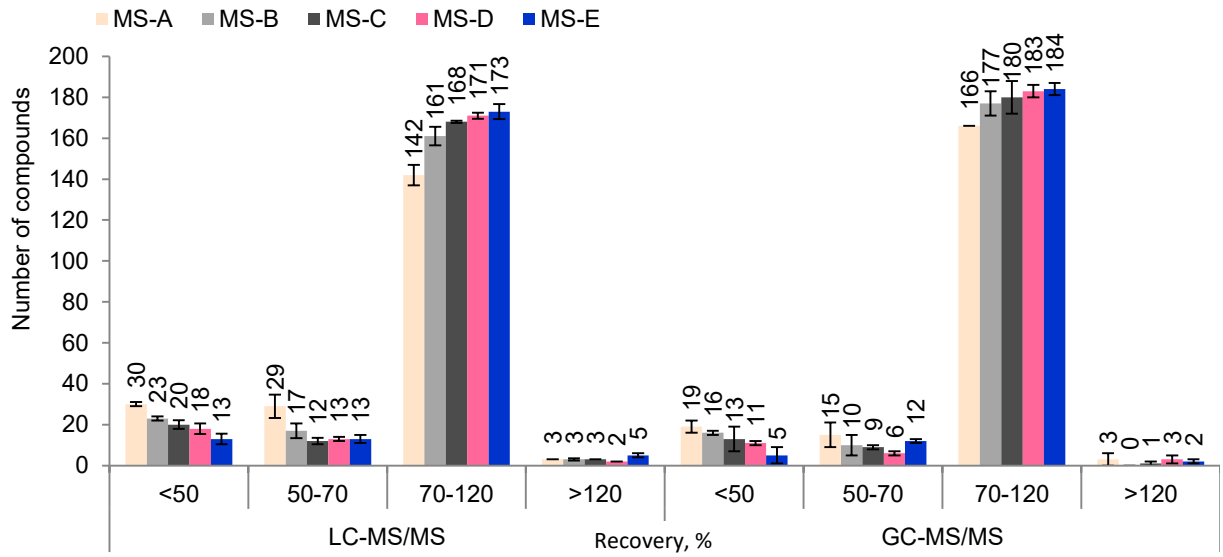

Fig. 3-1. Comparison of the recoveries obtained by the analysis of pesticide residues using different mixed-mode SPE sorbents (LC-MS/MS: 204 compounds; GC-MS/MS: 203 compounds; n = 3). MS-A: GCB (500 mg); MS-B: PSA/GCB (500 mg/500 mg); MS-C: d-SPE (250 mg C18) + PSA/GCB (500 mg/500 mg); MS-D: d-SPE (500 mg C18) + PSA/GCB (500 mg/500 mg); MS-E: C18 (500 mg/6 mL) connected to PSA/GCB (500 mg/500 mg/6 mL)

When 250 mg d-SPE C18 was added to the extraction solution, prior to passing through the mixed-mode GCB/PSA SPE cartridge (MS-C), the numbers of compounds with 70–120% recoveries increased by seven (for LC) and three (for GC), respectively, in comparison to MS-B. It was clear that the C18 sorbent removed just lipids and sterols in the matrix solution without absorbing pesticides. When the C18 content was increased from 250 mg (MS-C) to 500 mg (MS-D), the numbers of pesticides increased slightly, with three more compounds for both LC and GC. When using two SPE cartridges (MS-E), the numbers of pesticides with 70–120% recoveries were best (173 compounds for UPLC-MS/MS and 184 compounds for GC-MS/MS).

During the MS-A experiment, we observed that the solution was yellow after elution. This result showed that extraction clean-up was not efficient and the solution still contained many interfering compounds. In contrast, with the addition of PSA, especially addition of C18, the solution after elution was clear and almost colorless.

Thus, the C18 SPE cartridge paired with SPE GCB/PSA was ideal for complex matrices such as tea. The effectiveness of this combination will be discussed further under ―Matrix effect".

3.3.1.2. Elution volume of the SPE process

Elution volume is also an important factor affecting recovery. If the volume is too low, the analyte would not be released; if the volume is too high, interfering substances would be co-eluted. The experiments were conducted with elution volumes of 10 mL (EV-A), 15 mL (EV-B), 20 mL (EV-C) and 25 mL (EV-D). Solutions were spiked with 50 µg/L of standards prior to loading. Recoveries were calculated based on matrix-matched calibration and are reported in Fig. 3-2. With 10 mL of solvent, 43 pesticides (21.1% of the compounds analysed by LC-MS/MS) and 45 pesticides (22.2% of the compounds analysed by GC-MS/MS) were obtained, but recoveries were less than 70%. With 20 mL of solvent, 172 pesticides (84.3%of the compounds analysed by LC-MS/MS) and 147 pesticides (72.4% of the compounds analysed by GC-MS/MS) were recovered (70–120%). With 25 mL, recovery of some of the compounds decreased, because interfering compounds were eluted simultaneously and caused ion suppression (UPLC-MS/MS) or ion enhancement (GC-MS/MS). Therefore, an elution solvent volume of 20 mL (ACN/toluene, 3/1, v/v) was chosen for SPE clean-up.

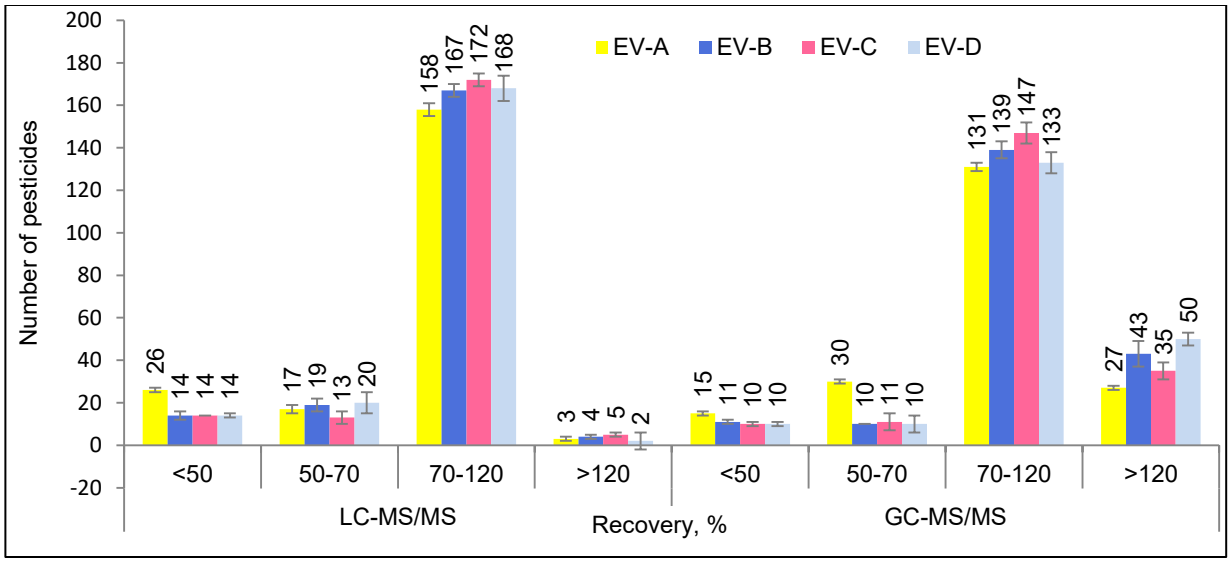

Fig. 3-2. Comparison of the recoveries obtained by analysis of pesticide residues using different elution volumes (LC-MS/MS: 204 compounds; GC-MS/MS: 203 compounds; n = 3). EV-A: 10 mL; EV-B: 15 mL; EV-C: 20 mL; EV-D: 25 mL

3.3.1.3. Evaporation optimization

Compounds in the elution solution can decompose or evaporate during solvent evaporation, meaning temperature and dryness need to be managed carefully. Fan et al. (Fan et al., 2013) reported that 40 °C and a nearly dry solution (0.3–0.5 mL) were the best conditions for 201 pesticides and chemical pollutants in a solvent mixture (ACN/toluene, 3/1, v/v). The temperature used in our study was fixed at 40 °C.

Investigations on impact of dryness for 407 pesticides were carried out by adding the standard solution (50 µl, 1 mg/L) to 25 mL of solvent (5 mL ACN containing 1% AA and 20 mL ACN/toluene, 3/1, v/v). The solvent was evaporated until either (i) the remaining volume was 1 mL (EC-A) or (ii) the sample was dry (EC-B). A blank sample was prepared in the same way, up to the concentration step, and a similar standard mix solution was added to obtain 25 mL of the final elution solution (EC-C). The results for these are reported in Fig. 3-3.

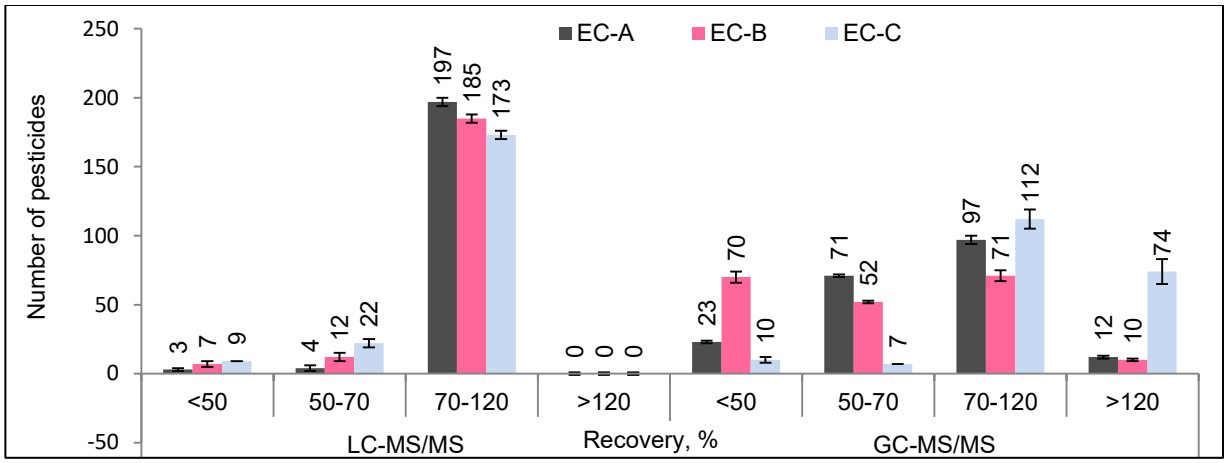

Fig. 3-3. The number of pesticides in each recovery range (according to SANTE/11945/2015) obtained from LC-MS/MS and GC-MS/MS methods under different evaporation conditions (n=3). EC-A: 1 mL remaining volume without sample matrix; EC-B: evaporation to dry; EC-C: 1 mL remaining volume with sample matrix

For UPLC-MS/MS, EC-A was best with 197 compounds (96.5%, 70–120%), meaning 1 mL remaining volume was better than concentrating samples to completely dry (Figure 3). When the tea matrix was present (EC-C), the numbers of compounds with recoveries in the range 70–120% was lower than in the other two cases (EC-A and EC-B) due to ion suppression effects. In turn, components present in the matrix acted as protective agents that reduced losses of some degradable substances (Fig. 3-4).

For GC-MS/MS, the numbers of compounds with recoveries greater than 70% were 109 (53.7%) and 81 (39.9%) for the EC-A and EC-B conditions, respectively.

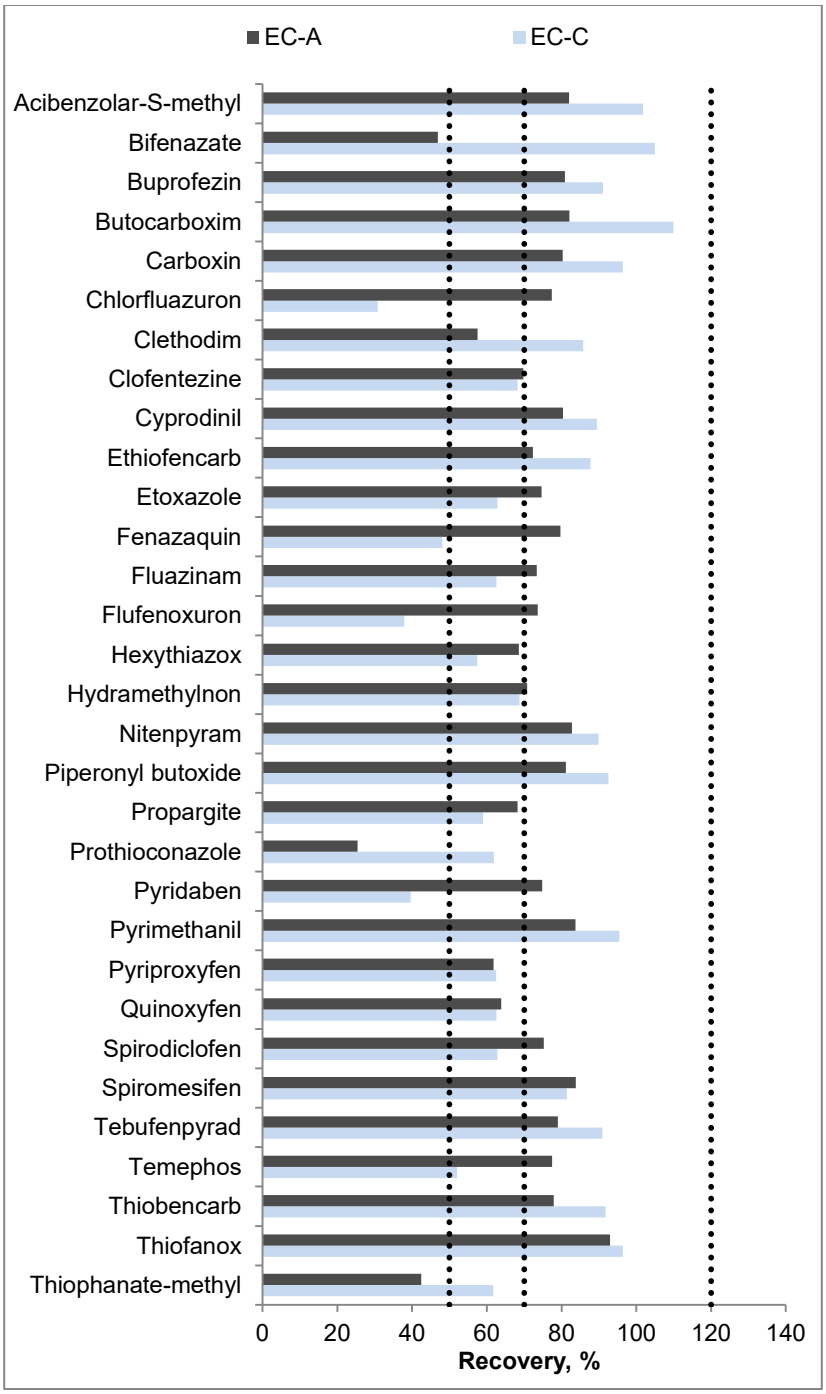

Fig. 3-4. Comparison of recovery of degradable pesticides under two evaporation conditions (EC-A and EC-C: 1 mL remaining volume without and with sample matrix, respectively)

The numbers of compounds with recoveries greater than 70% using GC-MS/MS was lower than those achieved with the LC method, probably because pesticides have lower vaporization temperatures. However, in the presence of the matrix (EC-C), the

results were significantly improved with 186 compounds (91.6%) having recoveries greater than 70%. However, there were 74 (36.4%) compounds with recoveries greater than 120% due to enhancement effects.

Based on these results, 1 mL remaining volume was chosen for evaporation.

3.3.2. Method validation

In the extraction and clean-up, four compounds analyse using UPLC-MS/MS (cyromazine, thidiazuron, hydramethylnon and pymetrozine) and three compounds analysed by GC-MS/MS (acequinocyl, captan and endrin aldehyde) had very low recoveries (< 30%) due to degradation. Hence, method validation was for 200 pesticides for UPLC-MS/MS and 200 pesticides for GC-MS/MS.

3.3.2.1. Matrix effect

Ion suppression and enhancement are two causes of matrix effects (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Uclés et al., 2017). Our study aimed to develop a method that analysed multi-pesticide residues with high recoveries and sensitivities and low matrix effects. By combining QuEChERS and a variety of SPE sorbents, matrix effects decreased and, thus, reliability of the results increased. Thus, evaluation of matrix effects was a prerequisite. The matrix effects were assessed by comparing slopes of matrix-matched calibration curves with slopes of solvent calibration curves (Equation 1).

Calibration curves (5 points from 10 to 100 μg/L) were prepared in the: (i) solvent (MeOH/H_2O for UPLC-MS/MS and IS solution for GC-MS/MS) and (ii) matrix (blank green tea solutions obtained from the preparation procedure). The matrix effects (%) are summarized in Table 3-1 (for details, see in Tables A-4 and A-5 of the Appendix Table). According to SANTE/11945/2015, matrix effects (%) must be in the range ± 20% to meet performance acceptability criteria. Our results showed that 154 compounds (77%) for UPLC-MS/MS and 71 compounds (35.5%) for GC-MS/MS met

or exceeded that criterion, meaning 225 pesticides (56.25% of the 400 pesticides) could be quantified using solvent calibration curves. Previous studies on eliminating/reducing interferences in tea samples are limited (Cajka et al., 2012; Hou et al., 2016; Z. Huang et al., 2007; Huang et al., 2009) and assessments of matrix effects are fewer still. We found only two research groups that had assessed matrix effects in tea (Li et al., 2012; J. Wang et al., 2011). For LC-MS/MS, Wang et al.(J. Wang et al., 2011) reported that, depending on the type of tea, 11-22 compounds (8-16% of the studied 141 pesticides) had matrix effects in the range –30% and +10% using QuEChERS-dSPE preparation. For GC-MS, Li et al. (Li et al., 2012) showed only 8 compounds in green tea (4.3% of the studied 186 pesticides) had matrix effects in the range ±20% using QuEChERS-SPE sample preparation. Compared to these results, our study had matrix effects in the range ±20% with more compounds recovered (154, 77%) for UPLC-MS/MS and (71, 35.5%) for GC-MS/MS. Additionally, by observing total ion chromatogram (TIC) of blank green tea samples (Fig. A-2 of the AFs) (HE-A), our method had the lowest background signals, which also implies the lowest matrix effects. In conclusion, combining SPE sorbents in the clean-up step was more effective in eliminating/reducing matrix effects for green tea samples.

Table 3-1. Evalutating matrix effect on two analytical methods

Matrix effect (%)	UPLC-MS/MS	GC-MS/MS
	Number of pesticides (% proportion)	
< (–50)	12 (6.0)	3 (1.5)
(–50) ÷ (–20)	33 (16.5)	4 (2.0)
(–20) ÷ (+20)	154 (77.0)	71 (35.5)
(+20) ÷ (+50)	1 (0.5)	38 (19.0)
> (+50)	0 (0)	84 (42.0)

We recognized that, for the UPLC-MS/MS method, ion suppression was more common. Ion suppression occurs when matrix components decrease droplet and ions

formation (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Uclés et al., 2017). A total of 45 compounds suffered this phenomenon, with retention times ranging from 2.62 min for aminocarb (log K_{ow} 1.90) to 18.46 min for moxidectin (log K_{ow} 6). One compound at 18.76 min (ivermectin, log K_{ow} 5.83) also showed ion enhancement. Thus, the matrix effects in LC-MS/MS method did not depend on properties of the analyte so much as co-eluting components (Kittlaus et al., 2011; SANTE/11945/2015).

In GC-MS/MS, it was more common to find signal enhancement (125 compounds or 61.5%). However, matrix effects also improved peak shapes (less tailing, more symmetry and higher intensity) when compared to standard solution peaks. Interfering compounds in the matrix seemed to block active sites on the GC column and injector, meaning more pesticides reached the MS detector. Some pesticide groups suffered more from matrix effects (*e.g.* carbamate, phosphate, carboxyl, azole, hydroxyl, amino group, urea, imidazole and benzimidazole), which is consistent with previous publications (Li et al., 2012; Rahman, El-Aty, et al., 2013).

Matrix effects outside the range ± 20% can be compensated by: (i) dilution; (ii) use of a standard addition; (iii) addition of isotope internal standards; and/or (iv) matrix-matched calibration (Kittlaus et al., 2011; Uclés et al., 2017). Dilution is a simple and effective method for reducing matrix effects, but requires highly sensitive analytical equipment to detect pesticide MRLs in food subsequently. The use of standard addition is not suitable for routine analysis. Isotope internal standards are very expensive and, usually, not available for all substances. Hence, matrix-matched calibration can be the best way to overcome matrix effects and generate highly accurate results.

3.3.2.2. Linearity

Matrix-matched calibration was performed in the range 1–200 µg/L and 1–100 µg/L for LC-MS/MS and GC-MS/MS, respectively. Responses were considered linear when

the correlation coefficient was equal to or greater than 0.99. Linear ranges and correlation coefficients are summarized in Tables A-4 and A-5 of the Appendix Table. It can be seen that regression coefficients were all greater than 0.99, except for three compounds (biphenyl, dichlobenil and captafol), although regression coefficients for these compounds were still acceptable ($R^2 > 0.97$). Excellent linear relationships were obtained for all the pesticide residues tested in our study.

3.3.2.3. Recovery and reproducibility

Blank green tea samples were spiked at 10, 50 and 100 μg/kg (6 samples for each level over 2 days) prior to analysis. The reproducibility and recoveries for these samples are presented in Table 3-2. Using the matrix-matched calibration curves, relative standard deviations (RSD_R, %) were less than 20% and recoveries were between 70–120% for most pesticides. These results indicated that our method had appropriate accuracy for quantification of multi-pesticide residues in tea according to SANTE/11945/2015.

Table 3-2. The number of pesticides that meets the SANTE/11945/2015 standard for recovery (ranging from 70 to 120%), RSD (≤ 20%) and LOQ (recovery in the range of 70 - 120% and RSD ≤ 20%) at different levels

Validation parameters	Concentration (µg/kg)	UPLC-MS/MS	GC-MS/MS	Total
		Number of pesticides (% proportion)		
Recovery (70–120%)	10	191 (95.5)	182 (91)	373 (93)
	50	195 (97.5)	196 (98)	391 (97.75)
	100	196 (98)	196 (98)	392 (98)
RSD (< 20%)	10	197 (98.5)	193 (96.5)	390 (97.5)
	50	199 (99.5)	199 (99.5)	398 (99.5)
	100	199 (99.5)	198 (99)	397 (99.25)
LOQ	1	0 (0)	19 (9.5)	19 (4.75)
	2	192 (96.0)	31 (15.5)	223 (55.75)
	5	7 (3.5)	137 (68.5)	144 (36.0)
	10	1 (0.5)	9 (4.5)	10 (2.5)
	25	0 (0)	3 (1.5)	3 (0.75)
	50	0 (0)	1 (0.5)	1 (0.25)

3.3.2.4. LOQ determination

Pesticide standards at different concentrations were added to samples to determine the LOQs. The results obtained showed that LOQs ranged from 2 and 5 µg/kg for most pesticides, although four pesticides had LOQs greater than 10 µg/kg (25 µg/kg for bioallethrin, carbophenothion, chlorbenside and 50 µg/kg for captafol) (Table 3-2). However, LOQs of chlorbenside and captafol were less than 100 µg/kg, which is also the MRL in EU regulations for tea products (EU MRL). There are no regulated MRLs for bioallethrin and carbophenothion.

3.4. Conclusions

A sample preparation method for the analysis of multi-pesticide residues in green tea combining several sorbents for clean-up was developed. Using QuEChERS extraction and an SPE purification technique with three different sorbents (C18, GCB and PSA), to eliminate the matrix effects, prior to liquid and gas chromatography systems coupled to MS, final solutions were almost colourless and results showed low co-extraction interference. Therefore, 225 pesticides (154 for UPLC-MS/MS and 71 for GC-MS/MS) were quantified using solvent calibration curves. In addition, using matrix-matched calibration curves to overcome matrix effects, a total of 400 compounds were quantified with high recovery and repeatability, and low LOQs. At 10 µg/kg, 373 pesticides (93%) met SANTE/11945/2015 standards for recovery (70 to 120%) and 390 pesticides (97.5%) met regulations for RSD (≤ 20%). LOQs for almost all pesticides (386 or 96.5%) were < 10 µg/kg, which is lower than MRLs for these pesticides in tea (from 5 µg/kg to 70 mg/kg). In future research, we will continue to investigate matrix effects in white, black and oolong teas to evaluate whether this method can be applied to these types of commodities.

Chapter 4. Evaluating and overcome matrix effects in several types of tea

4.1. Eliminating matrix effects by mixed-mode SPE clean-up

In chapter 3, to eliminate interferences in GT as much as possible, mixed-mode SPE cleanup, including a C18 SPE paired with a GCB/PSA cartridge, was performed after QuEChERS extraction (Fig. 4.1). The ME results are presented in Fig. 4-2.

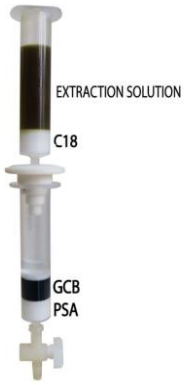

Fig. 4-1. The mixed-mode SPE for clean-up green tea extraction, including C18, GCB, and PSA sorbent

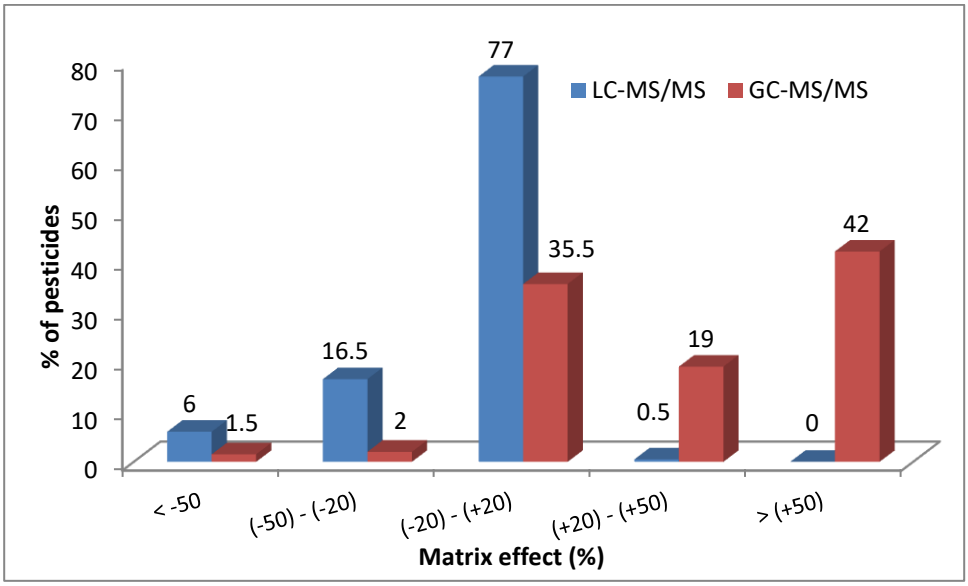

Fig. 4-2. Percentage of pesticides in each ME range (according to SANTE/11945/2015) obtained by UPLC-MS/MS and GC-MS/MS of green tea; QuEChERS extraction and mixed-mode SPE cleanup; and 3 and 2 µL injection for UPLC-MS/MS and GC-MS/MS, respectively

According to SANTE/11945/2015, MEs must be within the range of ±20%, meaning that the analyte has no ME (SANTE/11945/2015). Meanwhile, medium ME must be |ME| > 20% and strong ME must be |ME| > 50%. Moreover, ME less than or greater

than zero is considered ―ionsuppression" or ―ionenhancement," respectively. As shown in Fig. 4-2, the UPLC-MS/MS method had the highest number of pesticides (154 compounds, accounting for 77%) within the ME range of ±20%. Meanwhile, 16.5% and 6% of the cases were medium and strong suppression, respectively, and only one pesticide (ivermectin, accounting for 0.5%) exhibited medium enhancement. Excluding compounds with no ME, the results showed 98% ion suppression and only 2% ion enhancement for the UPLC-MS/MS method. This result proves that the common ME phenomenon in LC is ion suppression, consistent with that reported in previous studies (Uclés et al., 2017; J. Wang et al., 2011). Thus far, the enhancement mechanism in LC has not been explicitly proposed to explain this phenomenon (Uclés et al., 2017). Conversely, most of the opinions agree with the ion suppression phenomenon because matrix components decrease droplet and ion formation (Kittlaus et al., 2011; Taylor, 2005; Uclés et al., 2017). Moreover, we observed that ion suppression most commonly occurred at the beginning and end regions of the chromatogram, corresponding to polar and nonpolar impurities in the samples on the UPLC column (Fig. 4-3). Statistics show that 45.4% (10 out of 22 pesticides) and 74.2% (23 out of 31 pesticides) of medium or strong suppression were found in the polar (retention time lower than 3.6 min) and nonpolar (retention time higher than 14 min) ranges, respectively. The corresponding effect for the medium-polar range was only 8.2% (12 out of 147 pesticides). A total of 45 compounds exhibited medium/strong suppression, with retention times ranging from 2.62 min for aminocarb ($\log K_{ow}$ = 1.90) to 18.46 min for moxidectin ($\log K_{ow}$ = 6). Consequently, the MEs in the UPLC-MS/MS method did not depend on the properties of the analyte as much as the co-eluting components, consistent with that reported in previous studies (Kittlaus et al., 2011; Stahnke et al., 2009).

For GC-MS/MS, the calibration curve with or without IS needs to be considered before evaluating the MEs. Evidently, the IS is also influenced by MEs, but these MEs are different from those influencing the analytes. Therefore, in this study, GC

calibration curves were conducted with an external standard, and trifluralin-d14 (IS) was used to check the system stability. As shown in Fig. 4-2, the number of compounds exhibiting signal enhancement (122 pesticides, 61%) was larger than those showing signal suppression (7 pesticides, 3.5%) and no ME (71 pesticides, 35.5%). After removing the data of compounds with no ME, the results showed 94.5% enhancement and 5.5% suppression, which is consistent with that reported in previous studies (Li et al., 2012; Rahman, El-Aty, et al., 2013). The enhancement could be attributed to interfering compounds in the matrix that seemed to block active sites on the GC column and injector, meaning more pesticides reached the MS detector.

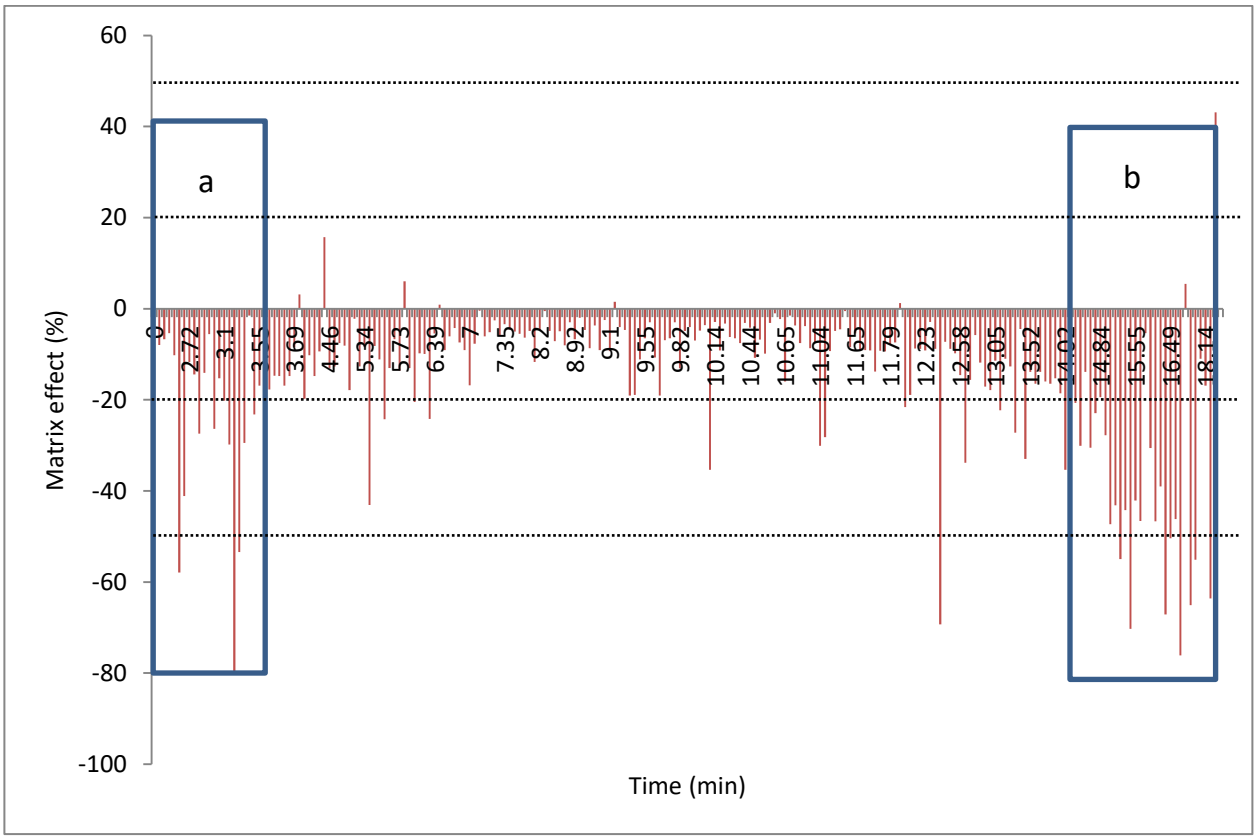

Fig. 4-3. MEs of 200 pesticides according to retention time in the UPLC-MS/MS method; 3 µL injection volume; a and b: elution regions of the polar and nonpolar compounds, respectively

Meanwhile, the mechanism of signal suppression in GC-MS/MS, until now, has not been explained (Uclés et al., 2017). A total of 84 compounds (42%) exhibited strong signal enhancement (Table A-10 in the Appendix Table). Among them, organophosphate (27), pyrethroid (16), dinitroaniline (5), and thiocarbamate (3) were the compounds most detected, whereas the rest had only one or two substances. Such compounds contain one or more functional groups interacting with the active sites on the liner and column, such as carbamate (–O–CO–NH–), carboxyl (–COOH), amino (–R–NH–), azole (–N=), benzimidazole, hydroxyl (–OH), imidazole, organophosphate (–P=O, –P=S), and urea (–NH–CO–NH–) (Li et al., 2012; Rahman, El-Aty, et al., 2013; Rutkowska et al., 2019). Considering the organophosphate group, only 10 out of 45 compounds (22.2%) did not exhibit MEs, whereas 8 (17.8%) and 27 (60%) compounds exhibited medium and strong signal enhancement, respectively. As shown in Fig. 4-4, ion enhancement was usually observed after 19 min in 23 out of 24 compounds (96%). These results showed that MEs depended not only on the pesticides‘ structure but also on the combination of the interferences in the samples (Li et al., 2012; Rahman, El-Aty, et al., 2013; Rutkowska et al., 2019).

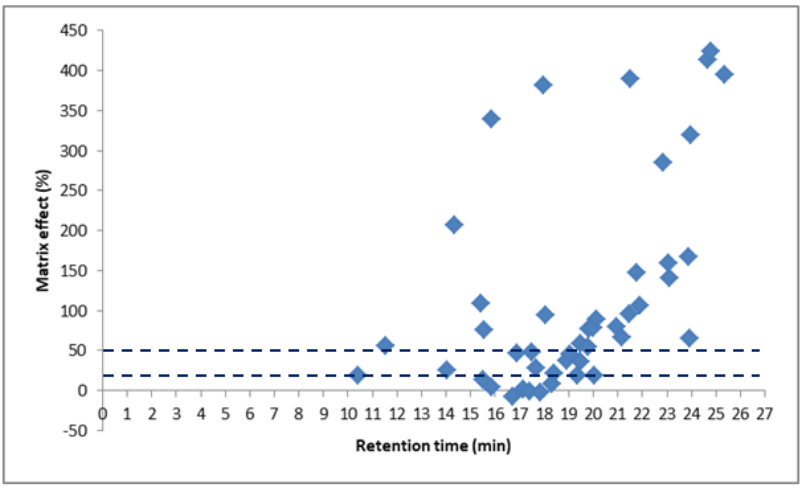

Fig. 4-4. Matrix effect distribution according to the retention time of the organophosphate group in the GC-MS/MS method

Thus far, the AP solution is often used to overcome ion enhancement in the GC-MS method. However, for multi-pesticide residue analysis, analyte protectants cannot always overcome the overestimation problems, as a matrix-matched calibration curve (Rahman, El-Aty, et al., 2013). In this study, the AP solution was prepared according to the EU Reference Laboratories report (EURL-SRM), but only 35.5% of the compounds were within the ME range of ± 20%. Thus, the AP solution is unsuitable for complex matrices, such as tea. However, some compounds, i.e., chlorothalonil, linuron, *N*-(2,4-dimethylphenyl)formamide, norflurazon, prochloraz, and tricyclazole, exhibited better signal and peak shape than those without AP solution (Fig. 4-5).

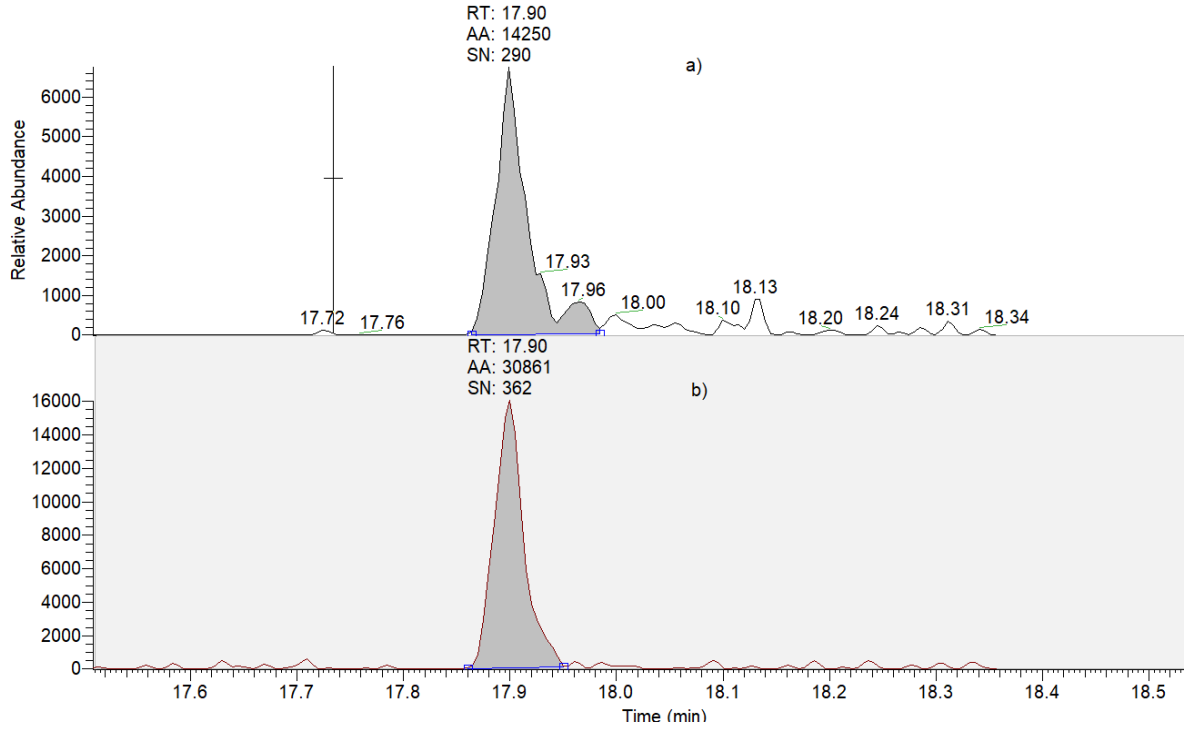

Fig. 4-5. Comparison of the peak shape and area (AA) of tricyclazole in 10 µg/L solvent with (a) and without (b) analyte protectants

This study utilized QuEChERS extraction and mixed-mode SPE cleanup, including C18, GCB, and PSA sorbents. In our previous study, C18 and PSA only removed organic acids, sugars, caffeine, and fatty acids without adsorbing pesticides, whereas

GCB removed chlorophylls and some pesticides with planar structures (Ly et al., 2020). Therefore, the combination of these three sorbents has eliminated much interference and reduced the MEs. Compared with other studies of MEs in tea, this method yielded a significantly larger number of pesticides without MEs. For UPLC-MS/MS, Wang et al. reported that, depending on the type of tea, only 8% to 16% of 141 pesticides did not exhibit MEs during QuEChERS-dSPE sample preparation (J. Wang et al., 2011). For GC/MS, only eight out of 186 pesticides (for GT) were within the ME range of ±20% during QuEChERS-SPE sample preparation (Li et al., 2012). In conclusion, improving sample extraction by mixed-mode SPE cleanup is an effective way to eliminate the MEs in pesticide analysis of tea.

4.2. Overcoming MEs by reducing the injection volume

In the ―Introductin," we mentioned that several methods can be used to overcome or compensate for the MEs. Among them, dilution is a simple but effective method. Thus far, many studies have applied this method to UPLC-MS/MS but almost none for GC-MS/MS (Kittlaus et al., 2011). In this study, another form of dilution was investigated, that is, reducing the injection volume. Accordingly, the injection volumes were reduced from 3 µL to 1 µL for UPLC-MS/MS and from 2 µL to 1 µL for GC-MS/MS. The results are shown in Fig. 4-6 (the details are presented in Tables A-8 and A-9 of the Appendix Table).

Results in Fig. 4-6 show that the number of pesticides with no ME significantly increased from 154 to 194 compounds (up to 26%) for UPLC-MS/MS and from 71 to 140 compounds (up to 97%) for GC-MS/MS. The percentage of pesticides with no, medium, and strong MEs was 97%, 2.5%, and 0.5% for UPLC-MS/MS, respectively, and 70%, 23%, and 7% for GC-MS/MS, respectively. To our knowledge, this is the first time that the injection volume has been reduced to overcome MEs. The results indicate that the combination of the mixed-mode SPE cleanup method and the

reduction of the injection volume may be an effective way to overcome or compensate for the MEs, particularly for UPLC-MS/MS.

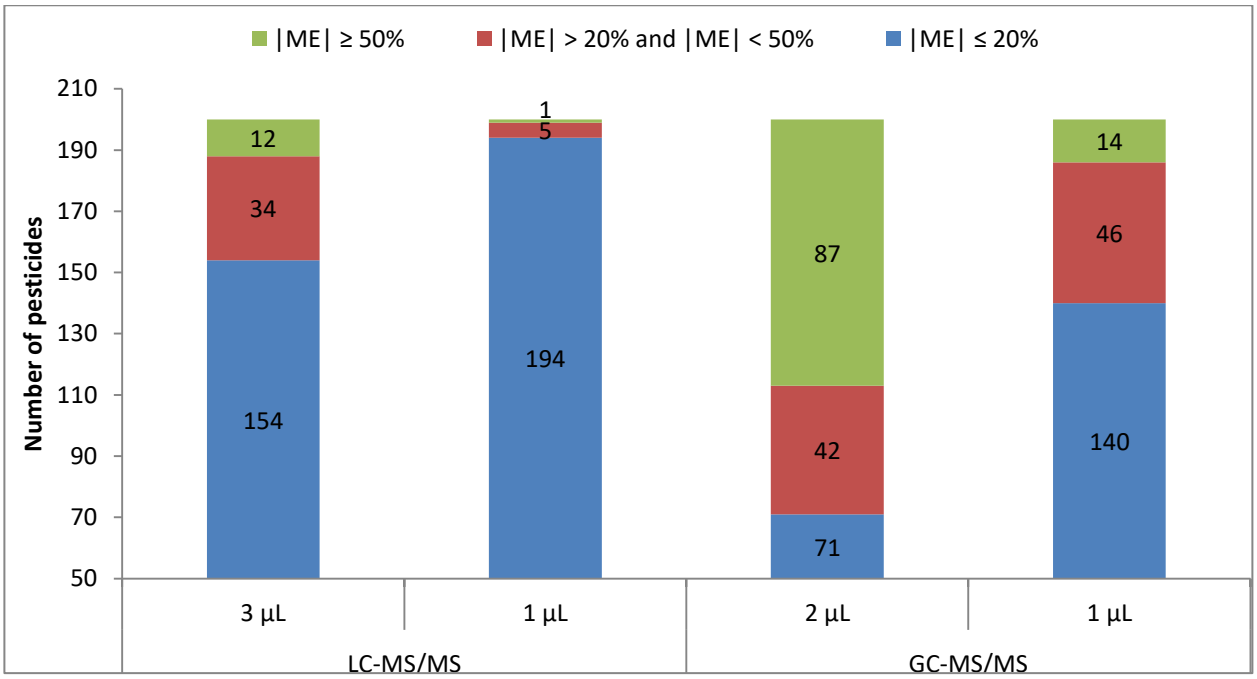

Fig. 4-6. Comparison of the number of pesticides according to ME range (SANTE/11945/2015) in green tea with two injection volumes, that is, 3 and 1 µL for UPLC-MS/MS and 2 and 1 µL for GC-MS/MS

In UPLC-MS/MS, suppression has been overcome for most of the pesticides, expect for propamocarb (2.7 min), carbendazim (3.24 min), dicrotophos (3.33 min), thiabendazole (3.58 min), fuberidazole (3.7 min), and ivermectin (18.76 min). Again, they were eluted in the polar and nonpolar regions. Notably, there was no ME in the medium-polar range. The decrease in injection volume aims to reduce the co-eluting interferences in the ion source; thus, the analyte is ionized more easily. The lesser the injection volume used, the lesser the column overload phenomenon is observed, contributing to the decrease in MEs (Taylor, 2005). Typically, the ideal injection volume for UPLC columns is from 1 µL to 3 µL (Perkin Elmer, 2009). If the volume falls below 1 µL, then the error caused by the needle will be large. Hence, the injection volume for UPLC-MS/MS was fixed at 1 µL.

Similarly, the number of pesticides within the ME range of ± 20% increased from 71 to 140 (nearly doubled), which is inversely proportional to the decrease in injection volume from 2 µL to 1 µL for the GC-MS/MS method. The medium ME range increased slightly from 42 to 46 compounds, but the strong ME range decreased sharply from 87 to 14 compounds (approximately six times). As a result of the decrease in interferences, ion enhancement was reduced. After removing the data of no ME pesticides, ion enhancement was more commonly observed in 57 pesticides (95%), whereas ion suppression was only detected in three pesticides (5%), equivalent to an injection volume of 3 µL. Twelve compounds (42%) exhibited strong signal enhancement, a sharp decrease compared with 84 substances in 3 µL injection volume (Table 4-1). The organophosphate group, with 10 compounds (83.3%), was most affected by MEs. Overall, this result showed that the MEs had been significantly improved. Therefore, in subsequent experiments, 1 µL injection volume was used for GC-MS/MS analysis.

Table 4-1. Pesticide groups that exhibited strong ion enhancement in GC-MS/MS of green tea; 1 µL injection volume

Compound	ME (%)	RT (min)	Group	Log*P*
Phorate	145	14.34	Organophosphate	3.86
Terbufos	161	15.42	Organophosphate	4.51
Disulfoton	11,515	15.85	Organophosphate	3.95
Linuron	66	17.62	Urea	3
Fenthion	128	17.97	Organophosphate	4.84
Tetrachlorvinphos	66	19.49	Organophosphate	3.53
Fenamiphos	244	19.81	Organophosphate	3.3
Tricyclazole	77	20.19	Triazolobenzothiazole	1.4
Sulprofos	151	21.53	Organophosphate	5.48
p,p‘-DDT	54	22.05	Organochlorine	6.91
Phosmet	70	23.08	Organophosphate	2.8
Pyraclofos	50	24.8	Organophosphate	3.77

4.3. Overcoming MEs by dilution

Although the MEs had been significantly improved by reducing the injection volume, some compounds did not reach the range of ± 20%, particularly in GC-MS/MS. Therefore, solvent calibration curves are unsuitable for quantification (SANTE/11945/2015). We continued to dilute the post-extraction solutions (the dilution factor was two for sample extraction) to overcome MEs, with different dilution factors of 4, 10, and 20 for GT. All of the data are presented in Tables A-8 and A-9 of the Appendix Table and summarized in Figs. 4-7 and 4-9. It should be noted that the more diluting, the higher LOQs were.

Fig. 4-7 shows a slight increase in the number of compounds within the ME range of ± 20% from 97% (194 compounds) to 98.5% (197 compounds) when the dilution factor increased from 2 to 4 and remained the same up to 20. At $f = 4$, most pesticides did not exhibit MEs, except for carbendazim (3.5 min, log$P$ = 1.48), fuberidazole (3.73 min, log$P$ = 2.71), and prothioconazole (12.23 min, log$P$ = 2; Fig. 4-8). When increasing the dilution factor from 2 to 20, the ME of carbendazim tended to decrease slightly, that of fuberidazole decreased sharply at $f = 4$ and then remained the same, and that of prothioconazole fluctuated stably and remained nearly unchanged.

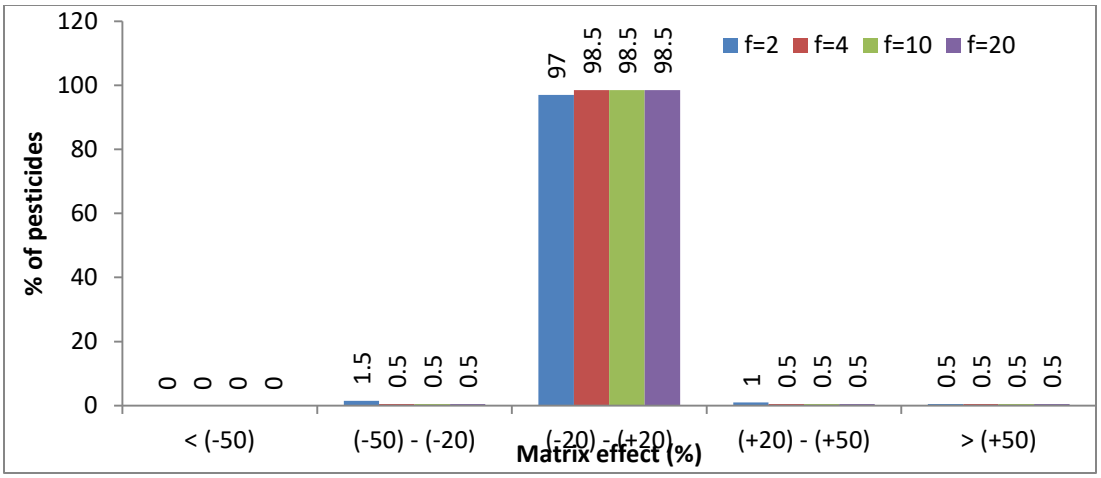

Fig. 4-7. Percentage of pesticides in each ME range (according to SANTE/11945/2015) obtained by UPLC-MS/MS of green tea with dilution factors (f) of 2, 4, 10, and 20

However, even at f = 20, all three substances did not meet the SANTE/11945/2015 requirements. Probably, these substances need to be more diluted; however, this will increase their LOQ (Kittlaus et al., 2011).

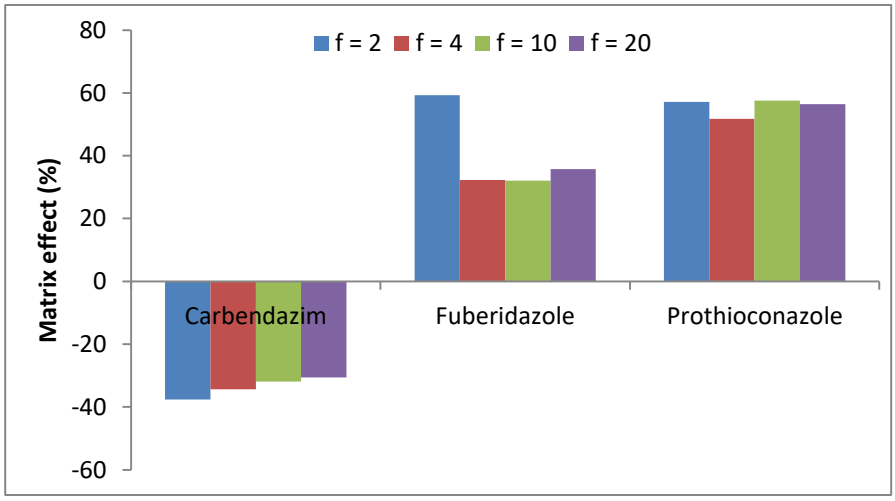

Fig. 4-8. MEs of carbendazim, fuberidazole, and prothioconazole in green tea with dilution factors of 2, 4, 10, and 20 obtained by UPLC-MS/MS; 1 µL injection volume

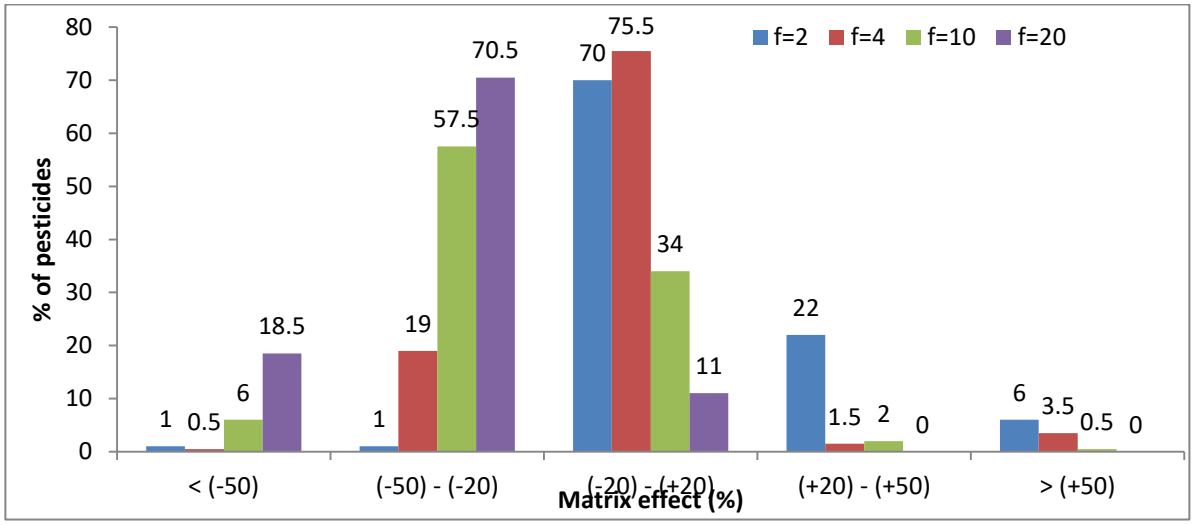

Fig. 4-9. Percentage of pesticides in each ME range (according to SANTE/11945/2015) obtained by GC-MS/MS of green tea with dilution factors of 2, 4, 10, and 20

Considering the GC-MS/MS method, the more diluted the post-extraction solutions, the more the compounds moved to the suppression region (Fig. 4-9). Indeed, enhancement compounds rapidly decreased from 28% ($f = 2$) to 0% ($f = 20$), whereas suppression compounds significantly increased from 2% to 89%. The no ME region reached a peak of 75.5% of compounds (151) at $f = 4$ and then decreased to 11% at $f = 20$. Most substances (198 out of 200 compounds) tended to move toward the suppression region, except for two substances (i.e., pentachloroaniline and pentachlorobenzene) with nearly constant ME, for example, the MEs of acrinathrin, *p*,*p*′-DDT, and phorate, as shown in Fig. 4-10. No studies have ever described this phenomenon in GC-MS/MS. Most studies agree that the enhancement phenomenon in GC-MS occurs mainly because the active sites on the injection port and GC column are blocked. However, this result showed that ion suppression occurs during MS with an ionization source. Thereby, the ME on GC-MS/MS could be the sum of these two phenomena. When undiluted, the enhancement phenomenon occurs more strongly than the suppression phenomenon; thus, the resulting ME is positive. When diluted, the enhancement phenomenon decreases faster than the suppression phenomenon; thus, the resulting ME is negative. The prediction of ME depletion of *p*,*p*′-DDT is simulated

in Fig. 4-11. However, more studies are needed to confirm this hypothesis. A study similar to the post-column infusion method for UPLC-MS/MS would be the appropriate way to isolate ion enhancement on the GC system.

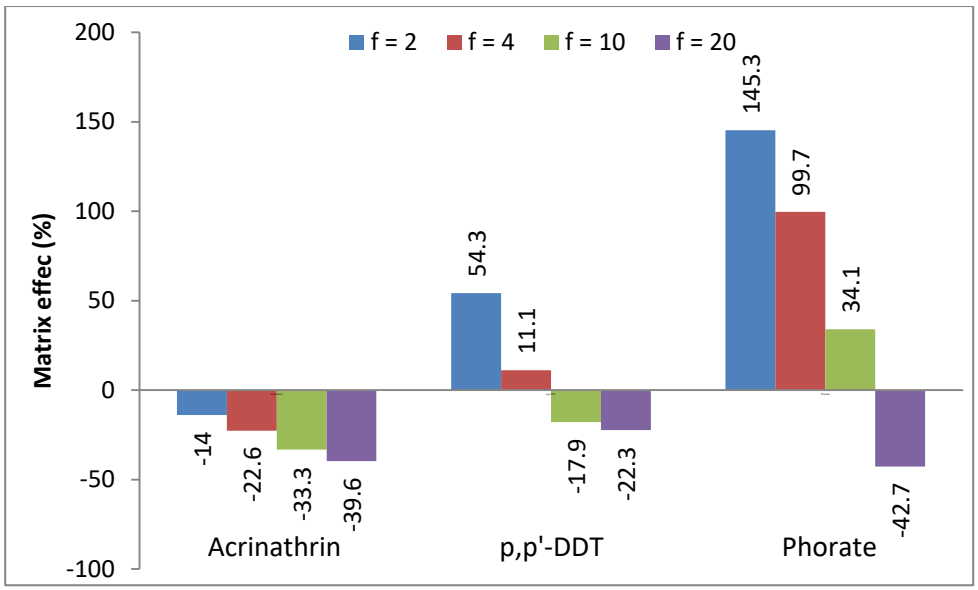

Fig. 4-10. MEs of acrinathrin (pyrethroid), p,p'-DDT (organochlorine), and phorate (organophosphate) in green tea with different dilution factors obtained by GC-MS/MS; 1 µL injection volume

In general, with a dilution factor of 4, both the UPLC-MS/MS and GC-MS/MS methods achieved the highest number of pesticides within the ME range of ±20%. Nevertheless, in our other study, many substances had LOQs higher than 10 µg/kg with f = 4, which did not meet the EU maximum residue limits (MRLs) for both methods (EU MRL). Considering the MEs and LOQs, dilution is unnecessary for the UPLC-MS/MS method because 97% of the compounds did not exhibit MEs with f = 2. For GC-MS/MS, MEs improved peak shapes (less tailing, more symmetry and higher intensity). Therefore, it is better to take advantage of this phenomenon than eliminate it (Michelangelo Anastassiades et al., 2003; Cajka et al., 2005; Rahman, El-Aty, et al., 2013). In conclusion, enhancing sample preparation by mixed-mode SPE cleanup and reducing the injection volume were selected for the determination of 400 pesticide residues in tea.

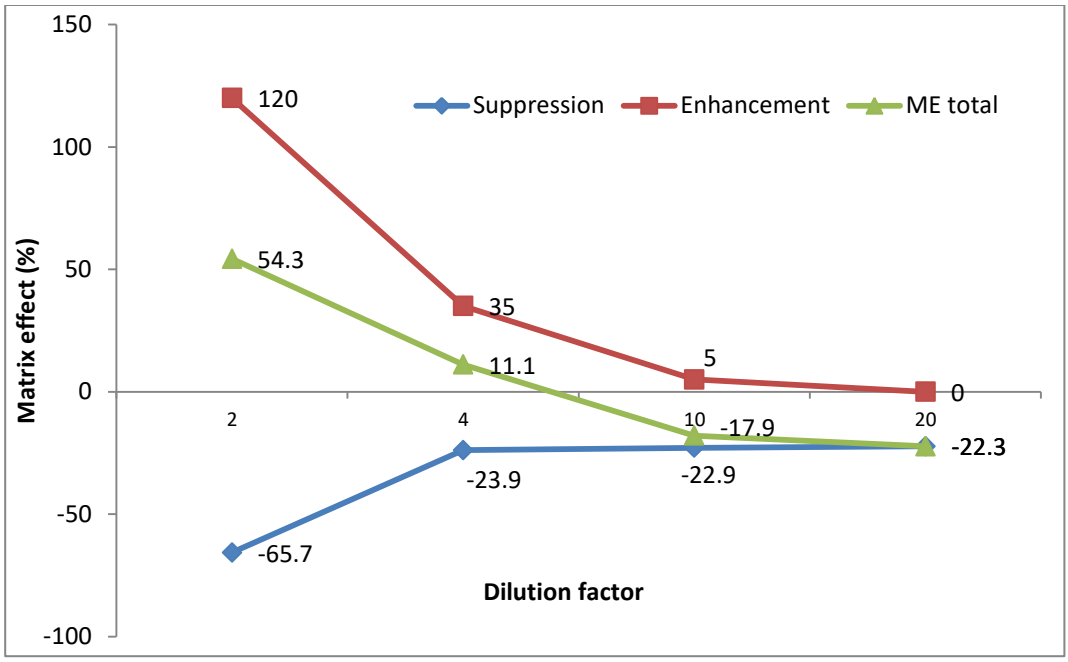

Fig. 4-11. Simulating the matrix effect of p, p'-DDT according to the dilution factor in GC-MS/MS method; matrix effects in GC-MS/MS could be sum of ion suppression and ion enhancement

4.4. Comparison of matrix effects in white, green, oolong, and black tea

On the basis of the previously presented results, we used mixed-mode SPE cleanup and 1 μL injection volume to investigate the differences of MEs in WT, GT, OT, and BT. The data are shown in Tables A-8 and A-9 of the Appendix Table and summarized in Fig. 4-12.

Fig. 4-12 shows that OT exhibited the lowest MEs for both LC and GC methods, with 197 (98.5%) and 170 (85%) compounds within the ME range of ±20%, respectively. Meanwhile, for BT, 191 (95.5% for LC) and 81 (40.5% for GC) compounds were detected in this region. The corresponding MEs were 193 (LC) and 132 (GC) compounds for WT and 194 (LC) and 140 (GC) compounds for GT. The MEs of GC could be divided into three groups, namely, strong (BT), medium (GT and WT), and soft (OT) MEs. This result could be attributed to the manufacturing process of BT

(fully oxidized), WT and GT (slightly oxidized), and OT (semi-oxidized), consistent with that reported in a previous study (Li et al., 2018).

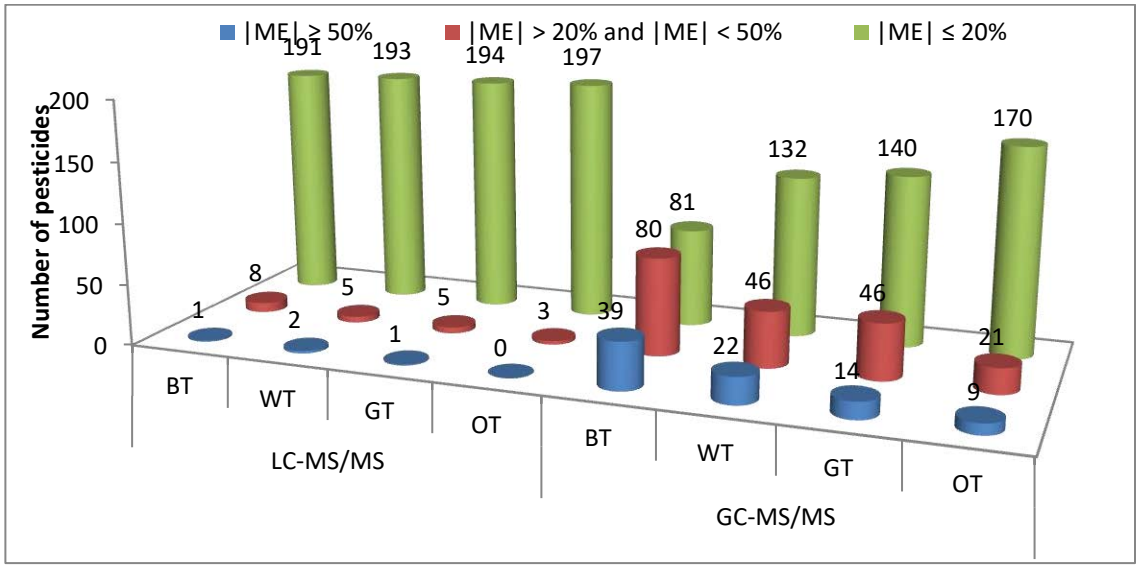

Fig. 4-12. Comparison of MEs in different types of tea, namely, black tea (BT), white tea (WT), green tea (GT), and oolong tea (OT), obtained by UPLC-MS/MS and GC-MS/MS; 1 µL injection volume

For UPLC-MS/MS, most of the compounds did not exhibit MEs, accounting for 95.5% (BT) to 98.5% (OT). Compounds exhibiting enhancement or suppression are presented in Table 4-2. Although some pesticides exhibited similar MEs (difference of <20%), some substances exhibited significantly different MEs (i.e., fuberidazole, ivermectin, propamocarb, and prothioconazole). This finding proved that the ME depends not only on the analyte but also on the matrix.

Table 4-2. Compounds that exhibited enhancement or suppression in UPLC-MS/MS of black tea (BT), white tea (WT), green tea (GT), and oolong tea (OT)

Compound	Matrix effect (%)			
	BT	WT	GT	OT
Aldicarb sulfoxide	−24.4	−16.1	−15.8	−5.6
Bifenazate	−22.6	−6.2	−16.4	−2.2
Carbendazim	−51.9	−52.9	−37.6	−30.7
Dicrotophos	−32.2	−31.6	−23.6	−17.5
Dinotefuran	−24.5	−18.2	−14.5	0.2
Dioxacarb	−23.3	−20.0	−19.9	−7.3
Fuberidazole	12.9	17.4	59.3	31.4
Ivermectin	14.5	50.6	36.7	14.3
Monocrotophos	−25.4	−25.2	−14.3	−6.9
Propamocarb	−33.1	−21.8	−22.5	−4.3
Prothioconazole	25.9	28.6	57.1	47.3

Moreover, to confirm the dilution method, the post-extraction solutions of WT, OT, and BT were diluted in the same manner as GT, as discussed in Section 4.3.3. The results are summarized in Table A-11 in the Appendix Table. For UPLC-MS/MS, compounds with no ME slightly increased from 193 to 197 and from 191 to 197 for WT and BT, respectively; meanwhile, OT remained constant with 197 compounds. Three pesticides, namely, carbendazim, fuberidazole, and prothioconazole, were not within the ME range of ±20%. For GC-MS/MS, the highest numbers of pesticides within the ME range of ±20% were obtained at a dilution factor of 4, that is, 175, 176, and 180 pesticides for WT, OT, and BT, respectively. Moreover, most pesticides tended to move toward the suppression region with increasing dilution. This phenomenon occurred in GC-MS/MS despite the type of tea.

Again, the dilution factor of four was the best for all types of tea. However, as mentioned in Section 4.3.3, our other study results showed that the LOQs hardly

reached the threshold of 10 µg/kg, according to the EU MRLs. Finally, no dilution may be a suitable option for pesticide residue analysis at trace levels.

In conclusion, by QuEChERS extraction, mixed-mode SPE cleanup (including C18, GCB, and PSA sorbents), and injection volume of 1 µL, solvent calibration curves could be applied to a total of 191 to 197 compounds (for *UPLC-MS/MS*) and 81 to 170 compounds (for GC-MS/MS), depending on the type of tea. Moreover, to overcome the MEs in 200 compounds (for GC-MS/MS), matrix-matched calibration curves (mix of four types of tea) should be employed according to SANTE guideline *(SANTE/11945/2015)*. However, the quantitative results using the matrix-matched calibration curves on a mixture of teas will not be as accurate as those on each type of teas.

4.5. Comparison of MEs in the UPLC-MS/MS and GC-MS/MS methods

Among 400 pesticides, 27 were detected by both the UPLC-MS/MS and GC-MS/MS methods (Table A-12 in the Appendix Table). The comparison of the MEs of four types of tea obtained by both methods is presented in Fig. 4-13.

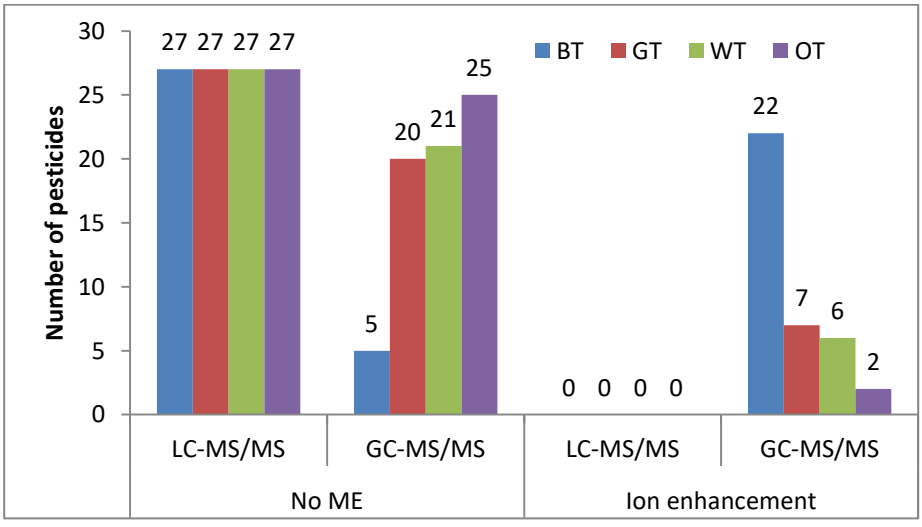

Fig. 4-13. Comparison of the MEs of 27 compounds in black tea (BT), green tea (GT), white tea (WT), and oolong tea (OT) obtained by both UPLC-MS/MS and GC-MS/MS

Undoubtedly, UPLC-MS/MS presented no MEs for all 27 compounds despite the type of tea. By contrast, GC-MS/MS exhibited ion enhancement for 22, 7, 6, and 2 pesticides in BT, GT, WT, and OT, respectively. Notably, both methods injected the same post-extraction solution (in the extraction and cleanup steps, before adding different standard mix solutions). Therefore, the ME is not only influenced by extraction, cleanup, and matrix but also by analytical techniques. UPLC-MS/MS is generally affected by ion suppression; thus, improving the sample extraction and cleanup steps could eliminate the MEs. By contrast, the MEs in GC are more complex, as discussed in Section 4.3.3. This result indicates that compounds that are compatible with both methods should be analyzed by UPLC-MS/MS.

4.6. Conclusions

In this study, the MEs of 400 pesticides were estimated by both the UPLC-MS/MS and GC-MS/MS methods for different types of tea, namely, WT, GT, OT, and BT. By using QuEChERS extraction and mixed-mode SPE cleanup (including C18, GCB, and PSA sorbents), a total of 154 (77%) and 71 (35.5%) pesticides estimated by UPLC-MS/MS and GC-MS/MS, respectively, met the requirement of MEs within the range of ±20% for GT. The common matrix phenomenon was ion suppression for UPLC-MS/MS and signal enhancement for GC-MS/MS. For UPLC-MS/MS, ion suppression most commonly occurred at the beginning and end regions of the chromatogram. For GC-MS/MS, organophosphate (27), pyrethroid (16), dinitroaniline (5), and thiocarbamate (3) were the compounds most detected. By reducing the injection volume, the ME was significantly improved for both UPLC-MS/MS and GC-MS/MS. Accordingly, there were 194 and 140 compounds with no ME obtained for UPLC-MS/MS and GC-MS/MS, respectively. To our knowledge, this is the first time that the injection volume has been reduced to overcome MEs. Moreover, compensation by dilution showed the best results at $f = 4$ for both methods. Regarding the types of tea, BT exhibited a strong ME with 128 out of 400 compounds within the ME range of ±20%, followed by WT (75 out of 400), GT (66 out of 400), and OT (33 out of 400).

Moreover, UPLC-MS/MS presented no MEs for all 27 compounds detected by both methods; a good result in comparison with that of GC-MS/MS. Furthermore, MEs in GC-MS/MS could be the sum of two ion enhancement and ion suppression phenomena. Therefore, more studies are needed to retest this phenomenon.

Chapter 5. Method validation and assessment of 397 pesticide residues in several types of tea from different countries

5.1. Method validation for several types of teas

In chapter 3, the analytical methods of 400 pesticides in green tea by QuEChERS extraction, mixed-mode SPE cleanup, and determination by tandem mass spectrometry (200 compounds for each of UPLC-MS/MS and GC-MS/MS) have been developed. However, there are three unstable compounds (captafol, chlorothalonil, and folpet) following this multi-residue analysis method due to their tendency to degrade in solution as well as during GC-injection (EURL-SRM, 2017; EURL-SRM for chlorothalonil). Hence, total of 200 compounds for UPLC-MS/MS and 197 compounds for GC-MS/MS were selected for method validation in WT, GT, OT, and BT.

5.1.1. Matrix effects

The matrix effects for WT, GT, OT, and BT were investigated in Session 4.1.4 of chapter 4 and the results were summarized in Fig. 5-1.

A matrix effect is considered soft, medium, or strong if its absolute value ranges from 0-20%, 20-50%, or > 50%, respectively. Fig. 5-1 shows that the UPLC-MS/MS method had an approximately soft ME for all types of teas (BT, WT, GT, and OT) with 191 (95.5%), 193 (96.5%), 194 (97.0%), and 197 compounds (98.5), respectively. According to the SANTE/11945/2015 standard, this method can employ the calibration curves in solvent for quantitation (SANTE/11945/2015).

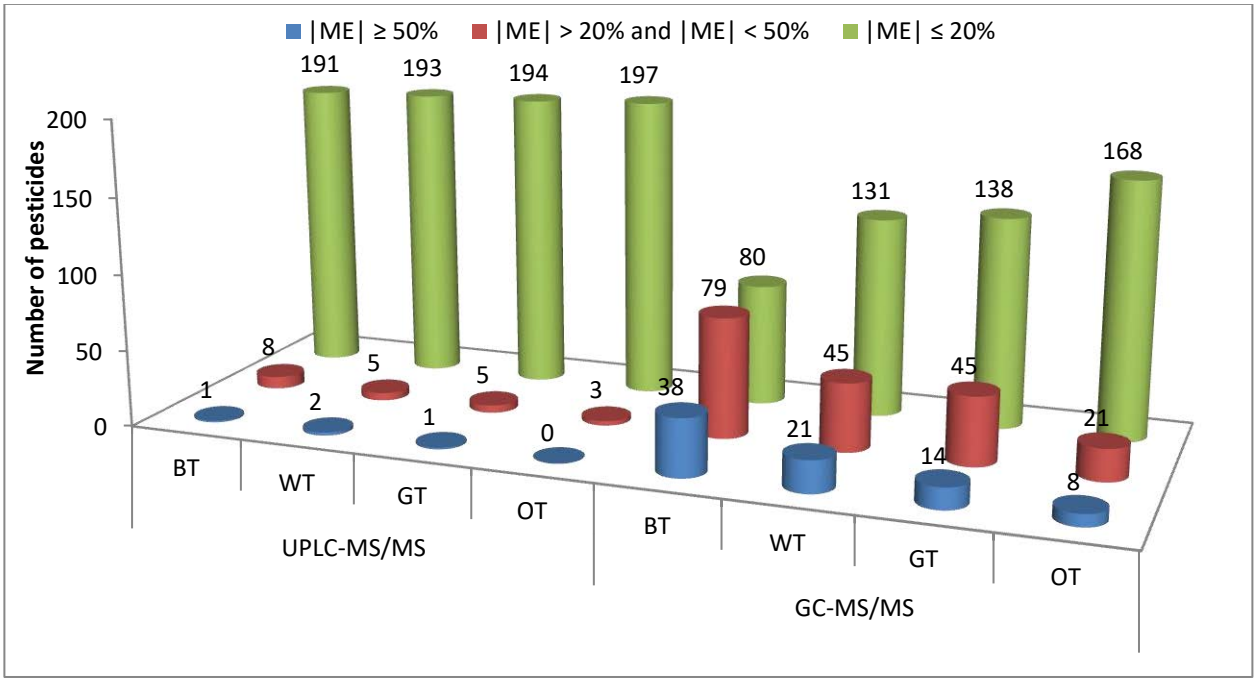

Fig. 5-1. Distribution of matrix effect in GC-MS/MS and UPLC-MS/MS method for black tea (BT), white tea (WT), green tea (GT), and oolong tea (OT)

For the GC-MS/MS method, the MEs are more complicated depending on the processing, such as non-oxidized (WT and GT), partially oxidized (OT), and completely oxidized (BT). Figure 5-1 shows that the distribution of the MEs is significantly different between teas. For example, with a soft ME, the best results in order are oolong tea, green tea, white tea, and finally black tea with 168 (85.3%), 138 (70.1%), 131 (66.5%), and 80 substances (40.6%), respectively. The black tea results show that most compounds had medium to strong MEs, with 79 (40.1%) and 38 compounds (19.3%), respectively. Due to its complete oxidation and more complex matrix, black tea is more severely affected than green and other teas (Li et al., 2012). Notably, among 36 compounds with strong "ion enhancement" (ME > 50%) in black tea, there were 25 organophosphate compounds (69.4%). We found that the ME in

GC-MS/MS can enhance the signal and peak sharpness, so that it can be considered a positive point. This phenomenon can be explained by the interferences in the matrix solutions blocking the active sites of the GC column and injector, especially polar compounds such as organophosphates; thus, more pesticides can quickly reach the MS detector (Li et al., 2012; Rahman, El-Aty, et al., 2013). To overcome MEs in GC-MS MS, especially the significant difference between different kinds of tea, a blank extraction solution of the four types of tea was mixed and a matrix-matched calibration curve was prepared from this mixed extraction solution, according to SANTE (SANTE/11945/2015).

5.1.2. Linearity

The linear ranges and correlation coefficients are summarized in Tables A-13 and A-14 of the Appendix Table. In most cases, the coefficient of determination (R^2) was higher than 0.99, with a concentration range between 0.5 and 100 µg/kg. However, among particular cases, linearity concentration ranges were different (Table 5-1), but the sensitivity remains acceptable.

Table 5-1. Compounds with linearity range of 1 – 100 µg/kg in LC-MS/MS (a) and GC-MS/MS (b) method

Linearity range, µg/kg	Compounds	
	UPLC-MS/MS	GC-MS/MS
1 – 100	Acibenzolar-S-methyl, avermectin, bitertanol, butocarboxim, butoxycarboxim, iprovalicarb, isocarbophos, propham, prothioconazole, and thiofanox	Acrinathrin, cypermethrin, o,p‘-DDT, p,p‘-DDT, fluridone, flutriafol, methoxychlor, paclobutrazole, parathion, prochloraz, and tricyclazole
5 – 100	Formetanate hydrochloride	Azinphos-methyl, dichlofluanid, resmethrin, and tolyfluanid

5.1.3. Recovery and repeatability

Standard pesticide solutions were added to five replicate blank matrix samples at concentrations of 10, 50, and 100 µg/kg. The reproducibility and recovery obtained with this method are presented in detail in Tables A-13 and A-14 of the Appendix Table, and summarized in Table 5-2. The repeatability for most pesticides (> 99%) for different teas was within 20%, as required by SANTE.

For the UPLC-MS/MS method, the number of compounds that met recoveries of 70 – 120% ranged from 172 (86%) to 188 (94%), for GT and OT at 100 µg/kg, and WT at 100 µg/kg, respectively. The results show that this method has high accuracy, even if it uses the solvent calibration curve and does not use the stable isotope internal standard. Substances with low recoveries (< 30%) were thiophanate-methyl (all types of tea), chlorfluazuron (OT), carboxin, and spirotetramat (BT). Thiophanate-methyl converted to carbendazim during extraction, resulting in low recovery (Singh et al., 2007). However, the repeatability for these compounds was acceptable (RSD ≤ 20%).

Table 5-2. The number of pesticides meets the SANTE/11945/2015 regulation for recovery (70 to 120%) and RSD (≤ 20%) at different levels for the UPLC-MS/MS (a), and GC-MS/MS method (b)

Validation parameters	Concentration, µg/kg	Number of pesticides (% proportion)			
		WT	GT	OT	BT
Recovery (70 - 120%)	10	182 (91)[a] 181 (91.9)[b]	177 (88.5)[a] 185 (93.9)[b]	175 (87.5)[a] 164 (83.2)[b]	184 (92)[a] 184 (93.4)[b]
	50	186 (93)[a] 189 (95.9)[b]	167 (83.5)[a] 181 (91.9)[b]	170 (85)[a] 169 (85.8)[b]	178 (89)[a] 189 (95.9)[b]
	100	188 (94)[a] 187 (94.9)[b]	172 (86)[a] 186 (94.4)[b]	172 (86)[a] 172 (87.3)[b]	175 (87.5)[a] 190 (96.4)[b]
RSD (< 20%)	10	200 (100)[a] 196 (99.5)[b]	200 (100)[a] 195 (99)[b]	198 (99)[a] 196 (99.5)[b]	199 (99.5)[a] 197 (100)[b]
	50	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]
	100	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]	200 (100)[a] 197 (100)[b]

Similarly, the GC-MS/MS method has high accuracy, ranging from 164 substances (83.2% for OT at 10 µg/kg) to 190 (96.4% for BT at 100 µg/kg), which were in the recovery range of 70-120%. Moreover, there was no compound with a less than 30% recovery. Despite the ME difference between teas, the use of matrix-matched curves and the mixture of matrices, has compensated for the MEs.

5.1.4. LOQ

LOQs were evaluated by determining the lowest concentration spike for the sample in which the recovery and repeatability were within 70–120% and less than 20%, respectively. In some instances, and typically with multi-residue methods, a mean recovery below 70% and RSD ≤ 20% may be acceptable. So, for each kind of tea blank, five samples were spiked at 1, 2, 5, 10, 50, and 100 µg/kg for evaluating LOQ. Each compound with the lowest concentration must meet the above conditions for all four matrices to be considered LOQ.

Fig. 5-2 summarizes the LOQ distribution of the UPLC-MS/MS and GC-MS/MS methods. In general, both methods are highly sensitive, with more than 200 (100%) and 189 substances (95.9%) for UPLC-MS/MS and GC-MS/MS, respectively, with LOQs of 10 µg/kg or less. Hence, these compounds meet a general default MRL of 10 µg/kg (EC, 396/2015). Eight compounds with LOQs of 50 µg/kg were all from GC-MS/MS method, *i.e.*, azinphos-methyl, bioallethrin, deltamethrin, disulfoton, endosulfan ether, fluridone, pentachloroaniline, and prochloraz. Most of them are lower than European MRL regulations, except bioallethrin and fluridone (MRL at 10 µg/kg for both compounds). Globally, 395 total compounds (99.5%) met the EU MRL regulations.

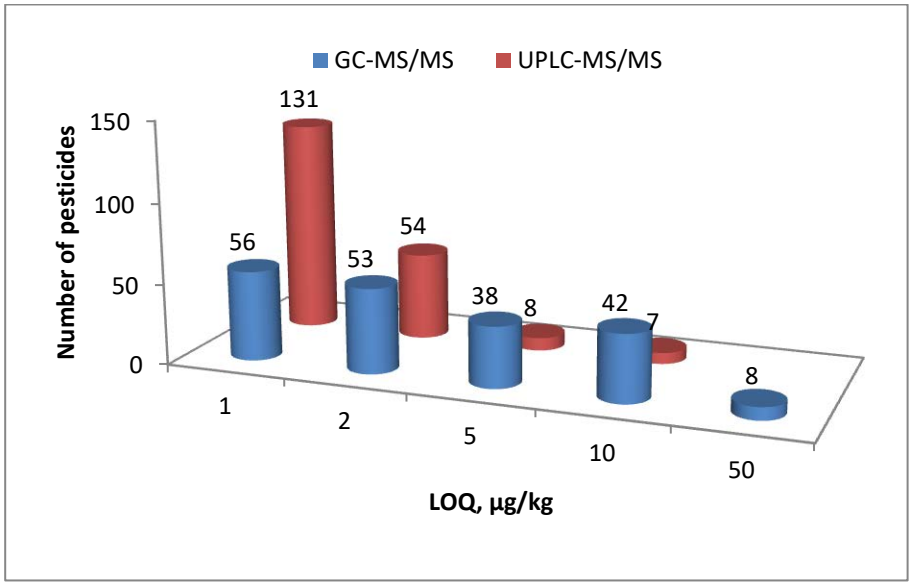

Fig. 5-2. Distribution of LOQs in the GC-MS/MS and UPLC-MS/MS method

The sensitivity and MEs of the 27 pesticides analyzed simultaneously by both methods were presented in Table 5-3. The results show that the UPLC-MS/MS method has a sensitivity of 2 to 50 times higher than GC-MS/MS, except six compounds with the same LOQs. In addition, while all 27 compounds had MEs in the range of ±20% for UPLC-MS/MS, 22 ones (accounting of 81.5%) exhibited ion enhancement (MEs > 20%) for GC-MS/MS. This result indicates that compounds, which were compatible with both methods, should be analysed by UPLC-MS/MS.

Table 5-3. Comparison of LOQs and MEs for 27 compounds analyzed by the UPLC-MS/MS (a) and GC-MS/MS (b) methods

#	Compound	LOQ, µg/kg		MEs, % (*)	
		UPLC-MS/MS	GC-MS/MS	UPLC-MS/MS	GC-MS/MS
1.	Bupirimate	1	2	−5.5	19.6
2.	Cyprodinil	1	2	−6.9	20.7
3.	Fenarimol	1	5	−6.4	24.1
4.	Fipronil	2	2	−9.8	12
5.	Fludioxonil	2	10	−12.7	44.2
6.	Fluquinconazole	2	2	−9.6	29.7
7.	Flusilazole	1	2	−7.6	22.9
8.	Flutolanil	1	2	−7.9	34.0
9.	Flutriafol	1	2	−7.76	27.3
10.	Linuron	2	10	−7.9	70.6
11.	Metalaxyl	1	2	−5.9	12.4
12.	Mevinphos	2	2	−13.0	27.6
13.	Myclobutanil	1	1	−6.7	22.4
14.	Paclobutrazol	1	5	−8.3	39.3
15.	Penconazole	1	2	−11.6	23.9
16.	Piperonyl butoxide	1	2	−7.8	33.5
17.	Prochloraz	1	50	−10.1	54.9
18.	Propargite	2	10	−9.3	29.5
19.	Pyridaben	1	10	−6.4	28.3
20.	Pyrimethanil	1	1	−6.3	17.5
21.	Pyriproxyfen	1	5	−7.7	32.0
22.	Tebuconazole	1	2	−11.1	35.1
23.	Tebufenpyrad	1	1	−5.9	32.0
24.	Triadimefon	1	2	−6.9	17.5
25.	Triadimenol	1	5	−8.7	26.3
26.	Tricyclazole	1	10	−7.1	112.4
27.	Triflumizole	2	2	−15.8	24.5

(*): MEs obtained from BT

5.2. Pesticides residues in tea

One hundred and six tea samples were analyzed and assessed for 397 pesticide residues according to European standards (EC, 396/2015). The tea sample was considered to be in noncompliance when its pesticide residue exceeds the EU MRL at least on one compound (EU MRLs). Furthermore, a default MRL of 0.01 mg/kg applies for pesticides without an explicit MRL (EC, 396/2015).

The pesticide analysis results are reported in Table A-16 (Appendix Table). Among 106 samples, 33 samples (31.1%) had no detectable pesticide residues (pesticide concentration lower than LOQ), 47 samples (44.3%) had detectable compliant pesticide residues (pesticide concentration lower than MRL), and 26 samples (24.6%) contained at least a single residue in noncompliance of the EU MRL (Fig. 5-3).

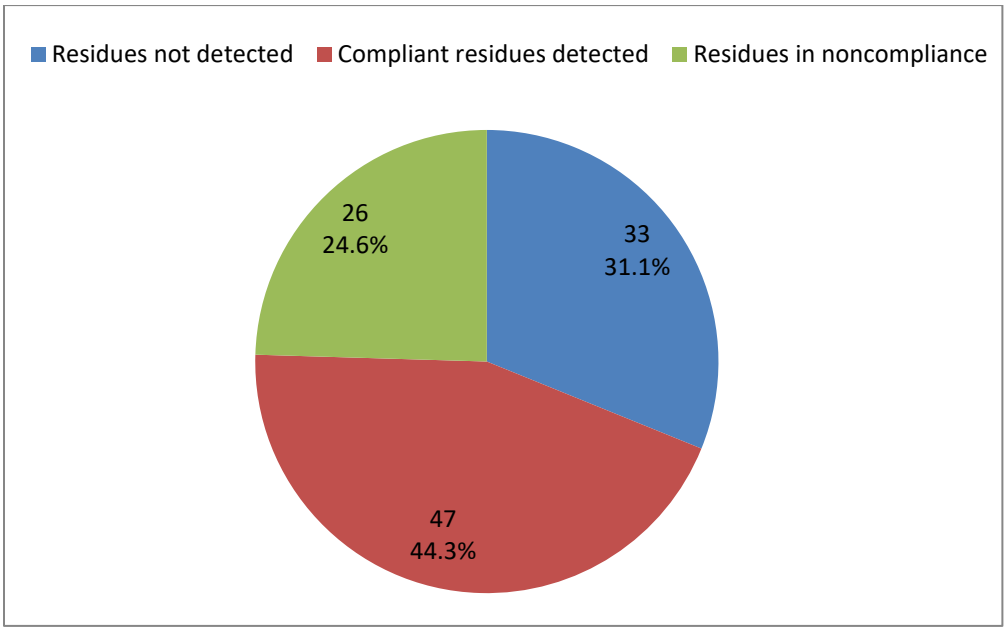

Fig. 5-3. Distribution of tea samples with residues not detected, compliant residues detected, and residues in noncompliance (number of samples and percentage)

- *Residues not detected: samples contained pesticide at level lower than LOQ.*
- *Compliant residue detected: samples detected pesticide at level lower than MRL.*
- *Residues in noncompliance: samples contained at least a single residue higher than MRL.*

As shown in Fig. 5-4, tea samples frequently contained more than one pesticide residue, with numerous individual tea samples containing both compliant pesticide residues and residues in noncompliance of applicable MRLs. Sixteen samples had one pesticide residue per sample, 26 samples with 2–5 pesticide residues, 14 samples with 6–10 pesticide residues, 9 samples with 11–15 pesticide residues, and 8 samples contained 16 to a maximum of 22 pesticide residues. Among 73 samples of detected

pesticides, 57 samples had two or more pesticide residues (78.1%), compared to 16 samples (21.9%) with only one pesticide residue. This is assumed to be due to pesticide formulation (often a mixture of many ingredients) and/or the practice of using multiple pesticides during their spreading. In addition, seventeen samples (16%) contained more than 10 pesticides, equivalent to previous studies (Huang et al., 2019; Lozano et al., 2012). There were 5 and 13 samples detected more than 10 pesticides per sample, reported by Huang and Lozano, respectively.

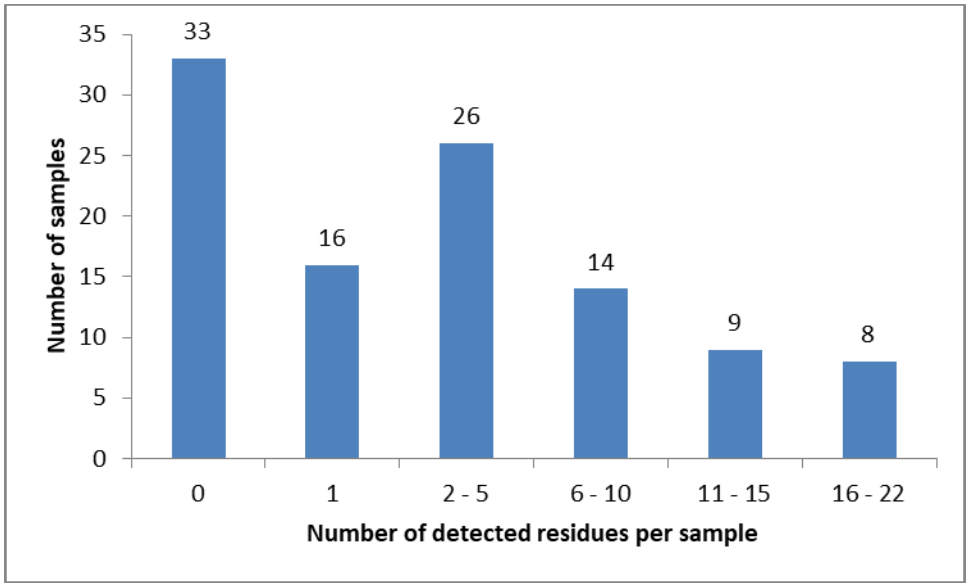

Fig. 5-4. Distribution of samples by the number of detected residues per sample

5.2.1. Residues assessing by the type of teas

A summary of sample and pesticide residue detections and noncompliances by tea type was reported in Table 5-4. Regarding samples with detected pesticides, OT had the highest rate at 100% (n = 17), followed by GT at 71.1% (n = 38), BT at 64.3% (n = 42), PT at 33.3% (n = 3), and WT at 16.7% (n = 6). In terms of sample noncompliance (at least one pesticide with a concentration exceeding the MRL), oolong tea had the most (7 samples, 41.2%), followed by green tea (14 samples, 36.8%), and black tea (5 samples, 11.9%). In contrast, WT and PT did not have any samples in this category.

Table 5-4. Summary of pesticide residue detections and noncompliances by tea type

Tea type (number of samles)	Number of detected pesticide samples[(1)] (Number of detected pesticides)	Average number of detected pesticides [(2)]	Number of noncompliance samples[(3)] (Number of noncompliance residues)	Average number of noncompliance residues[(4)]
Oolong tea (17)	17 (124)	7.3	7 (17)	2.4
Green tea (38)	27 (230)	8.5	14 (21)	1.5
Black tea (42)	27 (109)	4	5 (5)	1
White tea (6)	1 (3)	3	0 (0)	0
Pu-Erh tea (3)	1 (3)	3	0 (0)	0

Note: (1) Sample which at least one pesticide higher than LOQ

(2) Average number of detected pesticides = Number of detected pesticides / Number of detected pesticide samples

(3) Sample that at least one pesticide higher than MRL

(4) Average number of noncompliance residues = Number of noncompliance residues / Number of noncompliance samples

Among six samples of WT, there were three samples coming from the ancient tea garden in Vietnam, *i.e*, WT001, WT003, and WT004 (Yen Bai and Tay Con Linh). These Shan Tuyet tea were located in high mountain with an altitude of over 1400 meters above sea level and the tea trees here are usually grown naturally, without any chemicals or fertilizers. Two samples (WT002 and WT006) came from organic tea garden in Nepal. The other sample WT005 came from China, which detected low levels of bifenthrin (6.9 µg/kg), lambda-cyhalothrin (4.9 µg/kg) and thiamethoxam (1.5 µg/kg), complying with the EU MRL.

For 17 oolong tea, Vietnam and Taiwan have 7 samples, followed by China (2) and Thailand (1). The most dectected residues were dinotefuran (65% of samples), difenoconazole, chlorpyrifos (47%), buprofezin, imidacloprid (41%), fenpropathrin, and lambda-cyhalothrin (35%). Among them, neonicotinoid insecticides, such as dinotefuran and imidacloprid are regularly used in tea cultivation to control false-eye leafhopper (Ikenaka et al., 2018).

In this targeted survey, OTs had the highest average number of noncompliance residues at 2.4 detected residues per sample, followed by green tea with 1.5 and black

tea with 1 residue detection per sample. The number of samples with detected residues (64.3% of 42 samples) as well as the average number of pesticide residue noncompliances at 1 (5 compounds per 5 samples) in black tea was lower than oolong and green tea. Our results are consistent with previous studies, which have also found that black tea had less pesticide residue than other teas (Z. Huang et al., 2007; Lozano et al., 2012). This could be due to the complete oxidation of black tea.

In 27 organic tea samples, 20 ones (74%) were free of pesticides and 7 ones (26%) contained pesticide residues with concentrations ranging from 4.6 (ethion) to 70.2 µg/kg (cypermethrin). All samples were contaminated with only one pesticide and were below the MRL threshold.

5.2.2. Number of pesticides detected in tea

Seventy-one different pesticides, out of 397 validated compounds in this study, were detected, 16 compounds of which were frequently detected in tea (Table 5-5). Lambda-cyhalothrin, with concentrations ranging from 2.2 to 1252.9 µg/kg, was the most detected one (31 samples) and violated insecticide limits (14 samples). While the MRL of this compound in EU is low at 10 µg/kg, in most other countries it is relatively high, for example, it is 2,000 in Canada and Taiwan and 15,000 µg/kg in Japan (Canada MRLs; Japan MRLs; Taiwan MRLs). Because of the high MRL in some countries, lambda-cyhalothrin is still widely used in tea cultivation. Among the 71 detected pesticides, there were 29 approved and 42 non-approved by the European Commission (EC No. 1107/2009). Almost all the detected pesticides (except permethrin, fenobucarb, hexaconazole, chlorfluazuron, and hexythiazox) were also reported as noncompliances in tea according to the European Food Safety Authority (EFSA, 2017), the Canadian Food Inspection Agency (CFIA, 2011), and the US Food and Drug Administration (FDA, 2014). The neonicotinoid group (acetamiprid, clothianidin, imidacloprid, thiacloprid, dinotefuran, and thiamethoxam) has been used frequently in insecticides due to its lower toxicity in birds and mammals than in

insects. In tea cultivation, these compounds are often used to control pests, such as *Empoasca vitis* (false-eye leafhopper) (Ikenaka et al., 2018). Similarly, the synthetic pyrethroid insecticide group (cyhalothrin-lambda, bifenthrin, cypermethrin, fenpropathrin, and permethrin), a broad spectrum of insecticidal activity coupled with low mammalian toxicity, is commonly used in farming. For example, fenpropathrin is widely applied to control red spider mites on tea (Seenivasan & Muraleedharan, 2011). Triazole fungicides (difenoconazole, hexaconazole, and tebuconazole) are also commonly used to treat blight disease in tea (Subbiah, 2006). Beside pesticides, anthraquinones were also detected in eight samples, in which one exceeding MRL (20 µg/kg) at 70.4 µg/kg. Anthraquinone is a widely spread contaminant in tea samples, possibly migrating from the packaging to the tea, in addition to other currently unknown sources (Wang et al., 2018).

Table 5-5. Summary of pesticides frequently found in tea (n ≥ 10)

Compound	MRL (µg/kg)	Lowest level (µg/kg)	Highest level (µg/kg)	Number of detected samples (% detected frequencecies(1))	Number of noncompliance samples
Lambda-Cyhalothrin	10	2.2	1252.9	31 (29)	14
Bifenthrin	30000	2.4	2297.8	29 (27)	0
Thiamethoxam	20000	1.1	36.8	24 (23)	0
Chlorpyrifos	2000	3.3	261.6	23 (22)	0
Cypermethrin	500	11.9	3700.8	22 (21)	2
Acetamiprid	50	1.3	61.4	20 (19)	1
Buprofezin	50	2.0	294.7	20 (19)	2
Imidacloprid	50	2.1	311.4	18 (17)	2
Chlorfenapyr	50000	10.9	497.8	18 (17)	0
Thiacloprid	10000	1.3	80.1	15 (14)	0
Fenpropathrin	2000	2.4	2080.4	14 (13)	1
Dinotefuran	10	2.6	58.5	14 (13)	5
Permethrin, cis-	100	5.2	29.6	13 (12)	0
Permethrin, trans-	100	5.2	35.0	13 (12)	0
Difenoconazole	50	1.2	64.9	13 (12)	1
Carbendazim	100	1.9	1997.0	13 (12)	2

(1) Detected frequenceies: percentage number of detected samples per 106 samples

5.2.3. Residues assessing by origins

As presented in Table 5-6, in four countries studied, Taiwan had the most pesticide-contaminated samples with 83.3% (n = 10), followed by China (73.7%, n = 19), Vietnam (64.7%, n = 34), and India (55%, n = 20). In terms of average residue concentration per sample, the highest was China, at 918 µg/kg, followed by Taiwan (460 µg/kg), Vietnam (298 µg/kg) and India (82 µg/kg). The samples from India were the least pesticide-contaminated ones, with respect to detected pesticide samples, the average concentration of residues, and the number of detected compounds. For seven of these black Indian teas, one reason could be due to their origin from gardens, for which neither pesticides nor fertilizers have been applied since several years to reach organic standards. China and Taiwan, with rather the same farming practices, have similar numbers of detected compounds, with 40 and 39 compounds, respectively, of which 22 pesticides were commonly used. Due to the small sample size (n < 4 for other countries) or no information (unknown), the remaining samples (n = 21) do not have enough data for a comparison by origin.

Table 5-6. Summary of pesticide residue detections by origin

Origin	Samples	Number of pesticide detected samples (% detected samples)	Sum of residues (Average residues per sample) (µg/kg)	Number of detected compounds
Vietnam	34	22 (64.7)	6548 (298)	32
India	20	11 (55)	901 (82)	21
China	19	14 (73.7)	12848 (918)	40
Taiwan	12	10 (83.3)	4596 (460)	39
Other	13	8 (61.5)	509 (64)	12
Unknow	8	8 (100)	1887 (236)	13
Total	106	73 (68.9)	27289 (374)	71

5.3. Conclusion

Analytical methods with high sensitivity and accuracy were successfully validated according to SANTE/11945/2015 for determining 397 pesticide residues in different types of tea as white, green, oolong, and black teas. The LOQs obtained for most compounds were at or below 10 µg/kg. Totally 395 compounds (99.5% of the total) met the EU MRL regulations. The number of compounds with recoveries within 70-120% ranged from 172 (86%) to 188 (94%) for UPLC-MS/MS, and from 164 (83.2%) to 190 (96.4%) for GC-MS/MS. For UPLC-MS/MS method, the solvent calibration curves can be used for quantification. For GC-MS/MS, matrix-matched calibration curves on a mixed blank matrix (including WT, GT, OT, and BT) were used for all types of tea due to the complexity of matrix effect. The intraday precisions for more than 99% of pesticides were below 20%. Strong linear relationships were observed, with correlation coefficients $R^2 \geq 0.99$ for all compounds.

The overall compliance ratio for pesticide residues in the 106 tea samples in this targeted investigation was 75.4%. For the samples with detected pesticides, 57 samples had two or more pesticide residues (78.1%) compared to 16 samples (21.9%) with only one pesticide residue (in average, 6.4 pesticides per sample). There were 26 noncompliance samples with 43 pesticide residue noncompliances, but none from the organic tea category. Oolong teas had the highest number of samples with detected pesticides, at 100% (n = 17), followed by green tea at 71.1% (n = 38), black tea at 64.3% (n = 42), Pu‘Erh tea at 33.3% (n = 3) and white tea at 16.7% (n = 6). Black teas were the lowest contaminated ones with pesticides with respect to green and oolong teas, possibly due to the their processing. The most frequently detected pesticides were neonicotinoids, synthetic pyrethroids, and triazole fungicides. In terms of origin, Taiwan had the most pesticide-contaminated samples with 83.3%; followed by China (73.7%), Vietnam (64.7%), and India (55%). Multi-pesticide residues with respect to 106 tea samples showed that samples exceeding EU MRLs regulations were still high

with 24.6%. Therefore, assessments of multi-pesticide residues in tea need to be continued.

Chapter 6. Conclusions and perspectives

6.1. Conclusions

The different objectives of this thesis are:

- to develop analytical methods of multi-pesticide residues with high sensitivity, selectivity, and reliability for reaching the requirements as SANTE/11945/2015 of the EU in order to detect and quantify 400 pesticides at the MRLs in accordance with the European standard EC No. 396/2005 (0.005 - 350 mg kg^{-1}, depending on the combination of pesticides in commercial products) in several types of tealeaves (white, green, oolong and black teas);

- to carry out the matrix effects evaluation in different type of tea, including white, green, oolong, and black tealeaves cause by the above extraction method on LC-MS/MS and GC/MS/MS, respectively, by applying some appropriate ways to overcome/compensate matrix effects;

- to assess and control pesticide residues in tea products (white, green, oolong, and black tealeaves) in Vietnam and the world.

Some results were obtained as following:

- QuEChERS extraction combined with mixed-mode SPE (C18 SPE cartridge paired with SPE GCB/PSA) proved to be the most effective clean-up method. It enabled 397 pesticide residues to be quantified (200 residues using UPLC-MS/MS and 197 residues using GC-MS/MS).
- An elution solvent volume of 20 mL (ACN/toluene, 3/1, v/v) was chosen for SPE clean-up.
- A 1 mL remaining volume was chosen for evaporation.
- 1 mL injection volume was chosen for both UPLC-MS/MS and GC-MS/MS to reducing matrix effect. Hence more than 190 pesticides (> 95% of the 200 ones)

had the matrix effect within the range of ± 20% for UPLC-MS/MS. Therefore, they can be quantified using solvent calibration curves. However, a total of 15 to 59.5% of 200 pesticides presented medium and strong matrix effect for GC-MS/MS, depending on the types of teas, meaning that matrix-matched calibration curves should be used to overcome matrix effects. Moreover, we recognized that matrix effects in GC-MS/MS were not only signal enhancement but also suppression

- The analytical methods were validated fully in accordance with the SANTE/11945/2015 (EU) for 4 types of teas including white, green, oolong and black tea.
    - In almost of cases, the coefficient of determination (R^2) was higher than 0.99, with a concentration between 0.5 and 100 µg/kg. Some pesticides were out of this linear range, from 1 to 100 µg/kg. However, the sensitivity is still acceptable.
    - For the UPLC-MS/MS method, the number of compounds that met recoveries of 70 – 120% ranged from 172 (86%) to 188 (94%), for GT and OT at 100 µg/kg, and WT at 100 µg/kg, respectively. The results show that this method gives high accuracy, even if this method uses the calibration curve in solvent and does not use stable isotope internal standards. Substances with low recoveries (< 30%) were thiophanate-methyl (all types of tea), chlorfluazuron (OT), carboxin, and spirotetramat (BT). Thiophanate-methyl converted to carbendazim during extraction, resulting in low recovery (Singh et al., 2007). However, the repeatability for these compounds was acceptable (RSD ≤ 20%).
    - Similarly, the GC-MS/MS method has high accuracy, ranging from 164 substances (83.2% for OT at 10 µg/kg) to 190 (96.4% for BT at 100 µg/kg), which were in the recovery range of 70-120%. Moreover, there was no compound with a less than 30% recovery. Despite the ME

difference between teas, the use of matrix-matched curves, using a mixture of matrices, has compensated for the MEs.

- Pesticide residues assessment for 106 teas showed that 26 tea samples (24.6%) were containing at least one pesticide noncompliance, with 43 pesticide residue noncompliances. Among them, black tea had the lowest number of detected pesticides and the number of noncompliance residues. Organic teas, of which 74% of samples did not contain pesticides, and 26% detected compliant pesticide residues were considered safe for consumers. The most frequently detected pesticides were neonicotinoids, synthetic pyrethroids, and triazole fungicides. In terms of origin in this study, Taiwan had the most pesticide-contaminated samples with 83.3%, following by China (73.7%), Vietnam (64.7%), and India (Darjeeling) (55.0%).

In conclusion, an accurate, robust, precis and reliable method was validated according to SANTE/11945/2015 to determine 397 pesticide residues (captafol, chlorothalonil, and folpet unstable) in several types of tea, including white, green, oolong, and black teas. The limits of quantifications (LOQs) for almost of compounds were at or below 10 μg/kg. In total, there were 395 compounds (accounting of 99.5%) that met the EU MRL regulations. Number of compounds that met recoveries 70-120% ranged from 172 (86%) to 188 ones (94%) for UPLC-MS/MS; and from 164 (83.2%) to 190 ones (96.4%) for GC-MS/MS respectively.

6.2. Perspectives

- In GC, matrix-matched calibration curves on a mixture of four types of teas, according to SANTE/11945/2015. Although this is preferable to the use of calibration standards in solvent, compared to exact matrix matching, it is likely that the calibration will be less accurate. For more accuracy, 3 types of matrix-matched calibration curves should be apply for each matrix, one for oolong tea, one for black tea, and one for both green tea and white tea.
- Some pesticides are unstable and have low recoveries, *e.g.*, cyromazine, thidiazuron, hydramethylnon, pymetrozine, acequinocyl, captan, endrin aldehyde, captafol, chlorothalonil, and folpet. Thus, they must be analyzed by different methods. For instance, cyromazine is a polar compound and should be analysed by quick polar pesticides method (QuPPe). Captan, folpet, and captafol show a tendency to thermally degrade within the hot GC-liner, with tetrahydrophthalimide (THPI) and phthalimide (PI) showing up as additional peaks. Thus, LC-MS/MS was recommend for testing these compounds and their metabolites (EURL-SRM - Analytical Observations Report). The susceptibility of chlorothalonil to losses depends on the pH value during extraction and clean-up. In SPE clean-up step, PSA sorbent is the most critical step for chlorothalonil losses as it causes a considerable pH increment. Hence, the sample is acidified to pH ~ 1 with sulfuric acid before extracting with QuEChERS (EURL-SRM for chlorothalonil).
- For sample preparations, toluene was used to elute pesticides out of SPE cartridge. However, toluene is a very toxic solvent for human health and the environment. Therefore, more experiments are needed to replace or reduce the use of this solvent. In some investigated experiments, if touluene was removed from the eluate, 70% of 400 compounds achieved recoveries within 70 – 120%.

- Matrix effect on GC-MS/MS is much more complex than LC-MS/MS. It is possible that matrix effect is combined by both ion suppression and ion enhancement. Therefore, more experiments are needed to understand the mechanisms of matrix effect in GC-MS/MS. For instance, if standard solutions could be loaded directly to mass spectrometer, we could distinguish the MEs caused by injection port, column, and ion sources. Furthermore, it is necessary to compare ME with other difficult matrices, such as pepper and coffee.
- These methods could be improved for analyzing pesticide residues in soil, tea liquors …
- It could be applied of these methods in a way of regulation for official control of pesticide residues in tea. However, a complex procedure must be pursued to certify these methods as official methods.
- With these methods, it could be made the tea reference materials for ―non detected pesticides" also ―detected pesticides". However, it requires the cooperation of many laboratories to jointly validate these methods on the same tea.
- These methods will be applied to control pesticide residues in tea in Vietnam, contributing to protecting consumer‘ health and supporting export.

Appendix figure

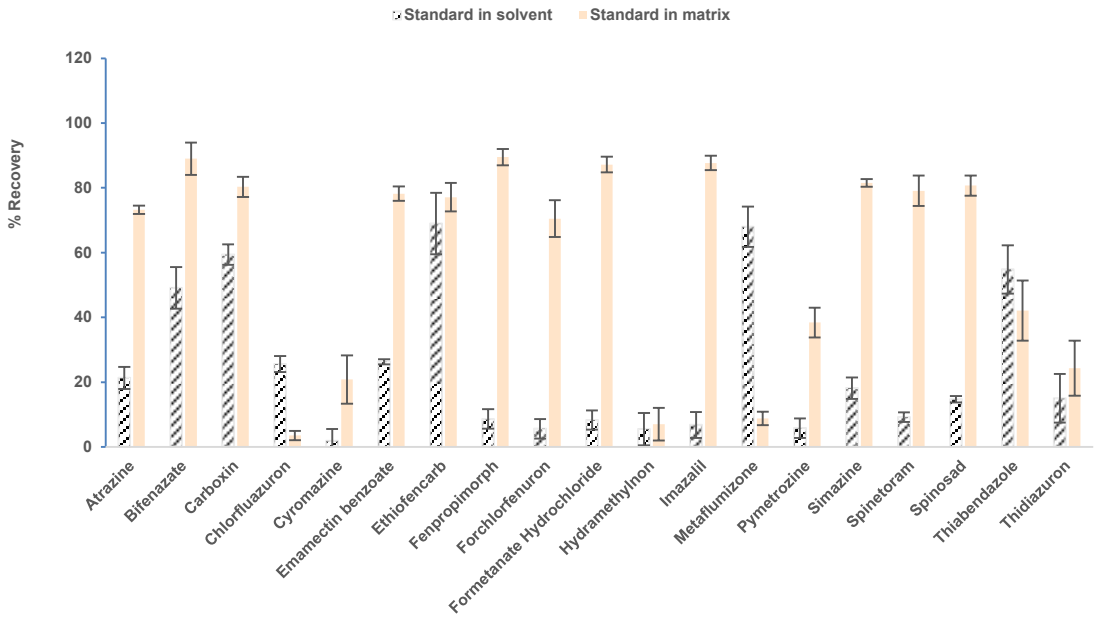

Fig. A-1. Recoveries of strong interacting pesticides (spiked at 50 µg/L) with GCB sorbent (chapter 3)

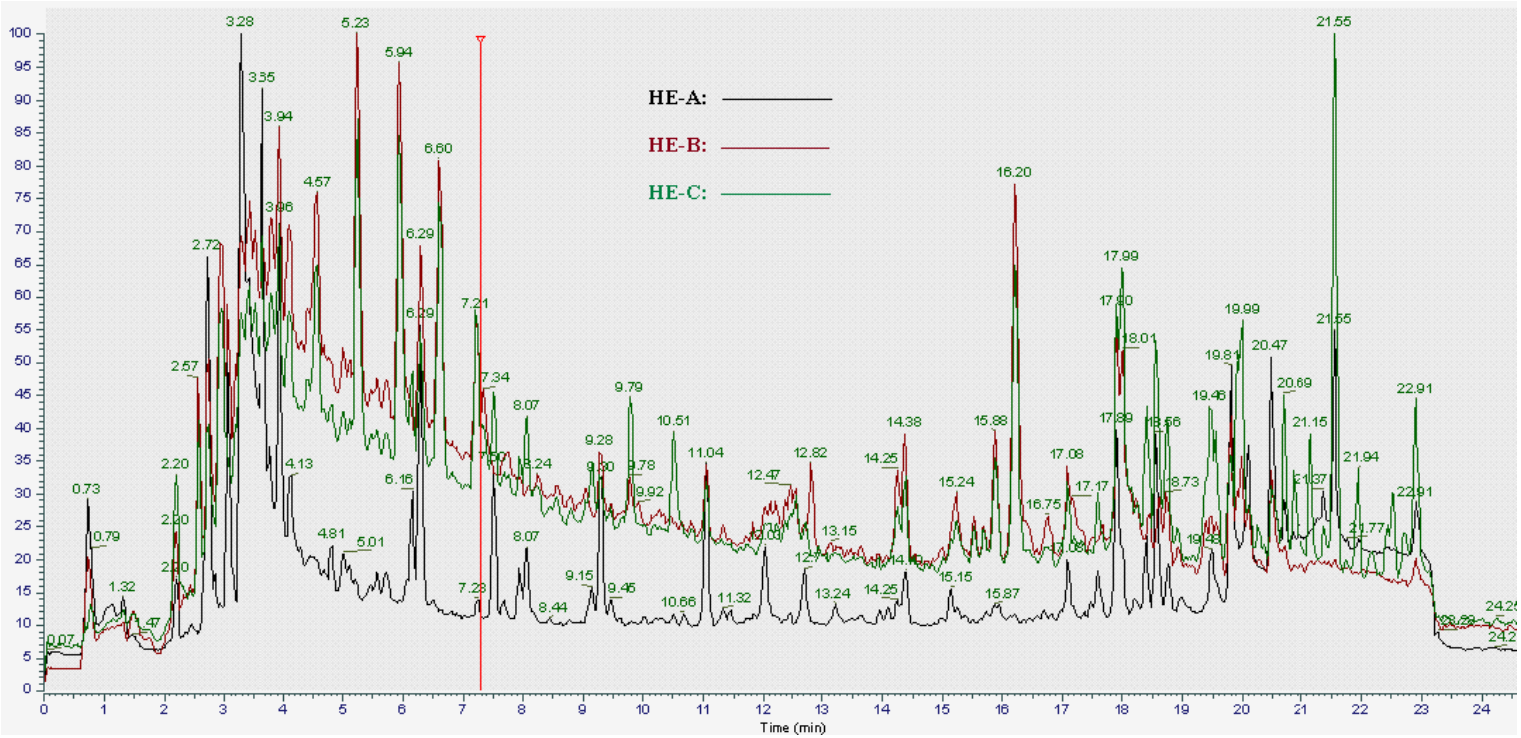

Fig. A-2. Example of total ion chromatogram (TIC) of blank green tea samples obtained from three extraction methods (HE-A: study method; HE-B: AOAC 2007.01 method; HE-C: EN 15662 method) (Chapter 3).

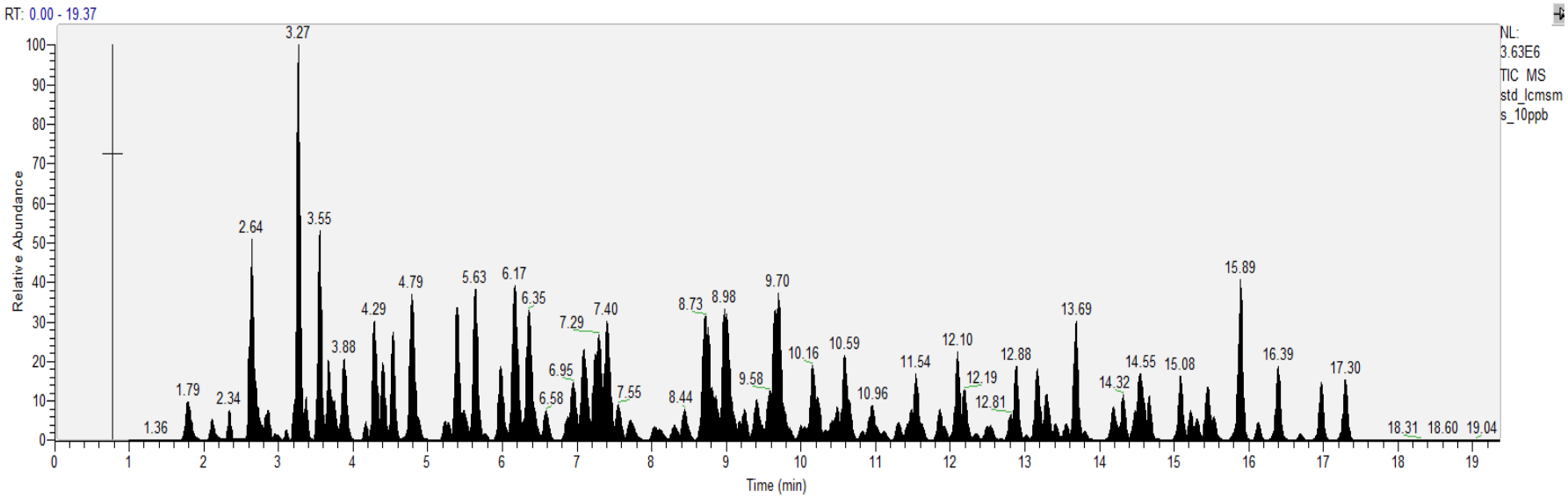

Fig. A-3. The UPLC-MS/MS TIC chromatogram of 200 pesticide standards at 10 µg/L.

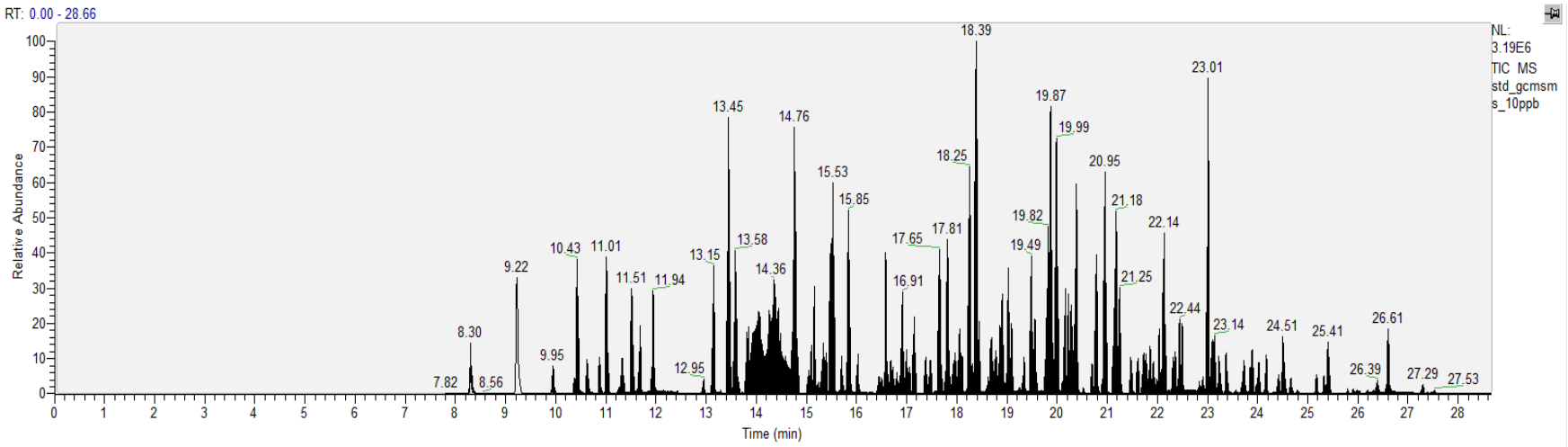

Fig. A-4. The GC-MS/MS TIC chromatogram of 203 pesticide standards at 10 µg/L (including 2 surrogates and 1 internal standard).

Appendix table

Table A-1. The Codex MRLs for pesticides in tea (Codex MRLs).

#	Compound	MRL, mg/kg
1	Bifenthrin	30
2	Chlorfenapyr	60
3	Chlorpyrifos	2
4	Clothianidin	0.7
5	Cypermethrins	15
6	Deltamethrin	5
7	Dicofol	40
8	Endosulfan	10
9	Etoxazole	15
10	Fenpropathrin	3
11	Fenpyroximate	8
12	Flubendiamide	50
13	Flufenoxuron	20
14	Hexythiazox	15
15	Imidacloprid	50
16	Indoxacarb	5
17	Methidathion	0.5
18	Paraquat	0.2
19	Permethrin	20
20	Propargite	5
21	Pyraclostrobin	6
22	Spiromesifen	70
23	Thiamethoxam	20

Table A-2. The EU MRLs for pesticides in tea (EU MRL, 2019).

#	Name	MRL
1	1,1-dichloro-2,2-bis(4-ethylphenyl)ethane	0.1
2	1,2-dibromoethane (ethylene dibromide)	0.02
3	1,2-dichloroethane (ethylene dichloride)	0.02
4	1,3-Dichloropropene	0.05
5	1-methylcyclopropene	0.05
6	1-Naphthylacetamide and 1-naphthylacetic acid (sum of 1-naphthylacetamide and 1-naphthylacetic acid and its salts, expressed as 1-naphythlacetic acid)	0.1
7	2,4,5-T (sum of 2,4,5-T, its salts and esters, expressed as 2,4,5-T)	0.05
8	2,4-DB (sum of 2,4-DB, its salts, its esters and its conjugates, expressed as 2,4-DB)	0.05
9	2,4-D (sum of 2,4-D, its salts, its esters and its conjugates, expressed as 2,4-D)	0.1
10	2,5-Dichlorobenzoic acid methylester	0.01
11	2-amino-4-methoxy-6-(trifluormethyl)-1,3,5-triazine (AMTT), resulting from the use of tritosulfuron	0.01
12	2-naphthyloxyacetic acid	0.05
13	2-phenylphenol (sum of 2-phenylphenol and its conjugates, expressed as 2-phenylphenol)	0.05
14	3-decen-2-one	0.1
15	8-hydroxyquinoline (sum of 8-hydroxyquinoline and its salts, expressed as 8-hydroxyquinoline)	0.01
16	Abamectin (sum of avermectin B1a, avermectin B1b and delta-8,9 isomer of avermectin B1a, expressed as avermectin B1a)	0.05
17	Acephate	0.05
18	Acequinocyl	0.02
19	Acetamiprid	0.05
20	Acetochlor	0.05
21	Acibenzolar-S-methyl (sum of acibenzolar-S-methyl and acibenzolar acid (free and conjugated), expressed as acibenzolar-S-methyl)	0.05
22	Aclonifen	0.05
23	Acrinathrin	0.05
24	Alachlor	0.05
25	Aldicarb (sum of aldicarb, its sulfoxide and its sulfone, expressed as aldicarb)	0.05
26	Aldrin and Dieldrin (Aldrin and dieldrin combined expressed as dieldrin)	0.02
27	Ametoctradin	0.01
28	Amidosulfuron	0.05
29	Aminopyralid	0.02
30	Amisulbrom	0.01
31	Amitraz (amitraz including the metabolites containing the 2,4 - dimethylaniline moiety expressed as amitraz)	0.1
32	Amitrole	0.05
33	Anilazine	0.05
34	Anthraquinone	0.02
35	Aramite	0.1

36	Asulam	0.1
37	Atrazine	0.1
38	Azadirachtin	0.01
39	Azimsulfuron	0.05
40	Azinphos-ethyl	0.05
41	Azinphos-methyl	0.1
42	Azocyclotin and Cyhexatin (sum of azocyclotin and cyhexatin expressed as cyhexatin)	0.05
43	Azoxystrobin	0.05
44	Barban	0.05
45	Beflubutamid	0.05
46	Benalaxyl including other mixtures of constituent isomers including benalaxyl-M (sum of isomers)	0.1
47	Benfluralin	0.1
48	Bensulfuron-methyl	0.05
49	Bentazone (Sum of bentazone, its salts and 6-hydroxy (free and conjugated) and 8-hydroxy bentazone (free and conjugated), expressed as bentazone)	0.1
50	Benthiavalicarb (Benthiavalicarb-isopropyl(KIF-230 R-L) and its enantiomer (KIF-230 S-D) and its diastereomers(KIF-230 S-L and KIF-230 R-D), expressed as benthiavalicarb-isopropyl)	0.05
51	Benzalkonium chloride (mixture of alkylbenzyldimethylammonium chlorides with alkyl chain lengths of C8, C10, C12, C14, C16 and C18)	0.1
52	Benzovindiflupyr	0.05
53	Bifenazate (sum of bifenazate plus bifenazate-diazene expressed as bifenazate)	0.1
54	Bifenox	0.05
55	Bifenthrin (sum of isomers)	30
56	Biphenyl	0.05
57	Bispyribac	0.05
58	Bitertanol (sum of isomers)	0.05
59	Bixafen	0.01
60	Bone oil	0.01
61	Boscalid	0.01
62	Bromadiolone	0.01
63	Bromide ion	70
64	Bromophos-ethyl	0.05
65	Bromopropylate	0.05
66	Bromoxynil and its salts, expressed as bromoxynil	0.05
67	Bromuconazole (sum of diasteroisomers)	0.05
68	Bupirimate	0.05
69	Buprofezin	0.05
70	Butralin	0.05
71	Butylate	0.05
72	Cadusafos	0.01
73	Camphechlor (Toxaphene)	0.05
74	Captafol	0.1
75	Captan (Sum of captan and THPI, expressed as captan)	0.1
76	Carbaryl	0.05

77	Carbendazim and benomyl (sum of benomyl and carbendazim expressed as carbendazim)	0.1
78	Carbetamide (sum of carbetamide and its S isomer)	0.05
79	Carbofuran (sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran)	0.05
80	Carbon monoxide	0.01
81	Carboxin (carboxin plus its metabolites carboxin sulfoxide and oxycarboxin (carboxin sulfone), expressed as carboxin)	0.1
82	Carfentrazone-ethyl (determined as carfentrazone and expressed as carfentrazone-ethyl)	0.02
83	Cartap	0.1
84	Chlorantraniliprole (DPX E-2Y45)	0.02
85	Chlorbenside	0.1
86	Chlorbufam	0.05
87	Chlordane (sum of cis- and trans-chlordane)	0.02
88	Chlordecone	0.02
89	Chlorfenapyr	50
90	Chlorfenson	0.1
91	Chlorfenvinphos	0.05
92	Chloridazon (sum of chloridazon and chloridazon-desphenyl, expressed as chloridazon)	0.1
93	Chlormequat (sum of chlormequat and its salts, expressed as chlormequat-chloride)	0.05
94	Chlorobenzilate	0.1
95	Chloropicrin	0.025
96	Chlorothalonil	0.05
97	Chlorotoluron	0.05
98	Chloroxuron	0.05
99	Chlorpropham	0.05
100	Chlorpyrifos	2
101	Chlorpyrifos-methyl	0.05
102	Chlorsulfuron	0.05
103	Chlorthal-dimethyl	0.05
104	Chlorthiamid	0.05
105	Chlozolinate	0.05
106	Chromafenozide	0.02
107	Cinidon-ethyl (sum of cinidon ethyl and its E-isomer)	0.1
108	Clethodim (sum of Sethoxydim and Clethodim including degradation products calculated as Sethoxydim)	0.1
109	Clodinafop and its S-isomers and their salts, expressed as clodinafop	0.1
110	Clofentezine	0.05
111	Clomazone	0.05
112	Clopyralid	0.5
113	Clothianidin	0.7
114	Copper compounds (Copper)	40
115	Cyanamide including salts expressed as cyanamide	0.01
116	Cyantraniliprole	0.05

117	Cyazofamid	0.05
118	Cyclanilide	0.1
119	Cyclaniliprole	0.05
120	Cycloxydim including degradation and reaction products which can be determined as 3-(3-thianyl)glutaric acid S-dioxide (BH 517-TGSO2) and/or 3-hydroxy-3-(3-thianyl)glutaric acid S-dioxide (BH 517-5-OH-TGSO2) or methyl esters thereof, calculated in total as cycloxydim	0.05
121	Cyflufenamid: sum of cyflufenamid (Z-isomer) and its E-isomer	0.05
122	Cyfluthrin (cyfluthrin including other mixtures of constituent isomers (sum of isomers))	0.1
123	Cyhalofop-butyl	0.1
124	Cymoxanil	0.1
125	Cypermethrin (cypermethrin including other mixtures of constituent isomers (sum of isomers))	0.5
126	Cyproconazole	0.05
127	Cyprodinil	0.1
128	Cyromazine	0.1
129	Dalapon	0.1
130	Daminozide (sum of daminozide and 1,1-dimethyl-hydrazine (UDHM), expressed as daminozide)	0.1
131	Dazomet (Methylisothiocyanate resulting from the use of dazomet and metam)	0.02
132	DDT (sum of p,p′-DDT, o,p′-DDT, p-p′-DDE and p,p′-TDE (DDD) expressed as DDT)	0.2
133	Deltamethrin (cis-deltamethrin)	5
134	Denathonium benzoate	0.05
135	Desmedipham	0.05
136	Di-allate (sum of isomers)	0.05
137	Diazinon	0.05
138	Dicamba	0.05
139	Dichlobenil	0.05
140	Dichlorprop (Sum of dichlorprop (including dichlorprop-P), its salts, esters and conjugates, expressed as dichlorprop	0.1
141	Dichlorvos	0.02
142	Diclofop (sum diclofop-methyl and diclofop acid expressed as diclofop-methyl)	0.05
143	Dicloran	0.05
144	Dicofol (sum of p, p′ and o,p′ isomers)	20
145	Didecyldimethylammonium chloride (mixture of alkyl-quaternary ammonium salts with alkyl chain lengths of C8, C10 and C12)	0.1
146	Diethofencarb	0.05
147	Difenoconazole	0.05
148	Diflubenzuron	0.05
149	Diflufenican	0.05
150	Difluoroacetic acid (DFA)	0.1
151	Dimethachlor	0.05
152	Dimethenamid including other mixtures of constituent isomers including dimethenamid-P (sum of isomers)	0.05
153	Dimethipin	0.1

154	Dimethoate	0.05
155	Dimethomorph (sum of isomers)	0.05
156	Dimoxystrobin	0.05
157	Diniconazole (sum of isomers)	0.05
158	Dinocap (sum of dinocap isomers and their corresponding phenols expressed as dinocap)	0.1
159	Dinoseb (sum of dinoseb, its salts, dinoseb-acetate and binapacryl, expressed as dinoseb)	0.1
160	Dinoterb (sum of dinoterb, its salts and esters, expressed as dinoterb)	0.05
161	Dioxathion (sum of isomers)	0.05
162	Diphenylamine	0.05
163	Diquat	0.05
164	Disulfoton (sum of disulfoton, disulfoton sulfoxide and disulfoton sulfone expressed as disulfoton)	0.05
165	Dithianon	0.01
166	Dithiocarbamates (dithiocarbamates expressed as CS2, including maneb, mancozeb, metiram, propineb, thiram and ziram)	0.1
167	Diuron	0.05
168	DNOC	0.05
169	Dodemorph	0.01
170	Dodine	0.05
171	Emamectin benzoate B1a, expressed as emamectin	0.02
172	Endosulfan (sum of alpha- and beta-isomers and endosulfan-sulphate expresses as endosulfan)	30
173	Endrin	0.01
174	Epoxiconazole	0.05
175	EPTC (ethyl dipropylthiocarbamate)	0.05
176	Ethalfluralin	0.01
177	Ethametsulfuron-methyl	0.02
178	Ethephon	0.1
179	Ethion	3
180	Ethirimol	0.05
181	Ethofumesate (Sum of ethofumesate, 2-keto–ethofumesate, open-ring-2-keto-ethofumesate and its conjugate, expressed as ethofumesate)	0.1
182	Ethoprophos	0.02
183	Ethoxyquin	0.1
184	Ethoxysulfuron	0.05
185	Ethylene oxide (sum of ethylene oxide and 2-chloro-ethanol expressed as ethylene oxide)	0.1
186	Etofenprox	0.05
187	Etoxazole	15
188	Etridiazole	0.05
189	Famoxadone	0.05
190	Fenamidone	0.05
191	Fenamiphos (sum of fenamiphos and its sulphoxide and sulphone expressed as fenamiphos)	0.05
192	Fenarimol	0.05
193	Fenazaquin	10
194	Fenbuconazole	0.05

195	Fenbutatin oxide	0.05
196	Fenchlorphos (sum of fenchlorphos and fenchlorphos oxon expressed as fenchlorphos)	0.1
197	Fenhexamid	0.05
198	Fenitrothion	0.05
199	Fenoxaprop-P	0.1
200	Fenoxycarb	0.05
201	Fenpicoxamid	0.05
202	Fenpropathrin	2
203	Fenpropidin (sum of fenpropidin and its salts, expressed as fenpropidin)	0.05
204	Fenpropimorph (sum of isomers)	0.05
205	Fenpyrazamine	0.05
206	Fenpyroximate	8
207	Fenthion (fenthion and its oxigen analogue, their sulfoxides and sulfone expressed as parent)	0.05
208	Fentin (fentin including its salts, expressed as triphenyltin cation)	0.1
209	Fenvalerate (any ratio of constituent isomers (RR, SS, RS & SR) including esfenvalerate)	0.1
210	Fipronil (sum fipronil + sulfone metabolite (MB46136) expressed as fipronil)	0.005
211	Flazasulfuron	0.05
212	Flonicamid (sum of flonicamid, TFNA and TFNG expressed as flonicamid)	0.1
213	Florasulam	0.05
214	Florpyrauxifen-benzyl	0.05
215	Fluazifop-P (sum of all the constituent isomers of fluazifop, its esters and its conjugates, expressed as fluazifop)	0.05
216	Fluazinam	0.1
217	Flubendiamide	0.02
218	Flucycloxuron	0.05
219	Flucythrinate (flucythrinate including other mixtures of constituent isomers (sum of isomers))	0.05
220	Fludioxonil	0.05
221	Flufenacet (sum of all compounds containing the N fluorophenyl-N-isopropyl moiety expressed as flufenacet equivalent)	0.05
222	Flufenoxuron	15
223	Flufenzin	0.1
224	Flumetralin	0.05
225	Flumioxazine	0.1
226	Fluometuron	0.02
227	Fluopicolide	0.02
228	Fluopyram	0.05
229	Fluoride ion	350
230	Fluoroglycofene	0.02
231	Fluoxastrobin (sum of fluoxastrobin and its Z-isomer)	0.05
232	Flupyradifurone	0.05
233	Flupyrsulfuron-methyl	0.1
234	Fluquinconazole	0.05

235	Flurochloridone (sum of cis- and trans- isomers)	0.05
236	Fluroxypyr (sum of fluroxypyr, its salts, its esters, and its conjugates, expressed as fluroxypyr)	0.05
237	Flurprimidole	0.05
238	Flurtamone	0.05
239	Flusilazole	0.05
240	Flutianil	0.05
241	Flutolanil	0.05
242	Flutriafol	0.05
243	Fluxapyroxad	0.01
244	Folpet (sum of folpet and phtalimide, expressed as folpet)	0.1
245	Fomesafen	0.05
246	Foramsulfuron	0.05
247	Forchlorfenuron	0.05
248	Formetanate: Sum of formetanate and its salts expressed as formetanate(hydrochloride)	0.05
249	Formothion	0.05
250	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl)	5
251	Fosthiazate	0.05
252	Fuberidazole	0.05
253	Furfural	1
254	Glufosinate-ammonium (sum of glufosinate, its salts, MPP and NAG expressed as glufosinate equivalents)	0.1
255	Glyphosate	2
256	Guazatine (guazatine acetate, sum of components)	0.05
257	Halauxifen-methyl (sum of halauxifen-methyl and X11393729 (halauxifen), expressed as halauxifen-methyl)	0.1
258	Halosulfuron methyl	0.02
259	Haloxyfop (Sum of haloxyfop, its esters, salts and conjugates expressed as haloxyfop (sum of the R- and S- isomers at any ratio))	0.05
260	Heptachlor (sum of heptachlor and heptachlor epoxide expressed as heptachlor)	0.02
261	Hexachlorobenzene	0.02
262	Hexachlorocyclohexane (HCH), alpha-isomer	0.01
263	Hexachlorocyclohexane (HCH), beta-isomer	0.01
264	Hexaconazole	0.05
265	Hexythiazox	4
266	Hymexazol	0.05
267	Imazalil	0.1
268	Imazamox (Sum of imazamox and its salts, expressed as imazamox)	0.1
269	Imazapic	0.01
270	Imazaquin	0.05
271	Imazosulfuron	0.05
272	Imidacloprid	0.05
273	Indolylacetic acid	0.1
274	Indolylbutyric acid	0.1
275	Indoxacarb (sum of indoxacarb and its R enantiomer)	5

276	Iodosulfuron-methyl (sum of iodosulfuron-methyl and its salts, expressed as iodosulfuron-methyl)	0.05
277	Ioxynil (sum of ioxynil and its salts, expressed as ioxynil)	0.05
278	Ipconazole	0.02
279	Iprodione	0.05
280	Iprovalicarb	0.05
281	Isofetamid	0.05
282	Isoprothiolane	0.01
283	Isoproturon	0.05
284	Isopyrazam	0.01
285	Isoxaben	0.02
286	Isoxaflutole (sum of isoxaflutole and its diketonitrile-metabolite, expressed as isoxaflutole)	0.1
287	Kresoxim-methyl	0.05
288	Lactofen	0.05
289	Lambda-cyhalothrin (includes gamma-cyhalothrin) (sum of R,S and S,R isomers)	0.01
290	Lenacil	0.1
291	Lindane (Gamma-isomer of hexachlorocyclohexane (HCH))	0.01
292	Linuron	0.05
293	Lufenuron (any ratio of constituent isomers)	0.05
294	Malathion (sum of malathion and malaoxon expressed as malathion)	0.5
295	Maleic hydrazide	0.5
296	Mandestrobin	0.05
297	Mandipropamid (any ratio of constituent isomers)	0.05
298	MCPA and MCPB (MCPA, MCPB including their salts, esters and conjugates expressed as MCPA)	0.1
299	Mecarbam	0.05
300	Mecoprop (sum of mecoprop-p and mecoprop expressed as mecoprop)	0.1
301	Mefentrifluconazole	0.05
302	Mepanipyrim	0.05
303	Mepiquat (sum of mepiquat and its salts, expressed as mepiquat chloride)	0.1
304	Mepronil	0.05
305	Meptyldinocap (sum of 2,4 DNOPC and 2,4 DNOP expressed as meptyldinocap)	0.1
306	Mercury compounds (sum of mercury compounds expressed as mercury)	0.02
307	Mesosulfuron-methyl	0.05
308	Mesotrione	0.05
309	Metaflumizone (sum of E- and Z- isomers)	0.1
310	Metalaxyl and metalaxyl-M (metalaxyl including other mixtures of constituent isomers including metalaxyl-M (sum of isomers))	0.05
311	Metaldehyde	0.1
312	Metamitron	0.1
313	Metazachlor (Sum of metabolites 479M04, 479M08 and 479M16, expressed as metazachlor)	0.1
314	Metconazole (sum of isomers)	0.1
315	Methabenzthiazuron	0.05

316	Methacrifos	0.05
317	Methamidophos	0.05
318	Methidathion	0.1
319	Methiocarb (sum of methiocarb and methiocarb sulfoxide and sulfone, expressed as methiocarb)	0.1
320	Methomyl	0.05
321	Methoprene	0.1
322	Methoxychlor	0.1
323	Methoxyfenozide	0.05
324	Metolachlor and S-metolachlor (metolachlor including other mixtures of constituent isomers including S-metolachlor (sum of isomers))	0.05
325	Metosulam	0.05
326	Metrafenone	0.05
327	Metribuzin	0.1
328	Metsulfuron-methyl	0.05
329	Mevinphos (sum of E- and Z-isomers)	0.02
330	Milbemectin (sum of milbemycin A4 and milbemycin A3, expressed as milbemectin)	0.1
331	Molinate	0.05
332	Monocrotophos	0.05
333	Monolinuron	0.05
334	Monuron	0.05
335	Myclobutanil	0.05
336	Napropamide	0.05
337	Nicosulfuron	0.05
338	Nicotine	0.6
339	Nitrofen	0.02
340	Novaluron	0.01
341	Omethoate	0.05
342	Orthosulfamuron	0.01
343	Oryzalin	0.05
344	Oxadiargyl	0.05
345	Oxadiazon	0.05
346	Oxadixyl	0.02
347	Oxamyl	0.05
348	Oxasulfuron	0.05
349	Oxathiapiprolin	0.05
350	Oxycarboxin	0.05
351	Oxydemeton-methyl (sum of oxydemeton-methyl and demeton-S-methylsulfone expressed as oxydemeton-methyl)	0.05
352	Oxyfluorfen	0.05
353	Paclobutrazol (sum of constituent isomers)	0.05
354	Paraffin oil (CAS 64742-54-7)	0.01
355	Paraquat	0.05
356	Parathion	0.1
357	Parathion-methyl (sum of Parathion-methyl and paraoxon-methyl expressed as Parathion-methyl)	0.05
358	Penconazole (sum of constituent isomers)	0.05

359	Pencycuron	0.05
360	Pendimethalin	0.05
361	Penoxsulam	0.05
362	Penthiopyrad	0.02
363	Permethrin (sum of isomers)	0.1
364	Pethoxamid	0.05
365	Petroleum oils (CAS 92062-35-6)	0.01
366	Phenmedipham	0.05
367	Phenothrin (phenothrin including other mixtures of constituent isomers (sum of isomers))	0.05
368	Phorate (sum of phorate, its oxygen analogue and their sulfones expressed as phorate)	0.05
369	Phosalone	0.05
370	Phosmet (phosmet and phosmet oxon expressed as phosmet)	0.1
371	Phosphamidon	0.02
372	Phosphane and phosphide salts (sum of phosphane and phosphane generators (relevant phosphide salts), determined and expressed as phosphane)	0.02
373	Phoxim	0.1
374	Picloram	0.01
375	Picolinafen	0.05
376	Picoxystrobin	0.05
377	Pinoxaden	0.05
378	Pirimicarb	0.05
379	Pirimiphos-methyl	0.05
380	Prochloraz (sum of prochloraz and its metabolites containing the 2,4,6-Trichlorophenol moiety expressed as prochloraz)	0.1
381	Procymidone	0.05
382	Profenofos	0.05
383	Profoxydim	0.05
384	Prohexadione (prohexadione (acid) and its salts expressed as prohexadione-calcium)	0.05
385	Propachlor: oxalinic derivate of propachlor, expressed as propachlor	0.1
386	Propamocarb (Sum of propamocarb and its salts, expressed as propamocarb)	0.05
387	Propanil	0.05
388	Propargite	10
389	Propham	0.05
390	Propiconazole (sum of isomers)	0.05
391	Propineb (expressed as propilendiamine)	0.1
392	Propisochlor	0.05
393	Propoxur	0.1
394	Propoxycarbazone (propoxycarbazone, its salts and 2-hydroxypropoxycarbazone expressed as propoxycarbazone)	0.1
395	Propyzamide	0.05
396	Proquinazid	0.05
397	Prosulfocarb	0.05
398	Prosulfuron	0.05

399	Prothioconazole: prothioconazole-desthio (sum of isomers)	0.05
400	Pymetrozine	0.1
401	Pyraclostrobin	0.1
402	Pyraflufen-ethyl (Sum of pyraflufen-ethyl and pyraflufen, expressed as pyraflufen-ethyl)	0.1
403	Pyrasulfotole	0.02
404	Pyrazophos	0.05
405	Pyrethrins	0.5
406	Pyridaben	0.05
407	Pyridalyl	0.02
408	Pyridate (sum of pyridate, its hydrolysis product CL 9673 (6-chloro-4-hydroxy-3-phenylpyridazin) and hydrolysable conjugates of CL 9673 expressed as pyridate)	0.05
409	Pyrimethanil	0.05
410	Pyriproxyfen	15
411	Pyroxsulam	0.02
412	Quinalphos	0.05
413	Quinclorac	0.05
414	Quinmerac	0.1
415	Quinoclamine	0.05
416	Quinoxyfen	0.05
417	Quintozene (sum of quintozene and pentachloro-aniline expressed as quintozene)	0.1
418	Quizalofop (sum of quizalofop, its salts, its esters (including propaquizafop) and its conjugates, expressed as quizalofop (any ratio of constituent isomers))	0.05
419	Resmethrin (resmethrin including other mixtures of consituent isomers (sum of isomers))	0.05
420	Rimsulfuron	0.05
421	Rotenone	0.02
422	Saflufenacil (sum of saflufenacil, M800H11 and M800H35, expressed as saflufenacil)	0.03
423	Silthiofam	0.05
424	Simazine	0.05
425	Sodium 5-nitroguaiacolate, sodium o-nitrophenolate and sodium p-nitrophenolate (Sum of sodium 5-nitroguaiacolate, sodium o-nitrophenolate and sodium p-nitrophenolate, expressed as sodium 5-nitroguaiacolate)	0.15
426	Spinetoram (XDE-175)	0.1
427	Spinosad (spinosad, sum of spinosyn A and spinosyn D)	0.1
428	Spirodiclofen	0.05
429	Spiromesifen	50
430	Spirotetramat and its 4 metabolites BYI08330-enol, BYI08330-ketohydroxy, BYI08330-monohydroxy, and BYI08330 enol-glucoside, expressed as spirotetramat	0.1
431	Spiroxamine (sum of isomers)	0.05
432	Sulcotrione	0.1
433	Sulfosulfuron	0.05
434	Sulfoxaflor (sum of isomers)	0.05
435	Sulfuryl fluoride	0.02

436	Tau-Fluvalinate	0.01
437	Tebuconazole	0.05
438	Tebufenozide	0.05
439	Tebufenpyrad	0.05
440	Tecnazene	0.05
441	Teflubenzuron	0.05
442	Tefluthrin	0.05
443	Tembotrione	0.05
444	TEPP	0.02
445	Tepraloxydim (sum of tepraloxydim and its metabolites that can be hydrolysed either to the moiety 3-(tetrahydro-pyran-4-yl)-glutaric acid or to the moiety 3-hydroxy-(tetrahydro-pyran-4-yl)-glutaric acid, expressed as tepraloxydim)	0.1
446	Terbufos	0.01
447	Terbuthylazine	0.05
448	Tetraconazole	0.02
449	Tetradifon	0.05
450	Thiabendazole	0.05
451	Thiacloprid	10
452	Thiamethoxam	20
453	Thifensulfuron-methyl	0.05
454	Thiobencarb (4-chlorobenzyl methyl sulfone)	0.05
455	Thiodicarb	0.05
456	Thiophanate-methyl	0.1
457	Thiram (expressed as thiram)	0.2
458	Tolclofos-methyl	0.05
459	Tolylfluanid (Sum of tolylfluanid and dimethylaminosulfotoluidide expressed as tolylfluanid)	0.1
460	Topramezone (BAS 670H)	0.02
461	Tralkoxydim (sum of the constituent isomers of tralkoxydim)	0.05
462	Triadimefon	0.05
463	Triadimenol (any ratio of constituent isomers)	0.05
464	Tri-allate	0.1
465	Triasulfuron	0.1
466	Triazophos	0.02
467	Tribenuron-methyl	0.05
468	Trichlorfon	0.05
469	Triclopyr	0.05
470	Tricyclazole	0.05
471	Tridemorph	0.05
472	Trifloxystrobin	0.05
473	Triflumizole: Triflumizole and metabolite FM-6-1(N-(4-chloro-2-trifluoromethylphenyl)-n-propoxyacetamidine), expressed as Triflumizole	0.1
474	Triflumuron	0.05
475	Trifluralin	0.05
476	Triflusulfuron (6-(2,2,2-trifluoroethoxy)-1,3,5-triazine-2,4-diamine (IN-M7222)	0.05

477	Triforine	0.05
478	Trimethyl-sulfonium cation, resulting from the use of glyphosate	0.05
479	Trinexapac (sum of trinexapac (acid) and its salts, expressed as trinexapac)	0.05
480	Triticonazole	0.02
481	Tritosulfuron	0.05
482	Valifenalate	0.02
483	Vinclozolin	0.05
484	Warfarin	0.01
485	Ziram	0.2
486	Zoxamide	0.05

Table A-3. LC and GC multi-residue pesticide kits

#	Catalogue number	Group	Number of compounds
LC multi-residue pesticide kit (Restek 31971 – 100 µg/mL each in acetonitrile)			
1	Restek 31972	Organophosphorus compounds	13
2	Restek 31973	Carbamate/Uron compounds	16
3	Restek 31974	Carbamate/Uron compounds	38
4	Restek 31975	Organonitrogen compounds	63
5	Restek 31976	Organonitrogen compounds	30
6	Restek 31977	Organonitrogen compounds	28
7	Restek 31978	Organonitrogen compounds	7
8	Restek 31979	Organonitrogen compounds	1
9	Restek 31980	Carbamate/Uron compounds	7
10	Restek 31981	Carbamate/Uron compounds	1
GC multi-residue pesticide kit (Restek 32562 – 100 µg/mL each in toluene)			
11	Restek 32563	Organophosphorus compounds	16
12	Restek 32564	Organochlorine compounds	40
13	Restek 32565	Organonitrogen compounds	25
14	Restek 32566	Organonitrogen compounds	28
15	Restek 32567	Organonitrogen compounds	34
16	Restek 32568	Synthetic pyrethroid compounds	18
17	Restek 32569	Herbicide methyl esters	10
18	Restek 32570	Organophosphorus compounds	24
19	Restek 32571	Organophosphorus compounds	8

Table A-4. List of pesticides, method parameters and data validation of UPLC-MS/MS method for green tea (chapter 3)

#	Compound	RT (min)	ESI mode	RF lens (V)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
												10 µg/kg	50 µg/kg	100 µg/kg
1	Acephate	2.31	+	75	184.045 > 143.046 (9)	184.045 > 95.174 (21)	1-200	0.9988	–6.71	0.6	2	92.5 (3.3)	98.1 / 3.5)	99.3 / 3.1)
2	Acetamiprid	3.81	+	117	223 > 126 (20)	223 > 90.1 (35)	1-200	0.9989	–10.2	0.6	2	100.5 (2.4)	100.3 (2.2)	99.4 (3)
3	Acibenzolar-S-methyl	9.62	+	89	211 > 136.1 (30)	211 > 140 (24)	1-200	0.9983	–10.7	0.6	2	90.2 (5.4)	85 (3.2)	87.6 (3.5)
4	Aldicarb	4.47	+	58	208.152 > 116.1 (10)	208.152 > 89.15 (10)	1-200	0.9992	–12.7	0.6	2	101.4 (3.5)	101.3 (2.4)	101 (3.2)
5	Aldicarb sulfoxide	2.72	+	59	207.1 > 132.04 (8)	207.1 > 89.15 (10)	1-200	0.999	–11.7	0.6	2	96.3 (6.9)	96.2 (5)	98.7 (6.2)
6	Aldicarb-sulfone	2.85	+	81	240.175 > 86.273 (23)	240.175 > 63.325 (31)	1-200	0.999	–14.1	0.6	2	99.8 (3.2)	99.9 (3.1)	101.4 (3.6)
7	Ametryn	7.16	+	173	228.1 > 186.1 (20)	228.1 > 138.1 (23)	1-200	0.9999	–6.08	0.6	2	97.4 (4.4)	97.8 (2.6)	96.3 (2.8)
8	Aminocarb	2.62	+	105	209.1 > 137.1 (23)	209.1 > 152.1 (15)	1-100	0.9992	–57.9	0.6	2	107.3 (6.3)	105.5 (4)	103.9 (4.1)
9	Amitraz	12.22	+	154	294.2 > 148.3 (16)	294.2 > 91.2 (40)	1-200	0.9998	–8.82	0.6	2	97.3 (4.6)	97 (2.8)	99.3 (3.7)
10	Atrazine	7	+	38	216.1 > 174.063 (20)	216.1 > 104.164 (31)	1-100	0.9993	–16.8	0.6	2	99.9 (2.8)	98.9 (2.6)	97.3 (2.7)
11	Avermectin (B1a) (*)	17.43	+	77	890.47 > 305.183 (24)	890.47 > 567.28 (14)	1-200	0.9969	–11.0	0.6	2	98.6 (4.2)	91.8 (3.1)	92.1 (4.5)
	Avermectin (B1b) (*)	16.92	+	76	876.5 > 291 (21)	876.5 > 553.4 (13)								
12	Azoxystrobin	9.08	+	144	404.12 > 372.067 (16)	404.12 > 344.076 (27)	1-200	0.9985	–2.47	0.6	2	102 (2.2)	104.5 (2.1)	102.9 (2.6)
13	Benalaxyl	12.23	+	128	326.23 > 148.174 (24)	326.23 > 121.197 (32)	1-100	0.9997	–9.16	0.6	2	99.1 (2.6)	101.6 (3)	100.9 (3.1)
14	Bendiocarb	5.47	+	94	224.175 > 167.126 (10)	224.175 > 109.174 (21)	1-200	0.9988	–11.1	0.6	2	97.9 (2.8)	98.8 (2.9)	99.7 (3)
15	Benzoximate	13.05	+	80	364.05 > 198.937 (9)	364.05 > 105.139 (23)	1-200	0.9995	–11.4	0.6	2	97.6 (3.5)	99.1 (2.4)	98 (6.1)
16	Bifenazate	10.53	+	93	301.2 > 198.1 (5)	301.2 > 152.138 (43)	1-200	0.9984	–9.88	0.6	2	96.1 (23.8)	99.6 (4.4)	99.6 (5.7)
17	Bitertanol	12.92	+	40	338.19 > 269.2 (9)	338.19 > 70.1 (12)	1-200	0.998	–5.78	0.6	2	95.7 (5.2)	92.2 (2.9)	91.8 (3.8)
18	Boscalid	9.55	+	189	343.04 > 307.065 (21)	343.04 > 272.091 (34)	1-200	0.9996	–6.52	0.6	2	95.1 (2.1)	95.8 (2.2)	95.3 (2.3)
19	Bromucanozole (*)	10.19, 11.65	+	178	377.935 > 159.015 (30)	377.935 > 161.018 (31)	1-200	0.9991	–9.16	0.6	2	96.1 (2.7)	96.5 (2.4)	96.6 (3.1)
20	Bupirimate	10.38	+	185	317.21 > 166.143 (27)	317.21 > 272.096 (21)	1-200	0.9998	–7.52	0.6	2	94.1 (2.2)	96.4 (2.2)	95.8 (3.6)
21	Buprofezin	14.36	+	112	306.235 > 106.219 (28)	306.235 > 57.448 (25)	1-200	0.9996	–20.7	0.6	2	98.1 (8.9)	95.6 (4.1)	95 (9.4)
22	Butafenacil	10.76	+	144	492.11 > 331.005 (26)	492.11 > 348.993 (17)	1-200	0.9997	–3.81	0.6	2	96.7 (2.4)	99.9 (2.6)	100.2 (3.4)
23	Butocarboxim	4.37	+	46	213.03 > 75.058 (16)	213.03 > 155.99 (10)	1-100	0.9958	15.7	0.6	2	95.1 (4)	95.4 (3.8)	97.5 (2.6)
24	Butoxycarboxim	2.82	+	75	223.03 > 166 (15)	223.03 > 106.11 (17)	1-200	0.9984	–27.4	0.6	2	99.6 (7.1)	97.8 (4.8)	96.1 (2.9)
25	Carbaryl	6.17	+	82	202.165 > 145.11 (11)	202.165 > 127.152 (31)	1-200	0.9977	–20.5	0.6	2	95.7 (3.8)	98.3 (2.8)	98.7 (2.9)
26	Carbendazim	3.24	+	132	192.1 > 160.1 (20)	192.1 > 105.2 (32)	1-100	0.9963	–53.4	0.6	2	98.9 (9.3)	94.6 (3.5)	93 (5.6)
27	Carbetamide	4.94	+	89	237.1 > 192 (9)	237.1 > 120 (17)	1-200	0.9995	–2.18	0.6	2	97.3 (3)	99.1 (2.7)	99.7 (2.6)
28	Carbofuran	5.45	+	100	222.185 > 165.129 (15)	222.185 > 123.16 (25)	1-200	0.9991	–8.15	0.6	2	101.5 (2.7)	103.2 (2.3)	102.3 (2.9)
29	Carbofuran-3-hydroxy	3.67	+	121	238.2 > 181.1 (12)	238.2 > 163.1 (18)	1-100	0.9982	–14.8	0.6	2	101.1 (3.3)	100.1 (3.4)	98.1 (3.3)
30	Carboxin	6.05	+	111	236.145 > 143.095 (18)	236.145 > 87.224 (28)	1-200	0.9995	–13.0	0.6	2	82.2 (9.9)	77.5 (12.8)	86.4 (3.8)
31	Carfentrazone-ethyl	11.83	+	180	412.1 > 346.1 (23)	412.1 > 366.1 (19)	1-200	0.9977	1.26	0.6	2	100.4 (4)	99.1 (3.7)	97.9 (4.1)
32	Chlorantraniliprole	8.25	+	149	481.88 > 450.948 (17)	481.88 > 283.955 (13)	1-200	0.9996	–0.50	0.6	2	95.9 (2.6)	97.7 (2.6)	97.9 (2.9)
33	Chlorfluazuron	16.87	+	149	539.995 > 382.974 (23)	539.995 > 346.999 (46)	1-200	0.9986	–76.1	0.6	2	110.6 (23.8)	115.3 (6.5)	109.6 (11)

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												10 µg/kg	50 µg/kg	100 µg/kg
34	Chlorotoluron	6.88	+	121	213.18 > 72.31 (21)	213.18 > 140.094 (27)	1-200	0.9996	–4.22	0.6	2	94.4 (2)	97.5 (2.5)	98 (2.7)
35	Chloroxuron	10.5	+	164	291.1 > 72.4 (23)	291.1 > 218.1 (27)	1-200	0.9991	–6.80	0.6	2	96.8 (1.9)	101.7 (2.8)	101.6 (2.8)
36	Clethodim (*)	10.1, 14.01	+	140	360.1 > 164.2 (20)	360.1 > 166.3 (22)	1-200	0.9996	–35.4	0.6	2	95 (15.1)	90.9 (10.5)	91.9 (9)
37	Clofentezine	13.47	+	100	303.061 > 138.06 (11)	303.061 > 102.11 (31)	1-50	0.9973	–33.0	0.6	2	98.6 (9.4)	95.8 (7.3)	98.7 (13.3)
38	Clothianidin	3.55	+	101	250.1 > 169.1 (13)	250.1 > 132.2 (14)	1-200	0.9977	–23.2	0.6	2	95.4 (5.4)	95 (3.7)	96 (4.3)
39	Cyazofamid	11.37	+	103	325 > 108.169 (17)	325 > 217.067 (21)	1-200	0.9993	–4.88	0.6	2	95 (2.1)	94.8 (2.7)	95.8 (3.7)
40	Cycluron	7.56	+	130	199.255 > 89.243 (17)	199.255 > 72.318 (25)	1-200	0.9997	–5.03	0.6	2	92.6 (2.1)	95.1 (2.9)	96.3 (2.8)
41	Cymoxanil	13.06	+	123	199 > 183.93 (16)	199 > 141 (25)	1-200	0.9994	–11.0	0.6	2	100.3 (3.9)	99.1 (2.9)	97.3 (5.9)
42	Cyproconazole (*)	9.78, 10.32	+	150	292.17 > 70.326 (22)	292.17 > 125.121 (30)	1-200	0.9997	–6.48	0.6	2	95.6 (2.7)	94 (2.8)	94.6 (3.2)
43	Cyprodinil	11.06	+	178	226.205 > 93.226 (37)	226.205 > 118.164 (34)	1-200	0.9997	–28.2	0.6	2	94.8 (7.7)	93.5 (5.3)	92.8 (8.7)
44	Desmedipham	8.2	+	101	318.09 > 182.126 (16)	318.09 > 136.142 (29)	1-200	0.9995	–4.64	0.6	2	95.5 (7.2)	95.9 (4.3)	96.1 (7.4)
45	Diclobutrazol	11.79	+	169	328.1 > 70.3 (32)	328.1 > 159 (34)	1-200	0.9992	–9.21	0.6	2	98.6 (3.8)	97.2 (3.2)	97.3 (3.5)
46	Dicrotophos	3.33	+	106	238.055 > 112.235 (15)	238.055 > 193.074 (10)	1-200	0.9989	–29.5	0.6	2	96.1 (3.6)	102.5 (3.2)	101.7 (3.8)
47	Diethofencarb	8.62	+	92	268.2 > 124.163 (35)	268.2 > 180.143 (20)	1-200	0.9996	–4.97	0.6	2	96 (2.6)	95.1 (2.8)	96.6 (2.5)
48	Difenoconazole (*)	13.52, 13.65	+	188	406 > 251.015 (26)	408 > 253 (26)	1-200	0.9997	–13.9	0.6	2	94.8 (4.6)	95.6 (4)	94.5 (6.7)
49	Diflubenzuron	11.6	+	126	311.1 > 157.9 (14)	311.1 > 141.1 (25)	1-200	0.9996	–8.48	0.6	2	97.2 (4.4)	94.7 (2.8)	95.5 (3.4)
50	Dimethoate	3.74	+	83	230.06 > 125.085 (24)	230.06 > 79.24 (33)	1-200	0.9978	–19.8	0.6	2	97.4 (4.2)	100 (3)	98.8 (4.1)
51	Dimethomorph (*)	9.24, 9.86	+	202	388.155 > 301.105 (23)	388.155 > 165.118 (34)	1-200	0.9991	–4.04	0.6	2	95.1 (1.8)	95.5 (2.5)	97.1 (2.4)
52	Dimoxystrobin	11.65	+	105	327.1 > 116.1 (20)	327.1 > 238.1 (13)	1-200	0.9997	–5.41	0.6	2	96.4 (2.2)	99.3 (2.5)	99.2 (2.8)
53	Diniconazole	13.19	+	191	326.155 > 70.303 (27)	326.155 > 159.041 (32)	1-200	0.9986	–12.7	0.6	2	95.5 (4.4)	91.1 (2.9)	91.6 (5.2)
54	Dinotefuran	2.75	+	79	203.11 > 129.16 (12)	203.11 > 114.161 (8)	1-100	0.9991	–14.4	0.6	2	99.1 (9.8)	99 (3.8)	98 (3.6)
55	Dioxacarb	3.69	+	91	224.165 > 123.172 (19)	224.165 > 95.242 (29)	1-100	0.9975	–8.47	0.6	2	110.7 (7.3)	108.2 (5.6)	102.8 (6.6)
56	Diuron	7.77	+	134	233.095 > 72.33 (21)	233.095 > 46.519 (19)	1-200	0.9988	–6.33	0.6	2	95.8 (3)	100.2 (2.8)	100.1 (3)
57	Doramectin	18.14	+	78	916.509 > 331.24 (22)	916.509 > 593.35 (12)	1-200	0.9961	–16.9	0.6	2	102.1 (5.7)	95 (3.9)	94 (7)
58	Emamectin benzoate (B1a) (*)	15.73	+	76	886.505 > 158.19 (39)	886.505 > 82.301 (47)	1-200	0.999	–5.36	0.6	2	75.1 (11.6)	80.5 (5.8)	80.1 (6.3)
	Emamectin benzoate (B1b) (*)	15.13	+	76	872.495 > 158.178 (37)	872.495 > 82.279 (46)								
59	Epoxiconazole	11.04	+	55	330.13 > 121.163 (15)	330.13 > 101.195 (35)	1-200	0.9993	–30.1	0.6	2	98.8 (1.9)	97.8 (2.3)	96.7 (3)
60	Eprinomectin	17.09	+	85	914.469 > 186 (27)	914.469 > 154 (27)	1-200	0.9982	5.45	0.6	2	99.6 (5)	95.9 (4.2)	93.6 (4.7)
61	Etaconazole (*)	10.74, 10.9	+	172	328.1 > 159 (23)	328.1 > 205 (18)	1-200	0.9997	–7.56	0.6	2	94.8 (1.4)	95.3 (2.6)	97 (2.9)
62	Ethiofencarb	6.32	+	86	226.165 > 107.183 (18)	226.165 > 77.279 (45)	1-200	0.9993	–24.2	0.6	2	86.6 (12.9)	84.9 (10.4)	89.4 (7.3)
63	Ethiprole	9.33	+	167	397.015 > 350.942 (23)	397.015 > 254.978 (39)	1-100	0.9988	–18.9	0.6	2	100.2 (3.2)	104.5 (2.6)	105.2 (3)
64	Ethirimol	4.46	+	165	210.2 > 140.1 (23)	210.2 > 98.2 (28)	1-200	0.9992	–13.1	0.6	2	67.6 (6)	72.8 (2.2)	74 (3.6)
65	Ethofumesate	8.92	+	143	287 > 121.2 (20)	287 > 259.1 (11)	1-200	0.9992	–6.74	0.6	2	99.9 (3.7)	98.3 (2.9)	99.3 (2.8)
66	Etoxazole	16.02	+	167	360.1 > 141.1 (27)	360.1 > 304 (19)	1-100	0.9996	–39.0	0.6	2	111.3 (6.7)	109.9 (8.4)	101.7 (12.2)
67	Famoxadone	12.88	+	90	392.18 > 331.11 (10)	392.18 > 238.11 (20)	1-100	0.9981	–15.6	0.6	2	98.9 (5.6)	94.8 (4.6)	92.8 (7.1)
68	Fenamidone	9.21	+	62	312.07 > 236 (15)	312.07 > 165 (16)	1-200	0.9992	1.48	0.6	2	99.1 (3.2)	99.6 (2.3)	98.1 (2.6)

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												10 µg/kg	50 µg/kg	100 µg/kg
69	Fenarimol	10.66	+	170	330.95 > 268.159 (24)	330.95 > 138.987 (37)	1-200	0.9996	–1.54	0.6	2	96.8 (2.8)	98.6 (2.9)	97.8 (3)
70	Fenazaquin	17.33	+	161	307.23 > 161.188 (19)	307.23 > 57.448 (25)	1-200	0.996	–55.1	0.6	2	113.5 (8.1)	106.5 (10.5)	103.7 (11.8)
71	Fenbuconazole	11.45	+	182	337.17 > 125.113 (30)	337.17 > 70.304 (22)	1-200	0.999	–4.56	0.6	2	94.5 (2.5)	91.4 (2.7)	93.2 (2.9)
72	Fenhexamid	10.44	+	125	302.12 > 97.255 (26)	302.12 > 55.424 (39)	1-200	0.9996	–4.15	0.6	2	96.4 (3.2)	96.9 (2.4)	97.8 (3)
73	Fenobucarb	8.59	+	99	208.23 > 95.244 (18)	208.23 > 152.1 (13)	1-200	0.9998	–7.12	0.6	2	94.5 (3.1)	94.8 (3)	96.2 (3.3)
74	Fenoxycarb	11.72	+	111	302.165 > 88.233 (21)	302.165 > 116.1 (10)	1-200	0.9988	–9.14	0.6	2	98.3 (3.6)	101.4 (2.7)	101 (4.4)
75	Fenpropimorph	9.05	+	181	304.31 > 147.189 (32)	304.31 > 132.193 (44)	1-200	0.9999	–3.67	0.6	2	87.9 (2.2)	90.1 (2.6)	89.6 (3)
76	Fenpyroximat	16.49	+	151	422.1 > 366.1 (15)	422.1 > 214.1 (24)	1-200	0.9989	–50.4	0.6	2	109.4 (10.5)	102.9 (10.2)	98.7 (12.9)
77	Fenuron	3.67	+	40	165.2 > 72.311 (15)	165.2 > 77.287 (30)	1-100	0.9973	–16.9	0.6	2	101 (4.9)	100.1 (4.2)	96.1 (4.7)
78	Fipronil	11.84	+	71	436.939 > 367.849 (17)	436.939 > 290 (25)	1-50	0.9983	–21.6	0.6	2	103.6 (5.7)	103.1 (3.7)	99.5 (3.2)
79	Flonicamid	3.1	+	123	230.03 > 203 (15)	230.03 > 174 (16)	1-200	0.9979	–20.2	0.6	2	97.2 (3.4)	96 (3.3)	97.3 (4.9)
80	Fluazinam	15.31	−	158	462.9 > 415.9 (22)	462.9 > 397.9 (19)	1-200	0.9995	–43.2	0.6	2	100.8 (6.9)	96.9 (6.4)	96.5 (13.3)
81	Flubendiamide	12.27	+	62	683.019 > 407.889 (10)	683.019 > 273.889 (32)	1-200	0.9993	–2.88	0.6	2	98.2 (4.8)	98 (3.2)	98.5 (3.2)
82	Fludioxonil	9.82	+	70	266.03 > 228.93 (10)	266.03 > 157.99 (32)	1-100	0.9979	–13.1	0.6	2	104.4 (5)	100.7 (2.8)	97.3 (3.4)
83	Flufenacet	10.86	+	106	364.1 > 152.2 (19)	364.1 > 124.2 (36)	1-200	0.9994	–8.69	0.6	2	97.4 (1.5)	100.3 (2.4)	99.6 (3)
84	Flufenoxuron	16.31	+	182	489.04 > 158.09 (21)	489.04 > 141.09 (43)	1-200	0.9987	–67.1	0.6	2	124.4 (9.4)	107.7 (5.5)	102.7 (12.7)
85	Fluometuron	6.66	+	126	233.165 > 72.322 (22)	233.165 > 160.076 (30)	1-200	0.9996	–6.08	0.6	2	95.4 (3)	97.8 (2.6)	97.9 (2.5)
86	Fluoxastrobin	10.73	+	191	459.1 > 427 (18)	459.1 > 188.1 (34)	1-200	0.9994	–3.71	0.6	2	99.6 (2.3)	101.8 (2.2)	100.9 (3.1)
87	Fluquinconazole	10.49	+	130	376 > 349.076 (19)	376 > 307.1 (22)	1-200	0.9975	–10.8	0.6	2	99 (2.7)	100.4 (2.2)	100.3 (3)
88	Flusilazole	11.68	+	188	316.06 > 247.092 (20)	316.06 > 165.152 (33)	1-200	0.9986	–9.07	0.6	2	98.3 (2.8)	100.7 (2.5)	99 (3.3)
89	Flutolanil	9.9	+	136	324.17 > 242.076 (28)	324.17 > 262.055 (20)	1-200	0.9968	–7.00	0.6	2	103.3 (2)	105.8 (2.3)	103.4 (2.5)
90	Flutriafol	7.21	+	128	302.16 > 70.334 (20)	302.16 > 123.111 (30)	1-200	0.9996	–5.17	0.6	2	94.1 (3.1)	95.8 (2.2)	97.5 (2.6)
91	Forchlorfenuron	7.81	+	128	248.035 > 129.127 (20)	248.035 > 93.236 (36)	1-200	0.9997	–4.90	0.6	2	54.9 (15.9)	58.8 (13.1)	59.4 (13.2)
92	Formetanate hydrochloride	2.6	+	111	222.1 > 164.9 (16)	222.1 > 120.1 (26)	1-200	0.9975	–10.2	1.5	5	58.1 (7.9)	62.2 (3.7)	62.1 (5.7)
93	Fuberidazole	3.7	+	138	185.1 > 157.1 (23)	185.1 > 65.4 (48)	1-200	0.9998	3.14	0.6	2	85 (6.1)	79.3 (5.7)	81.2 (6.9)
94	Furalaxyl	8.85	+	125	302.19 > 242.115 (18)	302.19 > 270.077 (11)	1-200	0.9989	–3.00	0.6	2	98.6 (1.9)	101.3 (2.3)	100.8 (2.2)
95	Furathiocarb	14.49	+	133	383.21 > 195.072 (21)	383.21 > 167.081 (27)	1-200	0.9995	–13.9	0.6	2	97 (4.4)	97.1 (3.6)	96.2 (7.1)
96	Halofenozide	9.32	+	76	331.01 > 275.111 (8)	331.01 > 105.028 (18)	1-200	0.9995	–19.1	0.6	2	104.2 (4.9)	104.4 (3.6)	106.2 (4)
97	Hexaconazole	12.51	+	161	314.2 > 70.4 (18)	314.2 > 159.024 (28)	1-200	0.9993	–9.78	0.6	2	96.9 (3)	91.3 (3.8)	92 (3.7)
98	Hexaflumuron	14.45	−	105	458.92 > 438.932 (14)	458.92 > 174.866 (37)	1-50	0.9955	–30.1	0.6	2	115.3 (8.7)	107 (5.7)	92.7 (7.1)
99	Hexythiazox	15.51	+	122	353 > 227.9 (15)	353 > 168 (24)	1-200	0.9997	–44.2	0.6	2	103.1 (10.5)	93.6 (7.4)	88.8 (29.7)
100	Imazalil	7.15	+	187	297.135 > 159.043 (26)	297.135 > 255.025 (23)	1-200	0.9996	–0.43	0.6	2	79.4 (5.9)	81.4 (3.1)	85.2 (3.1)
101	Imidacloprid	3.5	+	109	256 > 209 (16)	256 > 175 (18)	1-200	0.9998	–1.48	0.6	2	94.5 (3.3)	97.1 (2.3)	97.7 (3.5)
102	Indoxacarb	14	+	184	528.055 > 203.023 (38)	528.055 > 150.06 (25)	1-200	0.9995	–15.3	0.6	2	100.7 (5.8)	97.6 (4.5)	94 (10)
103	Ipconazole (*)	13.52, 13.88	+	166	334.2 > 70 (27)	334.2 > 125 (33)	1-200	0.9994	–16.5	0.6	2	98.6 (3.2)	96.4 (3.7)	96.8 (7.1)
104	Iprovalicarb (*)	10.41, 10.57	+	111	321.3 > 119.3 (18)	321.3 > 91.4 (54)	1-200	0.9996	–3.11	0.6	2	97.1 (2.5)	95.7 (2.6)	96.8 (2.5)

#	Compound	RT (min)	ESI mode	RF lens (V)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
												10 µg/kg	50 µg/kg	100 µg/kg
105	Isocarbophos	7.58	+	61	307.1 > 231 (18)	307.1 > 273.2 (5)	1-200	0.9985	–5.50	0.6	2	103.8 (2.3)	104.8 (3.2)	104 (3.1)
106	Isoprocarb	6.99	+	89	194.195 > 95.22 (18)	194.195 > 137 (10)	1-200	0.9997	–9.09	0.6	2	93.1 (2.8)	96.6 (3.6)	97.6 (4.3)
107	Isoproturon	7.35	+	133	207.225 > 72.312 (21)	207.225 > 134.182 (26)	1-100	0.9992	–3.39	0.6	2	96.9 (2.7)	100.8 (2.4)	99.4 (2.4)
108	Ivermectin	18.76	+	76	892.7 > 569.222 (13)	892.7 > 307.097 (22)	1-200	0.9975	43.1	0.6	2	115.7 (14.3)	92.9 (8.6)	94.3 (7.6)
109	Kresoxim-methyl	11.77	+	80	314.09 > 222.122 (15)	314.09 > 235.099 (19)	1-100	0.9993	–13.8	0.6	2	101.2 (3.6)	100.2 (2.9)	99 (4.6)
110	Linuron	9.07	+	112	249.095 > 182.077 (18)	249.095 > 160.041 (21)	1-100	0.9985	–9.08	0.6	2	99.4 (2.9)	100 (2.3)	98.7 (2.6)
111	Lufenuron	15.71	−	76	509 > 325.9 (10)	509 > 175 (20)	1-50	0.997	–46.6	0.6	2	124.3 (10)	118.1 (9.2)	105.7 (9.8)
112	Mandipropamid	9.9	+	152	412.1 > 328.1 (15)	412.1 > 356 (11)	1-200	0.9995	–4.82	0.6	2	99.2 (2.6)	101.4 (2.8)	101.1 (3)
113	Mefenacet	10.25	+	111	299.1 > 148.3 (16)	299.1 > 120.3 (27)	1-200	0.9992	–6.24	0.6	2	97.2 (2.3)	101 (2.4)	99.9 (3)
114	Mepanipyrim	10.65	+	169	224.195 > 77.278 (39)	224.195 > 106.194 (29)	1-200	0.9991	–16.0	0.6	2	97.7 (3.2)	99.6 (3.5)	97.5 (5.3)
115	Mepronil	9.83	+	137	270.225 > 119.15 (26)	270.225 > 228.085 (16)	1-100	0.999	–4.91	0.6	2	100.4 (2.4)	101.4 (2.5)	98.7 (2.2)
116	Metaflumizone	15.53	+	177	507.183 > 177.92 (23)	507.183 > 286.9 (23)	1-200	0.9992	–70.3	0.6	2	119.5 (6.6)	115.7 (13.6)	111.4 (14.2)
117	Metalaxyl	7.32	+	116	280.225 > 220.15 (16)	280.225 > 192.175 (21)	1-200	0.9975	–2.55	0.6	2	99 (1.8)	102.2 (2.1)	101.7 (2.3)
118	Metconazole	12.71	+	179	320.1 > 70.335 (24)	320.1 > 125.1 (40)	1-200	0.9996	–33.8	0.6	2	103.5 (7)	104 (6.2)	102.9 (6.7)
119	Methabenzthiazuron	7.34	+	98	222.145 > 165.105 (19)	222.145 > 150.104 (36)	1-200	0.9981	–5.77	0.6	2	100.9 (2.3)	100.9 (2.5)	98 (2.5)
120	Methamidophos	1.73	+	80	142.135 > 94.176 (16)	142.135 > 125.049 (16)	1-200	0.9995	–7.97	0.6	2	88.6 (3.3)	92.3 (3.6)	93.4 (3.7)
121	Methiocarb	9.03	+	84	226 > 169.082 (10)	226 > 121.045 (36)	1-100	0.9994	–8.68	0.6	2	97.5 (2.8)	100.3 (3.3)	98.9 (3.1)
122	Methomyl	3.07	+	59	163.1 > 88.3 (10)	163.1 > 73.3 (28)	1-200	0.9984	–15.3	0.6	2	99.7 (2.6)	102.2 (2.3)	103.8 (3.2)
123	Methoprotryne	7.35	+	171	272.2 > 198.1 (23)	272.2 > 240 (20)	1-200	0.9999	–4.58	0.6	2	95.4 (2.5)	96.7 (2.6)	95.8 (2.5)
124	Methoxyfenozide	10.22	+	95	369.1 > 149.1 (18)	369.1 > 313.1 (6)	1-200	0.9982	–3.25	0.6	2	100.6 (2.5)	104.6 (2.7)	104 (2.9)
125	Metobromuron	7.07	+	119	259.06 > 169.993 (22)	259.06 > 170.981 (29)	1-200	0.9993	–7.69	0.6	2	92.9 (2.9)	96.8 (3.1)	97.5 (2.8)
126	Metribuzin	5.29	+	151	215.075 > 187.131 (20)	215.075 > 171.115 (24)	1-200	0.9985	–12.7	0.6	2	98.2 (3.5)	97.7 (2.8)	98.6 (3)
127	Mevinphos (*)	3.67, 4.16	+	88	225.125 > 127.093 (19)	225.125 > 109.14 (34)	1-200	0.9997	–14.8	0.6	2	92.5 (5.2)	94.8 (4.1)	96.7 (4.6)
128	Mexacarbate	3.55	+	117	223.1 > 151.1 (24)	223.1 > 166.1 (16)	1-200	0.9988	–16.9	0.6	2	98.4 (2.9)	100.7 (2.7)	98.4 (3.9)
129	Monocrotophos	3.22	+	88	224 > 193.012 (9)	224 > 127.111 (10)	1-100	0.9992	–79.7	0.6	2	96.8 (9.3)	86.3 (3.4)	87.7 (8.2)
130	Monolinuron	6.48	+	94	215.135 > 126.11 (20)	215.135 > 99.16 (36)	1-200	0.9994	–9.09	0.6	2	99.1 (2.7)	103.3 (2.9)	102.7 (3.1)
131	Moxidectin	18.46	+	68	640.331 > 528.222 (10)	640.331 > 498.222 (10)	1-200	0.9977	–63.6	1.5	5	124.3 (9.6)	108.6 (7.6)	105.1 (15)
132	Myclobutanil	10.14	+	142	289.17 > 70.316 (21)	289.17 > 125.107 (33)	1-200	0.9996	–2.88	0.6	2	95 (2.7)	95.9 (2.5)	97.5 (3.1)
133	Neburon	11.81	+	121	275.03 > 88.22 (14)	275.03 > 57.39 (18)	1-200	0.9967	–7.39	0.6	2	103.4 (2.7)	104.4 (2.5)	100.9 (3.1)
134	Nitenpyram	2.97	+	120	271.15 > 237.098 (21)	271.15 > 224.099 (18)	1-200	0.999	–26.4	0.6	2	84.3 (7.2)	90.3 (3.2)	92.8 (3.2)
135	Novaluron	14.6	−	119	490.985 > 470.974 (14)	490.985 > 304.961 (19)	1-50	0.9973	–30.5	0.6	2	114.1 (8.6)	105.4 (5.9)	93.2 (6.9)
136	Nuarimol	8.98	+	166	315 > 252 (23)	315 > 242.9 (26)	1-200	0.9997	–1.97	0.6	2	95.7 (1.9)	97.7 (2.9)	99.1 (2.3)
137	Omethoate	2.58	+	101	214.1 > 182.9 (13)	214.1 > 125.1 (17)	1-200	0.9963	–5.35	0.6	2	96.8 (2.7)	98 (2.5)	97.4 (2.9)
138	Oxadixyl	4.77	+	99	279.2 > 219.071 (11)	279.2 > 133.155 (22)	1-200	0.9997	–17.9	0.6	2	97.6 (2.8)	99.4 (3.1)	100.1 (2.6)
139	Oxamyl	2.92	+	63	237.075 > 72.304 (17)	237.075 > 90.267 (11)	1-200	0.9996	–5.61	0.6	2	96.4 (2.8)	98.4 (3.2)	100.2 (2.9)
140	Paclobutrazol	9.66	+	145	294.19 > 70.324 (22)	294.19 > 125.114 (36)	1-200	0.9997	–19.1	0.6	2	94.8 (2.8)	94.1 (2.4)	94.6 (3)
141	Penconazole	11.95	+	142	284.1 > 159 (25)	284.1 > 70.4 (19)	1-200	0.9996	–18.9	0.6	2	94.4 (4.8)	96 (3.9)	96.8 (4.7)

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												10 µg/kg	50 µg/kg	100 µg/kg
142	Pencycuron	13.37	+	167	329.1 > 125.2 (21)	329.1 > 218 (16)	1-200	0.9992	–27.2	0.6	2	105.8 (14)	110.8 (11.2)	106.3 (14.5)
143	Phenmedipham	8.45	+	48	318.08 > 136 (25)	318.08 > 168 (12)	1-200	0.9998	–4.88	0.6	2	98.8 (2.9)	100 (2.6)	98.9 (2.8)
144	Phoxim	13.02	+	75	299.135 > 129.134 (13)	299.135 > 77.307 (29)	1-200	0.998	–17.1	0.6	2	98 (4.2)	97.4 (3.5)	97 (7.3)
145	Picoxystrobin	11.79	+	90	368.1 > 145.3 (22)	368.1 > 115.2 (50)	1-200	0.9996	–9.40	0.6	2	97.8 (3.3)	100.3 (1.9)	100.2 (3.9)
146	Piperonyl butoxide	14.84	+	107	356.2 > 177.1 (12)	356.2 > 119.2 (37)	1-200	0.9998	–19.4	0.6	2	97.2 (4.2)	98 (3.9)	96.9 (8.1)
147	Pirimicarb	4.52	+	123	239.225 > 182.157 (18)	239.225 > 72.307 (23)	1-200	0.9996	–7.57	0.6	2	95.7 (2.9)	97.4 (2.4)	97.2 (3.2)
148	Prochloraz	12.58	+	111	376.09 > 307.983 (14)	376.09 > 70.349 (27)	1-200	0.9996	–14.6	0.6	2	93.8 (3.5)	94.9 (3.3)	95.6 (5)
149	Promecarb	9.38	+	92	208 > 109.25 (16)	208 > 151.2 (9)	1-200	0.9997	–11.1	0.6	2	95.4 (3)	97 (2.8)	98.1 (3.2)
150	Prometon	6.22	+	163	226.2 > 142.1 (23)	226.2 > 184.1 (19)	1-200	0.9998	–9.96	0.6	2	95 (2.5)	97.6 (2.4)	96.4 (2.7)
151	Prometryn	8.83	+	179	242.2 > 158.1 (25)	242.2 > 200.1 (20)	1-200	0.9999	–8.03	0.6	2	95.5 (3.7)	96.3 (3)	94.7 (3.8)
152	Propamocarb	2.7	+	106	189.2 > 102.2 (20)	189.2 > 74.4 (15)	1-200	0.9998	–41.1	1.5	5	56.3 (9.2)	69.7 (3.3)	70.5 (5.6)
153	Propargite	15.98	+	111	368.14 > 107.198 (28)	368.14 > 57.44 (23)	1-200	0.9974	–46.7	0.6	2	117.6 (11.4)	104.4 (7.1)	97.7 (13.7)
154	Propham	6.95	+	25	180.122 > 138.04 (8)	180.122 > 120.11 (19)	1-200	0.9995	–7.43	1.5	5	92.6 (4.3)	87.7 (3.7)	91.9 (5.4)
155	Propiconazole (*)	12.31, 12.45	+	193	342.13 > 159.015 (30)	342.13 > 123.151 (37)	1-200	0.9987	–8.79	0.6	2	95.2 (2.6)	91.4 (2.9)	93.1 (3.7)
156	Propoxur	5.34	+	83	210.185 > 111.177 (17)	210.185 > 93.215 (27)	1-200	0.9995	–8.33	0.6	2	97.7 (2.6)	96.9 (3.2)	98 (3.3)
157	Prothioconazole	12.41	+	70	341.978 > 306.1 (15)	343.978 > 308.1 (15)	1-50	0.9961	–69.3	3	10	97.2 (23.6)	99.4 (21.4)	105.5 (16.2)
158	Pyracarbolid	5.73	+	61	218.152 > 125.11 (15)	218.152 > 97.125 (24)	1-200	0.9993	–13.6	0.6	2	120.4 (3.3)	113.3 (3.6)	110.8 (6.6)
159	pyraclostrobin	12.97	+	126	388.15 > 163.107 (26)	388.15 > 149.093 (31)	1-200	0.9997	–11.8	0.6	2	97.3 (3.6)	94.8 (2.7)	94.9 (5.1)
160	Pyridaben	17.12	+	90	365 > 309 (14)	365 > 147 (24)	1-200	0.9994	–65.1	0.6	2	121.6 (9.5)	112.3 (11.3)	107.9 (16.7)
161	Pyrimethanil	8.11	+	165	200.195 > 107.179 (25)	200.195 > 168.102 (33)	1-200	0.9996	–11.7	0.6	2	92.2 (2.8)	92.4 (3)	92.5 (4.1)
162	Pyriproxyfen	15.27	+	121	322.19 > 96.237 (19)	322.19 > 185.104 (25)	1-200	0.9995	–47.3	0.6	2	103.4 (11.2)	97.5 (6.4)	96.9 (13.6)
163	Quinoxyfen	15.55	+	213	308.075 > 197.022 (35)	308.075 > 162.098 (48)	1-200	0.9993	–42.1	0.6	2	101.7 (7)	94.8 (5.6)	93.6 (11)
164	Rotenone	11.51	+	206	395.15 > 213.086 (26)	395.15 > 191.115 (39)	1-100	0.9983	–0.55	0.6	2	94.9 (3.2)	91.8 (2.7)	93.3 (4.4)
165	Secbumeton	6.21	+	157	226.245 > 170.127 (21)	226.245 > 142.127 (26)	1-200	0.9996	–9.81	0.6	2	95.7 (2.2)	97.2 (2.3)	96 (2.6)
166	Siduron (*)	8.99, 9.31	+	101	233.152 > 94.151 (18)	233.152 > 137.04 (15)	1-200	0.9991	–4.66	0.6	2	98.6 (2.5)	101.6 (2.4)	101.1 (2.5)
167	Simazine	5.49	+	38	202.05 > 132.04 (20)	202.05 > 104.01 (26)	1-200	0.9961	–24.3	0.6	2	94.1 (4)	96.5 (2.3)	96.7 (3.5)
168	Simetryn	5.66	+	169	214.085 > 68.356 (36)	214.085 > 96.2 (27)	1-200	0.9998	–6.71	0.6	2	92.2 (2.6)	95 (2.8)	94.6 (3)
169	Spinetoram	14.33	+	200	748.5 > 142.2 (31)	748.5 > 98.1 (40)	1-100	0.9961	10.4	0.6	2	79.7 (11.9)	85.5 (2.6)	85.3 (4.5)
170	Spinosad A (*)	13.43	+	250	732.47 > 142.214 (26)	732.47 > 98.267 (41)	1-200	0.9956	–4.48	0.6	2	80 (11.1)	87.6 (4.6)	88.6 (5.5)
	Spinosad D (*)	14.3	+	250	746.455 > 142.203 (27)	746.455 > 98.269 (43)								
171	Spirodiclofen	16.51	+	141	411.085 > 313.027 (10)	411.085 > 71.376 (15)	1-200	0.9998	–46.2	0.6	2	111 (13.3)	101.4 (8.1)	97.9 (13.4)
172	Spiromesifen	15.97	+	76	371.3 > 273.3 (15)	371.3 > 255.2 (20)	1-200	0.9994	–30.6	0.6	2	106.6 (10.9)	99.6 (7.5)	94.6 (12.6)
173	Spirotetramat	10.6	+	152	374.2 > 302.15 (16)	374.2 > 330.207 (10)	1-200	0.9996	–1.01	0.6	2	91.8 (13.9)	98.3 (2.4)	99.6 (3)
174	Spiroxamine (*)	9.59, 9.78	+	142	298.3 > 144.1 (20)	298.3 > 100.2 (30)	1-200	0.9995	–2.98	0.6	2	82.4 (9.3)	87.1 (2.6)	87.5 (2.7)
175	Sulfentrazone	5.88	−	225	384.945 > 306.967 (25)	384.945 > 198.954 (40)	1-50	0.9946	6.00	0.6	2	109.6 (1.9)	105.3 (2.2)	96.4 (2.3)
176	Tebuconazole	12.08	+	160	308.2 > 70.338 (24)	308.2 > 125.106 (30)	1-200	0.9993	–8.77	0.6	2	94 (3.6)	93 (3.4)	94.8 (3.8)

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												10 µg/kg	50 µg/kg	100 µg/kg
177	Tebufenozide	11.79	+	96	353.27 > 133.153 (21)	353.27 > 297.2 (5)	1-100	0.9994	–7.94	0.6	2	103.3 (2.9)	104.1 (2)	104.1 (2.6)
178	Tebufenpyrad	14.62	+	207	334.15 > 145.054 (27)	334.15 > 117.161 (25)	1-200	0.9996	–22.9	0.6	2	97.8 (6.4)	96 (4.9)	95.6 (9.1)
179	Tebuthiuron	5.63	+	127	229.185 > 172.136 (20)	229.185 > 116.136 (30)	1-100	0.9991	–13.00	0.6	2	100.6 (2.7)	101.7 (2.4)	100.1 (2.8)
180	Teflubenzuron	15.26	−	95	378.939 > 338.89 (10)	378.939 > 358.89 (10)	1-50	0.9946	–27.8	0.6	2	112.6 (9.5)	104.5 (7.2)	92.5 (7.1)
181	Temephos	15.43	+	213	467.005 > 418.987 (22)	467.005 > 404.954 (17)	1-200	0.9992	–55.0	0.6	2	110 (9)	100.6 (11.8)	94.9 (16.4)
182	Terbumeton	6.39	+	140	226.1 > 170 (19)	226.1 > 142.1 (25)	1-200	0.9999	–5.45	0.6	2	94.7 (2.4)	96.3 (2.5)	95.6 (2.9)
183	Terbutryn	9.1	+	151	242.1 > 186.1 (21)	242.1 > 91.2 (29)	1-200	0.9999	–9.27	0.6	2	96.9 (3.9)	98 (2.9)	96.2 (4.4)
184	Tetraconazole	11.1	+	143	371.95 > 159.117 (28)	371.95 > 70.331 (24)	1-200	0.9985	–9.32	0.6	2	97.8 (2.8)	100.6 (2.6)	98.8 (3.4)
185	Thiabendazole	3.58	+	178	202.115 > 175.052 (28)	202.115 > 131.158 (36)	1-200	0.9996	–2.27	1.5	5	69 (7.9)	69 (5.1)	68.2 (3.3)
186	Thiacloprid	4.25	+	127	253.1 > 126.1 (22)	253.1 > 90.2 (41)	1-200	0.999	–9.35	0.6	2	100.8 (3.1)	100 (1.8)	99.3 (2.9)
187	Thiamethoxam	3.17	+	104	292 > 211 (13)	292 > 181 (23)	1-100	0.9994	–29.8	0.6	2	94.4 (6.1)	97.4 (2.4)	95.8 (5.9)
188	Thiobencarb	13.04	+	105	258.145 > 125.128 (21)	258.145 > 89.223 (50)	1-100	0.9987	–17.9	0.6	2	97.3 (5)	97.1 (3.4)	95.8 (6.6)
189	Thiofanox	6.47	+	46	241 > 184 (5)	219.2 > 61.1 (13)	1-100	0.9942	0.91	1.5	5	111.9 (6.4)	127.7 (3.1)	130.5 (5.1)
190	Thiophanate-methyl	5.36	+	135	343.1 > 151.2 (19)	343.1 > 311.2 (11)	1-100	0.9987	–43.1	1.5	5	106.4 (14.8)	96.2 (12.5)	97.8 (16.9)
191	Triadimefon	10.02	+	103	294.183 > 197 (14)	294.183 > 224.99 (12)	1-200	0.9995	–3.64	0.6	2	93.9 (3.5)	93.4 (2.4)	95.6 (2.8)
192	Triadimenol	9.66	+	58	296.07 > 70.04 (24)	296.07 > 126.946 (43)	1-200	0.9997	–6.92	0.6	2	94.2 (2.5)	95.9 (3)	96.8 (2.4)
193	Trichlorfon	3.64	+	112	256.905 > 109.146 (21)	256.905 > 79.26 (32)	1-100	0.9962	–17.7	0.6	2	95.3 (9.1)	100.3 (2.2)	97.2 (3.8)
194	Tricyclazole	4.66	+	150	190.1 > 163 (24)	190.1 > 136 (29)	1-200	0.9995	–8.13	0.6	2	92.8 (3.5)	92.2 (2.4)	91.6 (2.7)
195	Trifloxystrobin	13.87	+	139	409.14 > 186.086 (20)	409.14 > 145.085 (44)	1-200	0.9998	–16.0	0.6	2	97.4 (4.1)	98.5 (3.3)	96.2 (7.9)
196	Triflumizole	14.02	+	103	346.1 > 278 (5)	346.1 > 73.1 (15)	1-200	0.9974	–18.6	0.6	2	111.7 (3.9)	106.8 (4.3)	105.8 (7.9)
197	Triflumuron	13.05	+	118	359.06 > 156.06 (13)	359.06 > 138.99 (27)	1-100	0.9991	–22.3	0.6	2	100.9 (6.1)	102.5 (4.7)	100.6 (6.4)
198	Triticonazole	10.63	+	143	318.19 > 70.333 (19)	318.19 > 125.116 (45)	1-200	0.9993	–2.29	0.6	2	97.3 (4.3)	97.3 (2.3)	97.4 (3.6)
199	Vamidothion	3.64	+	94	288.1 > 146.118 (15)	288.1 > 118.142 (25)	1-200	0.9983	–14.7	0.6	2	96.1 (3.5)	99.1 (2.3)	98 (3.1)
200	Zoxamide	12.44	+	159	336 > 186.9 (20)	336 > 159 (42)	1-200	0.9996	–7.27	0.6	2	98.1 (3.4)	100.7 (3.2)	100.8 (3.6)

(*) Pesticides with two isomers, calculated with 2 peaks together.

Table A-5. List of pesticides, method parameters and data validation of GC-MS/MS method for green tea (chapter 3)

#	Compound	RT (min)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range (µg/kg)	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
										10 µg/kg	50 µg/kg	75 µg/kg
1	2,4'-Methoxychlor	22.15	121 > 78 (20)	227 > 121 (12)	2 - 100	0.9946	36.7	0.67	2	80.4 (8.4)	99 (7.2)	92.2 (8)
2	2-Phenylphenol	11.94	141 > 115 (12)	170 > 141 (22)	5 - 100	0.9961	22.1	1.67	5	87.1 (5.1)	115.8 (5.9)	107.5 (7.9)
3	4,4'-Methoxychlor olefin	21.74	238 > 152 (35)	238 > 195 (20)	5 - 100	0.995	12.3	1.67	5	70.5 (7.2)	101.2 (7.2)	96.7 (7.7)
4	Acetochlor	16.75	174 > 146 (12)	223 > 132 (20)	5 - 100	0.9959	-18.6	1.67	5	83.5 (8.7)	100.2 (5.9)	97.3 (10)
5	Acrinathrin	24.17	181 > 152 (22)	208 > 181 (8)	1 - 100	0.9951	71.8	0.33	1	89.5 (9.7)	106.6 (3.7)	103.8 (6.5)
6	Alachlor	16.91	188 > 130 (32)	188 > 160 (10)	5 - 100	0.994	-13.4	1.67	5	87.1 (6.4)	103.6 (8)	100.8 (5.9)
7	Aldrin	18.03	263 > 193 (32)	263 > 191 (30)	5 - 100	0.9943	2.98	1.67	5	73.2 (7.2)	103.2 (9.1)	99.4 (8.6)
8	Allidochlor	8.3	132 > 56 (6)	138 > 96 (8)	5 - 100	0.9964	6.01	1.67	5	75.6 (6.7)	124 (5.7)	68.1 (10.7)
9	Anthraquinone	18.07	180 > 152 (12)	208 > 180 (10)	5 - 100	0.9915	109.7	1.67	5	58 (10.4)	80.9 (8.8)	76.3 (6.7)
10	Atrazine	15.05	200 > 122 (10)	215 > 173 (8)	5 - 100	0.995	0.34	1.67	5	83.9 (7.8)	102.9 (6.6)	101.4 (6.8)
11	Azinphos-ethyl	24.67	132 > 77 (12)	160 > 132 (6)	5 - 100	0.9959	413.0	1.67	5	94 (7.7)	106.8 (4.9)	104.1 (6.1)
12	Azinphos-methyl	23.98	160 > 77 (16)	160 > 132 (6)	5 - 100	0.9956	319.7	1.67	5	95.5 (6.8)	102.5 (6.5)	104 (6.2)
13	Benfluralin	13.92	292 > 206 (12)	292 > 264 (8)	2 - 100	0.993	45.1	0.67	2	84.5 (1.8)	97.6 (5.9)	95.4 (5.5)
14	BHC, alpha-	14.49	181 > 145 (13)	219 > 183 (8)	5 - 100	0.9943	42.2	1.67	5	71.3 (5.4)	107 (6.7)	99.2 (5.5)
15	BHC, beta-	15.1	181 > 145 (15)	219 > 183 (8)	2 - 100	0.9943	-4.15	0.67	2	92.6 (9.7)	105.4 (7.4)	102.9 (6.1)
16	BHC, delta-	16.03	181 > 145 (13)	219 > 183 (8)	1 - 100	0.9968	-24.1	0.33	1	75.1 (13.4)	105.2 (8)	105.5 (7.1)
17	BHC, gamma-	15.34	181 > 145 (13)	219 > 183 (8)	5 - 100	0.9917	27.3	1.67	5	79 (19.9)	108.1 (6.1)	103.3 (7.8)
18	Bifenthrin	23.03	181 > 165 (25)	181 > 166 (10)	5 - 100	0.9952	50.4	1.67	5	81.9 (8.3)	104 (7)	100.4 (6.9)
19	Bioallethrin	18.93	123 > 81 (8)	136 > 93 (11)	25 - 100	0.9951	21.4	8.33	25	<LOQ	117.1 (19.7)	102.7 (7.1)
20	Biphenyl	9.95	154 > 115 (26)	154 > 127 (30)	5 - 100	0.9703	27.0	1.67	5	84.8 (12.4)	106.6 (5.9)	85.2 (12.7)
21	Bromfenvinphos	19.8	267 > 159 (15)	323 > 267 (10)	5 - 100	0.9954	55.0	1.67	5	80.6 (12.1)	100.7 (8.4)	99.5 (11.2)
22	Bromfenvinphos-methyl	18.9	109 > 79 (5)	295 > 109 (15)	5 - 100	0.9958	37.2	1.67	5	77.3 (11)	102.9 (6.7)	102.4 (7.9)
23	Bromophos methyl	18.4	329 > 314 (13)	331 > 316 (13)	5 - 100	0.9959	22.1	1.67	5	81.6 (7.5)	100.1 (9.3)	97.4 (10.8)
24	Bromophos-ethyl	19.35	331 > 303 (8)	359 > 303 (17)	1 - 100	0.996	19.2	0.33	1	92 (9.7)	107.5 (10.2)	104.6 (9.7)
25	Bromopropylate	23.16	183 > 155 (12)	341 > 183 (15)	2 - 100	0.9959	29.3	0.67	2	85.9 (7.6)	107 (7.2)	103.4 (7.4)
26	Bupirimate	20.32	273 > 108 (16)	273 > 193 (8)	5 - 100	0.9952	16.8	1.67	5	80.1 (10.8)	100.3 (5.7)	94.1 (3.4)
27	Captafol	22.33	150 > 79 (6)	150 > 77 (24)	50 - 200	0.9827	129.0	16.67	50	<LOQ	70.1 (16.7)	108.8 (10.9)
28	Carbophenothion	21.79	125 > 97 (6)	199 > 143 (10)	25 - 100	0.9939	147.5	8.33	25	<LOQ	104.2 (5.8)	99.4 (6.9)
29	Carfentrazone ethyl	21.62	330 > 310 (8)	340 > 312 (10)	5 - 100	0.9956	72.9	1.67	5	79.8 (5.8)	101.1 (6.3)	95.5 (5.1)
30	Chlorbenside	21.74	125 > 89 (17)	125 > 62.8 (28)	25 - 100	0.9976	-24.5	8.33	25	<LOQ	105.1 (15.3)	99 (15.9)
31	Chlordane, cis-	19.79	375 > 266 (21)	377 > 268 (19)	2 - 100	0.9948	-7.07	0.67	2	84 (8.8)	102.4 (9.3)	104.5 (8.9)
32	Chlordane, trans-	19.49	272 > 237 (13)	375 > 266 (18)	2 - 100	0.9971	2.39	0.67	2	90.2 (14.3)	107.3 (7.8)	103.4 (10.8)
33	Chlorfenapyr	20.54	137 > 102 (12)	249 > 112 (24)	5 - 100	0.9941	32.2	1.67	5	94.4 (13.4)	105.2 (9.9)	100.5 (5.1)
34	Chlorfenson	20	175 > 111 (8)	177 > 113 (8)	5 - 100	0.996	12.6	1.67	5	78.7 (8.5)	100.8 (6.7)	97.1 (7.4)
35	Chlorfenvinphos (*)	18.87, 19.5	267 > 159 (15)	323 > 267 (10)	10 - 100	0.997	35.8	3.33	10	76.9 (4.4)	85.2 (10.3)	92.4 (11.8)
36	Chlorobenzilate	20.97	139 > 111 (12)	251 > 139 (14)	5 - 100	0.9944	32.0	1.67	5	82.7 (7.8)	102.7 (6.4)	100.5 (7)
37	Chloroneb	11.68	191 > 113 (15)	193 > 115 (15)	5 - 100	0.9926	37.2	1.67	5	81.2 (13.3)	120.9 (6.7)	99.5 (8.4)
38	Chlorothalonil	15.72	264 > 168 (23)	266 > 133 (40)	5 - 100	0.994	-38.2	1.67	5	97.2 (6.4)	99.1 (9.6)	101 (13.9)
39	Chlorpropham	13.81	171 > 127 (8)	213 > 171 (8)	5 - 100	0.9945	6.54	1.67	5	81.6 (3.9)	102.1 (6.9)	98.5 (5.6)
40	Chlorpyrifos	17.85	197 > 169 (14)	314 > 258 (12)	5 - 100	0.9908	-2.16	1.67	5	80.7 (9.1)	100.6 (9.7)	97.2 (9.4)
41	Chlorpyrifos-methyl	16.73	286 > 93 (24)	286 > 271 (12)	5 - 100	0.9947	-8.01	1.67	5	71.3 (6.5)	108 (2.7)	103.3 (7.8)

#	Compound	RT (min)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range (µg/kg)	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
										10 µg/kg	50 µg/kg	75 µg/kg
42	Chlorthal-dimethyl	17.97	301 > 223 (24)	332 > 301 (8)	5 - 100	0.9944	-6.64	1.67	5	83.5 (7.2)	104.9 (7.6)	98.6 (9.3)
43	Chlorthiophos (*)	20.7	257 > 193 (16)	257 > 239 (12)	5 - 100	0.995	80.0	1.67	5	71.7 (6.8)	99.5 (5.8)	97.9 (6.9)
		20.93	297 > 269 (8)	325 > 269 (14)								
		21.2	297 > 269 (8)	325 > 269 (14)								
44	Chlozolinate	18.79	186 > 145 (16)	331 > 259 (8)	5 - 100	0.9945	-9.59	1.67	5	63.7 (15)	89.5 (7.5)	85.7 (9.5)
45	Clomazone	15.17	125 > 89 (13)	125 > 99 (17)	5 - 100	0.9935	13.7	1.67	5	81.8 (5)	104.2 (6.1)	99.4 (6.5)
46	Coumaphos	25.36	210 > 182 (10)	362 > 109 (17)	5 - 100	0.9934	395.0	1.67	5	89 (9.1)	105 (5.8)	109.6 (7.7)
47	Cycloate	13.59	154 > 83 (8)	215 > 154 (6)	5 - 100	0.9981	64.5	1.67	5	74.9 (9)	109.8 (5.6)	93.5 (6.4)
48	Cyfluthrin (*)	25.8, 25.92, 26, 26.05	163 > 91 (14)	163 > 127 (6)	1 - 100	0.9952	306.4	0.33	1	94.7 (6.5)	108.8 (5.4)	106.3 (6.3)
49	Cyhalothrin, lambda-	24.18	197 > 141 (10)	208 > 181 (8)	1 - 100	0.9968	73.7	0.33	1	92.8 (8.6)	108.8 (5.7)	107.2 (6.2)
50	Cypermethrin (*)	26.22, 26.32, 26.4, 26.45	181 > 127 (30)	181 > 152 (25)	5 - 100	0.9988	434.9	1.67	5	123.6 (9.5)	108 (7.5)	109.7 (8.7)
51	Cyprodinil	18.67	224 > 208 (20)	225 > 210 (12)	5 - 100	0.9943	7.59	1.67	5	76.7 (10.2)	97.7 (6.3)	95.9 (8.1)
52	DDD, o,p'-	20.4	235 > 165 (22)	235 > 199 (14)	5 - 100	0.9947	-6.68	1.67	5	76 (8)	102.6 (6.8)	99.3 (6.8)
53	DDD, p,p'-	21.19	235 > 165 (24)	237 > 165 (22)	5 - 100	0.9936	3.8	1.67	5	78.5 (7.9)	103.8 (7.2)	100.9 (8.2)
54	DDE, o,p'-	19.5	246 > 176 (32)	316 > 246 (15)	5 - 100	0.9925	-8.61	1.67	5	79.2 (9)	97.7 (8)	93.7 (8.6)
55	DDE, p,p'-	20.23	246 > 176 (28)	316 > 246 (20)	5 - 100	0.9955	-8.08	1.67	5	70.8 (6.8)	97.4 (8.6)	92.4 (8.1)
56	DDT, o,p'-	21.26	235 > 165 (21)	237 > 165 (22)	5 - 100	0.994	14.5	1.67	5	78.1 (8.8)	96.1 (9.1)	89.8 (7.4)
57	DDT, p,p'-	22.05	235 > 165 (21)	237 > 165 (22)	1 - 100	0.9956	45.9	0.33	1	78.5 (7.9)	93.5 (8.6)	86.6 (8.5)
58	Deltamethrin (*)	27.94, 28.17	181 > 152 (20)	253 > 174 (8)	5 - 100	0.9956	299.5	1.67	5	93.9 (30.3)	87.7 (6.9)	97.3 (7.3)
59	Diallate (*)	14.32, 14.57	234 > 150 (18)	234 > 192 (12)	5 - 100	0.9937	55.6	1.67	5	68.2 (10)	104.6 (8)	95.4 (7.9)
60	Diazinon	15.52	137 > 84 (12)	304 > 179 (10)	5 - 100	0.9948	14.2	1.67	5	79.3 (10.4)	103 (6.1)	97.9 (6.3)
61	Dichlofluanid	17.67	123 > 77 (16)	224 > 123 (12)	10 - 100	0.9928	-19.9	3.33	10	114 (2.9)	96.8 (3.8)	88.7 (9.3)
62	Dichloroaniline, 3,4'-	10.62	161 > 99 (21)	161 > 126 (8)	2 - 100	0.9957	-26.4	0.67	2	97.4 (10)	76.1 (5.6)	103.3 (8.6)
63	Dichlorobenzophenone, 4,4'-	18.26	139 > 75 (27)	139 > 111 (13)	2 - 100	0.9955	57.5	0.67	2	80.1 (4.4)	97.3 (7.7)	90.2 (6.7)
64	Diclobenil	9.23	171 > 100 (25)	171 > 136 (13)	5 - 100	0.9783	27	1.67	5	108.2 (7.4)	83.1 (14.3)	86.5 (14.7)
65	Dicloran	14.79	176 > 148 (10)	206 > 176 (10)	1 - 100	0.9956	36.8	0.33	1	91.7 (5.6)	104.1 (8.2)	102.1 (7.1)
66	Dieldrin	20.43	263 > 193 (34)	277 > 241 (8)	10 - 100	0.996	-4.8	3.33	10	115.6 (15)	105.8 (7.2)	100.8 (9.7)
67	Dimethachlor	16.65	134 > 105 (13)	197 > 148 (8)	5 - 100	0.9932	-64.4	1.67	5	95.5 (13)	103.1 (7.5)	100 (8.1)
68	Diphenamid	18.4	239 > 72 (10)	239 > 167 (8)	2 - 100	0.9968	3.7	0.67	2	81.8 (11.8)	98.8 (7.6)	97.5 (5.4)
69	Diphenylamine	13.45	168 > 167 (14)	168 > 139 (38)	5 - 100	0.9955	49.9	1.67	5	76.3 (11)	108.7 (7.1)	96.1 (8.2)
70	Disulfoton	15.85	88 > 60 (6)	142 > 109 (6)	5 - 100	0.9983	339.4	1.67	5	61.6 (8.2)	94.6 (5.9)	67.4 (8.7)
71	Edifenphos	21.88	109 > 65 (13)	173 > 109 (8)	5 - 100	0.993	106.2	1.67	5	80.2 (9.1)	102.4 (5.5)	105.2 (9)
72	Endosulfan ether	16.51	239 > 204 (13)	241 > 206 (13)	5 - 100	0.9917	-51.7	1.67	5	73.4 (11.1)	108.8 (7.3)	104 (8.5)
73	Endosulfan I	19.81	195 > 159 (6)	241 > 206 (10)	5 - 100	0.9932	-19.4	1.67	5	84.8 (9.5)	98.1 (11.6)	102.1 (12.3)
74	Endosulfan II	21.15	195 > 125 (23)	195 > 159 (8)	5 - 100	0.9954	4.23	1.67	5	92.6 (18.6)	102 (10.7)	100.5 (6.7)
75	Endosulfan sulfate	22	241 > 206 (8)	272 > 237 (10)	5 - 100	0.993	-11.9	1.67	5	71.5 (14.3)	98.1 (14.1)	101.2 (17.2)
76	Endrin	20.92	263 > 193 (30)	279 > 243 (8)	5 - 100	0.9958	7.52	1.67	5	86.4 (7.8)	102.6 (7.8)	96.4 (9.6)
77	Endrin ketone	23.09	315 > 279 (8)	317 > 281 (8)	5 - 100	0.9961	6.63	1.67	5	83 (15.7)	104.2 (9.1)	97.9 (7.7)
78	EPN	23.11	169 > 77 (22)	169 > 141 (8)	5 - 100	0.9973	141.1	1.67	5	93.7 (5.9)	100.7 (5)	98.5 (7.1)
79	Ethalfluralin	13.64	276 > 202 (15)	316 > 276 (10)	5 - 100	0.9929	58.6	1.67	5	84.2 (5.2)	102.2 (3.8)	97.4 (5.8)
80	Ethion	21.15	153 > 97 (10)	231 > 129 (24)	5 - 100	0.9953	66.1	1.67	5	76 (7.3)	99.1 (6.6)	98.3 (7.2)
81	Ethylan	20.8	223 > 167 (12)	223 > 179 (22)	5 - 100	0.9932	12.5	1.67	5	77.4 (10.2)	100.7 (7.3)	97.1 (8.1)
82	Etofenprox	26.62	163 > 107 (18)	163 > 135 (10)	5 - 100	0.9938	343.8	1.67	5	83.6 (9.3)	106.3 (6.4)	102.5 (6.7)
83	Etridazole	10.88	183 > 140 (16)	211 > 183 (10)	5 - 100	0.9906	82.8	1.67	5	76.7 (22.8)	92.8 (10.2)	96.2 (7.9)
84	Fenamiphos	19.81	303 > 195 (9)	303 > 154 (8)	2 - 100	0.9939	76.7	0.67	2	79.2 (3.8)	97 (6.7)	85.7 (6.4)

#	Compound	RT (min)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range (µg/kg)	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
										10 µg/kg	50 µg/kg	75 µg/kg
85	Fenarimol	24.53	139 > 111 (16)	219 > 107 (12)	2 - 100	0.9953	141.4	0.67	2	88.8 (9.6)	109.9 (5.9)	104.6 (7.2)
86	Fenchlorphos	17.16	285 > 270 (11)	287 > 272 (11)	5 - 100	0.9925	1.86	1.67	5	84.3 (9.8)	109.3 (8.7)	100.8 (9.3)
87	Fenitrothion	17.48	277 > 109 (18)	277 > 260 (6)	5 - 100	0.9939	48.6	1.67	5	73.6 (5.2)	98.1 (6.7)	96.5 (5.9)
88	Fenpropathrin	23.26	181 > 152 (24)	265 > 210 (8)	2 - 100	0.9961	51.3	0.67	2	82.8 (8.4)	106.4 (6.6)	100.8 (8.9)
89	Fenson	18.39	141 > 77 (8)	268 > 141 (8)	5 - 100	0.9967	7.9	1.67	5	78.9 (5.8)	100.8 (6.6)	96.5 (6.3)
90	Fenthion	17.97	278 > 109 (18)	278 > 169 (17)	5 - 100	0.9912	381.2	1.67	5	66.5 (7.2)	98 (6.6)	88.6 (5.2)
91	Fenvalerate (*)	27.3, 27.54	167 > 125 (8)	169 > 127 (10)	5 - 100	0.9961	376.9	1.67	5	95.6 (7.7)	109.9 (5.4)	107.3 (5.9)
92	Fipronil	18.67	367 > 213 (30)	369 > 215 (30)	2 - 100	0.9954	51.5	0.67	2	93.5 (9.7)	106.4 (6.9)	105.4 (9.1)
93	Fluazifop-P-butyl	20.71	383 > 268 (8)	383 > 282 (12)	5 - 100	0.9945	67.1	1.67	5	73.6 (9.9)	97.1 (4.8)	94.3 (7.7)
94	Fluchloralin	15.55	264 > 160 (15)	306 > 264 (8)	1 - 100	0.9973	18.9	0.33	1	87.7 (9.2)	95.8 (6.2)	95.7 (6)
95	Flucythrinate (*)	26.4, 26.63	157 > 107 (13)	199 > 157 (8)	2 - 100	0.9958	380.9	0.67	2	89.2 (9.5)	108.5 (5)	105.5 (7.3)
96	Fludioxonil	19.96	154 > 127 (8)	248 > 127 (30)	5 - 100	0.9965	93.4	1.67	5	80.2 (10)	104.2 (6.7)	102.9 (6.1)
97	Fluquinconazole	25.38	340 > 108 (42)	340 > 298 (14)	2 - 100	0.9948	155.1	0.67	2	91.1 (6.2)	106.1 (6.2)	105.7 (6.4)
98	Fluridone	26.87	328 > 189 (38)	328 > 259 (24)	5 - 100	0.9961	540.5	1.67	5	108.2 (8.4)	109.4 (6.5)	106.8 (7.3)
99	Flusilazole	20.33	233 > 152 (14)	233 > 165 (18)	5 - 100	0.9965	17.7	1.67	5	81.2 (10.2)	104.2 (9.2)	101.6 (6.9)
100	Flutolanil	19.89	173 > 145 (14)	281 > 173 (10)	5 - 100	0.9945	46.5	1.67	5	76.6 (11)	103.6 (6.6)	100.3 (7.8)
101	Flutriafol	19.84	123 > 95 (12)	219 > 123 (14)	2 - 100	0.9964	19.6	0.67	2	84.6 (6.7)	102.1 (7.9)	100.1 (7.7)
102	Folpet	19.27	104 > 76 (10)	260 > 130 (16)	5 - 100	0.9962	59	1.67	5	76.5 (27)	75.7 (10.4)	65.8 (9)
103	Fonofos	15.53	137 > 109 (6)	246 > 137 (8)	5 - 100	0.9914	76.3	1.67	5	69.6 (8.5)	102.5 (6.2)	96.1 (6.4)
104	Heptachlor	17.16	100 > 65 (12)	272 > 237 (13)	5 - 100	0.9923	36.8	1.67	5	81.7 (9.5)	112.4 (8.3)	102.2 (6.2)
105	Heptachlor epoxide	18.94	351 > 261 (11)	353 > 263 (13)	5 - 100	0.9933	-4.28	1.67	5	97.9 (14.5)	107.7 (6.5)	107.8 (10.3)
106	Hexachlorobenzene	14.59	249 > 214 (14)	284 > 249 (18)	5 - 100	0.9947	53.7	1.67	5	80.7 (6.6)	115.5 (9.2)	105.6 (10)
107	Hexazinone	22.12	171 > 71 (16)	171 > 85 (16)	2 - 100	0.9952	124.7	0.67	2	86.3 (8.1)	107.7 (6.7)	105.2 (7.5)
108	Iodofenfos	19.98	377 > 93 (34)	377 > 362 (15)	1 - 100	0.9928	78.5	0.33	1	87.1 (10.6)	101.6 (8.9)	103.3 (15.8)
109	Iprodione	22.85	314 > 245 (14)	314 > 271 (12)	5 - 100	0.9996	111	1.67	5	77 (18.7)	104.8 (6.8)	109 (7.1)
110	Isazophos	15.84	161 > 119 (8)	172 > 130 (8)	5 - 100	0.9943	3.9	1.67	5	76.4 (6.4)	101.1 (5.6)	96.9 (6.3)
111	Isodrin	18.74	193 > 123 (30)	193 > 157 (19)	5 - 100	0.9941	-2.93	1.67	5	83.5 (14.7)	107 (8.1)	102.3 (7.4)
112	Isopropalin	18.46	280 > 180 (10)	280 > 238 (8)	1 - 100	0.9963	52.3	0.33	1	84.7 (5.9)	93.9 (6.9)	91.1 (5.2)
113	Lenacil	21.94	136 > 53 (18)	153 > 136 (14)	5 - 100	0.9944	209.9	1.67	5	78.9 (8.3)	108 (6.8)	105.2 (8.5)
114	Leptophos	23.91	171 > 77 (18)	171 > 124 (8)	2 - 100	0.9955	65.1	0.67	2	84 (6.3)	101.9 (7)	98.6 (7.3)
115	Lindan-d6 (surrogate) (**)	14.39	224 > 150 (20)	224 > 187 (10)	10 - 100	0.9948	-	-	-	78.2 (11.3)	-	-
116	Linuron	17.62	187 > 124 (21)	248 > 61 (8)	10 - 100	0.9916	-13.3	3.33	10	56.5 (9.4)	88.3 (12.5)	95.5 (13.8)
117	Malathion	17.67	127 > 99 (6)	173 > 127 (6)	5 - 100	0.9922	28.5	1.67	5	72.5 (10.4)	96.3 (8.4)	94.8 (7)
118	Metalaxyl	17.11	160 > 130 (10)	220 > 160 (16)	10 - 100	0.9973	-15.3	3.33	10	93.2 (12.8)	116.1 (8.8)	108.1 (10)
119	Metazachlor	18.71	133 > 117 (25)	209 > 132 (15)	5 - 100	0.9969	2.89	1.67	5	83.1 (6.1)	102.5 (7.4)	97.9 (6.5)
120	Methacrifos	11.53	125 > 79 (6)	180 > 93 (8)	5 - 100	0.9964	55.5	1.67	5	66.5 (16.2)	112.9 (6)	81.4 (7.5)
121	Methoxychlor	23.25	227 > 141 (33)	227 > 169 (25)	2 - 100	0.9966	55.7	0.67	2	87.5 (7)	98.4 (7.9)	91.8 (7.5)
122	Methyl parathion	16.89	263 > 109 (10)	263 > 136 (8)	1 - 100	0.996	46.7	0.33	1	86.8 (5.6)	100.7 (6.1)	97.2 (8.5)
123	Metolachlor	17.82	238 > 133 (27)	238 > 162 (10)	2 - 100	0.9943	4.67	0.67	2	81.4 (8.5)	95.5 (7.6)	94.7 (4.9)
124	Mevinphos	10.43	127 > 109 (8)	192 > 127 (10)	5 - 100	0.9926	18.3	1.67	5	77.2 (25)	103.1 (6.8)	86.8 (9.8)
125	MGK 264 (*)	18.44, 18.74	164 > 67 (10)	164 > 98 (14)	5 - 100	0.9972	-0.36	1.67	5	109.2 (7.7)	105.5 (6.8)	97.5 (6.5)
126	Mirex	24.51	272 > 237 (15)	274 > 239 (15)	5 - 100	0.9959	-9.39	1.67	5	82.8 (12.7)	108 (10.3)	109.1 (10.6)
127	Myclobutanil	20.29	179 > 125 (14)	179 > 152 (8)	5 - 100	0.9959	22.7	1.67	5	83.8 (7.6)	103.8 (6.5)	102.1 (7.2)
128	N-(2,4-Dimethylphenyl)formamide	11.32	120 > 77 (15)	121 > 106 (8)	5 - 100	0.995	10.9	1.67	5	74.8 (10)	106.4 (7.7)	100 (7.6)
129	Nitralin	22.44	274 > 216 (6)	316 > 274 (8)	5 - 100	0.9975	69	1.67	5	91.6 (7)	93.5 (6.2)	91.4 (7)

#	Compound	RT (min)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range (µg/kg)	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
										10 µg/kg	50 µg/kg	75 µg/kg
130	Nitrofen	20.8	202 > 139 (20)	283 > 202 (10)	1 - 100	0.996	113.4	0.33	1	82.3 (7.5)	96.8 (6.1)	95.3 (9.6)
131	Nonachlor, cis-	21.24	409 > 300 (23)	409 > 302 (20)	5 - 100	0.9984	4.84	1.67	5	97.3 (17.1)	111.8 (10.9)	108 (14.8)
132	Nonachlor, trans-	19.85	409 > 300 (20)	409 > 302 (22)	5 - 100	0.9922	4.94	1.67	5	80.1 (24)	99.9 (15.4)	100.9 (16.5)
133	Norflurazon	21.77	145 > 95 (18)	303 > 145 (17)	2 - 100	0.997	289.5	0.67	2	88.7 (7.4)	109.5 (5.9)	106.7 (7.4)
134	Oxadiazon	20.17	175 > 112 (13)	258 > 175 (8)	5 - 100	0.9939	1.29	1.67	5	80.7 (8.7)	103.4 (8.1)	99.8 (7.3)
135	Oxyfluorfen	20.28	252 > 146 (33)	300 > 223 (15)	2 - 100	0.9963	119.4	0.67	2	85.2 (9.5)	100.4 (6.2)	98 (11.7)
136	Paclobutrazol	19.57	236 > 125 (12)	236 > 167 (10)	5 - 100	0.9949	34.9	1.67	5	81.5 (9)	103.1 (5.9)	100.2 (8.2)
137	Parathion	18.04	109 > 81 (8)	139 > 109 (8)	5 - 100	0.9955	94.1	1.67	5	90.3 (10.7)	96.1 (5.5)	93.6 (6.1)
138	Parathion-d10 (surrogate) (**)	17.94	115 > 83 (10)	301 > 115 (10)	-	0.9923	-	-	-	82.6 (8.6)	-	-
139	Pebulate	11.02	128 > 57 (8)	161 > 128 (6)	10 - 100	0.9949	67.6	3.33	10	75.3 (1.6)	117.8 (5.8)	63.4 (19.9)
140	Penconazole	18.8	248 > 157 (26)	248 > 192 (16)	5 - 100	0.9941	12	1.67	5	80.3 (5.3)	101.6 (7.9)	98.1 (5.5)
141	Pendimethalin	18.63	252 > 162 (10)	252 > 191 (8)	5 - 100	0.9974	65.4	1.67	5	93.8 (4.7)	98.3 (8.1)	95.3 (6.2)
142	Pentachloroaniline	16.45	263 > 192 (20)	265 > 194 (22)	5 - 100	0.9969	-51.9	1.67	5	97.2 (7)	106.9 (9)	104 (6.8)
143	Pentachloroanisole	14.73	265 > 237 (12)	267 > 239 (10)	5 - 100	0.9965	39.9	1.67	5	80.8 (10.3)	119.6 (9.8)	107.7 (8.3)
144	Pentachlorobenzene	11.96	250 > 179 (30)	250 > 215 (20)	1 - 100	0.9951	59.6	0.33	1	114.8 (16.4)	101 (9.8)	99.1 (10.2)
145	Pentachlorobenzonitrile	15.3	273 > 238 (17)	275 > 205 (30)	5 - 100	0.994	37.3	1.67	5	70.8 (11.5)	111.5 (9.1)	103.5 (6.5)
146	Pentachlorothioanisole	17.65	296 > 263 (12)	298 > 265 (8)	5 - 100	0.9969	6.96	1.67	5	72.4 (8.9)	108.8 (11.6)	103.1 (10.6)
147	Permethrin, cis-	25.19	163 > 127 (6)	183 > 168 (10)	2 - 100	0.9945	192.2	0.67	2	85.4 (6.5)	103.7 (5.9)	100.8 (7.4)
148	Permethrin, trans-	25.34	163 > 127 (6)	183 > 153 (14)	5 - 100	0.9957	177	1.67	5	96.7 (7.9)	107.1 (7.4)	108.4 (9.2)
149	Phenothrin (*)	23.58, 23.71	183 > 153 (14)	183 > 168 (12)	10 - 100	0.9908	141.2	3.33	10	91.5 (17.4)	97.8 (7.1)	89.8 (26.3)
150	Phorate	14.34	121 > 65 (10)	260 > 75 (8)	5 - 100	0.9941	207.2	1.67	5	69.6 (13.8)	108.2 (6.7)	87.8 (8.5)
151	Phosalone	23.87	182 > 111 (16)	182 > 138 (8)	2 - 100	0.9963	166.9	0.67	2	91 (7)	106.2 (5.7)	104.3 (7.3)
152	Phosmet	23.08	160 > 77 (24)	160 > 133 (10)	1 - 100	0.9958	159.7	0.33	1	85.3 (7.8)	103.3 (6.6)	104.4 (8.7)
153	Piperonyl butoxide	22.45	176 > 103 (26)	176 > 131 (14)	1 - 100	0.9947	80.8	0.33	1	89.3 (6.8)	104.1 (7)	100.4 (7.6)
154	Pirimiphos-ethyl	18.31	318 > 166 (12)	318 > 182 (8)	5 - 100	0.9945	8	1.67	5	82.8 (11.5)	100.3 (6.8)	96 (7.4)
155	Pirimiphos-methyl	17.39	290 > 233 (10)	305 > 180 (8)	5 - 100	0.9907	-0.92	1.67	5	69.8 (5.8)	97.6 (9.5)	96.2 (6.7)
156	Pretilachlor	20.03	162 > 132 (18)	262 > 202 (8)	5 - 100	0.9946	23.7	1.67	5	77.9 (12.9)	103 (7.2)	99.1 (7.6)
157	Prochloraz	25.43	180 > 138 (12)	308 > 70 (13)	5 - 100	0.9948	677.3	1.67	5	98.8 (8.3)	107.1 (5.3)	108.3 (7.6)
158	Procymidone	19.11	283 > 67 (28)	283 > 96 (10)	5 - 100	0.9954	-3	1.67	5	79.4 (8.2)	98.5 (7.3)	94 (5)
159	Prodiamine	17.41	279 > 203 (8)	321 > 279 (6)	1 - 100	0.9916	30.9	0.33	1	85.9 (2.8)	99.7 (8.3)	97.2 (6.2)
160	Profenofos	20.13	337 > 267 (13)	339 > 269 (13)	2 - 100	0.9939	89.6	0.67	2	85.4 (8.8)	107.1 (8.2)	103.8 (8.7)
161	Profluralin	15.25	318 > 199 (17)	330 > 69 (25)	5 - 100	0.9922	33.2	1.67	5	77 (12.6)	99.6 (4.7)	96.5 (5.2)
162	Propachlor	13.15	120 > 77 (19)	176 > 57 (8)	5 - 100	0.991	22.7	1.67	5	78.6 (4.3)	100.5 (7.7)	93.6 (5.3)
163	Propanil	16.61	217 > 161 (8)	219 > 163 (8)	1 - 100	0.9978	16.2	0.33	1	90.6 (8.7)	104.2 (6.1)	102.2 (6.8)
164	Propargite	22.37	135 > 77 (24)	135 > 107 (14)	10 - 100	0.9924	49.8	3.33	10	85.6 (6.3)	106.5 (7.2)	103.9 (7.8)
165	Propisochlor	17.01	162 > 120 (13)	162 > 144 (10)	5 - 100	0.9934	-10.3	1.67	5	78.9 (8.5)	103.8 (8.4)	101.2 (8.6)
166	Propyzamide	15.49	173 > 109 (27)	173 > 145 (13)	5 - 100	0.9965	21.2	1.67	5	83.3 (5.2)	103.1 (5.9)	100.6 (7.4)
167	Prothiofos	20.03	267 > 239 (8)	309 > 239 (15)	5 - 100	0.9961	18.3	1.67	5	79.9 (6.1)	98.1 (7.6)	93.9 (9.2)
168	Pyraclofos	24.8	194 > 138 (18)	360 > 194 (10)	2 - 100	0.9948	424.5	0.67	2	86.3 (10.4)	107.6 (6.1)	107 (7.4)
169	Pyrazophos	24.42	221 > 193 (8)	232 > 204 (8)	1 - 100	0.9955	282	0.33	1	87.4 (6.1)	105.1 (6.2)	102.4 (6.6)
170	Pyridaben	25.42	147 > 117 (20)	147 > 132 (13)	2 - 100	0.9939	227.9	0.67	2	89.4 (8.7)	106.3 (6)	106.2 (8.4)
171	Pyridaphenthion	22.85	340 > 109 (20)	340 > 199 (8)	5 - 100	0.997	285.6	1.67	5	92.5 (4.8)	103.5 (6.3)	99.9 (6.1)
172	Pyrimethanil	15.68	198 > 118 (32)	198 > 183 (16)	5 - 100	0.9923	9.59	1.67	5	66.1 (15.9)	97.4 (6.1)	96.7 (6.8)
173	Pyriproxyfen	24.04	136 > 78 (20)	136 > 96 (12)	5 - 100	0.9939	204.6	1.67	5	83.2 (7.1)	105 (6.4)	101.2 (8.2)
174	Quinalphos	19.03	146 > 91 (24)	146 > 118 (10)	5 - 100	0.9947	45.3	1.67	5	80.1 (7.3)	100.2 (7.4)	97.7 (7)
175	Quintozene	15.21	235 > 141 (26)	295 > 237 (15)	5 - 100	0.9949	81.3	1.67	5	76.9 (22.7)	111.3 (12.7)	103.2 (11.4)

#	Compound	RT (min)	Quantitative peak (collision energy)	Confirm peak (collision energy)	Linear range (µg/kg)	R^2	Matrix effect (%)	LOD (µg/kg)	LOQ (µg/kg)	% Recovery (% RSD_R, n = 12)		
										10 µg/kg	50 µg/kg	75 µg/kg
176	Resmethrin (*)	22.37, 22.51	143 > 128 (10)	171 > 143 (6)	5 - 100	0.9938	82.3	1.67	5	111.8 (26.6)	125.7 (36.4)	92.1 (25.3)
177	Sulfotep	14.02	202 > 146 (10)	322 > 202 (10)	5 - 100	0.9924	25.7	1.67	5	83.2 (7.9)	105 (6.7)	97.5 (7.3)
178	Sulprofos	21.53	322 > 156 (13)	322 > 97 (24)	5 - 100	0.9972	389	1.67	5	75.4 (8.9)	98.7 (7.3)	87.5 (8.2)
179	tau-Fluvalinate (*)	27.41, 27.48	250 > 55 (23)	250 > 200 (19)	5 - 100	0.9957	146	1.67	5	93.6 (5.3)	110.5 (4.6)	108.7 (7.2)
180	Tebuconazole	22.35	125 > 89 (16)	250 > 125 (22)	5 - 100	0.9963	92.1	1.67	5	81.5 (9.3)	103.1 (5.6)	100.2 (7.3)
181	Tebufenpyrad	23.39	276 > 171 (10)	333 > 276 (8)	2 - 100	0.9947	94.2	0.67	2	84.9 (7.8)	103.5 (6.6)	99.9 (6.1)
182	Tecnazene	12.96	215 > 179 (8)	261 > 203 (13)	5 - 100	0.9979	76.7	1.67	5	82.9 (12.6)	112.8 (7.9)	94.4 (8.3)
183	Tefluthrin	15.86	177 > 127 (15)	177 > 137 (15)	5 - 100	0.9925	4.79	1.67	5	79.4 (5.6)	103.5 (6.6)	98.6 (6.4)
184	Terbacil	15.83	160 > 117 (8)	161 > 144 (14)	5 - 100	0.9948	29.5	1.67	5	97.8 (5.9)	106.1 (5.8)	104.4 (5.6)
185	Terbufos	15.42	231 > 129 (23)	231 > 175 (12)	5 - 100	0.9925	108.6	1.67	5	62.8 (11)	99.2 (8.3)	85.6 (10)
186	Terbutylazine	15.4	229 > 138 (12)	229 > 173 (8)	5 - 100	0.9951	4.6	1.67	5	83 (6.6)	98.7 (5.2)	96.5 (3.3)
187	Tetrachloroaniline, 2,3,5,6-	13.47	231 > 158 (20)	231 > 160 (22)	5 - 100	0.9908	58.8	1.67	5	79.5 (7.9)	113 (9.2)	102.2 (9.7)
188	Tetrachlorvinphos	19.49	331 > 109 (20)	333 > 109 (17)	5 - 100	0.9938	58.3	1.67	5	78.1 (8.7)	98.1 (6.4)	99.6 (10.8)
189	Tetradifon	23.75	159 > 111 (20)	159 > 131 (10)	5 - 100	0.9951	57.5	1.67	5	84.5 (13.1)	103.9 (6.9)	101.4 (8.3)
190	Tetrahydrophthalimide	11.51	151 > 80 (6)	151 > 122 (10)	5 - 100	0.9932	-17.7	1.67	5	80.4 (4.7)	100 (5.6)	97.5 (4.1)
191	Tetramethrin (*)	22.93, 23.11	164 > 77 (25)	164 > 107 (12)	2 - 100	0.9959	125.6	0.67	2	82.7 (6.5)	104.7 (5.6)	101.8 (8.2)
192	Tolclofos-methyl	16.93	265 > 250 (10)	267 > 252 (10)	5 - 100	0.9947	-9.57	1.67	5	81.2 (7.6)	103.1 (6.8)	97.6 (7)
193	Tolylfluanid	18.87	137 > 91 (17)	238 > 137 (10)	10 - 100	0.9972	10.9	3.33	10	103.7 (4.9)	93.3 (5.8)	87.6 (7.2)
194	Transfluthrin	16.94	163 > 91 (12)	163 > 143 (13)	5 - 100	0.9961	-7.26	1.67	5	85.9 (4.9)	103.4 (7.8)	97.3 (7)
195	Triadimefon	18.12	208 > 111 (24)	208 > 181 (10)	2 - 100	0.9957	13.4	0.67	2	82.7 (11.8)	97.5 (6.1)	95.2 (6.9)
196	Triadimenol	19.11	128 > 65 (22)	168 > 70 (10)	5 - 100	0.9966	25.1	1.67	5	71.5 (14.9)	104.3 (6.3)	101.1 (6)
197	Triallate	16.03	268 > 184 (20)	268 > 226 (10)	5 - 100	0.993	27.1	1.67	5	69.5 (5.1)	101.2 (7.3)	96.5 (6.6)
198	Triazophos	21.48	161 > 134 (8)	257 > 162 (8)	1 - 100	0.9952	95.9	0.33	1	86.1 (9.2)	107 (5.3)	102.4 (6.2)
199	Tricyclazole	20.19	189 > 135 (18)	189 > 162 (12)	5 - 100	0.9944	281.3	1.67	5	79.1 (11)	102.8 (3.7)	102.8 (6.9)
200	Triflumizole	19.11	206 > 179 (14)	206 > 186 (10)	5 - 100	0.9938	7.1	1.67	5	75.6 (10.2)	97.7 (7.1)	94.9 (8.5)
201	Trifluralin	13.85	306 > 206 (12)	306 > 264 (8)	2 - 100	0.9931	57.4	0.67	2	83.4 (2.6)	99.6 (5)	94.8 (5.1)
202	Trifluralin-d14 (IS) (**)	13.7	315 > 163 (25)	315 > 267 (10)	-	-	-	-	-	-	-	-
203	Vinclozolin	16.87	212 > 172 (12)	285 > 212 (12)	5 - 100	0.9952	-4.18	1.67	5	81.7 (6.5)	98.9 (10.6))	94.1 (6.4)

(*) Pesticides with more than one isomer, calculated all peaks together.
(**) Surrogate and internal standard compound.

Table A-6. Different types of sorbents for investigation (chapter 3).

Code	Sorbent
MS-A	GCB SPE cartridge (500 mg)
MS-B	mix-mode GCB/PSA SPE cartridge (500/500 mg)
MS-C	C18 d-SPE (250 mg) + mix-mode GCB/PSA SPE cartridge (500/500 mg)
MS-D	C18 d-SPE (500 mg) + mix-mode GCB/PSA SPE cartridge (500/500 mg)
MS-E	C18 SPE cartridge (500 mg) + mix-mode GCB/PSA SPE cartridge (500/500 mg)

Table A-7. Compounds with low recoveries when using SPE GCB/PSA (MS-B) compare with SPE GCB (MS-A) in chapter 3.

#	Name	Method	Recovery (%) (MS-A)	Recovery (%) (MS-B)	pKa (*)
1	Thidiazuron	UPLC-MS/MS	24.34	0.52	8.86 (weak acid)
2	Cyromazine	UPLC-MS/MS	19.72	0.78	5.22 (weak base)
3	Phorate	GC-MS/MS	83.03	11.2	-
4	Fenamiphos	GC-MS/MS	80.83	18.53	-
5	Terbufos	GC-MS/MS	99.04	20.27	-
6	Sulprofos	GC-MS/MS	94.0	20.43	-
7	Fenthion	GC-MS/MS	88.92	21.71	-
8	Methyl parathion	GC-MS/MS	86.03	38.84	-

(*) https://sitem.herts.ac.uk/aeru/iupac/atoz.htm

Table A- 8. List of pesticides, method parameters and matrix effects of UPLC-MS/MS method for 4 types of teas (chapter 4).

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
1	Acephate	2.31 75	184.045 > 143.046 (9) 184.045 > 95.174 (21)	-4.2	-9.7	-9	-14.4	-5.6	-12.1	-12.1	-11.3	-0.4	-13.7	-11.3	-13.9	-8.1	-17.5	-18.4	-15.3
2	Acetamiprid	3.81 117	223 > 126 (20) 223 > 90.1 (35)	-11.4	-10.7	-8.1	-12.2	-15.4	-16.3	-13	-9.5	-13.5	-18.9	-11.9	-13.4	-13.5	-18.1	-16.4	-12.5
3	Acibenzolar-S-methyl	9.62 89	211 > 136.1 (30) 211 > 140 (24)	-2.9	-9.4	-7.6	-13.5	-7.9	-10.7	-10.2	-10.1	0.6	-11.7	-9.1	-12.5	-8.2	-14.6	-16.2	-13
4	Aldicarb	4.47 58	208.152 > 116.1 (10) 208.152 > 89.15 (10)	-6.9	-8.3	-5.2	-14.2	-8	-11.2	-6.8	-11.3	-1.6	-13.9	-5.7	-14.8	-9.2	-18.6	-16.7	-16.1
5	Aldicarb sulfoxide	2.72 59	207.1 > 132.04 (8) 207.1 > 89.15 (10)	-16.1	-5.7	-7.4	-17.3	-15.8	-9.2	-7.7	-13.2	-5.6	-4.9	-5.4	-15.6	-24.4	-18.3	-19.2	-16.9
6	Aldicarb-sulfone	2.85 81	240.175 > 86.273 (23) 240.175 > 63.325 (31)	-8.4	-4.9	-10.4	-17.2	-8.4	-9.9	-12.7	-14.3	-3.6	-10.1	-11.5	-17.5	-11.6	-14.9	-18.9	-17.5
7	Ametryn	7.16 173	228.1 > 186.1 (20) 228.1 > 138.1 (23)	-2.3	-6.2	-5.6	-10.9	-4.5	-8.9	-9	-7.6	1.3	-10.1	-8.2	-11.6	-5.9	-14.4	-15	-12
8	Aminocarb	2.62 105	209.1 > 137.1 (23) 209.1 > 152.1 (15)	-8.5	-6.9	-9.3	-15.5	-10.6	-9.6	-12.1	-12.5	-2.7	-9.2	-10.2	-14.8	-14.1	-14.8	-18.3	-16.4
9	Amitraz	12.22 154	294.2 > 148.3 (16) 294.2 > 91.2 (40)	-1.2	-5.3	-5.3	-10.6	-4.9	-8.2	-8.8	-7.8	1.9	-8.6	-6.7	-11.7	-5	-13.6	-15.7	-11.1
10	Atrazine	7 38	216.1 > 174.063 (20) 216.1 > 104.164 (31)	-6.6	-7.3	-4.7	-8.1	-2.1	-5.3	-5.7	-12.7	1.8	-10.3	-1.3	-8.5	-7.1	-16.7	-16.6	-11.4
11	Avermectin (B1a) (*)	17.43 77	890.47 > 305.183 (24) 890.47 > 567.28 (14)	-0.1	0.2	-9.8	-17.6	-5.4	-5.3	-14.2	-16.1	-3	-2.2	-15.5	-17.3	-5.5	-12.8	-18.8	-17
	Avermectin (B1b) (*)	16.92 76	876.5 > 291 (21) 876.5 > 553.4 (13)																
12	Azoxystrobin	9.08 144	404.12 > 372.067 (16) 404.12 > 344.076 (27)	-2.4	-6.5	-6.4	-12.1	-5.1	-9.8	-10	-9	1.5	-10.5	-9.1	-12.6	-6.3	-14.3	-15.5	-13.2
13	Benalaxyl	12.23 128	326.23 > 148.174 (24) 326.23 > 121.197 (32)	-2.1	-6.4	-6.7	-11.4	-4.8	-9	-9.6	-9.2	0.4	-10.1	-8.1	-11.8	-6.8	-14.7	-16	-12.7
14	Bendiocarb	5.47 94	224.175 > 167.126 (10) 224.175 > 109.174 (21)	-5.7	-8.6	-8.3	-12.1	-5.9	-10.8	-10.2	-10.1	-0.3	-12.9	-9.7	-12.8	-9	-17.3	-17.2	-13.2
15	Benzoximate	13.05 80	364.05 > 198.937 (9) 364.05 > 105.139 (23)	-2	-7.4	-6.7	-11.8	-4.6	-9.9	-11.3	-8.2	0.7	-10.7	-8.9	-12.7	-5.8	-16.1	-16.4	-12.6
16	Bifenazate	10.53 93	301.2 > 198.1 (5) 301.2 > 152.138 (43)	-6.2	-2.7	-8	-12.3	-16.4	-8.7	-13.5	-11.3	-2.2	-5.4	-10.3	-14.2	-22.6	-30.4	-28	-16.2
17	Bitertanol	12.92 40	338.19 > 269.2 (9) 338.19 > 70.1 (12)	-1.7	-5.3	-6.2	-10.8	-0.9	-8.7	-12.2	-11.1	-2	-5.6	-10.6	-15.7	-4.4	-17.2	-17.5	-11.4
18	Boscalid	9.55 189	343.04 > 307.065 (21) 343.04 > 272.091 (34)	-4.6	-8.7	-8	-13.3	-6.4	-11.2	-11.2	-10.3	0.4	-11.9	-10.2	-13.3	-7.9	-15.8	-17.5	-14.8
19	Bromucanozole (*)	10.19, 11.65 178	377.935 > 159.015 (30) 377.935 > 161.018 (31)	-4.9	-8.7	-8.3	-12.9	-6	-11	-10.4	-9.4	-0.7	-11.9	-9.5	-12.7	-8.8	-17	-17.7	-14
20	Bupirimate	10.38	317.21 > 166.143 (27)	-1.5	-6	-5.7	-11.6	-4.5	-9	-8.9	-7.7	2	-9.3	-8.1	-11.4	-5.5	-14.8	-15.7	-11.4

#	Compound	RT (min) / RF lens (V)	Quantitative peak (CE) / Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
		185	317.21 > 272.096 (21)																
21	Buprofezin	14.36 112	306.235 > 106.219 (28) 306.235 > 57.448 (25)	-5.1	-8.7	-7.9	-12.4	-5.9	-11.1	-10.4	-9	0.8	-10.8	-9.5	-13	-9.7	-16.9	-17.3	-13.4
22	Butafenacil	10.76 144	492.11 > 331.005 (26) 492.11 > 348.993 (17)	-2.2	-8	-8.1	-14.5	-5	-11	-11.8	-10.7	0.6	-12.5	-10	-14.3	-5.3	-16.9	-18.8	-14.4
23	Butocarboxim	4.37 46	213.03 > 75.058 (16) 213.03 > 155.99 (10)	19.9	0.4	-6.3	-12.2	4.7	-5	-11.2	-10.9	8.7	-11.1	-8.8	-13.3	9.5	-12.3	-16.5	-15.8
24	Butoxycarboxim	2.82 75	223.03 > 166 (15) 223.03 > 106.11 (17)	-9.6	-8	-5.9	-15.6	-9.8	-11.3	-5.2	-16.4	-4.4	-15.5	-5.9	-18.9	-14.9	-14.6	-15.8	-16.3
25	Carbaryl	6.17 82	202.165 > 145.11 (11) 202.165 > 127.152 (31)	-12.3	-12.5	-10.7	-15.2	-17	-16.7	-14.3	-11.1	-12.6	-17.7	-12.3	-14.9	-14.5	-18.9	-18.8	-15
26	Carbendazim	3.24 132	192.1 > 160.1 (20) 192.1 > 105.2 (32)	-52.9	-44	-34.1	-34.7	-37.6	-34.4	-31.9	-30.6	-30.7	-34.9	-30.4	-32.4	-51.9	-46.5	-39.1	-33.7
27	Carbetamide	4.94 89	237.1 > 192 (9) 237.1 > 120 (17)	-3.5	-7.7	-7.7	-12.5	-4.8	-11.3	-11.1	-10.3	0.2	-11.4	-9.6	-13.1	-7.1	-15.2	-16.8	-14.3
28	Carbofuran	5.45 100	222.185 > 165.129 (15) 222.185 > 123.16 (25)	-4.1	-7.2	-7.3	-11.7	-5.2	-10.1	-10	-8.6	0.5	-11.5	-8.3	-12.1	-7.5	-15.9	-16.7	-12.7
29	Carbofuran-3-hydroxy	3.67 121	238.2 > 181.1 (12) 238.2 > 163.1 (18)	-10.4	-10.8	-9.3	-12.6	-8.1	-11.5	-11.5	-9.3	-3	-12.6	-9.1	-11.8	-13.4	-18.6	-16.9	-13
30	Carboxin	6.05 111	236.145 > 143.095 (18) 236.145 > 87.224 (28)	-5.5	-7.8	-7.5	-12	-7.5	-10.3	-10	-8.4	-0.7	-11.4	-8.8	-11.6	-9.3	-15.9	-16.1	-12.1
31	Carfentrazone-ethyl	11.83 180	412.1 > 346.1 (23) 412.1 > 366.1 (19)	-1.2	-7	-7.1	-13.8	-3.6	-9.8	-10.7	-9	2.3	-10.8	-9.1	-12.6	-5.1	-14.8	-16.4	-13.9
32	Chlorantraniliprole	8.25 149	481.88 > 450.948 (17) 481.88 > 283.955 (13)	-2.9	-7.2	-3.8	-12.8	-6.6	-10.7	-7.7	-10.3	0.1	-12	-6.3	-13.7	-5.9	-16.4	-15.3	-14
33	Chlorfluazuron	16.87 149	539.995 > 382.974 (23) 539.995 > 346.999 (46)	-5.4	-11	-3.5	-15.9	-10.9	-14.4	-6.4	-13.3	-3.8	-15.1	-5.9	-16.9	-9	-19.8	-13.4	-16.5
34	Chlorotoluron	6.88 121	213.18 > 72.31 (21) 213.18 > 140.094 (27)	-2.1	-6.2	-5.7	-10.4	-5.3	-7.8	-8.7	-6.8	-0.1	-10.1	-7.3	-10.8	-6.1	-14	-15.6	-10.9
35	Chloroxuron	10.5 164	291.1 > 72.4 (23) 291.1 > 218.1 (27)	-2.3	-4.4	-5.8	-10.5	-4.4	-8.1	-8.9	-8	1.7	-9	-7.9	-11.6	-5.9	-13.9	-15.3	-11.4
36	Clethodim (*)	10.1, 14.01 140	360.1 > 164.2 (20) 360.1 > 166.3 (22)	-4	-8	-6.5	-12.2	-6.2	-10.6	-10.2	-8.4	1.1	-10.6	-8.1	-11.9	-7.2	-15.8	-15.7	-11.8
37	Clofentezine	13.47 100	303.061 > 138.06 (11) 303.061 > 102.11 (31)	-6.8	-11.4	-6.8	-16.3	-8.8	-14.1	-10.3	-14.5	-2.4	-15.8	-10	-17.7	-10.9	-19.5	-16.9	-16.7
38	Clothianidin	3.55 101	250.1 > 169.1 (13) 250.1 > 132.2 (14)	-15.8	-13	-10.3	-12.8	-7.9	-12	-10.7	-9.4	-1.3	-13.1	-9.8	-13.5	-15.8	-18.9	-18	-14.1
39	Cyazofamid	11.37 103	325 > 108.169 (17) 325 > 217.067 (21)	-9	-11.4	-9.2	-13.1	-11.8	-12.4	-12.5	-11.2	-3.2	-14.1	-11.4	-14.3	-11.6	-19.3	-17.5	-14.1
40	Cycluron	7.56 130	199.255 > 89.243 (17) 199.255 > 72.318 (25)	-3	-6	-5.8	-11.5	-5.1	-9.1	-9.6	-8.5	0.6	-10.4	-7.9	-11.5	-6	-14.4	-15.3	-11.7
41	Cymoxanil	13.06 123	199 > 183.93 (16) 199 > 141 (25)	-1	-4.9	-4.9	-9.9	-4.1	-7.9	-8	-6.9	2	-9.4	-6.7	-10	-5.2	-13.6	-14.4	-10.5
42	Cyproconazole (*)	9.78, 10.32 150	292.17 > 70.326 (22) 292.17 > 125.121 (30)	-5.5	-8.5	-8.3	-14	-7	-11.1	-10.8	-9.9	-0.9	-13.3	-10.4	-14.1	-8.9	-16.6	-18	-13.6

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
43	Cyprodinil	11.06 178	226.205 > 93.226 (37) 226.205 > 118.164 (34)	-2.8	-7	-6.3	-11.5	-5.1	-9.6	-9.5	-8.8	0.7	-10.5	-8.5	-12.1	-7	-14.5	-15.8	-12.6
44	Desmedipham	8.2 101	318.09 > 182.126 (16) 318.09 > 136.142 (29)	-5.1	-10.6	-4.3	-15	-7.8	-13.6	-7.4	-13.2	-1.8	-14.7	-5.8	-16	-9.4	-18.4	-14.9	-16.9
45	Diclobutrazol	11.79 169	328.1 > 70.3 (32) 328.1 > 159 (34)	-5.3	-8.4	-8.2	-12.7	-7.5	-11.2	-11.7	-9.5	-1.6	-12.3	-9.7	-12.6	-8.8	-16.9	-16.9	-13.8
46	Dicrotophos	3.33 106	238.055 > 112.235 (15) 238.055 > 193.074 (10)	-31.6	-24.9	-18.3	-18.9	-23.6	-19.2	-15	-10.7	-17.5	-18.8	-12.3	-13.4	-32.2	-30.2	-25	-18.9
47	Diethofencarb	8.62 92	268.2 > 124.163 (35) 268.2 > 180.143 (20)	-3.6	-8.1	-8.2	-14	-5.7	-12.1	-11.5	-10	0.5	-12.7	-10.3	-13.2	-7.8	-15.9	-17.5	-14.8
48	Difenoconazole (*)	13.52, 13.65 188	406 > 251.015 (26) 408 > 253 (26)	-1.6	-7.3	-8.4	-13	-5.7	-10.9	-11.7	-10	0.9	-11.3	-9.8	-13.6	-5.1	-15.9	-17.6	-14.1
49	Diflubenzuron	11.6 126	311.1 > 157.9 (14) 311.1 > 141.1 (25)	-3.5	-8.7	-8.4	-14.3	-5.7	-11.5	-11.9	-11.1	-0.7	-12.3	-10.2	-13.3	-7.9	-16.4	-17.8	-14
50	Dimethoate	3.74 83	230.06 > 125.085 (24) 230.06 > 79.24 (33)	-13.5	-12.1	-9	-12.8	-10.2	-12.4	-11	-9.5	-1.6	-12.7	-8.5	-12.4	-15.9	-19.5	-18.4	-14.5
51	Dimethomorph (*)	9.24, 9.86 202	388.155 > 301.105 (23) 388.155 > 165.118 (34)	-0.3	-5.7	-5.5	-11.2	-4	-8.5	-9.2	-8	2.2	-10	-7.9	-11.5	-4.6	-13.3	-15.5	-11.6
52	Dimoxystrobin	11.65 105	327.1 > 116.1 (20) 327.1 > 238.1 (13)	-2.1	-6.8	-6.8	-12.7	-4.3	-9.3	-11.4	-9.6	0.9	-10.9	-9.4	-13.1	-6.2	-15.1	-16.6	-13.2
53	Diniconazole	13.19 191	326.155 > 70.303 (27) 326.155 > 159.041 (32)	-3.4	-9.6	3.4	-13.5	-7.1	-12.4	-0.6	-9.4	-2.1	-13.2	1.4	-14.2	-8.3	-17	-8.1	-13.7
54	Dinotefuran	2.75 79	203.11 > 129.16 (12) 203.11 > 114.161 (8)	-18.2	-5.5	-10.7	-14.8	-14.5	-6.4	-11.2	-10.3	0.2	-4.2	-10.7	-12.9	-24.5	-17.1	-18.8	-14.5
55	Dioxacarb	3.69 91	224.165 > 123.172 (19) 224.165 > 95.242 (29)	-20	-11.7	-9.4	-18.4	-19.9	-14	-12.6	-15.2	-7.3	-6.1	-3.6	-13.6	-23.3	-19	-18.3	-18.7
56	Diuron	7.77 134	233.095 > 72.33 (21) 233.095 > 46.519 (19)	-4.6	-8.1	-7.6	-12.2	-7	-11	-11.2	-9.9	-1.3	-12.4	-10.1	-12.7	-8.5	-16.9	-17.5	-13.8
57	Doramectin	18.14 78	916.509 > 331.24 (22) 916.509 > 593.35 (12)	-0.7	-10.2	-7.6	-15	-4.1	-14.8	-8.7	-12.8	-1	-14.2	-8.1	-15.8	-7.7	-19.6	-15.8	-16.3
58	Emamectin benzoate (B1a) (*)	15.73 76	886.505 > 158.19 (39) 886.505 > 82.301 (47)	0.7	-5.2	-4.4	-9.2	1.6	-7.7	-8	-7.9	3.9	-8.7	-6.7	-10.4	-3	-12.9	-14.4	-9.9
	Emamectin benzoate (B1b) (*)	15.13 76	872.495 > 158.178 (37) 872.495 > 82.279 (46)																
59	Epoxiconazole	11.04 55	330.13 > 121.163 (15) 330.13 > 101.195 (35)	-1.5	-5	-5.7	-10.8	-4	-8.7	-8.8	-7.7	1.6	-9.4	-7.2	-11.1	-6.1	-14.3	-15.1	-11.3
60	Eprinomectin	17.09 85	914.469 > 186 (27) 914.469 > 154 (27)	6	-3	-3.5	-10.6	1.3	-4.3	-8.1	-6.5	6.8	-7.4	-6	-11.4	-1.2	-8.8	-16.5	-10
61	Etaconazole (*)	10.74, 10.9 172	328.1 > 159 (23) 328.1 > 205 (18)	-2.7	-6.6	-6.5	-12.2	-5	-10.1	-10.9	-8.5	1.1	-10.5	-8.8	-12.1	-6.1	-14.5	-15.8	-12.8
62	Ethiofencarb	6.32 86	226.165 > 107.183 (18) 226.165 > 77.279 (45)	-7.7	-10.4	-8.4	-12.8	-9.6	-12.3	-11.3	-9.1	-3.8	-13.9	-9.9	-13	-10.3	-16.3	-17.1	-13.5
63	Ethiprole	9.33 167	397.015 > 350.942 (23) 397.015 > 254.978 (39)	-3.3	-8.9	-7.9	-13.4	-5.9	-11	-10.9	-9.5	1.3	-12.2	-10.2	-12.9	-7.9	-15.6	-17.8	-14.1
64	Ethirimol	4.46 165	210.2 > 140.1 (23) 210.2 > 98.2 (28)	-7	-7.6	-6.7	-11.2	-6.7	-9.1	-8.8	-8.3	-0.3	-11.5	-7.8	-11.3	-10.6	-15.4	-15.6	-11.4

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
65	Ethofumesate	8.92 143	287 > 121.2 (20) 287 > 259.1 (11)	-3.9	-8.7	-8	-13	-6.9	-11.4	-12	-11	-0.8	-12.5	-10.3	-13.7	-8.3	-15.8	-17.8	-15.2
66	Etoxazole	16.02 167	360.1 > 141.1 (27) 360.1 > 304 (19)	-12.1	-6.6	-8.5	-16.8	-16.8	-11.2	-12.2	-15.1	-5.4	-1.3	-2.6	-13	-17.5	-15.6	-17.9	-17.1
67	Famoxadone	12.88 90	392.18 > 331.11 (10) 392.18 > 238.11 (20)	-4.6	-9.9	-7	-16.4	-5	-9.4	-11.2	-10.1	-2.5	-13.4	-9.9	-14.8	-7	-18.4	-19.9	-14.2
68	Fenamidone	9.21 62	312.07 > 236 (15) 312.07 > 165 (16)	-1.1	-4.9	-4.8	-9.6	-4.6	-7	-8.5	-7	2.5	-8.7	-7	-9.8	-5.5	-12.5	-14.4	-11.3
69	Fenarimol	10.66 170	330.95 > 268.159 (24) 330.95 > 138.987 (37)	-2.1	-7	-8.2	-13.1	-5.9	-11.2	-12.4	-9.9	0.4	-12.3	-9.8	-14.6	-6.4	-17	-18.6	-15.1
70	Fenazaquin	17.33 161	307.23 > 161.188 (19) 307.23 > 57.448 (25)	-9	-8.6	-9.2	-17.5	-12.5	-12	-12	-14.9	-3.7	-7.3	-6.5	-15.3	-13.7	-16.5	-17.8	-17.8
71	Fenbuconazole	11.45 182	337.17 > 125.113 (30) 337.17 > 70.304 (22)	-2.2	-8	-8.2	-12.8	-5.6	-10.5	-11.2	-9.2	0.5	-11.2	-10	-12.9	-7.2	-15.6	-17.1	-12.7
72	Fenhexamid	10.44 125	302.12 > 97.255 (26) 302.12 > 55.424 (39)	-1.3	-5.2	-6.4	-11.1	-2.7	-9.1	-8.5	-9	2.7	-8.6	-9.2	-11.9	-4.4	-15.4	-15.8	-11
73	Fenobucarb	8.59 99	208.23 > 95.244 (18) 208.23 > 152.1 (13)	-2.9	-7.9	-7.8	-12.5	-5.7	-10.5	-11.1	-9.8	0	-12.7	-9.8	-13	-7.7	-16.5	-17.6	-14.2
74	Fenoxycarb	11.72 111	302.165 > 88.233 (21) 302.165 > 116.1 (10)	-0.5	-7.3	-7.1	-12.5	-3.7	-9.8	-10.1	-9	2.1	-10.4	-9.1	-12.1	-4.5	-14.8	-15.8	-12.3
75	Fenpropimorph	9.05 181	304.31 > 147.189 (32) 304.31 > 132.193 (44)	-1.4	-4.7	-5	-10.7	-3.4	-7.2	-8.6	-7.5	2.4	-9.3	-6.6	-10.3	-5.2	-12.6	-14.5	-11.7
76	Fenpyroximat	16.49 151	422.1 > 366.1 (15) 422.1 > 214.1 (24)	-1.3	-8.1	-9.1	-13.5	-5.6	-11.5	-12.1	-11.2	-0.1	-12.7	-10.7	-14.2	-4.8	-16.8	-18	-14.4
77	Fenuron	3.67 40	165.2 > 72.311 (15) 165.2 > 77.287 (30)	-9	-9.1	-7.3	-11.4	-7.9	-10.3	-9.7	-8	-1.3	-10.6	-7.3	-11	-11.9	-16.8	-16.8	-13.4
78	Fipronil	11.84 71	436.939 > 367.849 (17) 436.939 > 290 (25)	-4.5	-10.2	-8.5	-12.3	-7.9	-11.8	-11	-9.6	-0.4	-12.5	-10.9	-12.7	-9.8	-16.7	-18	-13.8
79	Flonicamid	3.1 123	230.03 > 203 (15) 230.03 > 174 (16)	-7.8	-8.9	-5	-10.5	-4.3	-8.9	-8	-5.7	-1.2	-10.2	-5.1	-8.8	-10.5	-15.3	-14	-9.3
80	Fluazinam	15.31 158	462.9 > 415.9 (22) 462.9 > 397.9 (19)	-2.9	-10.9	-6.7	-16.4	-8.9	-15.3	-11.4	-14.3	-2.3	-15.4	-10	-16.3	-8.4	-19.6	-16.8	-17.5
81	Flubendiamide	12.27 62	683.019 > 407.889 (10) 683.019 > 273.889 (32)	-1.7	-8.6	-2.9	-14	-3.7	-12	-10.2	-9	-0.2	-13.9	-10.4	-11.4	-2.8	-15.7	-12	-15.5
82	Fludioxonil	9.82 70	266.03 > 228.93 (10) 266.03 > 157.99 (32)	-9.4	-13.3	-4.5	-14.3	-6.8	-12.8	-7.5	-11.4	-2.4	-14.5	-7.5	-15.9	-12.7	-18.2	-15.8	-15.8
83	Flufenacet	10.86 106	364.1 > 152.2 (19) 364.1 > 124.2 (36)	-1.7	-6.8	-7.5	-12.3	-5.8	-10.5	-10.2	-9.8	0.5	-12.1	-9.5	-12.6	-6.4	-16.1	-16.7	-13.4
84	Flufenoxuron	16.31 182	489.04 > 158.09 (21) 489.04 > 141.09 (43)	-3.4	-10	-2.1	-15.4	-8	-13.3	-6.4	-12.7	-2.5	-14.6	-5	-15.7	-8.7	-18.8	-12.5	-16.6
85	Fluometuron	6.66 126	233.165 > 72.322 (22) 233.165 > 160.076 (30)	-4.1	-7.3	-7.8	-10.9	-7.1	-10.4	-10.4	-9.2	-1.7	-11.9	-8.6	-12.1	-7.9	-16	-16.2	-12.3
86	Fluoxastrobin	10.73 191	459.1 > 427 (18) 459.1 > 188.1 (34)	-2.9	-6	-6.3	-11.4	-5.3	-9.5	-9.9	-8.9	1.4	-10.2	-8.2	-11.3	-5.1	-14.8	-16.2	-12.5
87	Fluquinconazole	10.49 130	376 > 349.076 (19) 376 > 307.1 (22)	-5.1	-10.1	0.5	-14.1	-6.8	-12.9	-1.3	-11	-0.9	-12.7	-1.3	-14.8	-9.6	-16.9	-9.6	-15.1

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
88	Flusilazole	11.68 188	316.06 > 247.092 (20) 316.06 > 165.152 (33)	-3.7	-7.5	-6.6	-10.9	-5.8	-10.5	-11.1	-8.4	0.4	-10.5	-8.9	-12.1	-7.6	-15.2	-16	-12.6
89	Flutolanil	9.9 136	324.17 > 242.076 (28) 324.17 > 262.055 (20)	-4	-7.6	-8.2	-13.5	-5.9	-10.3	-9.9	-9.7	-0.1	-12.1	-9.5	-13.1	-7.9	-15.8	-17	-13.4
90	Flutriafol	7.21 128	302.16 > 70.334 (20) 302.16 > 123.111 (30)	-4.9	-7.5	-6.6	-11.4	-6.3	-10.3	-10.1	-8.6	-1.4	-12.2	-9.4	-11.5	-7.8	-15.5	-15.9	-12.3
91	Forchlorfenuron	7.81 128	248.035 > 129.127 (20) 248.035 > 93.236 (36)	-5	-8.6	-7.9	-12.8	-6.8	-11	-10.7	-9.4	-1.8	-12.1	-10	-13.2	-10.3	-17.3	-17.3	-13.7
92	Formetanate hydrochloride	2.6 111	222.1 > 164.9 (16) 222.1 > 120.1 (26)	-4.2	-8.4	-8.3	-13.5	-7	-11.2	-11	-10.5	0.1	-12	-10.1	-12.7	-8	-16.4	-17.5	-13.1
93	Fuberidazole	3.7 138	185.1 > 157.1 (23) 185.1 > 65.4 (48)	17.4	35.3	36.8	29.4	59.3	32.3	32.1	35.7	31.4	31	38.3	29.8	12.9	22.1	23.1	28.3
94	Furalaxyl	8.85 125	302.19 > 242.115 (18) 302.19 > 270.077 (11)	-2.9	-6.8	-6.1	-11.7	-4.7	-9.5	-9.7	-8.7	0.8	-10.6	-8.4	-12	-6.4	-14.2	-15.3	-12.5
95	Furathiocarb	14.49 133	383.21 > 195.072 (21) 383.21 > 167.081 (27)	-1.9	-6.8	-6.7	-11.8	-4.2	-10	-10.2	-8.9	1.2	-10.4	-8.3	-12.8	-5.4	-15.7	-16.4	-12.6
96	Halofenozide	9.32 76	331.01 > 275.111 (8) 331.01 > 105.028 (18)	-3.5	-7.3	-7	-11.8	-6.8	-11.4	-13.7	-12	0.3	-11.7	-10.9	-13.1	-5.4	-17.7	-16.9	-12.8
97	Hexaconazole	12.51 161	314.2 > 70.4 (18) 314.2 > 159.024 (28)	-4.9	-8	-8.4	-13	-6.3	-11.3	-10.9	-9.7	0.1	-11.5	-10.4	-13.3	-9.1	-16.4	-17.6	-14.2
98	Hexaflumuron (-)	14.45 105	458.92 > 438.932 (14) 458.92 > 174.866 (37)	4.6	-2.6	-6.2	-10.6	-1.7	-8.2	-9.9	-8	4.9	-9.9	-8.1	-11.8	1	-11.7	-15.6	-12.1
99	Hexythiazox	15.51 122	353 > 227.9 (15) 353 > 168 (24)	-6.2	-10.9	-9.4	-14.8	-11.6	-14.3	-13.2	-12.1	-5.3	-14.6	-12.2	-15.4	-10.9	-19.3	-19	-15
100	Imazalil	7.15 187	297.135 > 159.043 (26) 297.135 > 255.025 (23)	-0.1	-5.1	-4.7	-9.5	-3.1	-6.8	-7.7	-6.8	2.8	-8.5	-5.8	-9.8	-5	-12.9	-13.9	-9.9
101	Imidacloprid	3.5 109	256 > 209 (16) 256 > 175 (18)	9.8	4.8	1.1	-7.8	7	-1.7	-6.4	-7.5	14.9	-2.9	-4.6	-11.2	9	-3.2	-9.5	-9.4
102	Indoxacarb	14 184	528.055 > 203.023 (38) 528.055 > 150.06 (25)	-2.2	-8	-8.4	-14.6	-6	-12.4	-11.3	-11.7	0.3	-13.6	-10.3	-15.6	-5.3	-18.3	-18.6	-15.3
103	Ipconazole (*)	13.52, 13.88 166	334.2 > 70 (27) 334.2 > 125 (33)	-4.2	-7.8	-7.8	-12.2	-6.1	-10.8	-11	-8.8	-0.3	-10.8	-9	-12.7	-7.8	-16.4	-16.5	-12.7
104	Iprovalicarb (*)	10.41, 10.57 111	321.3 > 119.3 (18) 321.3 > 91.4 (54)	-3.1	-6.4	-7.4	-11.7	-4.9	-9.9	-10.5	-8.5	0.7	-10.9	-9	-12.2	-6.7	-15.2	-15.5	-13.2
105	Isocarbophos	7.58 61	307.1 > 231 (18) 307.1 > 273.2 (5)	-4.8	-7.4	-5.4	-12.2	-6.3	-14	-7.3	-6	-0.7	-14.2	-7.3	-7.6	-8.7	-16.9	-14.8	-12.7
106	Isoprocarb	6.99 89	194.195 > 95.22 (18) 194.195 > 137 (10)	-3.9	-8.9	-8.6	-13.3	-6.6	-10.2	-11.8	-10.6	-0.4	-12.7	-10.4	-13.7	-7.9	-17.4	-18.5	-14.2
107	Isoproturon	7.35 133	207.225 > 72.312 (21) 207.225 > 134.182 (26)	-1.5	-5.3	-5.6	-10.3	-4	-8.6	-8.7	-8.4	1.7	-9.6	-7.7	-10.7	-4.9	-14.3	-15.1	-11.5
108	Ivermectin	18.76 76	892.7 > 569.222 (13) 892.7 > 307.097 (22)	50.6	14.2	14	-1.2	36.7	15.9	4.3	3.8	14.3	1.4	3.8	-3.2	14.5	8.5	17.8	6.1
109	Kresoxim-methyl	11.77 80	314.09 > 222.122 (15) 314.09 > 235.099 (19)	-5.6	-10.1	-9.3	-14.7	-7.7	-12.6	-12.9	-11.8	-2.3	-13.4	-13.1	-14.2	-8.5	-17.8	-19.5	-15.4
110	Linuron	9.07 112	249.095 > 182.077 (18) 249.095 > 160.041 (21)	-3.7	-7.8	-6.3	-11.9	-5.4	-8.9	-9.6	-9.1	0.7	-10.7	-8.5	-13.3	-8	-15.1	-16	-12.5

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
111	Lufenuron (-)	15.71 76	509 > 325.9 (10) 509 > 175 (20)	-1.8	-6.9	-2.1	-17.1	-8.8	-13.2	-3.9	-14.8	-1.3	-14	-2.6	-17.2	-7	-17.5	-10.9	-18
112	Mandipropamid	9.9 152	412.1 > 328.1 (15) 412.1 > 356 (11)	-2.4	-6.9	-6.9	-12.9	-6.1	-10.5	-10.5	-10.5	0.9	-12	-9.7	-13.3	-6.5	-15.9	-17.2	-14.4
113	Mefenacet	10.25 111	299.1 > 148.3 (16) 299.1 > 120.3 (27)	-3.3	-6.6	-6.8	-12.1	-5.5	-9.4	-10.1	-9.2	0.4	-10.7	-8.2	-12.9	-7.2	-15.3	-16.7	-12.8
114	Mepanipyrim	10.65 169	224.195 > 77.278 (39) 224.195 > 106.194 (29)	-2.1	-5.6	-4.6	-10.9	-4.8	-8.4	-9.3	-7.2	1.9	-9.5	-7.5	-10.6	-5.5	-14.3	-14.7	-11.6
115	Mepronil	9.83 137	270.225 > 119.15 (26) 270.225 > 228.085 (16)	-1	-5.3	-4.5	-9.8	-4.2	-7.2	-7.5	-6.7	1.8	-9.1	-6.5	-10.7	-5.9	-12.4	-14.1	-10.6
116	Metaflumizone	15.53 177	507.183 > 177.92 (23) 507.183 > 286.9 (23)	-6.1	-11.3	0.3	-15	-10.7	-15.7	-4.5	-12.5	-2.2	-14.5	-2.3	-15.6	-11.1	-19.6	-10.2	-16.5
117	Metalaxyl	7.32 116	280.225 > 220.15 (16) 280.225 > 192.175 (21)	-2.1	-6.5	-6.7	-11.1	-5	-9.4	-9.2	-8.6	1.1	-10.1	-8.2	-11.6	-5.9	-14.2	-15.6	-12.6
118	Metconazole	12.71 179	320.1 > 70.335 (24) 320.1 > 125.1 (40)	-7.4	-10.6	-9.7	-14	-10.6	-13.4	-11.7	-10.8	-4.5	-14.1	-10.1	-14.3	-11.5	-18.1	-18.2	-13.6
119	Methabenzthiazuron	7.34 98	222.145 > 165.105 (19) 222.145 > 150.104 (36)	-1.9	-5.6	-5.5	-10.6	-4.6	-8.2	-8.6	-6.5	1.6	-10.1	-7.4	-10.2	-6.5	-13.8	-14.2	-10.9
120	Methamidophos	1.73 80	142.135 > 94.176 (16) 142.135 > 125.049 (16)	-4.8	-9.1	-8.5	-13.2	-5.3	-11.2	-11.3	-10.1	-0.3	-12.9	-10.3	-13.5	-8	-17.2	-17.9	-14.3
121	Methiocarb	9.03 84	226 > 169.082 (10) 226 > 121.045 (36)	-4.7	-8.5	-7.9	-13.2	-6.8	-10.2	-11	-10.4	-0.1	-12.2	-9.9	-13	-7.7	-16	-17.4	-13.8
122	Methomyl	3.07 59	163.1 > 88.3 (10) 163.1 > 73.3 (28)	-5.3	-7.5	-7.5	-12.2	-5.9	-10.9	-10	-8.9	-0.9	-11.3	-8	-11.6	-8.3	-14.5	-16.6	-11.8
123	Methoprotryne	7.35 171	272.2 > 198.1 (23) 272.2 > 240 (20)	-1.8	-5.4	-4.8	-10.6	-4.7	-7.9	-8.6	-7.3	2.4	-9.7	-7.4	-10.6	-5.2	-13.4	-14.7	-11.3
124	Methoxyfenozide	10.22 95	369.1 > 149.1 (18) 369.1 > 313.1 (6)	-1.8	-8	-7.5	-12	-6.5	-11.3	-10.5	-9.8	0.3	-12.4	-10	-13.5	-6.8	-15.4	-17.2	-14
125	Metobromuron	7.07 119	259.06 > 169.993 (22) 259.06 > 170.981 (29)	-5.9	-8.3	-6.8	-11.3	-6.3	-10.2	-10	-8.4	-1.6	-12.1	-8.2	-12.7	-8.1	-15.5	-16.4	-12.8
126	Metribuzin	5.29 151	215.075 > 187.131 (20) 215.075 > 171.115 (24)	-6.2	-7.5	-5.5	-10.8	-6.6	-9.1	-8.3	-7.2	-0.4	-10.3	-7.3	-10.5	-8.9	-14.8	-14.8	-10.8
127	Mevinphos (*)	3.67, 4.16 88	225.125 > 127.093 (19) 225.125 > 109.14 (34)	-9.7	-3.8	-6.6	-16.4	-10.9	-5.3	-9.3	-12.8	-4.4	-8.5	-7.3	-15.4	-13.1	-13.1	-17.1	-17.6
128	Mexacarbate	3.55 117	223.1 > 151.1 (24) 223.1 > 166.1 (16)	-12.2	-13.7	-10.5	-15.8	-9.9	-13.5	-12.6	-11.7	-3	-15	-10.9	-14.4	-13.9	-19.6	-19.7	-15.6
129	Monocrotophos	3.22 88	224 > 193.012 (9) 224 > 127.111 (10)	-25.2	-15.1	-5.6	-15.9	-14.3	-10.2	-5.6	-10.8	-6.9	-9.7	-2.8	-13.2	-25.4	-20.4	-14.1	-16.9
130	Monolinuron	6.48 94	215.135 > 126.11 (20) 215.135 > 99.16 (36)	-2.6	-5.1	-5.6	-10.5	-4.6	-8.3	-8.2	-6.5	1.2	-9.5	-6.8	-10.2	-6	-13.5	-15.5	-11.5
131	Moxidectin	18.46 68	640.331 > 528.222 (10) 640.331 > 498.222 (10)	-4.9	0.2	-9.4	-13.1	-10.5	-4.5	-10.8	-11.8	-5.5	-5.8	-10.7	-12	-9.7	-10.4	-19.1	-15.6
132	Myclobutanil	10.14 142	289.17 > 70.316 (21) 289.17 > 125.107 (33)	-2	-7.4	-7.8	-14.1	-5	-10.3	-11.1	-10	-0.3	-11.9	-10.1	-13.6	-6.7	-16	-17	-13.8
133	Neburon	11.81 121	275.03 > 88.22 (14) 275.03 > 57.39 (18)	-6.3	-8.6	-1.7	-7.9	-9.5	-11.8	-5.7	-4.2	7.9	-11.4	-3.6	-8.8	-10.7	-16.4	-9.7	-8.5

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
134	Nitenpyram	2.97 120	271.15 > 237.098 (21) 271.15 > 224.099 (18)	-8.1	-13.1	-6	-16.9	-8	-16.5	-8.7	-13.6	-4.9	-17.4	-8.1	-15.6	-11.7	-19.1	-16.6	-18.2
135	Novaluron (-)	14.6 119	490.985 > 470.974 (14) 490.985 > 304.961 (19)	5.3	-2.6	-4.8	-9.6	-2.9	-7.3	-9.6	-8.1	5.3	-9.8	-7.1	-11.3	-1.9	-11.8	-14.9	-12.3
136	Nuarimol	8.98 166	315 > 252 (23) 315 > 242.9 (26)	-2.5	-8.3	-8.6	-14.1	-4.9	-10.8	-11.3	-10.6	0.7	-12.5	-10.2	-12.9	-6.8	-15	-17	-13.7
137	Omethoate	2.58 101	214.1 > 182.9 (13) 214.1 > 125.1 (17)	-3.3	-8.2	-8.3	-13.5	-5.4	-11.3	-10.8	-10.3	0	-12	-9.3	-12.5	-7.6	-16.3	-16.8	-13.5
138	Oxadixyl	4.77 99	279.2 > 219.071 (11) 279.2 > 133.155 (22)	2.9	-6.2	-7.4	-12.8	-0.6	-8.7	-11.4	-9.4	0.7	-9.4	-1.3	-12	-8	-14.9	-16	-7.6
139	Oxamyl	2.92 63	237.075 > 72.304 (17) 237.075 > 90.267 (11)	-4.9	-10.3	-7.6	-12.9	-6.8	-13.9	-10.2	-10.8	-2.3	-15.3	-10.3	-12.8	-8.6	-18.9	-17.1	-16.2
140	Paclobutrazol	9.66 145	294.19 > 70.324 (22) 294.19 > 125.114 (36)	-4.7	-8.1	-7.5	-12.4	-6	-11.2	-10.8	-9.3	0.1	-12	-9.1	-13.1	-8.3	-16.4	-17.1	-13.3
141	Penconazole	11.95 142	284.1 > 159 (25) 284.1 > 70.4 (19)	-7.1	-8.8	-7.2	-12.3	-9.1	-11.4	-11.2	-8.7	-2.6	-12.3	-9.2	-12.3	-11.6	-16.6	-17.1	-12.3
142	Pencycuron	13.37 167	329.1 > 125.2 (21) 329.1 > 218 (16)	-4	-8.9	-9.2	-13.3	-6.6	-11.9	-12.3	-11.3	-0.6	-12.9	-10.6	-14.7	-7.4	-17.4	-18.3	-14.5
143	Phenmedipham	8.45 48	318.08 > 136 (25) 318.08 > 168 (12)	-4.3	-10	-3.6	-14.9	-6.9	-13.3	-7	-11.1	-1.3	-14.1	-5.4	-15.5	-8.8	-17.8	-14.6	-16.2
144	Phoxim	13.02 75	299.135 > 129.134 (13) 299.135 > 77.307 (29)	-5.1	-8.3	-4.7	-11.1	-2.1	-7.7	-6.7	-15.7	0.7	-11.8	-3	-11	-5.2	-18.7	-17	-14
145	Picoxystrobin	11.79 90	368.1 > 145.3 (22) 368.1 > 115.2 (50)	-3.8	-8.2	-7.4	-13.1	-5.7	-9.8	-11.2	-9.1	-0.1	-11.5	-10.3	-13.3	-5.8	-16.2	-16	-13.2
146	Piperonyl butoxide	14.84 107	356.2 > 177.1 (12) 356.2 > 119.2 (37)	-2.6	-9.5	-7.2	-15.3	-7.3	-13.1	-11.3	-12.7	-1.6	-14.6	-9.5	-16.1	-7.8	-18.3	-17.3	-16.3
147	Pirimicarb	4.52 123	239.225 > 182.157 (18) 239.225 > 72.307 (23)	-6.3	-8.3	-6.9	-11.7	-7.1	-10.7	-10	-8.9	-1.1	-11.5	-8.3	-11.9	-9.2	-15.7	-17.1	-12.9
148	Prochloraz	12.58 111	376.09 > 307.983 (14) 376.09 > 70.349 (27)	-6.5	-10.5	-4.8	-14.1	-9.8	-13.8	-8.9	-11	-3.6	-14.6	-6.5	-15.2	-10.1	-18.8	-14.6	-15
149	Promecarb	9.38 92	208 > 109.25 (16) 208 > 151.2 (9)	-5	-9.1	-8.1	-13.3	-6.8	-11.5	-12.1	-10.7	0.7	-13.3	-10.4	-14.2	-7.8	-17.3	-18	-15.3
150	Prometon	6.22 163	226.2 > 142.1 (23) 226.2 > 184.1 (19)	-2.7	-5.7	-5.4	-10.8	-6.7	-9	-9	-7.5	0.3	-10.1	-7	-10.6	-5.7	-13.9	-14.5	-11.3
151	Prometryn	8.83 179	242.2 > 158.1 (25) 242.2 > 200.1 (20)	-1.5	-5.7	-6.1	-10.5	-4	-8.2	-9.3	-7.7	2.2	-9.4	-7	-10.8	-6.2	-13.6	-14.9	-12.3
152	Propamocarb	2.7 106	189.2 > 102.2 (20) 189.2 > 74.4 (15)	-21.8	-18.8	-13	-15.6	-22.5	-19.8	-14.2	-11.6	-4.3	-13.4	-9.8	-12	-33.1	-29.7	-23.6	-16.5
153	Propargite	15.98 111	368.14 > 107.198 (28) 368.14 > 57.44 (23)	-4.8	-11	-7.7	-16.2	-7.6	-13.6	-10.8	-13.1	-1.7	-15.2	-9.9	-16.5	-9.3	-19.8	-17	-15.6
154	Propham	6.95 25	180.122 > 138.04 (8) 180.122 > 120.11 (19)	0.2	-7.6	-6	-11.9	-4.7	-7.9	-13.1	-9.3	3.3	-12	-10.5	-14.4	-4	-12	-12	-11.2
155	Propiconazole (*)	12.31, 12.45 193	342.13 > 159.015 (30) 342.13 > 123.151 (37)	-2.6	-7.1	-7.4	-12.3	-5.6	-10.7	-10.6	-8.9	0.6	-11.2	-9.2	-12.3	-6.9	-15.3	-16.2	-13
156	Propoxur	5.34 83	210.185 > 111.177 (17) 210.185 > 93.215 (27)	-5.3	-8.2	-8.4	-12.5	-6.6	-11.1	-10.9	-11.4	-0.5	-12.8	-10	-13.3	-7.8	-17.3	-18.1	-14.5

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
157	Prothioconazole	12.41 70	341.978 > 306.1 (15) 343.978 > 308.1 (15)	28.6	67.2	62	51.8	57.1	51.7	57.6	56.4	47.3	56.1	62.4	54.9	25.9	47.1	47.9	56.4
158	Pyracarbolid	5.73 61	218.152 > 125.11 (15) 218.152 > 97.125 (24)	-12.8	-10.6	-9.5	-14.8	-14.6	-13.1	-12.6	-11.4	-8.4	-13.7	-11.5	-14.3	-15.9	-18.2	-19.2	-15.3
159	Pyraclostrobin	12.97 126	388.15 > 163.107 (26) 388.15 > 149.093 (31)	-2.6	-7.8	-8	-13.3	-5.6	-11.1	-10.8	-9.3	0	-11.6	-9.7	-13.9	-6.6	-16.4	-17.6	-13.5
160	Pyridaben	17.12 90	365 > 309 (14) 365 > 147 (24)	-3	-7.7	-7.7	-12.9	-7.7	-11.3	-10.8	-9.4	0.6	-12.1	-9.3	-13	-6.4	-16.1	-16.8	-13.1
161	Pyrimethanil	8.11 165	200.195 > 107.179 (25) 200.195 > 168.102 (33)	-1.6	-5.7	-6.1	-11.3	-5.3	-9.4	-9	-7.5	1.2	-10.3	-7.8	-11.6	-6.3	-14.5	-16.1	-12.1
162	Pyriproxyfen	15.27 121	322.19 > 96.237 (19) 322.19 > 185.104 (25)	-2.4	-7.1	-6.6	-12.1	-5.4	-9.9	-9.6	-8.9	1	-10.6	-8.2	-12.1	-7.7	-15.6	-16	-12.4
163	Quinoxyfen	15.55 213	308.075 > 197.022 (35) 308.075 > 162.098 (48)	-4.2	-8.1	-7.5	-12.7	-7.2	-11.1	-10.7	-9.7	-0.4	-11.3	-9.5	-12.5	-9.4	-16.1	-16.9	-12.9
164	Rotenone	11.51 206	395.15 > 213.086 (26) 395.15 > 191.115 (39)	-1.6	-7.6	-6.1	-15.1	-4.6	-10.4	-10.9	-11.6	2.2	-13.7	-8	-15.2	-5.8	-16.6	-17.5	-15.3
165	Secbumeton	6.21 157	226.245 > 170.127 (21) 226.245 > 142.127 (26)	-4.7	-8.1	-8.6	-14.2	-7.7	-11.7	-11.1	-10.6	-2.3	-13.3	-9.5	-13.7	-8.5	-16.4	-18	-13.5
166	Siduron (*)	8.99, 9.31 101	233.152 > 94.151 (18) 233.152 > 137.04 (15)	-0.1	-4.1	-4.5	-9.5	-3.5	-7.3	-7.9	-6.1	3	-8.4	-6.5	-9.6	-4.3	-12.4	-13.5	-10.7
167	Simazine	5.49 38	202.05 > 132.04 (20) 202.05 > 104.01 (26)	-9	-8.1	-6.2	-9	-4.4	-7.5	-5.6	-13.1	-2.6	-12.2	-1.8	-8	-10.6	-18.9	-17.9	-11.5
168	Simetryn	5.66 169	214.085 > 68.356 (36) 214.085 > 96.2 (27)	-3.5	-7.3	-7.1	-11.6	-6.1	-9	-10.5	-8.8	0.3	-10.5	-8.8	-12.4	-7.3	-15.2	-16	-12.8
169	Spinetoram	14.33 200	748.5 > 142.2 (31) 748.5 > 98.1 (40)	-1.8	-5.6	-5.5	-9.6	-1.7	-8.1	-9.3	-7.3	3.7	-9.4	-6.3	-10.1	-6.6	-13.6	-14.9	-11.1
170	Spinosad A (*)	13.43 250	732.47 > 142.214 (26) 732.47 > 98.267 (41)	-0.6	-5.3	-6.2	-10.6	-1.5	-8.4	-9.1	-7.6	2.8	-9.1	-7.3	-11.4	-4.5	-14	-15.2	-11.5
	Spinosad D (*)	14.3 250	746.455 > 142.203 (27) 746.455 > 98.269 (43)																
171	Spirodiclofen	16.51 141	411.085 > 313.027 (10) 411.085 > 71.376 (15)	-3.6	-9.6	-5	-15	-7.6	-12.3	-8.6	-11.5	-1.5	-14.1	-6.8	-15.7	-8.3	-18.9	-15.1	-16.8
172	Spiromesifen	15.97 76	371.3 > 273.3 (15) 371.3 > 255.2 (20)	-1.7	-6.9	-7.2	-12.2	-5.1	-10.5	-10.2	-9.8	-0.1	-11	-9.4	-11.3	-7.2	-16.1	-16.5	-12.5
173	Spirotetramat	10.6 152	374.2 > 302.15 (16) 374.2 > 330.207 (10)	-0.2	-5.5	-5.6	-10.4	-4.4	-8.8	-9.3	-7.6	1.7	-9.6	-8.4	-11.1	-4.5	-14.3	-15.5	-11.7
174	Spiroxamine (*)	9.59, 9.78 142	298.3 > 144.1 (20) 298.3 > 100.2 (30)	-1.3	-4.8	-4.7	-10.1	-4	-7.5	-8	-7.3	3.1	-8.9	-6.6	-10.5	-5.2	-13.5	-14.7	-11
175	Sulfentrazone (-)	5.88 225	384.945 > 306.967 (25) 384.945 > 198.954 (40)	1.4	-9.2	-7.9	-14.8	-1.5	-9.6	-12.2	-10.7	5.8	-11.7	-8.9	-13.1	-5.3	-15.8	-18.5	-14.3
176	Tebuconazole	12.08 160	308.2 > 70.338 (24) 308.2 > 125.106 (30)	-7.1	-11	-10.4	-14.4	-9.3	-13.6	-13.3	-11.9	-4.5	-14.1	-12.4	-15.2	-11.1	-18.6	-19.1	-15.8
177	Tebufenozide	11.79 96	353.27 > 133.153 (21) 353.27 > 297.2 (5)	-2.4	-6.9	-7.6	-13.4	-5.2	-10.6	-11.7	-9.8	0.7	-10.7	-10.3	-13.8	-6.3	-15.6	-16.3	-14.1
178	Tebufenpyrad	14.62	334.15 > 145.054 (27)	-1.4	-5.3	-6.1	-11.4	-5.9	-8.4	-9	-7.8	0.5	-9.9	-7.7	-11.5	-6	-14	-15.4	-11.5

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	Matrix effect (%)															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
		207	334.15 > 117.161 (25)																
179	Tebuthiuron	5.63 127	229.185 > 172.136 (20) 229.185 > 116.136 (30)	-3.4	-5.4	-5.2	-9.6	-4.9	-7.6	-7.4	-6.6	1.6	-9.1	-6.4	-10.1	-7	-13.4	-14.3	-11.1
180	Teflubenzuron (-)	15.26 95	378.939 > 338.89 (10) 378.939 > 358.89 (10)	19.2	9.9	4.5	-5.5	4.1	-4.4	-6.4	-5.4	8.5	-5.4	-4.1	-9.9	14	0.5	-7.6	-6.2
181	Temephos	15.43 213	467.005 > 418.987 (22) 467.005 > 404.954 (17)	2.9	-6.5	-8.1	-14.6	-5.6	-12.1	-12.5	-12.2	0.8	-12.8	-10.9	-14.6	-2.6	-15.6	-18.3	-15.5
182	Terbumeton	6.39 140	226.1 > 170 (19) 226.1 > 142.1 (25)	-7.8	-10.6	-6.2	-12.7	-10.3	-13.5	-8.6	-6.6	-3.1	-16.3	-6.7	-11.9	-10.4	-20	-17.1	-12.7
183	Terbutryn	9.1 151	242.1 > 186.1 (21) 242.1 > 91.2 (29)	-2.3	-6.8	-6.6	-10.9	-4.7	-8.9	-9.3	-8	2.1	-9.8	-7.8	-11.2	-6.5	-13.9	-15.5	-12.4
184	Tetraconazole	11.1 143	371.95 > 159.117 (28) 371.95 > 70.331 (24)	-3	-8.5	-7.3	-12.9	-6.3	-11.3	-11.4	-9.7	0	-11.2	-9.5	-13	-6.9	-16.6	-17.2	-13.3
185	Thiabendazole	3.58 178	202.115 > 175.052 (28) 202.115 > 131.158 (36)	4.5	15.1	19.6	12.5	50	15.2	16.5	17.1	15.8	14.4	14.5	14.4	0.8	6	7.3	12.4
186	Thiacloprid	4.25 127	253.1 > 126.1 (22) 253.1 > 90.2 (41)	-0.6	-4.2	-4.4	-9.5	-3.2	-7	-7.9	-6.4	2.1	-8.8	-5.9	-10.3	-5.1	-12.1	-14.5	-10.6
187	Thiamethoxam	3.17 104	292 > 211 (13) 292 > 181 (23)	-5.9	-8.7	-7.5	-13.7	-2.4	-9.9	-10.3	-9.3	0.7	-12.8	-8.5	-13.1	-5.9	-15.2	-16.8	-13.7
188	Thiobencarb	13.04 105	258.145 > 125.128 (21) 258.145 > 89.223 (50)	-2.5	-7.3	-6.1	-12.5	-4.9	-10.1	-9.8	-8.5	0	-10.8	-9.1	-11.9	-7.4	-15.9	-16.6	-13.5
189	Thiofanox	6.47 46	241 > 184 (5) 219.2 > 61.1 (13)	-2.6	-5.2	-5.2	-12.6	-6.5	-10.6	-7.5	-9	-3.2	-8.1	-5.2	-16.1	-8.2	-15.6	-14.1	-13.2
190	Thiophanate-methyl	5.36 135	343.1 > 151.2 (19) 343.1 > 311.2 (11)	-8.7	-3.5	-1.3	-5.1	-8.2	-4.4	-3.6	-2.1	-0.8	-5.7	-0.6	-4	-12.2	-11.9	-11.1	-6.8
191	Triadimefon	10.02 103	294.183 > 197 (14) 294.183 > 224.99 (12)	-2.6	-7.3	-7.1	-11.5	-4.6	-8.4	-10.4	-9.5	1.5	-10.7	-8.6	-12.4	-6.9	-15.2	-16.4	-13.8
192	Triadimenol	9.66 58	296.07 > 70.04 (24) 296.07 > 126.946 (43)	-5	-9.2	-7.1	-13.8	-7	-11.4	-11.5	-10.2	-0.2	-12.3	-10.7	-14.1	-8.8	-16.5	-17.5	-15
193	Trichlorfon	3.64 112	256.905 > 109.146 (21) 256.905 > 79.26 (32)	-16.3	-14.4	-10.1	-13.6	-10.7	-12.6	-10.6	-9.3	-5.2	-14.1	-9.3	-12.2	-17.4	-19.6	-17.3	-13.5
194	Tricyclazole	4.66 150	190.1 > 163 (24) 190.1 > 136 (29)	-3.6	-7.2	-6.3	-11.8	-5.4	-8.6	-9.2	-8.3	0.4	-10.9	-7.7	-11.4	-7.2	-14.6	-15.2	-12.3
195	Trifloxystrobin	13.87 139	409.14 > 186.086 (20) 409.14 > 145.085 (44)	-3.1	-6.5	-7.3	-12.2	-5.6	-10.3	-10.8	-9.1	0.8	-10.8	-9.1	-12.7	-5.9	-15.4	-17.1	-13.2
196	Triflumizole	14.02 103	346.1 > 278 (5) 346.1 > 73.1 (15)	-10.9	-9.3	-4.2	-16.7	-15.3	-13.9	-8.7	-14	-6.9	-10.6	-3.7	-15.9	-15.8	-18.2	-15	-17.5
197	Triflumuron	13.05 118	359.06 > 156.06 (13) 359.06 > 138.99 (27)	-3.7	-8.9	-7.9	-12.9	-6.5	-11.8	-11.6	-10.2	-0.2	-12.6	-9.9	-14	-8.3	-16.6	-18.4	-14.1
198	Triticonazole	10.63 143	318.19 > 70.333 (19) 318.19 > 125.116 (45)	-2.4	-6.7	-8	-11.1	-5.4	-11.4	-11.7	-8.8	1.2	-11.4	-9.9	-13.6	-5.8	-16.1	-16.6	-14.3
199	Vamidothion	3.64 94	288.1 > 146.118 (15) 288.1 > 118.142 (25)	-9.6	-11.1	-8.9	-14.6	-8.6	-12.8	-12.5	-9.9	-3.5	-13.4	-9.2	-13.4	-12.6	-18.1	-18.4	-14.3
200	Zoxamide	12.44 159	336 > 186.9 (20) 336 > 159 (42)	-0.5	-6.4	-6.8	-11.8	-4.5	-9.6	-10.4	-9.1	1	-10.3	-8.9	-12.4	-4.5	-15	-16.2	-13.2

(*) Pesticides with two isomers, calculated with 2 peaks together.
(-) Compounds scan in negative mode; the other ones scan in positive mode
CE: Colission energy (V)
f: dilution factor

Table A-9. List of pesticides, method parameters, and matrix effects of GC-MS/MS method for 4 types of teas with different dilution factor at 2, 4, 10, and 20; injection volume 1 μL (chapter 4).

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
1	2,4'-Methoxychlor	22.15	121 > 78 (20) 227 > 121 (12)	31.9	15.1	-25.9	-35	36.5	2.7	-23.8	-35	17.9	8.9	-22.5	-36.6	61.8	12.1	-10.4	-28
2	2-Phenylphenol	11.94	141 > 115 (12) 170 > 141 (22)	15.4	8.7	-21.1	-31.5	16.5	-2.3	-18.2	-29.5	13	8.8	-17.7	-32	25.2	2.6	-12.5	-24
3	4,4'-Methoxychlor olefin	21.74	238 > 152 (35) 238 > 195 (20)	15.7	12.4	-17.2	-26	20	0.8	-15.6	-25.2	10.4	11.6	-14	-26	18.4	6.6	-7.9	-19.1
4	Acetochlor	16.75	174 > 146 (12) 223 > 132 (20)	15.1	24.8	-4.4	-19.3	26.6	5.1	-15.2	-28	15.5	11.3	-17.9	-32	12.4	19.1	-0.3	-17.1
5	Acrinathrin	24.17	181 > 152 (22) 208 > 181 (8)	-23	-18.7	-33.9	-40.6	-14	-22.6	-33.3	-39.6	-24.2	-20.1	-31.7	-41.4	-16.9	-20.8	-27.4	-34.4
6	Alachlor	16.91	188 > 130 (32) 188 > 160 (10)	19.4	15.5	-16.8	-28.3	15.6	-4.3	-21.6	-31.7	8.2	4.9	-20.9	-33.9	21.3	5.6	-11.1	-23.9
7	Aldrin	18.03	263 > 193 (32) 263 > 191 (30)	9.5	11.2	-13.1	-21.7	11.4	-2.1	-12.7	-23.2	2.9	7.9	-13	-24.8	11.9	2.7	-6.8	-16.8
8	Allidochlor	8.3	132 > 56 (6) 138 > 96 (8)	4.2	0.4	-27	-34.2	-1.5	-16.8	-27.6	-35.7	-6	-9.4	-28.1	-35.8	10.8	-4.9	-20.6	-29.2
9	Anthraquinone	18.07	180 > 152 (12) 208 > 180 (10)	33	11	-28.6	-40.3	19.1	-14.4	-34.5	-46.5	12	-5.3	-34.7	-47.9	46.1	1.5	-22.3	-35.7
10	Atrazine	15.05	200 > 122 (10) 215 > 173 (8)	13.2	5.6	-27.2	-36.7	13.7	-7.8	-25.4	-37.2	8.6	3.7	-23.8	-37.1	20.9	-2.8	-18.7	-32
11	Azinphos-ethyl	24.67	132 > 77 (12) 160 > 132 (6)	54.9	3	-50.7	-66.6	46.3	-19.8	-56.7	-70.2	21.9	-15.7	-55.7	-70.5	75.5	4.3	-44.1	-62.1
12	Azinphos-methyl	23.98	160 > 77 (16) 160 > 132 (6)	14.2	-34.3	-70.5	-81.1	3.1	-58.5	-80.9	-83.9	-26.7	-56.3	-80	-90.9	22.4	-35.3	-71.6	-81
13	Benfluralin	13.92	292 > 206 (12) 292 > 264 (8)	-2.7	-14.6	-42.2	-49.3	-7.2	-28.6	-40.9	-47.7	-9.4	-17.1	-39.9	-48	17.4	-19.7	-35.5	-45
14	BHC, alpha-	14.49	181 > 145 (13) 219 > 183 (8)	0.2	1.7	-18.8	-23.6	0.4	-8.1	-17.8	-22.4	-3.3	-1.6	-16.2	-23.4	3.9	-6.8	-11.5	-20.2
15	BHC, beta-	15.1	181 > 145 (15) 219 > 183 (8)	7.1	3.3	-18.8	-27.3	5.6	-8.3	-19.1	-26.6	1.5	1.5	-18.8	-26.2	8.9	-2.7	-11.8	-22.4
16	BHC, delta-	16.03	181 > 145 (13) 219 > 183 (8)	-26	-15.9	-28.6	-30.5	-7.4	-14.9	-23.8	-28.7	-15.4	-11.8	-22.9	-29.7	-13.1	-19.4	-23.7	-25.7
17	BHC, gamma-	15.34	181 > 145 (13) 219 > 183 (8)	3.1	7.9	-13.6	-20.4	3.8	-1.4	-10.6	-18.5	-2.8	0.2	-9.4	-16.7	12.2	-0.3	-7.3	-15.7
18	Bifenthrin	23.03	181 > 165 (25) 181 > 166 (10)	14.9	-4	-35.9	-45.8	13.4	-17.3	-36.3	-46.3	3.2	-10.8	-35.7	-47.4	24.2	-8.9	-28.2	-39.9
19	Bioallethrin	18.93	123 > 81 (8) 136 > 93 (11)	11.4	-9.5	-42.6	-51.6	4	-26.4	-44.6	-50.7	0	-16.2	-41.2	-50.5	22.7	-16.8	-34.4	-47.2
20	Biphenyl	9.95	154 > 115 (26) 154 > 127 (30)	1.8	8.6	-1.1	-2.5	3.3	1.8	2.1	-1.8	-0.6	7.6	0.4	-2	3.6	0.6	4.4	3.2
21	Bromfenvinphos	19.8	267 > 159 (15)	44.1	16.2	-31.5	-43.5	46.5	5	-25.8	-42.8	24.2	3.2	-33.8	-51.1	65.5	11.3	-21.5	-39.3

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
			323 > 267 (10)																
22	Bromfenvinphos-methyl	18.9	109 > 79 (5) 295 > 109 (15)	42	19.3	-29.2	-44.5	32.8	-7.4	-35.7	-49.1	16.9	1.2	-32.8	-50.8	79.3	13.3	-20.9	-39.8
23	Bromophos methyl	18.4	329 > 314 (13) 331 > 316 (13)	24.6	13.9	-22.9	-34.6	18	-9	-28.3	-38.4	14.8	4.6	-23.5	-39.4	38.9	6.9	-14.9	-29.7
24	Bromophos-ethyl	19.35	331 > 303 (8) 359 > 303 (17)	31.1	23.7	-19.8	-35.3	33.1	23.4	2.7	-22.6	17.4	10.6	-22.8	-38.3	37.6	22.2	1.7	-21.9
25	Bromopropylate	23.16	183 > 155 (12) 341 > 183 (15)	10.1	-5.5	-37.6	-46.2	9.4	-19.3	-37.7	-45.9	0.6	-12.4	-37.1	-47.8	21.5	-7.6	-29.9	-40.9
26	Bupirimate	20.32	273 > 108 (16) 273 > 193 (8)	10.9	7.4	-22.1	-29.1	16.4	-3.5	-18.1	-27.5	5.2	3.3	-20	-30.8	19.6	-0.1	-11.7	-23.2
27	Carbophenothion	21.79	125 > 97 (6) 199 > 143 (10)	61.7	27.4	-26	-44.6	47.8	1.3	-29.9	-43.8	36.2	10.3	-29.8	-46	72.9	19.3	-14.3	-36.7
28	Carfentrazone ethyl	21.62	330 > 310 (8) 340 > 312 (10)	29.5	10.6	-30.6	-42.6	32.6	-4.6	-31	-42.4	17.9	4	-29.8	-44.7	36.7	6.1	-18.8	-35.9
29	Chlorbenside	21.74	125 > 89 (17) 125 > 62.8 (28)	22.6	2.7	-34	-44.9	24.7	-2	-23.3	-35	11.3	-6.1	-35.3	-47.4	34.8	0.9	-21.5	-36.8
30	Chlordane, cis-	19.79	375 > 266 (21) 377 > 268 (19)	5.9	5.5	-16.7	-26.3	9.5	-3.3	-14.7	-24.2	-1.6	2.1	-17.6	-27.5	11.1	-2.4	-8.3	-18.9
31	Chlordane, trans-	19.49	272 > 237 (13) 375 > 266 (18)	7.6	5.6	-17.5	-25.9	10.4	-0.4	-7.1	-21.2	2.6	3.5	-15.8	-26.2	11.5	0.5	-6	-15.8
32	Chlorfenapyr	20.54	137 > 102 (12) 249 > 112 (24)	17.8	5	-28.2	-37.5	15.8	-7.8	-24.5	-33.9	11	6.6	-26.1	-33.9	23	-0.9	-17.3	-31.7
33	Chlorfenson	20	175 > 111 (8) 177 > 113 (8)	14.9	12.1	-15.2	-23.1	15.8	2.3	-12.8	-23.5	7.1	7.4	-14.2	-25.4	13.5	4.6	-5.3	-16.5
34	Chlorfenvinphos (*)	18.87 19.5	267 > 159 (15) 323 > 267 (10)	28.2	7	-33.4	-45.5	19.8	-14.6	-37.5	-48.6	12.3	-6.2	-34.6	-50	50	0.3	-24.6	-41.5
35	Chlorobenzilate	20.97	139 > 111 (12) 251 > 139 (14)	11.3	-2.6	-32.9	-40.1	10.5	-14.8	-31.3	-39.1	3.7	-6.6	-31	-40	22.3	-7.2	-23.8	-34.1
36	Chloroneb	11.68	191 > 113 (15) 193 > 115 (15)	2.1	9.4	-3.9	-8.8	4.5	2.1	-0.5	-6.7	-1.3	8.7	-1.8	-7.9	5.6	1	1.5	-2.8
37	Chlorothalonil	15.72	264 > 168 (23) 266 > 133 (40)	-66.4	-46.8	-19.5	-16.3	-36.6	-20.4	-5.3	-12.3	-54.3	-23.8	-11.9	-4.4	-58.9	-24.2	-15	-9.8
38	Chlorpropham	13.81	171 > 127 (8) 213 > 171 (8)	9.2	-4.7	-34.3	-43.6	2.3	-20.5	-34.5	-42.6	-0.2	-10.7	-33.5	-43.5	18.2	-11	-27.9	-38.5
39	Chlorpyrifos	17.85	197 > 169 (14) 314 > 258 (12)	14.9	11	-18.4	-27.2	13.6	-3.9	-18.1	-29	7.6	2.8	-18.6	-29.7	22.5	1.1	-10.3	-22.3
40	Chlorpyrifos-methyl	16.73	286 > 93 (24) 286 > 271 (12)	1.7	31.6	-4.6	-18.1	26.9	6.5	-11.8	-24.5	15.7	11.5	-13.9	-28.2	37.2	16.8	1	-13.8
41	Chlorthal-dimethyl	17.97	301 > 223 (24) 332 > 301 (8)	5.2	10.8	-7.4	-12.4	10	1.1	-6.8	-13.1	2.4	7.2	-6.8	-14.9	7.5	1.6	0.4	-6.5
42	Chlorthiophos (*)	20.7	257 > 193 (16) 257 > 239 (12)	34.6	19.2	-20.6	-32.8	34.5	4.6	-17.7	-31.7	24.1	13.6	-17.9	-34.7	47	13.5	-8.1	-24.4
		20.93	297 > 269 (8) 325 > 269 (14)																

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
		21.2	297 > 269 (8) 325 > 269 (14)																
43	Chlozolinate	18.79	186 > 145 (16) 331 > 259 (8)	0.1	1.9	-19.8	-27.4	5	-10.6	-19.5	-28.3	-1	0.3	-17.5	-28.8	10.6	-6.8	-11.9	-20.9
44	Clomazone	15.17	125 > 89 (13) 125 > 99 (17)	14.7	6.7	-29.5	-37.8	10.5	-9.7	-28.1	-37.4	6.5	1.6	-27.2	-37.8	23	-0.7	-20.6	-33.2
45	Coumaphos	25.36	210 > 182 (10) 362 > 109 (17)	53.4	6	-44.7	-62.4	49.9	-17	-51.2	-66.1	22.1	-17.4	-49.2	-67.7	79.3	1.2	-39.4	-56.3
46	Cycloate	13.59	154 > 83 (8) 215 > 154 (6)	5.8	1.9	-25.1	-32.6	7.8	-8.7	-21.9	-31.4	3.3	2.5	-20.8	-31	11.1	-6	-17.3	-27.4
47	Cyfluthrin (*)	25.8 25.92 26.0 26.05	163 > 91 (14) 163 > 127 (6)	5.5	-9.1	-40.2	-51.5	10.3	-21.7	-41.9	-52.2	-3.1	-17.8	-39.7	-53.4	16.8	-12	-34.3	-44.7
48	Cyhalothrin, lambda-	24.18	197 > 141 (10) 208 > 181 (8)	-21.6	-15.1	-33.9	-40.2	-11.7	-22.7	-33.2	-39.8	-19.7	-20	-32.1	-42.3	-12.2	-18.7	-25.2	-34.7
49	Cypermethrin (*)	26.22 26.32,2 26.4 26.45	181 > 127 (30) 181 > 152 (25)	3.5	-8.9	-39.4	-51.1	11.5	-18.3	-38.9	-50.7	-2.4	-14.7	-38.2	-52.9	19.6	-11.3	-33.7	-44.4
50	Cyprodinil	18.67	224 > 208 (20) 225 > 210 (12)	14.9	6	-23.4	-31.6	14	-9.5	-23.7	-34	7.8	1.5	-21.2	-33.5	20.7	-1.9	-15.5	-26.2
51	DDD, o,p‘-	20.4	235 > 165 (22) 235 > 199 (14)	6.8	2.8	-18.5	-25.5	7.7	-8	-17.2	-24.8	1.5	-0.9	-17.3	-27	4	-3.7	-12.2	-19.7
52	DDD, p,p‘-	21.19	235 > 165 (24) 237 > 165 (22)	13.5	0.2	-27.7	-36.5	12.7	-11.9	-27.5	-38.2	5.6	-4.6	-27.1	-39	15.7	-4.3	-19.8	-30.5
53	DDE, o,p‘-	19.5	246 > 176 (32) 316 > 246 (15)	8.2	11.9	-8	-14.8	10.8	5.8	0	-9.9	4.4	10.8	-5.3	-14.6	8.5	4.6	2.3	-6
54	DDE, p,p‘-	20.23	246 > 176 (28) 316 > 246 (20)	5.4	12	-2.1	-3	9.7	3.7	2	-0.8	0.2	10.2	1.2	-3	7.4	2.5	5.5	3
55	DDT, o,p‘-	21.26	235 > 165 (21) 237 > 165 (22)	27.5	13.4	-18.1	-31.2	32.5	3.7	-22.1	-26	10.7	6.4	-17	-31.8	67.5	6.6	-10.7	-25.1
56	DDT, p,p‘-	22.05	235 > 165 (21) 237 > 165 (22)	41.2	22.5	-17.7	-26.8	54.3	11.1	-17.9	-22.3	20.4	13.1	-16.2	-30.3	105.5	16.7	-4.1	-20.4
57	Deltamethrin (*)	27.94 28.17	181 > 152 (20) 253 > 174 (8)	-26.3	-31.7	-59.8	-71.5	-23.3	-48.6	-62.6	-73.7	-34.3	-44.5	-61.1	-74.3	-1.1	-32.7	-56.1	-65.9
58	Diallate (*)	14.32, 14.57	234 > 150 (18) 234 > 192 (12)	5.2	2.1	-24.7	-33.9	6.3	-8.2	-22	-31	1.9	2.1	-20.5	-31.6	11.6	-4.3	-16.8	-28.5
59	Diazinon	15.52	137 > 84 (12) 304 > 179 (10)	1.9	8.6	-12.3	-19.2	8.5	-0.9	-8.4	-16.6	-0.2	8	-7.2	-16	6.6	0.2	-4	-14
60	Dichlofluanid	17.67	123 > 77 (16) 224 > 123 (12)	-15.2	4.1	-12	-23.9	3	-4.1	-14.4	-23.6	-19.9	0.6	-14.2	-24.6	-23.3	-5.1	-10.1	-20.3
61	Dichloroaniline, 3,4‘-	10.62	161 > 99 (21) 161 > 126 (8)	5.5	6.9	-16.6	-23.6	1.8	-9.2	-16.2	-23.1	-1.5	1	-16.3	-24.4	10.6	-2.7	-10.7	-17.8
62	Dichlorobenzophenone, 4,4‘-	18.26	139 > 75 (27) 139 > 111 (13)	14.2	-4.8	-37.2	-43.5	2.9	-23.7	-38.3	-46.4	0.4	-14.1	-37.7	-46.8	22.9	-12.3	-31.2	-40.2

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
63	Diclobenil	9.23	171 > 100 (25) 171 > 136 (13)	3.1	6	-6.4	-10.6	3.5	-1.3	-4.1	-10.3	-0.5	3.7	-5.5	-10.6	7.4	-1.2	-1.4	-4.8
64	Dicloran	14.79	176 > 148 (10) 206 > 176 (10)	14.1	-5.9	-37.8	-46.7	5.1	-23.2	-37.7	-47	4.8	-10.9	-36.3	-47.9	37.5	-12.2	-32.3	-42.9
65	Dieldrin	20.43	263 > 193 (34) 277 > 241 (8)	9.2	8.4	-14.8	-14.5	13.7	-2.5	-10	-19.9	8.2	-0.3	-13.8	-21.8	14.2	1.4	-8	-10.4
66	Dimethachlor	16.65	134 > 105 (13) 197 > 148 (8)	-74.6	26.7	-1.7	-11.2	25.2	11.4	-6.5	-23.8	15	13.9	-13.3	-30.7	21.2	14.9	5.3	-9.3
67	Diphenamid	18.4	239 > 72 (10) 239 > 167 (8)	9.8	7.7	-18	-31.1	10.6	-9.3	-25.1	-34	9.5	6.7	-18.4	-31	17.5	0.3	-12.4	-24.4
68	Diphenylamine	13.45	168 > 167 (14) 168 > 139 (38)	6.4	4.2	-18.8	-25.6	5.2	-6.6	-16.3	-24.7	0.8	1.6	-16.1	-25.2	11.1	-4	-11.1	-19.2
69	Disulfoton	15.85	88 > 60 (6) 142 > 109 (6)	11995	8642	92.1	-25.9	11515	8080.2	1819.1	-20	11081.7	7506.1	586.7	27.7	13188.5	9081.7	4483.2	87.2
70	Edifenphos	21.88	109 > 65 (13) 173 > 109 (8)	56.1	16.1	-43	-60.1	43.5	-17.7	-49	-64.4	20.9	-11.4	-44	-67.5	106.7	6.2	-36.4	-53.9
71	Endosulfan ether	16.51	239 > 204 (13) 241 > 206 (13)	-82.2	-80	-1.6	-7.9	-58.3	2.1	-4.1	-10.7	-22.2	9.5	-3.7	-11.5	-81.7	-76.1	3.4	-5
72	Endosulfan I	19.81	195 > 159 (6) 241 > 206 (10)	5.2	9.3	-14.8	-21.7	13	5.4	-8.6	-16.4	3.1	4.7	-13.4	-22.4	10.2	-0.1	-5.8	-16.7
73	Endosulfan II	21.15	195 > 125 (23) 195 > 159 (8)	17.9	6.4	-21.4	-30.4	15.5	-6.3	-17.8	-29.3	5.7	2.8	-20.1	-29.8	16.2	1.2	-13.7	-23.4
74	Endosulfan sulfate	22	241 > 206 (8) 272 > 237 (10)	-5.5	9.1	-15.6	-28.2	25.1	7.6	-10.1	-21	7.4	11.7	-14	-25.8	14.3	0.5	-10.6	-14.6
75	Endrin	20.92	263 > 193 (30) 279 > 243 (8)	21.2	13.1	-23.8	-35.5	19.6	-2.7	-23.5	-36.9	11	6.1	-22.4	-36.9	34.1	2.3	-15.9	-27
76	Endrin ketone	23.09	315 > 279 (8) 317 > 281 (8)	4.8	-1	-21.6	-30.9	12.2	-9.8	-22.3	-33.3	-3.5	-6.6	-21.1	-32.8	15.1	-3.2	-17.3	-29.1
77	EPN	23.11	169 > 77 (22) 169 > 141 (8)	21.6	-5.9	-44.9	-53.3	20.3	-22.2	-46.2	-55.8	5.1	-18	-45	-58.9	61.9	-9.9	-36.7	-50.8
78	Ethalfluralin	13.64	276 > 202 (15) 316 > 276 (10)	-4.1	-14.4	-40.7	-47.2	-5.4	-26.6	-38.9	-45.7	-6.7	-13.2	-37.1	-46.2	18.3	-19.8	-34.3	-43.1
79	Ethion	21.15	153 > 97 (10) 231 > 129 (24)	21.9	-5.7	-39.2	-49.6	13.3	-20.4	-39.5	-49.6	7.3	-12.6	-39.1	-51.6	40.4	-9.2	-31.6	-44.3
80	Ethylan	20.8	223 > 167 (12) 223 > 179 (22)	17.9	7.8	-21.8	-31.5	20.2	-2.9	-19.5	-30.1	12.6	6.1	-18.3	-30.7	24.5	2.4	-13.1	-24.3
81	Etofenprox	26.62	163 > 107 (18) 163 > 135 (10)	12.7	-1	-35	-47.6	19.8	-12.4	-35.4	-48.1	5	-7.3	-34.2	-49.7	31	-6.1	-28.8	-41
82	Etridiazole	10.88	183 > 140 (16) 211 > 183 (10)	14	1.1	-33.3	-41.6	6.5	-17.4	-33	-42.3	-1.8	-10.3	-34.8	-43	45.2	-5	-26.6	-36.9
83	Fenamiphos	19.81	303 > 195 (9) 303 > 154 (8)	245	140.6	-39.6	-69.2	243.5	116.6	11.8	-62.2	188.3	110.8	-20.6	-71.3	324.9	143.4	34.7	-46.1
84	Fenarimol	24.53	139 > 111 (16) 219 > 107 (12)	9.1	-17	-49.2	-58.6	7.4	-30	-50.3	-59.3	-2.5	-24.4	-49.2	-60.1	24.1	-17.7	-42.9	-53.5
85	Fenchlorphos	17.16	285 > 270 (11)	22.2	18.8	-11.6	-22	19.5	1.5	-14.5	-25.3	10.3	9.2	-13.7	-26.9	28.6	10.3	-3.1	-16.8

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
			287 > 272 (11)																
86	Fenitrothion	17.48	277 > 109 (18) 277 > 260 (6)	37.1	9.7	-36.5	-48.7	20.2	-19.4	-42	-54.4	10.7	-11.9	-41.8	-55.3	62.9	-0.4	-29.8	-44.8
87	Fenpropathrin	23.26	181 > 152 (24) 265 > 210 (8)	15.8	0	-33.1	-42.6	16.5	-13.5	-32.5	-41.6	5.9	-6.4	-31.9	-43.4	24.7	-6.4	-25	-36.6
88	Fenson	18.39	141 > 77 (8) 268 > 141 (8)	13.1	12.4	-9	-16.3	13.4	-0.2	-9.2	-18.8	9	11.7	-6.2	-17.4	16.9	6.2	-0.1	-8.2
89	Fenthion	17.97	278 > 109 (18) 278 > 169 (17)	129.7	120.3	0	-36.8	128.1	98.2	42.7	-30.6	111.4	103.7	21.7	-32.6	138.6	105.1	62.7	-2.3
90	Fenvalerate (*)	27.3 27.54	167 > 125 (8) 169 > 127 (10)	-1.1	-11	-41.6	-52.6	5.5	-24.3	-42.2	-55.4	-7	-18.6	-40.1	-55.8	12.9	-14.3	-36.2	-45.9
91	Fipronil	18.67	367 > 213 (30) 369 > 215 (30)	1	-18.5	-48.8	-57.3	-1.8	-32.9	-49.2	-56.7	-10.8	-22.5	-47.4	-57	12	-23.8	-40.8	-51
92	Fluazifop-P-butyl	20.71	383 > 268 (8) 383 > 282 (12)	22.1	10.2	-26.5	-37.2	26.9	-4.6	-24	-34.7	14.1	8	-24.3	-37.5	37.7	4	-15.9	-29.1
93	Fluchloralin	15.55	264 > 160 (15) 306 > 264 (8)	-1.4	2.8	-19.6	-26	9.3	-5.7	-16.1	-22	-0.3	4.6	-14.4	-22.8	29.2	-5.7	-13.3	-21
94	Flucythrinate (*)	26.4 26.63	157 > 107 (13) 199 > 157 (8)	2.5	-9.6	-39.4	-51.1	12.6	-18.9	-40	-53.6	-1.1	-14.2	-38.8	-53.9	16.1	-12	-34.3	-46.1
95	Fludioxonil	19.96	154 > 127 (8) 248 > 127 (30)	28.6	3.2	-34.2	-46.5	23.3	-11.6	-33.8	-47.4	12.2	-7.6	-36.8	-51.2	44.2	0	-25.7	-39.8
96	Fluquinconazole	25.38	340 > 108 (42) 340 > 298 (14)	11.6	-6	-41.5	-53.1	18	-19.5	-43.8	-55.3	0	-16.2	-42.2	-56.5	29.7	-9.9	-34.9	-47.7
97	Fluridone	26.87	328 > 189 (38) 328 > 259 (24)	30.1	-13.6	-57.3	-69.7	23.6	-37.2	-61.5	-74.8	3.2	-31.7	-58.7	-74.3	52	-17.1	-51.7	-65.3
98	Flusilazole	20.33	233 > 152 (14) 233 > 165 (18)	13.1	3.1	-26.4	-35.5	13.2	-8.6	-23.8	-33.6	5	-1.7	-25.7	-37	22.9	-2.9	-17.1	-28.7
99	Flutolanil	19.89	173 > 145 (14) 281 > 173 (10)	17.9	-1.8	-35.5	-46.7	17	-12.3	-31	-43.7	6.8	-9.3	-35.7	-48	34	-6	-26.4	-39.4
100	Flutriafol	19.84	123 > 95 (12) 219 > 123 (14)	17.7	3.3	-31.4	-42.2	19.3	-6.2	-26.3	-36.7	7.7	-2.2	-30.9	-42.8	27.3	-0.8	-20.9	-34.2
101	Fonofos	15.53	137 > 109 (6) 246 > 137 (8)	8.4	10.5	-11.5	-19.6	11.1	1.2	-7.3	-16.6	5.3	10	-6.5	-16.4	11.6	1.9	-3.1	-12.2
102	Heptachlor	17.16	100 > 65 (12) 272 > 237 (13)	16	17	-8.6	-15.4	16.7	5.5	-7.8	-12.8	8.4	9.7	-7.8	-16.6	26.8	9.2	-1.5	-9.3
103	Heptachlor epoxide	18.94	351 > 261 (11) 353 > 263 (13)	2.6	0.9	-19.3	-23.9	4.3	-9.2	-19.3	-26	0.1	0.6	-18.2	-27.7	5.4	-5.4	-10.2	-22
104	Hexachlorobenzene	14.59	249 > 214 (14) 284 > 249 (18)	1.6	5.5	-7.8	-13.2	3.5	-2.9	-5.3	-14.1	0.9	5.8	-6	-11.9	3.1	-0.8	-2.4	-7.8
105	Hexazinone	22.12	171 > 71 (16) 171 > 85 (16)	41	9.2	-37.3	-50.5	31.7	-11.7	-40.6	-54.7	20.7	-4.1	-39.3	-55.5	55.1	6.9	-26.4	-44.3
106	Iodofenfos	19.98	377 > 93 (34) 377 > 362 (15)	36.8	8.4	-40.4	-53.5	30	-15.9	-39.5	-53.9	14.7	-11.4	-42.1	-59.6	62	0.4	-26.4	-49.4
107	Iprodione	22.85	314 > 245 (14) 314 > 271 (12)	5.4	0	-20.9	-33.2	32.5	-3.5	-25.5	-37.8	9.1	1.8	-16.8	-40.4	44.6	3.7	-16	-23.7

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
108	Isazophos	15.84	161 > 119 (8) 172 > 130 (8)	10.5	10.2	-18.2	-25.9	10.4	-3.6	-16	-23.9	4.6	6.2	-14.9	-25.7	16.2	1.5	-9.9	-20.1
109	Isodrin	18.74	193 > 123 (30) 193 > 157 (19)	3	4.1	-17.7	-24.1	4.2	-7.5	-16.2	-25.1	-1	2.7	-14.6	-24.6	8.5	-3.6	-8.8	-19.1
110	Isopropalin	18.46	280 > 180 (10) 280 > 238 (8)	6.2	-8.3	-39.7	-47.9	2.5	-27.1	-42	-49.1	-1.6	-11.8	-38.2	-49.1	25.4	-14.2	-31.2	-43.1
111	Lenacil	21.94	136 > 53 (18) 153 > 136 (14)	45.3	-2.6	-48.3	-58.9	34.1	-18.5	-50.9	-64.5	18	-16.4	-49.1	-65	69.9	-0.6	-37.5	-54.7
112	Leptophos	23.91	171 > 77 (18) 171 > 124 (8)	24.4	-1	-37.9	-48.5	22.4	-16	-38.9	-50.7	8.1	-12.2	-38.3	-52.4	33.6	-3.7	-29.2	-42
113	Lindan-d6 (surrogate) (**)	14.39	224 > 150 (20) 224 > 187 (10)	8.4	4.4	-16.3	-23.9	8.4	-2.7	-15.1	-24.3	6	3.2	-14.7	-24.5	17	0.7	-9.8	-21
114	Linuron	17.62	187 > 124 (21) 248 > 61 (8)	48	94.7	34.9	33.3	65.9	58.2	36.6	4.1	40.8	55.7	26	3.4	70.6	70.2	66.5	27.2
115	Malathion	17.67	127 > 99 (6) 173 > 127 (6)	24.8	9.2	-27.4	-38.7	20.3	-8.4	-30.5	-40.2	10	-1.7	-29.7	-41.8	35.7	1.4	-21.4	-34.1
116	Metalaxyl	17.11	160 > 130 (10) 220 > 160 (16)	7.7	10.5	-14.3	-22.9	10.6	-2.2	-14.3	-22.9	4	6.2	-13.3	-25.5	12.4	0.8	-7.5	-17.9
117	Metazachlor	18.71	133 > 117 (25) 209 > 132 (15)	21.4	11.9	-22	-33.8	19.6	-6.2	-24.2	-36.1	10	3.5	-22	-36.7	25.7	4.2	-15.2	-27.2
118	Methacrifos	11.53	125 > 79 (6) 180 > 93 (8)	0.3	-4.3	-31.2	-37.9	-4.6	-19.1	-30.9	-37.4	-1.5	-2.2	-26.8	-35.9	7.7	-11	-25.2	-33.1
119	Methoxychlor	23.25	227 > 141 (33) 227 > 169 (25)	38	18	-27.1	-35.7	45.5	7.1	-23.9	-30.2	20.2	8.8	-24.1	-37.9	81.9	12.3	-12.7	-28.9
120	Methyl parathion	16.89	263 > 109 (10) 263 > 136 (8)	55.9	25	-27.6	-44.5	29.8	-11.9	-39.4	-49.6	17.5	-7.1	-39.3	-54.4	81.4	9.8	-22.6	-43
121	Metolachlor	17.82	238 > 133 (27) 238 > 162 (10)	14.3	5.6	-21.6	-34.2	12.4	-10.9	-26.5	-35.6	4.8	-1.1	-25.4	-37.2	16.9	-2.6	-18	-29.9
122	Mevinphos	10.43	127 > 109 (8) 192 > 127 (10)	17.5	1.2	-37.4	-47.1	-1.8	-25.1	-41.4	-48.8	-5.8	-16.4	-41.5	-49.6	27.6	-9.1	-32.3	-42.4
123	MGK 264 (*)	18.44 18.74	164 > 67 (10) 164 > 98 (14)	11.5	4.1	-24.3	-31.5	10.3	-9.9	-25.5	-33.3	8	3.6	-21.2	-32.9	20.4	-1.7	-16	-25.7
124	Mirex	24.51	272 > 237 (15) 274 > 239 (15)	-0.1	-3.2	-28.7	-32.7	-0.3	-13.6	-24.8	-33.9	-3	-6.6	-27.2	-32.4	6	-7.7	-20	-27.3
125	Myclobutanil	20.29	179 > 125 (14) 179 > 152 (8)	13.9	5.1	-25.6	-35.1	14.2	-7.2	-22.9	-34.1	8	-1.2	-25.5	-37.6	22.4	-0.9	-16.1	-28.4
126	N-(2,4-Dimethylphenyl)formamide	11.32	120 > 77 (15) 121 > 106 (8)	7.5	-10.5	-41.2	-47.2	-0.8	-30.1	-42.5	-49.6	-0.1	-14.1	-40	-48.9	20.8	-15.2	-35.3	-44.2
127	Nitralin	22.44	274 > 216 (6) 316 > 274 (8)	-10.9	2.3	-25	-24.6	20.1	-1.2	-19.5	-17.6	-0.4	4.3	-10.4	-25.9	48.7	-8.2	-14.9	-24.2
128	Nitrofen	20.8	202 > 139 (20) 283 > 202 (10)	22.3	2.3	-34.7	-43.5	20.5	-14.8	-33.7	-44.3	8.4	-5.5	-33.7	-46.3	57.5	-3.2	-26.9	-38
129	Nonachlor, cis-	21.24	409 > 300 (23) 409 > 302 (20)	5.3	-3.5	-22.8	-32.4	4.7	-12.3	-22.6	-35.9	-2.8	-4.7	-22.6	-33.9	17.1	-7.3	-19.1	-26.7
130	Nonachlor, trans-	19.85	409 > 300 (20)	9.7	6.4	-17.9	-27.9	9	-4.1	-15.3	-29.8	3.1	0.4	-18.7	-29.4	15.4	-0.9	-13	-23.8

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				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
			409 > 302 (22)																
131	Norflurazon	21.77	145 > 95 (18) 303 > 145 (17)	54.6	15.5	-36.2	-53.3	37.7	-11.9	-43.6	-59.3	24.9	-5.4	-41.9	-60.4	71.9	11.9	-28.2	-47.8
132	Oxadiazon	20.17	175 > 112 (13) 258 > 175 (8)	8.2	5.9	-20.4	-27	10.2	-3.5	-16.6	-23.7	3.3	3.7	-18.1	-26.3	8.9	-0.9	-10.3	-20.3
133	Oxyfluorfen	20.28	252 > 146 (33) 300 > 223 (15)	15.5	-2.5	-37.5	-45.2	13.9	-14.3	-35.8	-46.1	4.9	-12.2	-37.6	-50	42.4	-6	-27.8	-42.1
134	Paclobutrazol	19.57	236 > 125 (12) 236 > 167 (10)	22.8	0.6	-35.5	-45.6	27	-4.9	-23.3	-37	10	-6.7	-36.1	-49.2	39.3	-0.3	-22.8	-36.7
135	Parathion	18.04	109 > 81 (8) 139 > 109 (8)	18.7	0	-33.4	-43.5	7.1	-19.6	-37.9	-47.7	2.9	-12	-37.5	-48.8	39.2	-8.2	-28.8	-39.5
136	Parathion-d10 (surrogate) (**)	17.94	115 > 83 (10) 301 > 115 (10)	24.1	-2.4	-36.6	-46.2	10.5	-21.3	-40.4	-48.7	6.9	-16.1	-41.1	-49.5	49.9	-6.8	-30.9	-44.6
137	Pebulate	11.02	128 > 57 (8) 161 > 128 (6)	-0.1	-5	-30.2	-36.5	-3	-19.5	-29	-36.5	-7.5	-10.7	-29.7	-36.3	6.7	-10.8	-23.7	-31.6
138	Penconazole	18.8	248 > 157 (26) 248 > 192 (16)	13.4	1.8	-29.9	-38.8	9	-14.4	-30.2	-39.7	4.2	-5.3	-29.2	-40.5	23.9	-6.2	-21.9	-33.5
139	Pendimethalin	18.63	252 > 162 (10) 252 > 191 (8)	5.2	-10.5	-43.1	-51.2	-0.1	-28.4	-44.8	-52.8	-2.3	-16.6	-41.1	-51.8	28.9	-17.1	-34.7	-46.6
140	Pentachloroaniline	16.45	263 > 192 (20) 265 > 194 (22)	-73.4	-71.8	-57	-11.9	-70.2	-29.9	-6.4	-17.1	-71.8	-6.5	-7.6	-18.7	-73.5	-72.7	-30.4	-5.7
141	Pentachloroanisole	14.73	265 > 237 (12) 267 > 239 (10)	4.4	7.9	-6.8	-13.2	5	-0.3	-5.2	-12.9	0.6	6.3	-5.4	-12.9	8.3	-0.6	-1.5	-7.1
142	Pentachlorobenzene	11.96	250 > 179 (30) 250 > 215 (20)	-2.1	6.5	-7.1	-12.6	5.2	-5.2	-4.5	-10.6	-1.1	6.7	-4.6	-10.7	1.9	-0.4	0.6	-5.3
143	Pentachlorobenzonitrile	15.3	273 > 238 (17) 275 > 205 (30)	5.6	5.2	-17.2	-25.7	5.2	-6.7	-16	-25	0.4	2.1	-15.9	-25.5	7.2	-3.2	-9.7	-19.9
144	Pentachlorothioanisole	17.65	296 > 263 (12) 298 > 265 (8)	7.9	9.1	-13.3	-21.7	9.9	-2.7	-13.3	-22.4	4.2	3.4	-12.6	-24.3	11.9	-1.7	-8	-16.7
145	Permethrin, cis-	25.19	163 > 127 (6) 183 > 168 (10)	6.2	-7.1	-41.4	-51	12.2	-19.8	-41	-52.2	0.3	-14.5	-40.4	-53.1	24.1	-12.5	-33.5	-45.2
146	Permethrin, trans-	25.34	163 > 127 (6) 183 > 153 (14)	6.6	-12.3	-44.6	-56	16.2	-23.1	-46.1	-57.5	-0.6	-20.7	-45.1	-58.4	25.8	-16.8	-37.9	-50.4
147	Phenothrin (*)	23.58 23.71	183 > 153 (14) 183 > 168 (12)	16.1	-6.1	-39	-49.4	14.6	-19.7	-39.2	-50.2	2.3	-12.8	-38.6	-50.5	29.1	-8.9	-30.7	-44.8
148	Phorate	14.34	121 > 65 (10) 260 > 75 (8)	144.8	123.8	-16.8	-54.2	145.3	99.7	34.1	-42.7	144.9	123.7	13.3	-33.2	160.7	112.6	51.1	-20.3
149	Phosalone	23.87	182 > 111 (16) 182 > 138 (8)	47.4	5.3	-43.4	-58.5	36.7	-18.5	-48.7	-61.3	16.4	-16.2	-47.3	-63.1	60.9	5.7	-34.4	-52.5
150	Phosmet	23.08	160 > 77 (24) 160 > 133 (10)	93.2	26.5	-40.9	-59.2	70.4	-9	-47.8	-62.7	38	-11.7	-47.8	-67.1	105	18.1	-34.6	-53.6
151	Piperonyl butoxide	22.45	176 > 103 (26) 176 > 131 (14)	18	0.4	-34.2	-43.6	16.1	-14.3	-33.5	-43.9	9.3	-4.7	-32.8	-45.3	33.5	-3.3	-24.3	-37.4
152	Pirimiphos-ethyl	18.31	318 > 166 (12) 318 > 182 (8)	15.3	11	-16.6	-23.9	13.1	-5.5	-17	-25	11.1	11.3	-13.4	-24.3	21.3	4.7	-6	-17.6

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
153	Pirimiphos-methyl	17.39	290 > 233 (10) 305 > 180 (8)	13.7	12.3	-16.3	-24.9	15.3	-1.9	-16.8	-24.7	7.8	7.6	-15.9	-26.6	21.1	4.4	-7.4	-18.9
154	Pretilachlor	20.03	162 > 132 (18) 262 > 202 (8)	20.8	10.8	-28.5	-39.8	24	-1.7	-23.6	-36	13.3	4.8	-27.1	-41.2	35.9	5.3	-17.3	-31.3
155	Prochloraz	25.43	180 > 138 (12) 308 > 70 (13)	30.4	-8.9	-53.6	-66.6	25.7	-27.2	-57.4	-70.4	6	-25.7	-56.6	-70.7	54.9	-11.1	-46.9	-61.9
156	Procymidone	19.11	283 > 67 (28) 283 > 96 (10)	10.9	10.6	-17	-24.3	13.4	-2.1	-17.2	-25.8	7.8	9.1	-14.4	-25.8	15.5	2.9	-7.6	-17.7
157	Prodiamine	17.41	279 > 203 (8) 321 > 279 (6)	10.5	-4.9	-36.2	-44.7	4.4	-24.8	-38.7	-49.1	-1.3	-15.3	-39.1	-49.6	31.1	-13.8	-30.8	-41.1
158	Profenofos	20.13	337 > 267 (13) 339 > 269 (13)	50	18.7	-30.3	-44.9	46.5	-3.2	-32.7	-48.3	23.6	1.1	-33.3	-53.4	87.3	14.8	-21.3	-39.8
159	Profluralin	15.25	318 > 199 (17) 330 > 69 (25)	-1	-9.5	-35.7	-47	-1.5	-25.2	-38	-45	-7.1	-12.6	-36.3	-45.2	19.1	-16.7	-29.3	-40.5
160	Propachlor	13.15	120 > 77 (19) 176 > 57 (8)	9.8	0.6	-30.4	-39.6	4.2	-16.3	-31.3	-40.3	-0.6	-5.7	-29.9	-40.5	19	-6.8	-24.5	-34.8
161	Propanil	16.61	217 > 161 (8) 219 > 163 (8)	44.5	41.4	13.8	-7.2	37.9	23.1	-8.4	-28.1	33	24	-17.5	-37.3	42.6	30	18	-7.6
162	Propargite	22.37	135 > 77 (24) 135 > 107 (14)	14.3	-2	-36.6	-46	11.4	-12.3	-35.5	-45.9	5.6	-11.6	-34.2	-48	29.5	-9.2	-26.2	-39.5
163	Propisochlor	17.01	162 > 120 (13) 162 > 144 (10)	18.3	12.5	-18	-29.1	14.5	-4.6	-20.6	-31.1	6.3	2.9	-20.9	-32.5	17.9	2.8	-11.4	-23.1
164	Propyzamide	15.49	173 > 109 (27) 173 > 145 (13)	12.8	2.2	-29.5	-40.1	12.4	-9.2	-23.7	-36.6	7.7	4.9	-21.2	-35.5	21.4	-5.3	-22.7	-35.9
165	Prothiofos	20.03	267 > 239 (8) 309 > 239 (15)	17.4	7.2	-25.9	-35.2	17.5	-4.3	-21.5	-32.9	9.9	1.8	-23.5	-36.5	25.5	1.8	-15	-28.6
166	Pyraclofos	24.8	194 > 138 (18) 360 > 194 (10)	68.4	5.5	-51	-66.8	50.4	-21.9	-55.8	-71.5	21.8	-23.3	-54.1	-73	102.5	3.6	-43.5	-62.9
167	Pyrazophos	24.42	221 > 193 (8) 232 > 204 (8)	30.6	-8.1	-48.5	-62.1	22.6	-25.1	-52.6	-64.1	6.8	-22.9	-51.4	-65.7	51.2	-8	-40.9	-56.7
168	Pyridaben	25.42	147 > 117 (20) 147 > 132 (13)	10.5	-15.9	-50.6	-61.4	10.3	-30.2	-52.4	-63	-3.9	-25.7	-51.3	-64.1	28.3	-18.8	-44.2	-56.7
169	Pyridaphenthion	22.85	340 > 109 (20) 340 > 199 (8)	50.1	-6.2	-54.6	-67.1	31.8	-29.4	-58.8	-70.3	14.3	-24.3	-57.3	-70.8	78.1	-5.2	-44.9	-62.6
170	Pyrimethanil	15.68	198 > 118 (32) 198 > 183 (16)	9.5	6.7	-19.9	-29.1	10.3	-5.9	-18.5	-27.7	5.1	4.3	-16.5	-27.5	17.5	-1	-12.7	-23.5
171	Pyriproxyfen	24.04	136 > 78 (20) 136 > 96 (12)	21.2	3.9	-33.2	-44.5	22.2	-12.1	-35.2	-45.8	11	-5.5	-34	-47	32	1.1	-24.3	-38
172	Quinalphos	19.03	146 > 91 (24) 146 > 118 (10)	29.3	5.6	-31	-43.3	19.9	-14.8	-36.9	-46.5	12.7	-6.9	-36.1	-47.3	40.6	-2.1	-25.9	-39.8
173	Quintozene	15.21	235 > 141 (26) 295 > 237 (15)	7.5	4.5	-23.7	-31.9	7.9	-8.4	-21.9	-31.5	3.4	1.3	-20.7	-32.3	22.5	-3.6	-16.6	-27.2
174	Resmethrin (*)	22.37 22.51	143 > 128 (10) 171 > 143 (6)	15.6	-9.8	-41	-52.7	10.1	-25	-40	-50.6	-0.8	-15.4	-41.5	-52.7	30.9	-12.1	-38.5	-46.4
175	Sulfotep	14.02	202 > 146 (10)	6	2.1	-22	-29.7	7.2	-7.2	-19.7	-28.1	4.1	1.7	-18.9	-28.9	15.7	-3.2	-14.7	-24

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
			322 > 202 (10)																
176	Sulprofos	21.53	322 > 156 (13) 322 > 97 (24)	151.3	107.7	-25.6	-56.8	151	82.5	12	-49.7	138.8	105.7	-3.3	-54.5	173.1	103.4	34.4	-30.1
177	tau-Fluvalinate (*)	27.41 27.48	250 > 55 (23) 250 > 200 (19)	-20.4	-20.5	-45.3	-54.5	-6.8	-29.5	-45.1	-56.7	-18.9	-25.6	-41.8	-57.3	-2.6	-21.4	-39.5	-49.3
178	Tebuconazole	22.35	125 > 89 (16) 250 > 125 (22)	19.8	-1.7	-37.7	-48	17.9	-15.7	-37.5	-49.3	6.9	-9.5	-36.6	-50.5	35.1	-4.9	-28.5	-42.1
179	Tebufenpyrad	23.39	276 > 171 (10) 333 > 276 (8)	17.7	0.2	-36.9	-46.5	22.9	-15.4	-37.6	-45.8	5.3	-8.2	-36.8	-48.9	32	-4.6	-27.4	-41.5
180	Tecnazene	12.96	215 > 179 (8) 261 > 203 (13)	1.9	-2	-23.5	-30.2	0.2	-14.1	-22.4	-29.5	-6.1	-5.6	-22.1	-29.8	12.2	-9.2	-17.5	-24.9
181	Tefluthrin	15.86	177 > 127 (15) 177 > 137 (15)	7.2	3.6	-21.1	-27.9	6.5	-9.7	-18.1	-27.3	3.5	2.3	-17.1	-27.1	14.4	-4.3	-14.6	-22.7
182	Terbacil	15.83	160 > 117 (8) 161 > 144 (14)	30.4	-1.6	-42.4	-53.9	10.7	-24.1	-44	-55.3	8.6	-13.4	-44.1	-55.7	48.8	-8.4	-35.9	-49.8
183	Terbufos	15.42	231 > 129 (23) 231 > 175 (12)	161.9	140.8	-17.2	-54.6	160.5	116.5	40.1	-43.2	148.4	134.8	18.7	-47.8	175.3	124	56.7	-21.9
184	Terbuthylazine	15.4	229 > 138 (12) 229 > 173 (8)	9.9	4.4	-26.6	-37.5	9.4	-8.3	-23.8	-34.4	3.6	3.6	-20.4	-34.3	17.1	-4.5	-18	-31
185	Tetrachloroaniline, 2,3,5,6-	13.47	231 > 158 (20) 231 > 160 (22)	3	4.4	-14.7	-22.3	3.5	-6.1	-12	-21	-0.9	2.5	-12.3	-21.1	5.5	-3.6	-7.7	-14.6
186	Tetrachlorvinphos	19.49	331 > 109 (20) 333 > 109 (17)	51.9	33.3	-23	-35.9	65.5	23.6	-10.3	-26.6	27.4	17	-27	-47.5	88.6	34.2	-6.6	-28.3
187	Tetradifon	23.75	159 > 111 (20) 159 > 131 (10)	15.9	1.4	-26.2	-37	11.9	-8.6	-28.9	-41.1	1.6	-7.7	-27.3	-40.5	17	-5.3	-22.2	-29.7
188	Tetrahydrophthalimide	11.51	151 > 80 (6) 151 > 122 (10)	5.7	-4.8	-35.5	-44.4	-0.6	-22.9	-36.2	-44.2	-0.6	-8.3	-33.6	-43.7	9.5	-11.2	-28.5	-38.5
189	Tetramethrin (*)	22.93 23.11	164 > 77 (25) 164 > 107 (12)	21.7	-10.5	-47.6	-58.5	12.3	-27.2	-49	-59.8	2.9	-21.8	-49.1	-61	28.9	-13.2	-39.8	-52.8
190	Tolclofos-methyl	16.93	265 > 250 (10) 267 > 252 (10)	17	16.9	-6.6	-16.1	17.7	4.8	-8.3	-18.2	8	10.3	-8.6	-20.6	20.4	7.2	0.7	-11
191	Tolylfluanid	18.87	137 > 91 (17) 238 > 137 (10)	-4.8	3.9	-19.5	-28.8	5.2	-7.4	-20.4	-30	-18	-6	-19.9	-31.9	-16.7	-11.5	-14.4	-23.1
192	Transfluthrin	16.94	163 > 91 (12) 163 > 143 (13)	12.2	10.9	-16.5	-24.6	9.6	-4.7	-17.3	-24.6	4.1	3.2	-17.8	-26.7	15.2	1.8	-9.3	-20.1
193	Triadimefon	18.12	208 > 111 (24) 208 > 181 (10)	10.4	-0.3	-28.9	-37.9	5.5	-16.3	-30.1	-39.9	1	-7.5	-30.3	-40.5	17.5	-7.3	-23.5	-32.7
194	Triadimenol	19.11	128 > 65 (22) 168 > 70 (10)	14.8	-2.4	-32.9	-46.7	10.4	-20.1	-37.1	-47.5	6.4	-5.9	-34.8	-47.6	26.3	-5.9	-26.9	-40.6
195	Triallate	16.03	268 > 184 (20) 268 > 226 (10)	5.1	-2.3	-25.9	-33.8	2.6	-13.4	-24.6	-32	-0.6	-3	-22.6	-32.1	12.1	-8.3	-18.8	-28.6
196	Triazophos	21.48	161 > 134 (8) 257 > 162 (8)	59.3	22.1	-31.3	-45.2	49.2	0.2	-34.5	-47.9	30.8	2.8	-34.1	-51.4	69	14.9	-20.8	-40.2
197	Tricyclazole	20.19	189 > 135 (18) 189 > 162 (12)	109.4	60.4	-13.5	-38.2	76.8	18.7	-27.4	-46.7	54.2	19	-29.9	-49.7	112.4	46.1	-8.3	-32.9

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	ME, %															
				White tea				Green tea				Oolong tea				Black tea			
				f = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20	*f* = 2	*f* = 4	*f* = 10	*f* = 20
198	Triflumizole	19.11	206 > 179 (14) 206 > 186 (10)	17.7	5.7	-25.9	-35	13.6	-11.2	-26.7	-37.6	10.1	1.1	-24.5	-36.3	24.5	0.5	-17.7	-29.2
199	Trifluralin	13.85	306 > 206 (12) 306 > 264 (8)	-4	-15.3	-42.7	-49.5	-7.6	-28.7	-41.4	-47.8	-10.1	-18.1	-40.4	-48.3	18.4	-21	-35.9	-45.5
200	Vinclozolin	16.87	212 > 172 (12) 285 > 212 (12)	16.6	12.7	-16.5	-25.4	12.1	-4.8	-21.3	-30	6.9	3.3	-21.3	-31.4	19.6	2.4	-11.7	-22.9

(*) Pesticides with more than one isomer, calculated all peaks together.
(**) Surrogate and internal standard compound.
(CE): Colision energy (V)

Table A-10. Pesticide groups suffered strong ion enhancement in GC-MS/MS method for green tea; 3uL injection (chapter 4)

Group	Number of pesticides
Organophosphate	27
Pyrethroid	16
Dinitroaniline	5
Thiocarbamate	3
Chlorophenyl	2
Diphenyl ether	2
Phthalimide	2
Pyridazinone	2
Triazole	2
Aromatic hydrocarbon	1
Aryloxyphenoxypropionate	1
Bridged diphenyl	1
Chlorinated hydrocarbon	1
Cyclic aromatic	1
Dicarboximide	1
Imidazole	1
Organochlorine	1
Phenylpyrazole	1
Phenylpyrrole	1
Phosphorothiolate	1
Pyrazolium	1
Pyrimidine	1
Triazinone	1
Triazolobenzothiazole	1
Triazolone	1
Uracil	1
Unclassified	6
Total	**84**

Table A-11. Matrix effects summary according to the dilution factors (2, 4, 10, and 20) obtained by LC-MS / MS and GC-MS/MS method of white (WT), green (GT), oolong (OT), and black tea (BT); 1 µL injection (chapter 4).

Method	Matrix	f	Number of pesticides				
			Suppression		No ME	Enhancement	
			Strong	Medium		Medium	Strong
LC-MS/MS	WT	2	1	4	193	1	1
		4	0	2	196	1	1
		10	0	1	197	1	1
		20	0	1	197	1	1
	GT	2	0	3	194	2	1
		4	0	1	197	1	1
		10	0	1	197	1	1
		20	0	1	197	1	1
	OT	2	0	1	197	2	0
		4	0	1	197	1	1
		10	0	1	197	1	1
		20	0	1	197	1	1
	BT	2	1	7	191	1	0
		4	0	6	192	2	0
		10	0	4	194	2	0
		20	0	1	197	1	1
GC-MS/MS	WT	2	4	5	132	41	18
		4	2	4	175	11	8
		10	9	124	65	1	1
		20	37	140	22	1	0
	GT	2	2	2	140	44	12
		4	1	38	151	3	7
		10	12	115	68	4	1
		20	37	141	22	0	0
	OT	2	2	4	170	17	7
		4	1	15	176	1	7
		10	9	119	69	2	1
		20	48	133	18	1	0
	BT	2	3	1	81	79	36
		4	2	7	180	4	7
		10	3	90	100	2	5
		20	19	136	43	1	1

Table A-12. Matrix effects of 27 compounds obtained by LC-MS/MS and GC-MS/MS in green (GT), black (BT), white (WT), and oolong tea (OT) (chapter 4).

Matrix effect (%)	GT		BT		WT		OT	
Component Name	LC-MS/MS	GC-MS/MS	LC-MS/MS	GC-MS/MS	LC-MS/MS	GC-MS/MS	LC-MS/MS	GC-MS/MS
Cyprodinil	-5.1	14	-7	20.7	-2.8	14.9	0.7	7.8
Fenarimol	-5.9	7.4	-6.4	24.1	-2.1	9.1	0.4	-2.5
Fludioxonil	-6.8	23.3	-12.7	44.2	-9.4	28.6	-2.4	12.2
Fluquinconazole	-6.8	18	-9.6	29.7	-5.1	11.6	-0.9	0
Flusilazole	-5.8	13.2	-7.6	22.9	-3.7	13.1	0.4	5
Flutriafol	-6.3	19.3	-7.8	27.3	-4.9	17.7	-1.4	7.7
Linuron	-5.4	65.9	-8	70.6	-3.7	48	0.7	40.8
Metalaxyl	-5	10.6	-5.9	12.4	-2.1	7.7	1.1	4
Mevinphos	-10.9	-1.8	-13.1	27.6	-9.7	17.5	-4.4	-5.8
Myclobutanil	-5	14.2	-6.7	22.4	-2	13.9	-0.3	8
Paclobutrazol	-6	27	-8.3	39.3	-4.7	22.8	0.1	10
Piperonyl butoxide	-7.3	16.1	-7.8	33.5	-2.6	18	-1.6	9.3
Prochloraz	-9.8	25.7	-10.1	54.9	-6.5	30.4	-3.6	6
Propargite	-7.6	11.4	-9.3	29.5	-4.8	14.3	-1.7	5.6
Pyridaben	-7.7	10.3	-6.4	28.3	-3	10.5	0.6	-3.9
Tebuconazole	-9.3	17.9	-11.1	35.1	-7.1	19.8	-4.5	6.9
Tebufenpyrad	-5.9	22.9	-6	32	-1.4	17.7	0.5	5.3
Triadimefon	-4.6	5.5	-6.9	17.5	-2.6	10.4	1.5	1
Tricyclazole	-5.4	76.8	-7.2	112.4	-3.6	109.4	0.4	54.2

Table A- 13. List of pesticides, method parameters and data validation of UPLC-MS/MS method for 4 types of teas (chapter 5)

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5) 10 µg/kg	50 µg/kg	100 µg/kg
1	Acephate	2.31 75	184.045 > 143.046 (9) 184.045 > 95.174 (21)	0.999	–4.19/–5.59/–0.44/–8.08	1 50	95.3/99.4/99.6/97.1 1.7/1.7/2/2.5	95.8/97.3/95.9/96.5 2.2/1.3/1.4/1.3	97.1/96.5/98.1/97.8 1.2/1.3/1.6/1.2
2	Acetamiprid	3.81 117	223 > 126 (20) 223 > 90.1 (35)	0.9984	–11.42/–15.43/–13.53/–13.52	1 50	90.1/86.6/83.8/89.7 1.2/1.6/1.6/1.2	90.5/85/79.1/90.1 1.4/2.2/1.4/2.2	88.8/83.7/80.5/89.1 1.4/2.1/1.2/1.2
3	Acibenzolar-S-methyl	9.62 89	211 > 136.1 (30) 211 > 140 (24)	0.9977	–2.94/–7.93/0.63/–8.16	5 50	96.7/96.9/103.1/84.5 4/2.2/3.1/5.9	91.4/89.7/95.9/98 3.2/2.4/5.9/3.1	91.9/95.3/97.8/99.2 3.6/2.6/3/2.9
4	Aldicarb	4.47 58	208.152 > 116.1 (10) 208.152 > 89.15 (10)	0.9983	–6.91/–8.04/–1.65/–9.18	1 50	91.7/93.9/96.5/68.9 1.9/8.6/6/5.4	89.5/95.6/92.7/85.8 7/1.5/1.8/1.9	86.6/88.5/90.7/95.5 3.1/2/2/4
5	Aldicarb sulfoxide	2.72 59	207.1 > 132.04 (8) 207.1 > 89.15 (10)	0.9982	–16.14/–15.84/–5.56/–24.42	1 50	92.4/91.6/109.6/104.9 1.2/2.6/5.6/9.5	82.5/90.1/96.6/87.6 3.3/3/3.9/3.8	86/94.5/99.9/88 1.4/2.5/1.5/1.2
6	Aldicarb-sulfone	2.85 81	240.175 > 86.273 (23) 240.175 > 63.325 (31)	0.9993	–8.42/–8.41/–3.59/–11.64	2 50	93.8/97.3/100.3/101.5 1.5/5/1.9/2.3	94/97.4/98.2/95.6 1.8/2.2/3.7/1.8	95.8/99.6/101.2/98.6 1.3/2.2/1.6/1.7
7	Ametryn	7.16 173	228.1 > 186.1 (20) 228.1 > 138.1 (23)	0.9991	–2.33/–4.53/1.33/–5.9	1 10	99.2/100.2/100.5/87.7 3.5/1.2/2.8/3.3	96.7/94.2/94.5/95.1 2/1.6/1.4/1.7	98.7/96.1/98/94.9 1.3/1.3/1.3/1.6
8	Aminocarb	2.62 105	209.1 > 137.1 (23) 209.1 > 152.1 (15)	0.9998	–8.47/–10.59/–2.7/–14.06	1 10	97.1/102.2/105.8/86 1.7/1.9/1.5/4.1	91.9/97.4/98.8/96.8 1.9/1.4/1.5/2.2	95/98.2/100.8/96.7 1.3/2.6/1.9/1.2
9	Amitraz	12.22 154	294.2 > 148.3 (16) 294.2 > 91.2 (40)	0.9988	–1.16/–4.91/1.92/–4.96	2 100	97/98.4/96.7/88.9 1.3/1.3/1.2/2.7	94.9/93.6/92.1/94.3 1.6/1.3/1.3/1.3	99/96/96.2/96.3 1.3/1.2/2.1/1.2
10	Atrazine	7 38	216.1 > 174.063 (20) 216.1 > 104.164 (31)	0.9997	–6.63/–2.09/1.83/–7.12	1 100	89.2/93.3/93.5/75.8 3/2.1/1.7/4.9	88.1/91.1/89.3/88.9 1.2/2.2/1.2/2.2	90.4/90/91.3/88.2 1.2/1.7/1.4/1.4
11	Avermectin (B1a) (*) Avermectin (B1b) (*)	17.43 77 16.92 76	890.47 > 305.183 (24) 890.47 > 567.28 (14) 876.5 > 291 (21) 876.5 > 553.4 (13)	0.9975	–0.11/–5.37/–3.01/–5.51	2 10	106.1/89.7/97.9/98.2 4.7/9.3/1.8/7	99.1/85.4/89.6/92.1 4.3/6.5/3.7/2.4	98.8/86.9/92.6/94.2 1.3/4.6/5.3/1.8
12	Azoxystrobin	9.08 144	404.12 > 372.067 (16) 404.12 > 344.076 (27)	0.9987	–2.35/–5.09/1.54/–6.3	1 50	104/104.7/105.7/99.3 1.3/1.2/1.4/1.3	99.6/101.8/100.7/101.8 1.5/2.3/1.9/3	101/101.6/100.6/100.5 1.3/1.2/1.2/2.5
13	Benalaxyl	12.23 128	326.23 > 148.174 (24) 326.23 > 121.197 (32)	0.9986	–2.08/–4.79/0.37/–6.83	1 100	99/99.4/99.3/90.6 3.5/1.2/3.5/3.2	95.3/95.8/94.8/96.3 1.4/2/1.2/2	98.5/96.9/97.7/98.5 1.4/1.7/1.8/1.2
14	Bendiocarb	5.47 94	224.175 > 167.126 (10) 224.175 > 109.174 (21)	0.9987	–5.73/–5.87/–0.31/–9.01	2 10	96.9/99.4/99.3/84 2.7/1.5/1.6/2.9	96.6/99.1/95.1/95.6 1.4/2.3/1.2/3.3	97.6/98.6/98.2/97.2 1.5/3.4/1.4/1.3
15	Benzoximate	13.05 80	364.05 > 198.937 (9) 364.05 > 105.139 (23)	0.9985	–2.03/–4.57/0.65/–5.83	2 10	88.8/83.6/83.1/77.9 1.8/3.2/8.6/2.9	89.8/78.2/76.5/89.2 1.2/3/3.2/1.6	93/80.6/84.3/87.5 1.4/3.2/3.4/1.2
16	Bifenazate	10.53 93	301.2 > 198.1 (5) 301.2 > 152.138 (43)	0.9985	–6.2/–16.41/–2.2/–22.59	1 100	115.1/97.4/85/102.6 1.7/4.7/8.4/1.3	110.8/101.1/65.7/109.2 3.4/2.2/1.7/4.4	100.1/89.8/61.8/107.4 1.6/2.2/1.7/1.4
17	Bitertanol	12.92 40	338.19 > 269.2 (9) 338.19 > 70.1 (12)	0.9994	–1.75/–0.9/–1.98/–4.42	5 50	97.9/106.9/93.7/103 2/4.5/9.4/4.2	100.9/98/89.4/93.9 6.8/1.8/1.9/1.4	101.8/93.6/91.2/98 6.6/3.2/3/1.3
18	Boscalid	9.55 189	343.04 > 307.065 (21) 343.04 > 272.091 (34)	0.9996	–4.63/–6.36/0.44/–7.89	1 10	99/103.3/101.9/96.3 3.2/1.2/2.8/1.2	98.8/101.4/99.6/101.3 2/1.2/2.5/3.7	102.4/101.2/102/99.1 2.5/2.2/1.4/1.2
19	Bromucanozole (*)	10.19,	377.935 > 159.015 (30)	0.9986	–4.86/–6.04/–0.69/–8.77	1	93.8/96.5/93.9/91.6	93.9/90.9/91.1/92.3	96.8/92.4/93.6/92.1

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5) 10 µg/kg	 50 µg/kg	 100 µg/kg
		11.65 178	377.935 > 161.018 (31)			50	1.5/2.6/1.4/5.2	1.6/3.5/1.2/3.4	2/1.3/1.2/1.3
20	Bupirimate	10.38 185	317.21 > 166.143 (27) 317.21 > 272.096 (21)	0.9992	–1.46/–4.54/2/–5.51	1 50	94.7/93.9/94.3/87.8 3.7/1.2/3.3/3.8	93.6/89.7/88.7/91.6 1.3/3/1.8/1.7	97/90.6/92.8/89.1 1.5/2.3/1.4/1.8
21	Buprofezin	14.36 112	306.235 > 106.219 (28) 306.235 > 57.448 (25)	0.9992	–5.08/–5.89/0.85/–9.66	1 50	80.2/72.9/66.2/82.2 3.8/3.7/9.9/1.2	84.5/59.3/60.5/79.3 1.2/3.8/4.7/4.6	90.6/65.7/65.6/72.9 1.2/9.5/9.2/1.4
22	Butafenacil	10.76 144	492.11 > 331.005 (26) 492.11 > 348.993 (17)	0.9989	–2.2/–5.05/0.64/–5.35	1 10	102.7/103.7/105.5/99.5 1.5/1.2/1.8/1.2	101.7/102/99.9/103.7 2.1/1.7/1.6/3.9	104.2/100.7/98.9/101.5 1.4/1.3/4.4/1.2
23	Butocarboxim	4.37 46	213.03 > 75.058 (16) 213.03 > 155.99 (10)	0.9983	19.91/4.73/8.69/9.49	5 10	119/102.6/103.8/80.2 6.7/1.5/3.2/7.5	112.3/107.2/111.7/113.7 2/2.7/7/1.9	111.2/110.2/111.6/111.6 1.2/4.2/1.2/1.5
24	Butoxycarboxim	2.82 75	223.03 > 166 (15) 223.03 > 106.11 (17)	0.9988	–9.59/–9.76/–4.4/–14.89	5 10	107.2/116.5/107/90 19.5/4.3/1.7/2.1	92/99.7/98.6/99.2 5.5/5.5/1.5/3	95.2/97.9/100.7/98.4 6/1.6/6.6/2.8
25	Carbaryl	6.17 82	202.165 > 145.11 (11) 202.165 > 127.152 (31)	0.9995	–12.32/–17.03/–12.62/–14.47	2 50	91.9/90.8/87/88.7 1.3/2.3/2.5/1.6	93.5/88.6/83.7/92.4 2.2/1.3/1.5/2.4	93.2/89.5/83.7/94.1 1.2/1.5/1.2/1.4
26	Carbendazim	3.24 132	192.1 > 160.1 (20) 192.1 > 105.2 (32)	0.999	–52.86/–37.65/–30.71/–51.86	1 100	67.7/83.2/85.5/70.6 1.2/2/2.7/1.2	63.3/77/77.8/66.9 1.8/3/1.4/2	61.7/76.5/78.4/64.8 2/1.2/1.6/1.2
27	Carbetamide	4.94 89	237.1 > 192 (9) 237.1 > 120 (17)	0.9982	–3.47/–4.78/0.24/–7.08	2 50	100.6/102.5/103.7/97.1 1.8/1.9/2.4/2.9	98.6/100.6/99.2/100.6 1.4/1.3/1.3/2.9	102.2/100.5/102.5/103.4 1.3/1.8/1.2/1.6
28	Carbofuran	5.45 100	222.185 > 165.129 (15) 222.185 > 123.16 (25)	0.9991	–4.1/–5.2/0.52/–7.48	1 50	98.5/103/102.1/87.1 2.3/1.3/1.2/2.6	97.9/99.8/97.7/96.8 1.3/1.5/1.3/2.7	97.8/97.9/98/97.5 1.5/3.1/1.2/1.9
29	Carbofuran-3-hydroxy	3.67 121	238.2 > 181.1 (12) 238.2 > 163.1 (18)	0.9972	–10.37/–8.05/–2.97/–13.4	1 50	95.1/100.9/100/91.6 3.2/3.4/1.7/1.2	90.6/96.6/94.9/92.8 3.1/3.5/3.8/2.5	93.4/99.1/96/93.3 1.4/1.4/1.5/1.6
30	Carboxin	6.05 111	236.145 > 143.095 (18) 236.145 > 87.224 (28)	0.999	–5.49/–7.47/–0.68/–9.31	1 100	72/79.2/78.3/21.2 4/3.4/4.2/6.8	74/81.3/82.3/76 4/2.2/1.3/1.7	73.9/74.7/79.4/80 2.7/2.7/7.8/2.1
31	Carfentrazone-ethyl	11.83 180	412.1 > 346.1 (23) 412.1 > 366.1 (19)	0.999	–1.17/–3.61/2.29/–5.06	1 20	103.9/104.9/102.1/96.7 2.6/1.8/2.2/4.6	101.7/97.1/93.7/99.2 3.3/2.3/1.3/2.3	101.7/95.3/96.6/98.1 2.4/1.9/1.4/1.4
32	Chlorantraniliprole	8.25 149	481.88 > 450.948 (17) 481.88 > 283.955 (13)	0.9984	–2.93/–6.6/0.13/–5.88	1 20	97.7/96/98.1/96.1 4.2/1.9/1.2/5.5	95.4/97.9/94/96.3 1.2/1.5/1.5/3.7	99.1/95.9/98.4/98.9 2.9/1.4/1.2/1.3
33	Chlorfluazuron	16.87 149	539.995 > 382.974 (23) 539.995 > 346.999 (46)	0.9985	–5.44/–10.89/–3.83/–9	1 10	52.5/35.4/27.4/70.4 3.5/1.2/16.7/4.4	56.8/25.8/25.2/46.3 14.4/1.3/10.3/9.8	67.2/29.2/22.5/36.4 3.1/7.5/18.4/2.1
34	Chlorotoluron	6.88 121	213.18 > 72.31 (21) 213.18 > 140.094 (27)	0.9989	–2.13/–5.34/–0.09/–6.11	1 50	99.3/98/100/90.3 3.7/1.6/1.2/2.6	96.5/98.6/96/96.2 1.2/2.9/2.1/2.3	98.8/99.4/99.4/97.4 1.2/1.8/1.2/1.2
35	Chloroxuron	10.5 164	291.1 > 72.4 (23) 291.1 > 218.1 (27)	0.9996	–2.28/–4.45/1.73/–5.9	1 50	101.2/99/99.6/95.6 3.4/2.5/1.4/1.2	97.7/100.9/95.5/97.8 2.3/1.2/1.6/3.2	101.4/97.8/99.1/98.1 1.2/1.3/1.3/1.2
36	Clethodim (*)	10.1, 14.01 140	360.1 > 164.2 (20) 360.1 > 166.3 (22)	0.9984	–3.96/–6.18/1.14/–7.24	1 100	70.3/80.1/78.9/33.6 4.1/1.2/1.7/7.1	71.3/74.2/73/72.2 5.7/2.9/1.4/2.2	73.2/74.7/76.9/73.5 2.2/1.5/2.2/1.3
37	Clofentezine	13.47 100	303.061 > 138.06 (11) 303.061 > 102.11 (31)	0.9975	–6.79/–8.78/–2.37/–10.87	1 50	84.6/72.1/67/69 6.5/4.7/7.1/3.9	80.8/63.9/61/78.7 1.5/6/5.1/3.3	85.5/67.3/65.7/75.5 1.2/5.8/6/1.4
38	Clothianidin	3.55 101	250.1 > 169.1 (13) 250.1 > 132.2 (14)	0.9978	–15.81/–7.92/–1.28/–15.79	1 700	89.7/100.8/101.9/90.2 2.2/3.4/4.3/2.8	87.6/97.3/94.5/88.4 1.2/2.8/1.2/2.3	89.1/97.1/97.3/88.8 1.7/1.8/1.7/2.6
39	Cyazofamid	11.37 103	325 > 108.169 (17)	0.9949	–8.98/–11.78/–3.23/–11.57	2 50	103.4/102.7/102.1/91.2 3.1/3.3/1.2/5	98.9/98.8/94.6/100.4 1.4/1.4/1.2/3.9	103.1/97.8/98.7/102.6 1.3/1.5/1.2/1.2

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5)		
							10 µg/kg	50 µg/kg	100 µg/kg
			325 > 217.067 (21)						
40	Cycluron	7.56 130	199.255 > 89.243 (17) 199.255 > 72.318 (25)	0.9985	–2.98/–5.08/0.56/–6.04	2 10	97.7/99.2/100.2/86.2 1.9/1.2/1.3/6.5	98.7/99.2/97.7/98 1.4/1.2/2.2/3	100.7/99.6/98.3/99 1.3/2.1/1.2/1.5
41	Cymoxanil	13.06 123	199 > 183.93 (16) 199 > 141 (25)	0.9988	–1.04/–4.13/2.04/–5.23	1 100	94.9/87.9/85.4/78 4.3/4.1/7.8/7.5	92.2/79.9/79.2/90.4 1.2/4.4/2.1/1.9	92.8/80.3/82.5/88.3 1.9/4.3/3.1/1.3
42	Cyproconazole (*)	9.78, 10.32 150	292.17 > 70.326 (22) 292.17 > 125.121 (30)	0.9991	–5.53/–6.96/–0.94/–8.95	1 50	98.2/99.9/98.5/92.8 4.3/1.3/1.8/1.4	97.1/96.4/96/94.9 1.2/2.1/1.8/3.4	100.8/97.3/97.1/95.5 1.3/1.2/1.8/1.2
43	Cyprodinil	11.06 178	226.205 > 93.226 (37) 226.205 > 118.164 (34)	0.9983	–2.83/–5.12/0.72/–6.95	1 100	74.3/69.2/68.6/77.3 1.2/3.9/12.2/4.9	79.1/57.2/62.8/69.6 3.1/4.7/3.9/4.9	89/63.4/67.1/65.7 1.2/6.2/4.6/2
44	Desmedipham	8.2 101	318.09 > 182.126 (16) 318.09 > 136.142 (29)	0.9972	–5.06/–7.82/–1.78/–9.43	2 50	103.7/101.9/100.2/97.2 5.6/1.2/1.4/1.2	97.8/99.6/96.6/97.8 2.3/1.3/1.4/3.4	100.8/100.7/101.2/98.9 2.6/1.4/1.5/1.5
45	Diclobutrazol	11.79 169	328.1 > 70.3 (32) 328.1 > 159 (34)	0.9982	–5.33/–7.54/–1.61/–8.82	2 10	96.7/96.9/101/92.8 3.6/4.6/5/5.1	92.6/92.8/91.8/94.1 1.2/4.7/2.5/5.1	97.8/93.5/95.9/94.2 1.9/1.2/1.2/1.2
46	Dicrotophos	3.33 106	238.055 > 112.235 (15) 238.055 > 193.074 (10)	0.998	–31.61/–23.62/–17.5/–32.23	1 10	70.3/77.1/86.8/68.3 2.8/2.7/1.3/2.6	71.6/79/80.9/72.2 3/1.3/1.2/1.6	69.3/78.8/78.3/72.3 1.7/1.2/1.4/1.6
47	Diethofencarb	8.62 92	268.2 > 124.163 (35) 268.2 > 180.143 (20)	0.9984	–3.58/–5.71/0.46/–7.76	2 50	97.6/99.2/100.8/89.1 2.3/4.8/4/6.3	95.3/98.7/96.6/97.6 3.5/1.2/1.7/2.7	100.3/98.9/99.9/96.9 3.1/2.1/1.5/1.2
48	Difenoconazole (*)	13.52, 13.65 188	406 > 251.015 (26) 408 > 253 (26)	0.9988	–1.57/–5.71/0.92/–5.11	1 50	93/83.6/86.2/92.1 2/3.5/7.6/1.5	92.1/75.9/77.8/88.7 1.7/4.6/3.4/3.5	96.5/79.3/83.1/85.8 1.2/5.2/3.7/1.2
49	Diflubenzuron	11.6 126	311.1 > 157.9 (14) 311.1 > 141.1 (25)	0.9985	–3.5/–5.66/–0.66/–7.92	1 50	98.1/99.3/92/95 2/1.2/5.4/3.2	95.4/90.9/88.7/93.8 1.2/4.1/1.7/1.2	100/90.7/94.1/95.8 1.8/1.2/1.3/1.3
50	Dimethoate	3.74 83	230.06 > 125.085 (24) 230.06 > 79.24 (33)	0.9978	–13.53/–10.16/–1.59/–15.87	1 50	90.2/95.7/97.7/84.2 1.3/3.6/1.6/4.5	88.2/96.4/95.7/91.4 1.5/1.2/1.8/3.4	88.7/93.4/96.6/89.2 1.5/1.2/1.6/1.5
51	Dimethomorph (*)	9.24, 9.86 202	388.155 > 301.105 (23) 388.155 > 165.118 (34)	0.9985	–0.26/–3.98/2.18/–4.55	1 50	102.8/100.8/104.6/98.4 1.9/1.3/1.8/1.5	101.4/101.2/99.2/101.7 1.2/1.4/2.6/3.8	104/100.8/100.3/103.4 1.4/2.6/1.2/1.3
52	Dimoxystrobin	11.65 105	327.1 > 116.1 (20) 327.1 > 238.1 (13)	0.9985	–2.06/–4.31/0.89/–6.18	2 50	99.2/99.7/100.1/94.1 1.5/1.2/1.8/1.9	99.3/98.5/96.2/98.7 1.3/1.6/1.3/2	100.5/98/98.8/99.7 1.6/1.2/1.2/1.6
53	Diniconazole	13.19 191	326.155 > 70.303 (27) 326.155 > 159.041 (32)	0.9985	–3.4/–7.12/–2.12/–8.28	1 50	96.3/93.1/90.6/92.8 2.2/1.3/5.2/1.6	93.7/84.4/84.9/91.7 2/4.7/1.2/1.3	97.8/87.3/90.2/93 1.4/3.7/1.9/2.2
54	Dinotefuran	2.75 79	203.11 > 129.16 (12) 203.11 > 114.161 (8)	0.9996	–18.21/–14.46/0.16/–24.49	2 10	83.8/96.8/102.2/94 2.5/3.2/8.1/5.8	77.4/95.2/108.4/84.1 1.2/1.5/1.7/2.4	77/95.3/104.4/85.3 2.4/2.9/1.2/1.2
55	Dioxacarb	3.69 91	224.165 > 123.172 (19) 224.165 > 95.242 (29)	0.9971	–19.97/–19.85/–7.26/–23.27	2 10	103.8/116.7/106.2/98.8 1.2/3/1.4/1.5	107.1/110.5/109.9/107 1.2/1.4/2.5/2.7	106.9/111/113.6/104.8 1.7/1.9/1.3/1.2
56	Diuron	7.77 134	233.095 > 72.33 (21) 233.095 > 46.519 (19)	0.9981	–4.58/–6.97/–1.28/–8.46	1 50	99.4/100.6/101.2/90.6 1.4/2.5/2/2.8	96.7/98.9/97.7/96 1.9/1.5/2.2/2	100.2/100.3/99.3/96.4 1.5/1.3/2.2/1.2
57	Doramectin	18.14 78	916.509 > 331.24 (22) 916.509 > 593.35 (12)	0.9967	–0.7/–4.13/–0.99/–7.72	2 10	106.6/85.6/87.1/106 2.1/6.5/4.6/1.2	99.1/74.1/75.2/91.5 2.4/5/7.3/1.2	97.8/74.1/79.9/86.2 3.1/7/5.9/2.6
58	Emamectin benzoate (B1a) (*)	15.73 76	886.505 > 158.19 (39) 886.505 > 82.301 (47)	0.9984	0.66/1.63/3.86/–2.98	1 20	88.3/83.1/86.8/81.5 1.2/6.4/4.1/1.2	85.4/80/85.9/83.4 2.2/1.3/1.6/3.1	91.9/77.4/90.7/82.8 1.7/3.4/1.9/3.2
	Emamectin benzoate (B1b) (*)	15.13 76	872.495 > 158.178 (37) 872.495 > 82.279 (46)						

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5)		
							10 µg/kg	50 µg/kg	100 µg/kg
59	Epoxiconazole	11.04 55	330.13 > 121.163 (15) 330.13 > 101.195 (35)	0.9985	–1.49/–4.02/1.62/–6.05	2 50	100.5/100.6/100.7/92.3 3.6/2.7/1.3/1.4	97.6/97.8/96.5/97.5 2.6/1.6/2/3.2	102.5/97.3/99.4/98.3 2.1/2.2/1.3/1.2
60	Eprinomectin	17.09 85	914.469 > 186 (27) 914.469 > 154 (27)	0.9992	5.96/1.32/6.78/–1.23	2 10	104/98.1/98.4/100.3 3.3/2.5/3.3/3.4	92/89.7/97.8/97.5 1.2/2.1/1.6/1.6	98.7/89.4/93.8/91.1 2.3/4.4/1.8/4
61	Etaconazole (*)	10.74, 10.9 172	328.1 > 159 (23) 328.1 > 205 (18)	0.9973	–2.73/–4.99/1.14/–6.11	1 10	98.7/101.6/97.7/94.1 2.3/2.3/1.3/3.9	97.2/96.6/95/95.9 2.3/1.7/1.2/4.9	101/96.4/98.7/97.6 2.4/1.8/1.3/1.2
62	Ethiofencarb	6.32 86	226.165 > 107.183 (18) 226.165 > 77.279 (45)	0.999	–7.72/–9.56/–3.8/–10.27	5 10	77/88.8/83.5/73.9 5/3.3/3.9/1.2	69.7/79.9/77.9/74.8 6/1.6/1.8/2	69/73.9/79.8/77.4 2/2.9/1.4/1.9
63	Ethiprole	9.33 167	397.015 > 350.942 (23) 397.015 > 254.978 (39)	0.9989	–3.31/–5.88/1.35/–7.92	1 10	101.6/103.6/105.9/96.5 1.2/1.4/6.3/1.4	101.1/101/100.3/98.4 2.1/2/2.3/2.9	101.5/102.4/100.9/100 1.2/2.2/1.2/1.3
64	Ethirimol	4.46 165	210.2 > 140.1 (23) 210.2 > 98.2 (28)	0.9979	–7.04/–6.73/–0.31/–10.62	1 50	88.1/94.1/92.3/85 1.3/1.8/2/2	86.5/93.2/91/90.1 1.3/1.4/1.7/2.8	86.5/91.8/94.3/89.4 2/1.4/1.2/1.4
65	Ethofumesate	8.92 143	287 > 121.2 (20) 287 > 259.1 (11)	0.9975	–3.89/–6.87/–0.79/–8.33	2 100	99.3/101.8/100.6/88.7 1.6/1.7/4.3/6.3	98.4/101.3/97.8/98.4 3/1.8/2.7/1.6	100.9/101.2/99.9/99.9 3.3/1.2/1.3/1.2
66	Etoxazole	16.02 167	360.1 > 141.1 (27) 360.1 > 304 (19)	0.9965	–12.08/–16.82/–5.42/–17.47	2 15000	80.2/65.7/59.7/88.7 1.2/6.3/15.7/1.6	85.6/53.1/55.4/77.6 3.9/5.3/7.2/10	97.6/60.5/57.3/66.7 1.5/9.7/12.4/2.2
67	Famoxadone	12.88 90	392.18 > 331.11 (10) 392.18 > 238.11 (20)	0.9975	–4.59/–5.02/–2.47/–7.02	2 50	94.6/88.9/79.5/96.9 12.3/6.2/13.9/1.3	95.2/75.8/73/90.4 2.1/6.7/7.1/1.2	96.5/74.6/75/87 1.2/4.8/3.8/1.3
68	Fenamidone	9.21 62	312.07 > 236 (15) 312.07 > 165 (16)	0.9991	–1.14/–4.6/2.47/–5.52	1 50	98.7/101.2/101.4/98.2 1.2/1.7/1.5/2.9	97.6/99.1/96.5/99.8 1.9/2.1/1.7/1.9	98.7/98.7/100/99.5 1.6/1.7/1.2/1.7
69	Fenarimol	10.66 170	330.95 > 268.159 (24) 330.95 > 138.987 (37)	0.9971	–2.11/–5.93/0.37/–6.37	1 50	101.7/100.4/105.8/96.4 7.1/1.2/1.3/2.3	101/95.4/97.4/99.5 2.4/3/1.5/4	104.3/98.4/99.1/99.4 3/2.2/1.2/1.6
70	Fenazaquin	17.33 161	307.23 > 161.188 (19) 307.23 > 57.448 (25)	0.9997	–8.98/–12.54/–3.67/–13.67	2 10000	64.4/49.2/44.1/74.7 2.4/6.6/17.8/1.2	71.2/39.9/43.2/61.7 7.8/3.4/8.9/8.6	81.8/46.2/42.5/51.5 1.2/9.3/12.8/1.9
71	Fenbuconazole	11.45 182	337.17 > 125.113 (30) 337.17 > 70.304 (22)	0.9971	–2.24/–5.61/0.5/–7.16	1 50	101.5/96.7/103.8/96.1 1.7/1.2/2.7/3.1	97.9/95.5/93.3/98.4 1.9/3.1/2/3.3	101.8/97.1/97.5/99.8 1.4/1.2/1.2/1.8
72	Fenhexamid	10.44 125	302.12 > 97.255 (26) 302.12 > 55.424 (39)	0.9975	–1.29/–2.75/2.71/–4.44	1 50	100.1/95.4/106/99.7 6.3/3/1.2/4.3	97.7/99.2/96.9/98.4 2.1/2/1.4/4.6	100.4/98.8/99.3/98.3 1.4/1.2/2.8/2.7
73	Fenobucarb	8.59 99	208.23 > 95.244 (18) 208.23 > 152.1 (13)	0.9996	–2.92/–5.71/0.01/–7.7	2 10	95.9/98.7/98/80.2 3.6/3.1/2/7.5	95.8/97.5/96/97.2 1.6/1.3/2.3/1.6	98.2/98.1/98.2/96.4 1.8/2.2/1.2/1.5
74	Fenoxycarb	11.72 111	302.165 > 88.233 (21) 302.165 > 116.1 (10)	0.9983	–0.52/–3.73/2.12/–4.51	1 50	97.9/95.3/94.5/86.1 1.3/5.2/4/4.7	97.9/90.4/90.2/96.1 1.2/3.3/1.3/3.5	99.2/93.2/94.6/95.7 1.2/2.7/1.2/1.2
75	Fenpropimorph	9.05 181	304.31 > 147.189 (32) 304.31 > 132.193 (44)	0.9982	–1.4/–3.4/2.42/–5.2	1 50	77.5/68.6/75.1/61.9 1.5/14.5/16.8/2	82/64.6/83.7/71.4 1.2/2.5/2.3/8.6	88.4/64.1/87.4/67.6 1.2/8.6/2.8/2.8
76	Fenpyroximat	16.49 151	422.1 > 366.1 (15) 422.1 > 214.1 (24)	0.9995	–1.33/–5.6/–0.1/–4.82	1 8000	69.4/53.7/48.7/81.9 1.3/6.6/15.5/2.4	73.5/42/44.4/63.8 6.2/4.2/8.1/8.7	83.1/47.4/44.1/54.3 1.3/8.8/13.1/1.4
77	Fenuron	3.67 40	165.2 > 72.311 (15) 165.2 > 77.287 (30)	0.9974	–8.99/–7.94/–1.3/–11.9	2 10	93.3/106.2/98.8/86.7 1.2/3.1/1.2/4.3	91.2/97.5/94.5/91 1.4/1.4/2.2/2.7	90.1/94.8/93.8/90.8 1.9/1.2/1.5/1.2
78	Fipronil	11.84 71	436.939 > 367.849 (17) 436.939 > 290 (25)	0.999	–4.48/–7.87/–0.38/–9.83	2 5	105.8/105/109.8/92.2 8.9/11.7/2.3/5	97.5/103.1/99.1/97.2 4.2/1.2/5/6.4	100.1/99.4/102.6/97.8 3.8/1.7/3/5.3
79	Flonicamid	3.1 123	230.03 > 203 (15) 230.03 > 174 (16)	0.9959	–7.76/–4.34/–1.21/–10.46	2 100	92.9/103.2/104.1/91.2 1.8/2.9/2.4/2.1	94/98.9/94.5/97.5 2.4/1.3/1.4/2.9	95.2/100.1/96/96.2 2.2/2.7/4.1/1.4

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							10 µg/kg	50 µg/kg	100 µg/kg
80	Fluazinam	15.31 158	462.9 > 415.9 (22) 462.9 > 397.9 (19)	0.9976	–2.91/–8.89/–2.3/–8.41	1 100	71.8/55.6/47.4/80 1.3/3.4/12.2/1.2	70.1/40.8/40.1/64.7 4.4/7.3/6.2/8.4	80.7/46.5/40.5/55.1 2.2/8.1/12/2.3
81	Flubendiamide	12.27 62	683.019 > 407.889 (10) 683.019 > 273.889 (32)	0.9958	–1.7/–3.74/–0.17/–2.76	2 20	103.6/88.3/111.5/102.2 2.7/1.8/5.8/7.5	93.5/95.8/87.1/97.1 4.8/1.8/3/2	97.4/94.7/94.5/92.9 3/1.2/1.2/2.6
82	Fludioxonil	9.82 70	266.03 > 228.93 (10) 266.03 > 157.99 (32)	0.999	–9.42/–6.83/–2.45/–12.7	2 50	101.7/99.3/95.2/96.1 3.7/3.6/1.3/4.9	99.8/100.8/95.3/97.3 2.1/1.5/1.2/1.7	99.6/97.7/98/97.2 1.4/1.9/3/2.5
83	Flufenacet	10.86 106	364.1 > 152.2 (19) 364.1 > 124.2 (36)	0.999	–1.7/–5.78/0.52/–6.39	1 50	102.4/101.7/100.4/87.9 2.7/4.5/3.7/3.9	99.8/98.1/96.8/99.9 1.2/1.3/1.4/3.5	101.1/98.2/99.4/97.7 1.6/1.2/1.4/1.2
84	Flufenoxuron	16.31 182	489.04 > 158.09 (21) 489.04 > 141.09 (43)	0.9986	–3.44/–7.97/–2.46/–8.66	1 15000	59.7/41.8/34.8/76.1 1.2/6.1/21/5.2	63.2/31.1/30.6/53.8 9.6/4.2/11/10.5	73.6/35.2/29.4/44.6 2.6/8.9/15.2/1.2
85	Fluometuron	6.66 126	233.165 > 72.322 (22) 233.165 > 160.076 (30)	0.9994	–4.07/–7.14/–1.71/–7.89	1 20	98.4/100.5/99/88.7 2.2/1.2/1.4/2	97.2/99.7/95.5/95.8 1.6/2.2/1.5/1.4	100.6/99.6/98.6/97.8 1.2/1.3/1.5/1.3
86	Fluoxastrobin	10.73 191	459.1 > 427 (18) 459.1 > 188.1 (34)	0.9986	–2.87/–5.34/1.39/–5.06	1 50	103.8/103.2/107.7/100 2.9/1.2/1.4/1.2	100.2/102/99.4/101.9 2.3/1.5/1.5/4.6	104.1/100.3/98.6/100.9 1.6/1.4/3.1/1.2
87	Fluquinconazole	10.49 130	376 > 349.076 (19) 376 > 307.1 (22)	0.9974	–5.07/–6.8/–0.91/–9.56	2 50	103.5/102.8/98.5/94.8 1.2/1.5/4.3/3.2	96.4/96.9/91.4/96.4 1.7/1.8/1.6/5	98.9/97.1/95.6/94.7 1.7/1.5/1.2/1.2
88	Flusilazole	11.68 188	316.06 > 247.092 (20) 316.06 > 165.152 (33)	0.9991	–3.73/–5.84/0.42/–7.56	1 50	96.3/95.6/96.2/91 1.8/2.4/2.5/4.5	95.6/92.2/91.4/94.1 1.2/2.8/1.2/2.5	98/92.9/95.7/93.4 1.4/1.3/1.2/1.3
89	Flutolanil	9.9 136	324.17 > 242.076 (28) 324.17 > 262.055 (20)	0.9994	–3.96/–5.94/–0.07/–7.86	1 50	104.6/105.4/106.4/96.5 1.6/1.2/1.5/3.6	99.1/101.3/99/100.3 1.7/1.2/1.7/4.1	102.2/99.6/99.1/99.8 1.4/2.3/1.7/1.2
90	Flutriafol	7.21 128	302.16 > 70.334 (20) 302.16 > 123.111 (30)	0.9991	–4.9/–6.28/–1.36/–7.76	1 50	96.3/99.4/96.8/92.5 2.5/2.1/1.2/3.5	94.2/97.2/95/96.1 1.6/1.2/1.4/3.2	98.3/98/98.6/98.6 1.4/2.6/1.5/1.9
91	Forchlorfenuron	7.81 128	248.035 > 129.127 (20) 248.035 > 93.236 (36)	0.9982	–5.03/–6.81/–1.82/–10.26	1 50	72.4/77.3/73/71.4 1.3/7.3/2.2/4.2	72.8/86.9/76.2/62.9 1.9/1.6/2.2/5.1	77.9/94.4/73/69.7 3/1.6/2.2/3
92	Formetanate hydrochloride	2.6 111	222.1 > 164.9 (16) 222.1 > 120.1 (26)	0.9994	–4.21/–7.02/0.1/–7.97	2 50	104/116.8/87.4/113.7 4.2/1.3/1.6/3	83.9/83.2/76.3/103.9 4/1.7/1.3/3.1	73.5/69.7/75.5/105.6 1.3/2.7/2.3/1.6
93	Fuberidazole	3.7 138	185.1 > 157.1 (23) 185.1 > 65.4 (48)	0.9959	17.39/59.27/31.41/12.93	2 50	109.2/109.4/112.9/87.9 1.4/11.2/1.2/5.2	103.5/103.8/97.2/99.4 13.1/6.7/4.6/5.1	107.6/98.6/108.6/94.6 13.2/2/7.7/1.5
94	Furalaxyl	8.85 125	302.19 > 242.115 (18) 302.19 > 270.077 (11)	0.9986	–2.93/–4.73/0.79/–6.44	1 10	101.1/102.4/104.1/97.6 2.7/1.2/1.5/3.3	100.3/101.1/99.6/100.6 2/1.6/1.2/2.3	100.5/100.8/98.8/101.2 1.9/2.1/1.2/1.2
95	Furathiocarb	14.49 133	383.21 > 195.072 (21) 383.21 > 167.081 (27)	0.9988	–1.86/–4.2/1.25/–5.4	1 10	92.9/86.9/84.7/87.1 3.7/1.3/5.7/4.1	92.1/76.9/77.1/89.3 1.3/4.3/2.7/1.2	96/81.7/83.4/85.8 1.2/6.1/3.7/2
96	Halofenozide	9.32 76	331.01 > 275.111 (8) 331.01 > 105.028 (18)	0.9991	–3.52/–6.8/0.28/–5.39	2 10	103.3/99.5/104.3/97.3 2.4/7.9/8.9/4.3	105.5/100.5/99.8/103.2 2.1/4/1.4/1.2	103.2/106.3/101/105.6 2.4/1.2/6.3/7.6
97	Hexaconazole	12.51 161	314.2 > 70.4 (18) 314.2 > 159.024 (28)	0.9971	–4.92/–6.3/0.15/–9.14	1 50	100/91/92.7/84 4.3/1.3/5.7/3.2	91.7/88.2/88.1/90.7 1.4/1.5/1.5/1.5	95.7/88.8/91.5/91 1.4/1.2/1.5/1.3
98	Hexaflumuron (-)	14.45 105	458.92 > 438.932 (14) 458.92 > 174.866 (37)	0.9981	4.62/–1.74/4.88/0.98	2 10	107.5/83.4/71.1/111.1 4.2/1.2/13.4/3.9	104.9/66.2/68.3/98.5 1.3/5.6/7.4/4.7	109.3/71/68.6/87.1 1.2/6.1/9.6/1.6
99	Hexythiazox	15.51 122	353 > 227.9 (15) 353 > 168 (24)	0.9984	–6.18/–11.62/–5.29/–10.85	1 4000	64.2/52.4/44.7/69.1 1.2/4.8/16.5/1.9	67/40.3/38.9/59.8 2.3/5.6/7.4/9.4	75.4/46.1/39.6/53.3 1.9/10.2/12.6/2.2
100	Imazalil	7.15 187	297.135 > 159.043 (26) 297.135 > 255.025 (23)	0.9985	–0.09/–3.06/2.84/–4.97	1 100	94.5/91.4/95.6/82.8 1.2/2/4.3/2.7	95.5/89.3/94.9/91 1.5/2/1.4/2.2	97.7/87.6/98.7/92.1 1.3/2/1.3/1.2

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5) 10 µg/kg	 50 µg/kg	 100 µg/kg
101	Imidacloprid	3.5 109	256 > 209 (16) 256 > 175 (18)	0.9968	9.79/7.02/14.94/8.95	2 50	119.6/118.5/108.8/115.3 4.1/2.4/1.4/1.4	117.8/114.5/104.5/97.3 1.4/2.2/1.2/3.6	119.8/116.6/112.4/117.3 1.2/2.2/1.7/1.8
102	Indoxacarb	14 184	528.055 > 203.023 (38) 528.055 > 150.06 (25)	0.9982	–2.19/–5.97/0.25/–5.27	1 5000	93.1/80.4/81.6/94 4.9/5.4/13.2/3.3	90.1/71.1/69.7/88.1 1.4/5.1/3.7/3.6	97.5/74.8/76.1/86.6 1.8/5.5/3.6/1.5
103	Ipconazole (*)	13.52, 13.88 166	334.2 > 70 (27) 334.2 > 125 (33)	0.9992	–4.18/–6.1/–0.28/–7.78	1 20	90.1/82.8/82.3/87.5 2.4/1.8/8.3/1.2	90.1/74.3/76/85 1.6/5.1/2.5/2.8	93.3/76.9/80.6/82.2 1.3/5.4/3/1.2
104	Iprovalicarb (*)	10.41, 10.57 111	321.3 > 119.3 (18) 321.3 > 91.4 (54)	0.9987	–3.13/–4.88/0.75/–6.72	10 50	107.6/110.7/99.5/89 4/3.2/4/12.5	96.6/99.1/98.5/91.9 1.7/2.8/1.3/3.7	98.6/99.7/99.2/99 1.7/2/1.2/1.8
105	Isocarbophos	7.58 61	307.1 > 231 (18) 307.1 > 273.2 (5)	0.9996	–4.79/–6.33/–0.7/–8.74	5 10	94.3/100.1/102/69.4 4.6/1.6/11.9/3.1	101.5/104.9/96/92.2 7.8/1.2/1.2/5.8	101.6/90.3/87.9/96.1 8.8/1.7/1.6/5.3
106	Isoprocarb	6.99 89	194.195 > 95.22 (18) 194.195 > 137 (10)	0.9989	–3.89/–6.58/–0.38/–7.95	2 10	96.2/96.2/98.5/76.2 2.6/2/1.4/5.3	93.6/97.4/95.6/94.5 1.2/3.2/2.3/3.8	95.4/96.9/97.4/95.9 1.3/1.6/1.7/1.2
107	Isoproturon	7.35 133	207.225 > 72.312 (21) 207.225 > 134.182 (26)	0.9993	–1.46/–4.02/1.7/–4.87	1 50	100.8/101.9/100.9/91.2 3.3/1.3/1.9/2.1	100.2/100.8/99.3/98.7 2.3/1.3/1.5/1.5	101/99.2/101/99.7 1.3/2.7/1.4/1.2
108	Ivermectin	18.76 76	892.7 > 569.222 (13) 892.7 > 307.097 (22)	0.9996	50.58/36.69/14.29/14.49	5 10	176.9/108.7/97.7/108.9 2.1/2.8/10/4.5	180.8/104/79.8/81.8 5.3/10.6/5.3/2.5	201.2/113.6/86.6/112.3 3.4/4.4/3.8/1.2
109	Kresoxim–methyl	11.77 80	314.09 > 222.122 (15) 314.09 > 235.099 (19)	0.9975	–5.59/–7.75/–2.3/–8.53	1 50	92.9/96.3/97.5/84.1 1.9/3.2/5.5/3	94/91.8/87.5/95.3 1.3/2.6/3.3/1.6	96.5/93.4/93.4/93.1 1.2/1.5/1.3/4
110	Linuron	9.07 112	249.095 > 182.077 (18) 249.095 > 160.041 (21)	0.9986	–3.72/–5.4/0.7/–7.97	2 50	97/97.9/100.7/83.4 1.3/2.2/5.1/2.4	97.4/99/97.3/98.4 1.8/1.5/2.8/3.5	99.2/99.9/98.5/97.7 1.2/1.9/1.3/1.9
111	Lufenuron (–)	15.71 76	509 > 325.9 (10) 509 > 175 (20)	0.9994	–1.75/–8.83/–1.26/–7.01	1 50	80.8/53.7/55.5/83.4 1.3/8.5/15.9/1.4	77.6/44/46.9/70.2 2/1.2/4.7/8.5	86/49/45.7/63.4 6.3/7.3/13.8/2
112	Mandipropamid	9.9 152	412.1 > 328.1 (15) 412.1 > 356 (11)	0.9994	–2.37/–6.11/0.94/–6.53	2 50	100.1/103.4/104.5/99.6 1.6/1.3/3.2/2	101.4/102.4/98.6/102.8 2/1.2/1.6/2.8	104.2/101.6/100.4/102 1.2/2.5/1.2/1.2
113	Mefenacet	10.25 111	299.1 > 148.3 (16) 299.1 > 120.3 (27)	0.9993	–3.25/–5.47/0.39/–7.24	1 10	101.7/100.8/103/92.6 1.7/1.2/1.8/3.7	99.8/98.8/97.1/97.8 1.2/1.2/1.2/3.7	99.8/98.1/98.7/98.5 1.6/1.9/1.4/1.2
114	Mepanipyrim	10.65 169	224.195 > 77.278 (39) 224.195 > 106.194 (29)	0.9991	–2.12/–4.77/1.9/–5.47	1 50	89.6/86.8/84.3/81.7 1.5/3.6/6.8/4.6	90.8/81.3/82.6/87 1.2/2.2/2/1.2	96.2/84.8/87.1/85.5 1.6/4.4/2.4/1.3
115	Mepronil	9.83 137	270.225 > 119.15 (26) 270.225 > 228.085 (16)	0.9996	–0.96/–4.23/1.82/–5.88	1 50	103.6/105.2/106.3/97.8 1.3/1.2/1.5/3.5	101.5/102/99.5/101.1 1.2/1.4/2.3/1.8	103.2/100.6/101.8/99.8 1.2/2/1.5/1.3
116	Metaflumizone	15.53 177	507.183 > 177.92 (23) 507.183 > 286.9 (23)	0.9989	–6.1/–10.72/–2.17/–11.08	2 100	58.5/43.9/37.9/74.6 1.5/3.3/21/2.6	59.9/31.4/32/49.2 10.3/1.7/8.1/12.2	69.9/35.8/29.7/38.1 3.5/9.3/12.6/1.7
117	Metalaxyl	7.32 116	280.225 > 220.15 (16) 280.225 > 192.175 (21)	0.9989	–2.14/–5.02/1.13/–5.94	1 50	101.6/102.5/104.6/94.9 2.9/1.4/1.8/2.6	100.7/100.4/100.1/101 1.6/1.2/1.2/2.6	101.4/100.4/100.7/101.2 1.2/2.5/1.3/1.5
118	Metconazole	12.71 179	320.1 > 70.335 (24) 320.1 > 125.1 (40)	0.9991	–7.42/–10.64/–4.51/–11.51	1 100	94.9/91.6/90/88.6 1.3/1.3/3.5/1.9	92.5/85.5/85.1/91.1 1.2/2.1/1.6/1.7	96.9/87.1/89.6/90.4 1.5/3.8/2.8/1.6
119	Methabenzthiazuron	7.34 98	222.145 > 165.105 (19) 222.145 > 150.104 (36)	0.9988	–1.9/–4.57/1.56/–6.52	1 50	98.6/100.1/101.4/86.7 2.6/1.2/2.1/4.5	96.6/97.5/96.5/96.8 2.3/1.2/1.2/2.9	97.8/98/97.2/96.8 1.2/2.2/1.7/2
120	Methamidophos	1.73 80	142.135 > 94.176 (16) 142.135 > 125.049 (16)	0.9989	–4.84/–5.32/–0.28/–8.01	1 50	92.9/95.5/89.2/87.4 2.2/3.3/6.6/1.6	91.2/93.4/91.8/93.6 1.3/1.2/1.4/2	92.6/94.5/92.7/94.1 1.2/1.3/1.4/1.2

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							10 µg/kg	50 µg/kg	100 µg/kg
121	Methiocarb	9.03 84	226 > 169.082 (10) 226 > 121.045 (36)	0.9984	–4.73/–6.81/–0.08/–7.72	1 100	95.6/99.6/98.9/83.2 1.6/1.9/1.9/3.1	96.3/98.4/97/97.8 1.2/1.2/2.4/3.1	98.2/97.3/98.1/96.6 1.6/2.3/1.2/1.3
122	Methomyl	3.07 59	163.1 > 88.3 (10) 163.1 > 73.3 (28)	0.9988	–5.33/–5.86/–0.91/–8.34	1 50	92.9/99.4/98.8/95.3 3.9/5.6/1.2/2.4	95.5/95/96/96.3 1.2/1.7/3.9/1.4	96.7/97.7/97.7/99.8 1.5/3.2/1.2/4.1
123	Methoprotryne	7.35 171	272.2 > 198.1 (23) 272.2 > 240 (20)	0.9992	–1.78/–4.72/2.44/–5.23	1 10	100.3/101.8/101.5/90 1.6/2.4/2.3/2.1	98.5/98.3/98/97.3 1.3/1.2/1.7/2.4	100.4/98.4/99.6/97.3 1.2/1.4/1.5/1.4
124	Methoxyfenozide	10.22 95	369.1 > 149.1 (18) 369.1 > 313.1 (6)	0.9987	–1.75/–6.46/0.26/–6.76	2 50	97.8/98.7/100.4/92.1 1.5/2.3/1.6/2.7	95.4/96.2/94.5/94.4 1.2/1.9/2.2/6.2	96.5/95.3/93/95.9 1.4/1.7/1.9/1.2
125	Metobromuron	7.07 119	259.06 > 169.993 (22) 259.06 > 170.981 (29)	0.9987	–5.89/–6.25/–1.61/–8.11	2 10	95.8/97.7/98.5/80.7 4.6/1.4/1.4/6.6	93.9/96.3/96.4/96.6 1.8/1.2/1.2/4.1	97/97.4/98/96.4 1.2/3/1.2/2.5
126	Metribuzin	5.29 151	215.075 > 187.131 (20) 215.075 > 171.115 (24)	0.9997	–6.18/–6.56/–0.37/–8.88	1 100	61.1/68.1/62.5/44.6 10.2/16.8/4.8/3	64.1/64/58.9/60.3 7.3/15/1.7/3.6	69.2/58.7/61.7/59.2 2.6/1.6/1.4/3.4
127	Mevinphos (*)	3.67, 4.16 88	225.125 > 127.093 (19) 225.125 > 109.14 (34)	0.997	–9.71/–10.88/–4.45/–13.05	2 20	94.2/94.9/98.7/69.7 1.3/1.6/2.8/5.1	90.7/93.6/93.9/92.9 1.2/2.7/1.3/2.8	92.7/94.2/97.4/94.1 1.7/1.9/1.2/1.6
128	Mexacarbate	3.55 117	223.1 > 151.1 (24) 223.1 > 166.1 (16)	0.9975	–12.22/–9.85/–3.04/–13.88	1 10	90.7/94.8/96.5/80.7 2.3/3.8/2.1/2.6	84.3/92/90.8/89.3 1.7/2/1.2/2.3	84.5/90/92.8/89.4 1.6/2.3/1.2/1.3
129	Monocrotophos	3.22 88	224 > 193.012 (9) 224 > 127.111 (10)	0.9968	–25.17/–14.35/–6.91/–25.41	1 50	88.7/99.8/99.8/84.2 6.7/1.2/6.2/1.7	82.4/92.9/92.1/86.2 3.8/1.2/5/2.4	82.6/92.5/95.7/85.9 1.7/1.4/1.7/2.6
130	Monolinuron	6.48 94	215.135 > 126.11 (20) 215.135 > 99.16 (36)	0.9991	–2.63/–4.63/1.23/–6.05	2 50	95.5/96.9/96.2/77.3 2.8/2.7/1.5/5.5	94.1/97.4/97/94.5 2.1/1.6/1.2/1.8	97.2/96.7/96.8/96.6 1.2/1.8/1.4/1.6
131	Moxidectin	18.46 68	640.331 > 528.222 (10) 640.331 > 498.222 (10)	0.9966	–4.95/–10.49/–5.54/–9.67	10 10	56/45.6/36.4/82.8 5.9/12.5/14.5/6.1	62.9/31.7/35.7/55.8 9.7/5.2/13.5/6.8	72.3/36.4/30.3/44 3.2/8.8/18.2/1.2
132	Myclobutanil	10.14 142	289.17 > 70.316 (21) 289.17 > 125.107 (33)	0.9984	–2/–4.95/–0.3/–6.71	1 50	99.6/102.6/102.4/94.5 3.8/1.3/1.4/1.3	99.4/97.2/96.8/97 1.9/1.3/1.3/4.2	101.2/98.4/98.7/100 1.9/1.2/1.6/1.2
133	Neburon	11.81 121	275.03 > 88.22 (14) 275.03 > 57.39 (18)	0.9991	–6.31/–9.53/7.93/–10.66	10 10	79.9/74.7/75.1/72 9.2/5.6/5.7/4.1	87.5/80.4/84.4/88.1 1.3/2.9/3.4/8.6	91.6/88.2/88.1/88.5 1.5/3.1/2.4/1.3
134	Nitenpyram	2.97 120	271.15 > 237.098 (21) 271.15 > 224.099 (18)	0.9992	–8.05/–7.96/–4.95/–11.69	1 10	77.3/61.2/64.9/53.9 9/9/2.9/15.5	65.2/69.2/75.2/67.6 4.9/2.6/1.2/1.2	70.2/68.7/76.2/71 3.3/2.1/2.9/1.7
135	Novaluron (–)	14.6 119	490.985 > 470.974 (14) 490.985 > 304.961 (19)	0.9991	5.33/–2.91/5.31/–1.86	2 10	107.9/86.1/72.8/114.8 3.9/5.2/15.6/1.5	108.8/68.7/69.7/96.4 2/6.2/7.7/5.7	113.5/74.7/69.6/85.2 1.3/7.3/11.1/1.3
136	Nuarimol	8.98 166	315 > 252 (23) 315 > 242.9 (26)	0.9983	–2.45/–4.9/0.69/–6.85	2 10	104.4/100.5/102.2/93.1 1.6/1.2/3.7/1.5	99.8/98.5/98.5/100.6 1.2/1.4/1.2/1.4	103.2/101.3/100.3/101.9 2.8/2.5/1.3/3.3
137	Omethoate	2.58 101	214.1 > 182.9 (13) 214.1 > 125.1 (17)	0.9993	–3.31/–5.41/0.03/–7.64	1 50	101.6/103.6/105.3/92.9 1.2/2.4/1.5/1.3	98.3/102/101.9/99.6 1.2/1.7/2.2/1.9	99.7/100.6/102.3/101.3 1.3/1.4/1.4/1.6
138	Oxadixyl	4.77 99	279.2 > 219.071 (11) 279.2 > 133.155 (22)	0.9986	2.94/–0.58/0.67/–8	1 20	101.4/112.2/104.2/97.2 2.6/5.9/3.3/2	100.3/101.9/102.7/99.2 1.6/4.3/2.4/3.2	102.6/102.8/101.6/102.5 2.2/1.9/1.3/3.1
139	Oxamyl	2.92 63	237.075 > 72.304 (17) 237.075 > 90.267 (11)	0.9989	–4.88/–6.76/–2.25/–8.58	2 50	102/104.4/107.4/102 2.2/3.1/1.2/4.1	100.5/97.3/96.7/97.5 4.5/1.2/3.6/3.3	99.4/100.5/99.7/101.8 1.3/1.2/1.5/3.2
140	Paclobutrazol	9.66 145	294.19 > 70.324 (22) 294.19 > 125.114 (36)	0.9992	–4.73/–6/0.1/–8.28	1 50	97.2/101/101.9/95 3.3/1.3/1.9/4.5	98.1/97.5/97.8/97.2 1.2/1.2/1.3/2.1	99.9/99.2/99.7/97.2 1.9/2/1.5/1.3
141	Penconazole	11.95 142	284.1 > 159 (25) 284.1 > 70.4 (19)	0.9993	–7.1/–9.14/–2.57/–11.56	1 50	86.2/85.6/89.7/77 3/1.9/3.2/2.2	83.6/83.6/81.3/84.2 1.8/1.5/1.3/2.3	86.5/85.4/84.8/84.2 1.6/1.4/1.2/1.3

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							10 µg/kg	50 µg/kg	100 µg/kg
142	Pencycuron	13.37 167	329.1 > 125.2 (21) 329.1 > 218 (16)	0.9991	–3.96/–6.61/–0.61/–7.4	1 50	85.5/80.5/78.1/86.3 1.5/1.9/7.4/1.9	84.6/69.9/70.2/79.8 1.5/4.6/2.4/3.5	87.6/71.6/74.7/76.5 1.3/4.9/4.8/1.5
143	Phenmedipham	8.45 48	318.08 > 136 (25) 318.08 > 168 (12)	0.9976	–4.29/–6.86/–1.3/–8.79	2 50	103.3/101.6/101.5/95.9 1.5/3/1.5/1.4	97.3/101/96.6/98.2 2.6/1.2/1.8/3.3	102.1/99.8/100.4/98.2 2.9/1.9/1.7/1.4
144	Phoxim	13.02 75	299.135 > 129.134 (13) 299.135 > 77.307 (29)	0.9994	–5.12/–2.05/0.68/–5.2	1 100	85.9/85.4/76.3/73.7 1.2/3.4/10.2/5.9	87.3/74.3/71.7/85.7 2.4/4.4/3.5/2.4	90.6/76/76.8/83.2 1.3/4.7/2.8/1.5
145	Picoxystrobin	11.79 90	368.1 > 145.3 (22) 368.1 > 115.2 (50)	0.9981	–3.82/–5.71/–0.13/–5.79	2 50	97.5/98.4/97.7/90.6 5.8/3/5.9/5.6	96.8/94.9/92.2/98.8 1.2/3/1.2/3.2	98.8/95.2/97.8/97.6 2.7/1.4/3.1/1.2
146	Piperonyl butoxide	14.84 107	356.2 > 177.1 (12) 356.2 > 119.2 (37)	0.9993	–2.58/–7.26/–1.63/–7.82	1 10	87.5/79.1/76/80.1 4.1/2.2/11/4.9	87.7/69.8/70.9/83.1 1.7/4.9/4.7/3.7	92.3/73.7/76.5/78.9 1.2/6.2/5.4/1.5
147	Pirimicarb	4.52 123	239.225 > 182.157 (18) 239.225 > 72.307 (23)	0.998	–6.26/–7.05/–1.12/–9.2	1 50	96.9/100.1/100.1/81.7 2.7/1.2/1.8/3.3	92.5/96/97.2/95.7 1.3/1.2/1.2/2.6	94.8/96.2/98.4/96.2 1.5/2.4/1.2/2.7
148	Prochloraz	12.58 111	376.09 > 307.983 (14) 376.09 > 70.349 (27)	0.9984	–6.5/–9.81/–3.58/–10.1	1 100	90.1/89.6/90.4/88.4 3.1/3.3/7.2/1.5	91.6/83.1/84.2/89.4 2.4/3.1/1.2/1.2	95.1/83.8/89.4/88.3 1.4/3.7/1.6/1.2
149	Promecarb	9.38 92	208 > 109.25 (16) 208 > 151.2 (9)	0.9977	–5/–6.77/0.7/–7.82	1 10	97.2/97.8/99.2/84.3 2.5/1.3/3.8/4.2	97.4/99.1/97.4/99.5 3.4/1.8/1.2/2.8	98.7/99.5/99.9/98.6 1.5/2/1.4/1.5
150	Prometon	6.22 163	226.2 > 142.1 (23) 226.2 > 184.1 (19)	0.9996	–2.68/–6.71/0.34/–5.75	1 10	99.1/104.7/97.8/95.5 2.4/6.7/3/10.2	97.7/94.3/99.9/100.7 1.4/1.2/7.8/8.5	97.4/94.8/94.3/95.3 1.4/1.4/1.2/1.3
151	Prometryn	8.83 179	242.2 > 158.1 (25) 242.2 > 200.1 (20)	0.9986	–1.53/–3.97/2.21/–6.17	1 10	94.9/94.2/94.9/87.7 3.1/1.5/5.3/3.8	94.7/85.1/88/90 1.2/3.3/1.2/1.6	97.6/88.3/92.5/87 1.4/3.2/1.8/1.2
152	Propamocarb	2.7 106	189.2 > 102.2 (20) 189.2 > 74.4 (15)	0.9993	–21.76/–22.52/–4.26/–33.08	1 50	66.4/79.5/87.8/65.1 1.2/2.5/1.3/4.5	64.2/77.6/83.6/68.7 1.4/1.5/2.7/2	64.1/77/83.9/68.4 1.2/2/1.4/2.5
153	Propargite	15.98 111	368.14 > 107.198 (28) 368.14 > 57.44 (23)	0.9988	–4.85/–7.59/–1.74/–9.27	2 10000	66.1/56.3/45.8/77.1 6.8/2.7/16.4/3	70.9/41.2/40.1/62.5 4.9/6.5/10.4/10.5	81.9/46.5/41.2/53.6 1.6/8.6/13.4/1.4
154	Propham	6.95 25	180.122 > 138.04 (8) 180.122 > 120.11 (19)	0.9992	0.17/–4.69/3.33/–4.04	10 50	77.4/102.4/101.7/78.3 17.8/8.8/1.4/4.4	84.1/91.7/91.3/81.4 1.2/1.5/1.9/1.2	82.7/83.9/94.7/90.9 3.5/1.6/1.2/4.7
155	Propiconazole (*)	12.31, 12.45 193	342.13 > 159.015 (30) 342.13 > 123.151 (37)	0.9989	–2.61/–5.6/0.61/–6.87	1 50	89.6/91.8/93/81.3 1.3/1.2/3.8/2.7	85.7/85.9/83.2/88.3 3/3.3/1.2/1.7	90.4/86.9/89.2/89.7 1.7/2/1.6/1.2
156	Propoxur	5.34 83	210.185 > 111.177 (17) 210.185 > 93.215 (27)	0.9989	–5.27/–6.55/–0.54/–7.77	1 100	95.7/99.8/102.1/82.6 1.4/1.6/3.7/2.9	96/98.6/94.6/95.6 1.5/1.2/1.2/2.4	97.4/97.2/97.5/97.4 1.3/1.4/1.2/1.4
157	Prothioconazole	12.41 70	341.978 > 306.1 (15) 343.978 > 308.1 (15)	0.9982	28.63/17.12/47.26/25.92	10 50	55.3/55.5/57.1/52.6 1.3/5.9/6.9/8.2	49.9/50.5/60.2/47.9 4/1.6/4.3/1.3	57.1/47.3/55.5/49.5 2.9/1.7/2.5/2.1
158	Pyracarbolid	5.73 61	218.152 > 125.11 (15) 218.152 > 97.125 (24)	0.9991	–12.84/–14.64/–8.41/–15.91	1 10	97.5/99.5/101.6/90.7 2.1/1.5/2.1/1.5	97.7/98.4/98/96.8 1.7/1.3/1.4/3	98.9/98.9/100.4/99.8 1.3/1.6/2.2/1.9
159	Pyraclostrobin	12.97 126	388.15 > 163.107 (26) 388.15 > 149.093 (31)	0.9986	–2.58/–5.6/0.01/–6.59	2 100	95.4/92.5/91.8/92.2 1.9/2.9/5.4/1.5	96/85.1/84/94.6 1.5/3.9/3.2/1.3	98.1/87.1/88.2/92.4 1.3/3/2.4/1.7
160	Pyridaben	17.12 90	365 > 309 (14) 365 > 147 (24)	0.999	–3.05/–7.73/0.55/–6.43	1 50	51.2/41.3/35.5/62.7 1.4/2.4/19.7/3.9	57.1/30.5/33/49.2 10.3/2.7/10.4/10.8	67.3/37.1/31.1/39.9 1.2/9.2/17.6/1.4
161	Pyrimethanil	8.11 165	200.195 > 107.179 (25) 200.195 > 168.102 (33)	0.9988	–1.58/–5.31/1.19/–6.3	1 50	90.1/89.1/88.8/78.7 5.6/3/5.3/4.8	88.3/82.2/84/86.2 1.5/2.1/1.2/1.2	91.9/85.5/91.1/86.3 2.3/3.5/1.9/1.2
162	Pyriproxyfen	15.27 121	322.19 > 96.237 (19) 322.19 > 185.104 (25)	0.9993	–2.42/–5.43/0.95/–7.72	1 15000	67.3/54.4/45.8/70.2 4/7.1/16.6/2.6	70.4/42.8/43.7/65.3 3.2/4.6/9/8.6	78.2/48.7/44.1/56.9 1.2/9.8/12.8/1.5

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5)		
							10 µg/kg	50 µg/kg	100 µg/kg
163	Quinoxyfen	15.55 213	308.075 > 197.022 (35) 308.075 > 162.098 (48)	0.9988	–4.16/–7.19/–0.38/–9.42	1 50	72.6/56.5/51.6/71.2 3.5/7/13.9/1.3	75.4/48.1/51/65.8 2.1/3.3/6.5/6.8	82.7/52.8/52.5/61.1 1.5/6.7/8/1.6
164	Rotenone	11.51 206	395.15 > 213.086 (26) 395.15 > 191.115 (39)	0.9963	–1.63/–4.62/2.25/–5.78	2 20	100.8/94.5/89.9/79.2 1.6/1.2/3.5/3.2	90.9/87.7/85.2/91.7 1.8/3.2/1.4/1.2	95.5/86.2/89.7/95.5 2.6/2.7/2.4/1.3
165	Secbumeton	6.21 157	226.245 > 170.127 (21) 226.245 > 142.127 (26)	0.9997	–4.71/–7.72/–2.33/–8.53	1 10	97.3/98.1/97.5/88.8 1.9/1.2/1.8/2.7	96.2/93.6/92.5/94.9 2/1.2/1.2/1.6	97.7/94.4/92.7/95.2 1.3/1.9/1.7/1.2
166	Siduron (*)	8.99, 9.31 101	233.152 > 94.151 (18) 233.152 > 137.04 (15)	0.9981	–0.07/–3.45/2.95/–4.34	2 10	102/102.1/102.3/98.3 2.6/1.6/3.4/2.6	99.9/101.6/99.1/101.4 1.3/1.3/1.5/3.2	101.4/100/99.6/101.5 1.3/1.5/1.3/1.8
167	Simazine	5.49 38	202.05 > 132.04 (20) 202.05 > 104.01 (26)	0.9994	–9.03/–4.38/–2.6/–10.56	1 50	84.9/87.2/84.8/70.6 2/2.8/2/4.7	85.5/86.4/82/84 1.3/1.8/1.3/2.7	85.9/85.7/84.6/85.9 2.3/2.2/1.6/1.6
168	Simetryn	5.66 169	214.085 > 68.356 (36) 214.085 > 96.2 (27)	0.9983	–3.47/–6.14/0.34/–7.25	2 10	95.7/98.8/98.9/85.9 4.5/1.3/1.3/1.9	96.9/96.2/96.8/96.3 1.2/1.2/1.2/1.6	97.3/96.8/99.3/96.5 1.8/1.2/1.8/1.2
169	Spinetoram	14.33 200	748.5 > 142.2 (31) 748.5 > 98.1 (40)	0.9986	–1.82/–1.72/3.68/–6.56	1 100	86.1/77.6/87.1/78.9 1.9/7.5/7.2/4.5	86.9/75.4/87.7/77.6 2/2.5/1.2/5.3	89.1/72.7/92.2/76.7 1.5/6.6/1.2/1.4
170	Spinosad A (*)	13.43 250	732.47 > 142.214 (26) 732.47 > 98.267 (41)	0.9992	–0.56/–1.46/2.76/–4.54	1 100	90.8/84.7/92.1/82.4 3.2/5.5/3/3.4	90/84.6/89.6/84.4 1.7/3.5/1.2/4.2	90.2/80.2/92.9/82.8 1.2/3.7/1.2/1.5
	Spinosad D (*)	14.3 250	746.455 > 142.203 (27) 746.455 > 98.269 (43)			100			
171	Spirodiclofen	16.51 141	411.085 > 313.027 (10) 411.085 > 71.376 (15)	0.9979	–3.65/–7.6/–1.5/–8.28	1 50	67.8/53.5/47/76.2 3.8/3.9/16.8/2.8	70.8/42.4/42/63.5 6.3/6.7/9.5/9.4	81.2/47.3/42.4/54.1 1.3/9.3/15.2/1.3
172	Spiromesifen	15.97 76	371.3 > 273.3 (15) 371.3 > 255.2 (20)	0.9982	–1.73/–5.12/–0.06/–7.18	1 50000	79.3/68/59.5/78.3 2.3/6.9/9.9/1.9	80.6/51.7/53.2/73 9.5/7.2/9/4.8	90.4/60.3/57.1/66.3 5.1/6.1/9.9/1.3
173	Spirotetramat	10.6 152	374.2 > 302.15 (16) 374.2 > 330.207 (10)	0.9989	–0.25/–4.44/1.71/–4.53	10 100	70.4/68.1/64.1/28.6 9.2/5.5/4/38.6	70.8/67.1/62.8/75 2.5/5.6/1.2/4.8	69.1/63.5/61.6/73.4 1.2/1.9/4.3/1.5
174	Spiroxamine (*)	9.59, 9.78 142	298.3 > 144.1 (20) 298.3 > 100.2 (30)	0.9992	–1.3/–3.97/3.08/–5.19	1 50	95.2/91.5/99.1/74.5 2/4.6/3.6/3.2	96.1/92.1/99.8/90.7 1.3/2.1/1.5/2.1	99.3/88.8/101.4/90.3 1.7/2.7/1.2/1.5
175	Sulfentrazone (–)	5.88 225	384.945 > 306.967 (25) 384.945 > 198.954 (40)	0.9996	1.45/–1.49/5.83/–5.26	1 10	115.3/116.3/113.6/109.7 5.1/2/2.2/2.5	111.1/113.8/114.7/114.6 1.8/3/2.6/3.5	111.3/111.7/114.6/113.4 1.2/1.3/3/2.1
176	Tebuconazole	12.08 160	308.2 > 70.338 (24) 308.2 > 125.106 (30)	0.9988	–7.1/–9.28/–4.48/–11.08	1 50	91.1/87.5/88.8/83.2 3.5/1.2/1.9/2.1	87.5/85.1/84.8/86.8 1.3/2.1/1.3/1.3	91.2/86.8/87.9/87.3 1.5/1.5/1.6/1.2
177	Tebufenozide	11.79 96	353.27 > 133.153 (21) 353.27 > 297.2 (5)	0.9995	–2.4/–5.17/0.7/–6.28	1 50	100.8/101.3/105.1/100.9 5.3/1.5/2.8/2.7	97.7/101/99/99.2 3.3/2.1/3.3/1.2	98.6/97.5/99.6/97.7 1.8/1.3/2.5/4.3
178	Tebufenpyrad	14.62 207	334.15 > 145.054 (27) 334.15 > 117.161 (25)	0.9986	–1.4/–5.89/0.52/–5.96	1 50	84.6/75.7/69.9/83.3 2.6/6.4/11.3/6.8	87.9/65/65.2/83.5 1.3/5.6/3.9/4.2	93/69.7/70.4/77.3 1.3/7.9/7/1.4
179	Tebuthiuron	5.63 127	229.185 > 172.136 (20) 229.185 > 116.136 (30)	0.9995	–3.44/–4.86/1.61/–7.03	1 10	100.7/104/102.6/93.5 2.3/1.4/1.3/3.7	98.1/99.8/97.9/97.8 1.5/1.5/1.4/2.6	98/97.9/98.4/98.3 1.2/2.4/1.6/1.5
180	Teflubenzuron (–)	15.26 95	378.939 > 338.89 (10) 378.939 > 358.89 (10)	0.995	19.17/4.11/8.49/14.01	1 50	110/84.3/70.8/113.8 2.1/4/2.6/1.9	107.5/65.1/62.9/101.3 1.5/15.8/6.8/11.2	104.5/71.1/68.8/93.9 4.2/1.7/4.5/1.6
181	Temephos	15.43 213	467.005 > 418.987 (22) 467.005 > 404.954 (17)	0.9986	2.87/–5.6/0.8/–2.61	1 10	68/51/43.1/77.7 2.3/5.9/18.9/2.3	72.7/38.3/37/63.8 6/5.1/8.7/10.5	82.2/43.9/36.5/54.3 1.4/6.8/12.2/1.3
182	Terbumeton	6.39 140	226.1 > 170 (19) 226.1 > 142.1 (25)	0.9989	–7.83/–10.35/–3.13/–10.39	1 10	100.4/99.7/100.7/91 3.3/1.6/2.7/3.3	96.6/94.6/95.8/93.3 1.2/1.9/1.4/1.4	97.8/94.9/96.9/94 1.5/1.2/1.2/1.8

#	Compound	RT (min) RF lens (V)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/GT/OT/BT) (n = 5)		
							10 µg/kg	50 µg/kg	100 µg/kg
183	Terbutryn	9.1 151	242.1 > 186.1 (21) 242.1 > 91.2 (29)	0.9987	–2.32/–4.72/2.05/–6.49	1 10	94.1/91.1/93.5/86.9 2.6/1.7/5.1/3.2	93.2/83.4/87/88.6 1.5/4.6/1.2/1.7	97.1/85.1/91.3/85.3 1.5/4.1/3.1/1.3
184	Tetraconazole	11.1 143	371.95 > 159.117 (28) 371.95 > 70.331 (24)	0.9985	–3/–6.27/0.02/–6.94	1 20	98.8/100/96.7/91 4.4/1.2/3/1.2	97.5/97/93.5/96.9 1.2/1.9/1.9/3.2	101.5/96.3/98/97.2 1.2/1.3/1.2/1.2
185	Thiabendazole	3.58 178	202.115 > 175.052 (28) 202.115 > 131.158 (36)	0.996	4.53/50/15.76/0.8	1 50	79.4/94/113.8/89.6 11.1/13.7/1.6/10.7	94.7/99.4/93.9/90.5 16.7/14.5/8/8.3	98.8/88.5/99.4/84.3 15.7/1.3/11.6/1.7
186	Thiacloprid	4.25 127	253.1 > 126.1 (22) 253.1 > 90.2 (41)	0.9984	–0.56/–3.17/2.09/–5.09	1 10000	102.7/105.9/105.6/100.7 1.4/1.2/1.4/1.2	98.9/101.4/99/100.9 1.2/1.2/1.3/3.7	100.4/100.6/101.8/101 1.3/2.4/1.2/1.5
187	Thiamethoxam	3.17 104	292 > 211 (13) 292 > 181 (23)	0.999	–5.88/–2.39/0.68/–5.92	1 20000	95.9/101.2/103.5/98.2 1.3/1.2/1.2/3.6	93.1/96.9/95.7/96.4 2/2.7/2/2.7	92.4/96.7/97.8/96.5 1.2/3.7/2/2
188	Thiobencarb	13.04 105	258.145 > 125.128 (21) 258.145 > 89.223 (50)	0.9989	–2.52/–4.86/–0.01/–7.37	1 50	84.6/83.9/78.7/71 2.6/4.3/8.9/3.8	83.7/75.6/75.5/84.8 2.2/3.5/3.7/2.7	86.5/77.5/79.7/83.4 1.2/4.5/2.3/1.2
189	Thiofanox	6.47 46	241 > 184 (5) 219.2 > 61.1 (13)	0.9994	–2.56/–6.53/–3.17/–8.24	5 10	108.1/100.2/109.1/64.2 7.2/19.7/7.8/1.4	102.2/98/97.8/93.6 3.2/1.2/2.5/4.6	99.1/96.8/99.9/100.7 5/4.1/1.2/3.3
190	Thiophanate–methyl	5.36 135	343.1 > 151.2 (19) 343.1 > 311.2 (11)	0.9987	–8.7/–8.2/–0.79/–12.2	10 100	16.2/26.8/29.4/27.8 18.8/11.6/12.3/4.3	19.3/36.5/41/25.7 9.4/5/1.3/13.9	18.2/25.4/45.6/30.6 6.2/10.3/5.7/6
191	Triadimefon	10.02 103	294.183 > 197 (14) 294.183 > 224.99 (12)	0.9988	–2.57/–4.6/1.45/–6.91	1 50	99.9/98.8/97.1/89.4 1.3/3.3/1.2/3.2	96.9/96.6/97.6/96 2.9/1.5/1.2/4.4	101.1/99.8/98/97.7 1.6/1.3/1.7/1.5
192	Triadimenol	9.66 58	296.07 > 70.04 (24) 296.07 > 126.946 (43)	0.9996	–5.02/–7.01/–0.15/–8.77	1 50	98.5/97.1/96.3/95.6 4.2/1.9/1.5/5.2	94.2/96.5/93.8/98.1 1.6/1.2/1.7/3.1	97.5/97.7/99.6/95.8 1.4/1.2/1.8/1.4
193	Trichlorfon	3.64 112	256.905 > 109.146 (21) 256.905 > 79.26 (32)	0.997	–16.29/–10.68/–5.24/–17.44	2 50	91.2/104/105.6/89 3.2/4.2/1.6/1.8	87/95.9/91/86.8 2.1/2.7/1.8/2	84.9/93.9/92.1/85.1 1.2/2.8/1.2/1.3
194	Tricyclazole	4.66 150	190.1 > 163 (24) 190.1 > 136 (29)	0.9983	–3.58/–5.38/0.38/–7.15	1 50	101/103.9/104.2/95.4 1.2/1.8/1.2/1.2	96.8/100.5/99.9/99.1 1.9/1.6/1.3/2.9	99.1/99.8/101.9/98.8 1.2/2.1/1.3/1.2
195	Trifloxystrobin	13.87 139	409.14 > 186.086 (20) 409.14 > 145.085 (44)	0.9989	–3.07/–5.6/0.84/–5.91	1 50	95.8/88.5/83.6/89.4 1.3/3.2/5.9/2.1	93.9/77.1/75.6/89.3 1.2/5.5/3.7/2	96.7/79/80.7/86.3 1.5/5.3/4.1/1.3
196	Triflumizole	14.02 103	346.1 > 278 (5) 346.1 > 73.1 (15)	0.9989	–10.86/–15.26/–6.88/–15.81	2 100	76.4/82.5/83/88.7 2.7/14/7.4/2.7	87.7/69.8/73.1/81.2 1.7/7.2/6.1/2.7	94.6/74.4/78.3/79.7 1.6/7.4/5/1.5
197	Triflumuron	13.05 118	359.06 > 156.06 (13) 359.06 > 138.99 (27)	0.9993	–3.67/–6.53/–0.16/–8.32	1 50	94.3/83.8/82.5/91.3 1.3/3.2/7.6/1.2	92.4/74.1/72.2/88.8 1.6/7.1/3/2.3	96.4/77.5/76.9/83.9 1.2/6.1/3.9/1.6
198	Triticonazole	10.63 143	318.19 > 70.333 (19) 318.19 > 125.116 (45)	0.9995	–2.45/–5.36/1.19/–5.81	1 20	101/100.3/102.9/97.3 3.9/1.2/1.4/1.5	94.8/98.2/96/98 1.2/1.7/1.3/3.8	101.5/97.6/96.6/97 1.5/1.3/3/1.3
199	Vamidothion	3.64 94	288.1 > 146.118 (15) 288.1 > 118.142 (25)	0.9976	–9.62/–8.59/–3.47/–12.6	1 10	93.5/96.9/96.3/72.7 2.3/2.4/1.4/1.2	89/94.7/93.5/93 1.3/1.7/2.1/2.7	91.7/93.1/96.1/93.5 1.7/2.1/1.5/1.4
200	Zoxamide	12.44 159	336 > 186.9 (20) 336 > 159 (42)	0.9985	–0.49/–4.54/1.04/–4.48	1 50	96.4/94.2/92.5/87.5 2.3/1.5/4.8/6.3	94.1/89/85.8/95.2 2.6/3.5/1.2/1.8	95.9/90.9/89.6/94.5 1.2/2.2/1.6/1.6

(*) Pesticides with two isomers, calculated with two peaks together.
(-) Compounds scan in negative mode; the other ones scan in positive mode
CE: Collision energy (V)
WT, GT, OT, BT: white, green, oolong and black tea, respectively
ME: Matrix effect
MRL: maximum residue limit (EU MRL)

Table A-14. List of pesticides, method parameters, and data validation of GC-MS/MS method for 4 types of teas (chapter 5)

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5) 10 µg/kg	50 µg/kg	75 µg/kg
1	2,4'-Methoxychlor	22.15	121 > 78 (20) 227 > 121 (12)	0.9909	31.9/36.5/17.9/61.8	5 100	97.9/108.5/104.7/107.7 6.9/5.5/2.6/5.7	98/105.5/102.5/96.5 1.6/1.6/2.7/7.9	92.8/112.9/108.1/96.2 5.5/2.3/4.2/14.1
2	2-Phenylphenol	11.94	141 > 115 (12) 170 > 141 (22)	0.9951	15.4/16.5/13/25.2	10 50	93.5/113.2/113.7/96.6 3.3/5.7/3.2/7.9	104/113.8/112.3/102.5 2.4/2.7/1.6/1.3	110/113.5/114.3/106 1.2/2.7/1.2/1.2
3	4,4'-Methoxychlor olefin	21.74	238 > 152 (35) 238 > 195 (20)	0.9985	15.7/20/10.4/18.4	1 100	115/114.5/111.2/115.3 3.7/1.2/6.9/2.7	113.1/116.8/111.6/109.8 1.7/1.9/3/1.1	116.5/117.6/113/110.4 3.3/1.3/2.2/1.6
4	Acetochlor	16.75	174 > 146 (12) 223 > 132 (20)	0.9989	15.1/26.6/15.5/12.4	5 50	119.6/115.4/104.7/118.1 1.6/2.4/1.3/1.3	116.9/115.5/104.4/113.1 4/1.4/1.8/1.2	116.8/110.8/104.4/116.8 3.6/1.4/1.2/1.5
5	Acrinathrin	24.17	181 > 152 (22) 208 > 181 (8)	0.9921	–23/–14/–24.2/–16.9	1 50	101.8/104.4/91.4/113 1.4/1.2/1.5/6	95.1/92.1/82/103 1.1/1.5/2.2/5.8	99.2/97.9/87.4/110.8 3.4/1.3/5.9/2.5
6	Alachlor	16.91	188 > 130 (32) 188 > 160 (10)	0.9987	19.4/15.6/8.2/21.3	5 50	119/118.2/110.3/118 1.9/2.8/2.8/1.4	119/117.9/108.7/113.3 1.3/1.4/1.8/1.2	117.9/113.5/109.4/113.1 1.2/1.3/1.4/1.2
7	Aldrin	18.03	263 > 193 (32) 263 > 191 (30)	0.9988	9.5/11.4/2.9/11.9	5 20	117.6/115/101.3/107 3.2/1.3/10.9/3	112/103.6/91.5/98.8 1.3/2.1/1.2/1.2	115.8/105/93.6/94.5 2.5/2.7/4.2/3.8
8	Allidochlor	8.3	132 > 56 (6) 138 > 96 (8)	0.9987	4.2/–1.5/–6/10.8	10 10	59.1/90/88.1/50.8 19.4/4/1.2/15.7	60.7/84.7/79.4/61.6 1.5/17.4/1.2/5.6	44.1/79.5/75.7/55.5 11.3/9.7/4.4/6.8
9	Anthraquinone	18.07	180 > 152 (12) 208 > 180 (10)	0.9906	33/19.1/12/46.1	10 20	99.5/73.4/42.1/73.7 5.2/11.7/6.5/6.4	91.5/70.9/53.8/69.9 4.7/1.7/1.7/1.3	94.1/69.7/58.6/75.9 2.1/4.6/2.1/1.6
10	Atrazine	15.05	200 > 122 (10) 215 > 173 (8)	0.9983	13.2/13.7/8.6/20.9	2 100	107.9/115.7/113.3/99.8 6.7/1.2/3.4/9.5	103.3/111.3/111.3/96.1 2.8/1.5/1.2/3.7	104.2/108.4/110.9/97.4 1.8/1.1/1.2/3.8
11	Azinphos-ethyl	24.67	132 > 77 (12) 160 > 132 (6)	0.9973	54.9/46.3/21.9/75.5	10 50	72.4/83.1/55.3/104 10.7/14.4/3.3/2.6	72.7/64.6/50/89.4 1.2/3.1/7.4/1.4	72.4/71.2/56.6/89 5.1/4.2/3.8/7.3
12	Azinphos-methyl	23.98	160 > 77 (16) 160 > 132 (6)	0.991	14.2/3.1/–26.7/22.4	50 100	< LOQ	74/52.6/43/84.1 7.8/18.6/7.7/1.8	72.4/56.6/45.8/87.2 1.2/15.7/11.9/15.2
13	Benfluralin	13.92	292 > 206 (12) 292 > 264 (8)	0.9959	–2.7/–7.2/–9.4/17.4	1 100	102.6/106.3/102.8/106.2 3.4/1.3/2.3/4.2	95.6/96.9/94.4/97.3 1.1/1.9/1.1/1.7	96.3/97.1/95.6/97.1 1.7/1.1/1.2/1.7
14	BHC, alpha-	14.49	181 > 145 (13) 219 > 183 (8)	0.9989	0.2/0.4/–3.3/3.9	1 10	108.6/114.4/110.4/112.5 5.8/1.7/3.7/5.2	105.2/110.7/107.1/105.1 1.2/2.6/1.9/1.5	105.5/108.4/105.9/103.4 1.9/1.2/1.2/1.3
15	BHC, beta-	15.1	181 > 145 (15) 219 > 183 (8)	0.9981	7.1/5.6/1.5/8.9	1 10	115.6/118.4/114.3/118.5 3.2/1.9/1.5/2	118.1/119.6/119.4/108.5 1.7/1.4/1.3/1.2	118.6/118.5/118.3/113 1.6/2.2/1.4/1.3
16	BHC, delta-	16.03	181 > 145 (13) 219 > 183 (8)	0.9972	–26/–7.4/–15.4/–13.1	10 10	102.8/110.9/101.3/115.3 4.7/3.5/5.6/4.5	91.2/105.7/94.3/101.2 1.9/1.3/3.4/8.8	97.8/102/96/106.9 1.6/1.9/1.7/4.8
17	BHC, gamma-	15.34	181 > 145 (13) 219 > 183 (8)	0.9974	3.1/3.8/–2.8/12.2	1 10	111.9/109.8/116/111.9 5.5/5.5/1.2/5.5	108.8/115.1/108.8/107.3 6.3/1.2/1.7/2.1	111/116.5/110.4/105.9 1.4/5.9/1.2/2
18	Bifenthrin	23.03	181 > 165 (25) 181 > 166 (10)	0.9988	14.9/13.4/3.2/24.2	2 30000	105.6/114/102.9/113.9 4.6/2.3/1.1/2.2	104/106.8/97.5/105.8 1.2/1.2/2.7/1.2	106.4/110.7/103.2/106.9 3.3/2.3/3.9/1.5
19	Bioallethrin	18.93	123 > 81 (8) 136 > 93 (11)	0.9912	11.4/4/0/22.7	50 10	< LOQ	106.2/98/88.9/105.8 6.7/3/4/3.6	109.6/98.8/96.3/103.1 2.9/3.7/1.2/2.1
20	Biphenyl	9.95	154 > 115 (26) 154 > 127 (30)	0.9981	1.8/3.3/–0.6/3.6	10 50	40.7/110.7/119/51.9 19.7/9.2/2.1/13.2	50.2/85.8/92/43.8 1.4/19.8/1.2/6	39.2/75/77.3/36.4 18.8/8/4.1/9.7

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
21	Bromfenvinphos	19.8	267 > 159 (15) 323 > 267 (10)	0.9978	44.1/46.5/24.2/65.5	2 10	93.8/101.5/85.4/108.1 5.8/2/2.1/6.9	92.5/97.2/82.1/99 2/1.6/1.3/4.3	92.4/100.2/81.6/101.2 2.8/1.7/2.9/5.3
22	Bromfenvinphos-methyl	18.9	109 > 79 (5) 295 > 109 (15)	0.9976	42/32.8/16.9/79.3	10 10	88.3/70/63.4/105.3 13/12.4/4.9/12.3	87.7/68/64.7/96.4 1.7/2.9/2.6/10.1	82.5/72.3/62.9/96.3 1.3/2.5/4.3/3.8
23	Bromophos methyl	18.4	329 > 314 (13) 331 > 316 (13)	0.9975	24.6/18/14.8/38.9	1 10	106.6/100.2/89.9/112.4 2.8/1.3/2.3/4.4	99/95.1/89.2/98.2 2.2/3.5/2.7/3	100/94.3/89.5/100.6 1.4/1.1/2/3.3
24	Bromophos-ethyl	19.35	331 > 303 (8) 359 > 303 (17)	0.9991	31.1/33.1/17.4/37.6	1 50	108.8/114.8/99.5/118.4 4.3/4/2.2/2	104.3/115/94.4/111.7 2/1.2/1.7/1.9	105.8/113.5/95.8/112.9 2/9.6/1.1/1.4
25	Bromopropylate	23.16	183 > 155 (12) 341 > 183 (15)	0.9966	10.1/9.4/0.6/21.5	2 50	100.3/103.8/90.2/108.9 6.3/5.8/1.1/1.2	95.6/97.5/87.4/100.4 1.2/1.6/3.9/1.2	98.8/99.6/91.1/102.3 3.3/3.1/3.1/2
26	Bupirimate	20.32	273 > 108 (16) 273 > 193 (8)	0.9966	10.9/16.4/5.2/19.6	2 50	109.4/112.2/108.2/112.5 2.7/1.3/2.1/4	106.1/114.6/104.7/103.8 1.6/2.5/2.2/1.3	111.7/114.6/106.7/107.8 1.7/1.5/1.1/1.7
27	Carbophenothion	21.79	125 > 97 (6) 199 > 143 (10)	0.9983	61.7/47.8/36.2/72.9	5 10	105/91.9/80.8/104.5 5.7/3/5.2/3	101.6/93.5/85.8/101.2 1.9/1.8/2.6/5.9	100.4/98.7/87.9/105.1 3.4/2.4/4.5/4.6
28	Carfentrazone ethyl	21.62	330 > 310 (8) 340 > 312 (10)	0.9979	29.5/32.6/17.9/36.7	2 20	98.3/103.3/94.8/107.9 7.3/5.3/1.4/1.9	98.2/101.7/95.6/102.4 3.2/1.1/1.3/2.1	99.8/102.9/98.2/104.5 2.7/1.5/2.2/4.3
29	Chlorbenside	21.74	125 > 89 (17) 125 > 62.8 (28)	0.9921	22.6/24.7/11.3/34.8	5 100	74.6/107.1/73/94.6 1.7/5.8/12.8/6.6	100.2/116.1/91.2/102.2 3.4/6.9/3.8/1.3	104.1/117/98.2/108.7 1.2/1.4/1.7/1.9
30	Chlordane, cis-	19.79	375 > 266 (21) 377 > 268 (19)	0.9991	5.9/9.5/–1.6/11.1	1 20	113.6/116.3/107.6/106.3 5.3/4.2/1.1/8.4	116.4/111.9/109.2/114.4 1.1/1.2/1.8/1.2	112.2/119.4/116.5/114.4 1.2/1.9/4.5/1.1
31	Chlordane, trans-	19.49	272 > 237 (13) 375 > 266 (18)	0.9991	7.6/10.4/2.6/11.5	1 20	106.7/118.6/106.4/117.8 7.1/2.1/1.3/2.7	116/119.6/115.2/113.5 1.3/6.2/2.4/2	117.8/115.8/117.4/116 3.5/5/1.2/1.2
32	Chlorfenapyr	20.54	137 > 102 (12) 249 > 112 (24)	0.9989	17.8/15.8/11/23	10 50000	94.3/99.4/110.1/105.8 14.2/1.3/3.4/6.4	112.8/109.7/104.5/107.3 4/5.6/4.1/2.2	105/109.4/107.4/106.1 2.9/1.8/3/1.2
33	Chlorfenson	20	175 > 111 (8) 177 > 113 (8)	0.9977	14.9/15.8/7.1/13.5	5 100	107.4/116.8/103.3/108.1 3.9/1.2/3.3/4.6	109.9/113.4/105.2/104.4 1.2/1.6/1.9/1.8	113.8/117.1/107.3/108.2 2.9/2.1/1.7/1.6
34	Chlorfenvinphos (*)	18.87 19.5	267 > 159 (15) 323 > 267 (10)	0.9927	28.2/19.8/12.3/50	5 50	85.1/83.3/75/96 9.2/5.8/2.7/6.6	96.7/86.4/83.1/100.1 2.8/2.3/2/3.9	97.5/89.5/85.9/101.3 1.3/1.6/1.6/3.2
35	Chlorobenzilate	20.97	139 > 111 (12) 251 > 139 (14)	0.9972	11.3/10.5/3.7/22.3	5 100	103.1/110.7/99.2/109.9 5.1/1.7/1.6/2.5	102.5/109/101.1/103.4 1.7/2.3/3.1/1.1	107.5/109.9/102.3/105.2 2.1/2/1.4/1.9
36	Chloroneb	11.68	191 > 113 (15) 193 > 115 (15)	0.9993	2.1/4.5/–1.3/5.6	1 10	110.4/118.7/118.6/101.4 6.1/1.2/1.6/8.3	108.9/112.4/119.5/96.7 1.6/2.4/1.4/2	106.2/118.3/119.3/95.8 1.6/1.6/1.7/1.3
37	Chlorpropham	13.81	171 > 127 (8) 213 > 171 (8)	0.9974	9.2/2.3/–0.2/18.2	5 50	112.5/117.7/109.1/113 4.3/2.9/8.6/1.3	112.4/111.2/111.3/111.9 1.4/2.1/4.3/1.2	113.2/107.3/110.6/110.4 1.4/1.5/1.2/2
38	Chlorpyrifos	17.85	197 > 169 (14) 314 > 258 (12)	0.9983	14.9/13.6/7.6/22.5	2 2000	104.4/116.3/114.4/115.9 5.9/4.4/3.7/1.8	107.4/113/107.2/105.8 2/1.2/1.1/1.2	112.9/111.3/106.4/105.7 1.3/1.4/1.1/2.6
39	Chlorpyrifos-methyl	16.73	286 > 93 (24) 286 > 271 (12)	0.9989	1.7/26.9/15.7/37.2	1 50	118.1/107.3/94.6/116.9 1.6/4.3/2.1/2.1	112.6/99.5/92.9/104.6 1.1/1.3/1.8/1.2	112.5/98/92.3/105.7 1.7/1.8/1.2/1.9
40	Chlorthal-dimethyl	17.97	301 > 223 (24) 332 > 301 (8)	0.9992	5.2/10/2.4/7.5	1 50	115.7/103.8/119.3/119 1.7/3/1.4/1.5	118.9/114.1/117.4/113 1.1/1.2/2.3/1.2	118.7/118.8/115.7/116.2 1.2/1.5/3.8/1.1
41	Chlorthiophos (*)	20.7	257 > 193 (16) 257 > 239 (12)	0.998	34.6/34.5/24.1/47	1 10	106.9/113.9/107.9/112.4 3.8/4.6/3.2/3.3	103.8/106.7/101.4/102.6 1.2/1.4/2.1/1.2	107.3/105.9/103/103 2.7/2.3/1.7/2.2

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
		20.93	297 > 269 (8) 325 > 269 (14)						
		21.2	297 > 269 (8) 325 > 269 (14)						
42	Chlozolinate	18.79	186 > 145 (16) 331 > 259 (8)	0.9965	0.1/5/–1/10.6	10 50	66.7/92.4/95.3/62.8 16.4/14.9/16.5/6.2	74.2/92/92.6/67.5 3.7/2.7/5.8/1.2	72.1/95.6/98/74.1 3.2/1.2/2.6/3.3
43	Clomazone	15.17	125 > 89 (13) 125 > 99 (17)	0.9983	14.7/10.5/6.5/23	1 50	116.6/119.7/115.1/114 3.7/1.2/1.5/3	110.1/114.5/114/107.4 1.5/1.8/1.4/1.2	112/113.9/113.4/107.4 1.6/2.1/1.3/1.6
44	Coumaphos	25.36	210 > 182 (10) 362 > 109 (17)	0.9974	53.4/49.9/22.1/79.3	10 10	71.2/67.5/56.2/94.8 2.3/3.4/9.9/1.2	75.1/62.6/55.7/87.4 3.4/2.4/5/1.2	74.4/71.9/57/85.9 8.2/7.1/10.4/5.3
45	Cycloate	13.59	154 > 83 (8) 215 > 154 (6)	0.9986	5.8/7.8/3.3/11.1	2 10	101.2/97.3/103.6/104.5 14.7/1.7/7.1/6.3	101.4/116.3/119.3/98.2 1.1/3.8/1.2/1.2	96.7/113.6/116.5/94.3 5.9/1.6/1.6/2.7
46	Cyfluthrin (*)	25.8 25.92 26.0 26.05	163 > 91 (14) 163 > 127 (6)	0.9967	5.5/10.3/–3.1/16.8	5 100	91.8/91.4/78.6/116.2 4.5/4/4.7/3.9	87.5/87.6/70.8/101.6 2.2/1.5/1.6/4.2	87/90.8/74.2/100.3 2.1/2.1/4.1/2.8
47	Cyhalothrin, lambda-	24.18	197 > 141 (10) 208 > 181 (8)	0.9955	–21.6/–11.7/–19.7/–12.2	2 10	103.9/99.5/90.4/109.3 1.4/2.1/2/6.3	96.8/94.2/81.6/103.6 2.5/2.5/3.1/7.2	100.5/97.1/89.4/111.1 3.8/1.3/5/2.9
48	Cypermethrin (*)	26.22 26.32,2 26.4 26.45	181 > 127 (30) 181 > 152 (25)	0.9978	3.5/11.5/–2.4/19.6	10 500	105.6/88/72.7/98 13.4/7.6/4.9/4.6	81.3/79.7/77.2/104.9 5.6/4.5/4.6/3.5	81.5/85.6/77.3/99.6 5.3/2.8/6.7/2
49	Cyprodinil	18.67	224 > 208 (20) 225 > 210 (12)	0.9969	14.9/14/7.8/20.7	2 100	110.7/109.7/112.5/105.4 3.3/6/8.2/3.4	108.1/105.3/106.9/102.3 2.4/1.7/4.1/1.8	114/108.1/109.3/105.2 1.1/2.3/3.7/3.3
50	DDD, o,p‘-	20.4	235 > 165 (22) 235 > 199 (14)	0.9987	6.8/7.7/1.5/4	2 200	114.1/117.8/112.4/116.4 2/2.5/3.1/1.8	115/112.7/112.2/108.7 1.6/1.3/1.7/1.2	115.7/116.1/113.8/113.3 4.1/1.5/1.2/1.3
51	DDD, p,p‘-	21.19	235 > 165 (24) 237 > 165 (22)	0.9963	13.5/12.7/5.6/15.7	5 200	111.7/112/96/114.7 3/2.4/1.9/2.8	99.6/100.2/92.3/96.3 1.5/1.4/1.8/1.7	103.6/103.5/95.1/100.8 2.8/2.1/2/2.2
52	DDE, o,p‘-	19.5	246 > 176 (32) 316 > 246 (15)	0.9992	8.2/10.8/4.4/8.5	1 200	110.5/116.3/105.1/111.6 9/3.1/1.2/9.4	118.3/110/108.5/112.6 1.9/1.6/1.5/1.2	103/115.9/103.4/114.3 1.7/3.9/1.4/1.3
53	DDE, p,p‘-	20.23	246 > 176 (28) 316 > 246 (20)	0.9992	5.4/9.7/0.2/7.4	1 200	100.4/110.4/104.3/107.4 1.4/7.5/3/12.2	119.4/119.6/111.6/112.6 1.2/1.9/8.7/1.2	104.2/116.9/113.2/115.6 2.3/1.3/6.6/1.5
54	DDT, o,p‘-	21.26	235 > 165 (21) 237 > 165 (22)	0.9937	27.5/32.5/10.7/67.5	5 200	85/103.8/83.7/96.5 7.8/2.6/17.7/9.5	95.6/105.1/105.8/90.2 4.7/2.2/1.3/9.3	91.8/113.6/107.1/96.8 1.5/2.8/6/13.7
55	DDT, p,p‘-	22.05	235 > 165 (21) 237 > 165 (22)	0.9904	41.2/54.3/20.4/105.5	10 200	102.2/103.9/110.5/105.3 1.4/1.9/6.8/2.4	96.9/102.8/102/90.7 2.9/1.2/1.9/18	87.3/111.2/103/88.3 2.9/1.8/2.6/19.3
56	Deltamethrin (*)	27.94 28.17	181 > 152 (20) 253 > 174 (8)	0.9948	–26.3/–23.3/–34.3/–1.1	50 5000	< LOQ	59.9/36.4/34.4/105.2 3.5/6.2/1.1/13.1	62.1/39.2/39.7/110 9.4/1.2/6/1.9
57	Diallate (*)	14.32, 14.57	234 > 150 (18) 234 > 192 (12)	0.9992	5.2/6.3/1.9/11.6	2 50	115.2/109.4/106.8/111.2 6/1.4/2.4/6	111.2/117.2/118.2/105.1 1.2/2.2/1.1/1.4	108.5/115.7/117.7/103.2 3.6/1.2/1.2/1.9
58	Diazinon	15.52	137 > 84 (12) 304 > 179 (10)	0.9988	1.9/8.5/–0.2/6.6	1 50	116.9/115.4/111.2/115 3.4/1.3/3.4/2.8	111.3/119.4/118.9/104.5 1.5/1.3/1.3/2.2	114.6/117.4/118.3/105.8 1.6/1.2/1.2/1.6

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
59	Dichlofluanid	17.67	123 > 77 (16) 224 > 123 (12)	0.9929	–15.2/3/–19.9/–23.3	2 10	105/110.1/115.4/111.6 2.4/2/2.9/6.3	85.5/88.2/71.5/91.9 4.3/3/2.5/10.6	85.3/86.9/74.2/96.9 1.3/2/3.2/1.9
60	Dichloroaniline, 3,4‘-	10.62	161 > 99 (21) 161 > 126 (8)	0.9975	5.5/1.8/–1.5/10.6	5 10	95.4/103.1/96.1/87.6 3.7/1.6/2.5/4.6	93.1/96.5/93.6/87.2 1.9/1.4/1.2/2.3	97.6/94.5/95.9/87.9 1.2/2.4/1.3/1.1
61	Dichlorobenzophenone, 4,4‘-	18.26	139 > 75 (27) 139 > 111 (13)	0.9958	14.2/2.9/0.4/22.9	2 10	105/97.7/89.2/111.1 4.2/1.3/3.1/4.3	106.3/97.6/91.1/100.9 1.2/1.3/2.3/1.7	109.8/99.8/92.9/102.8 1.3/1.9/1.2/1.1
62	Diclobenil	9.23	171 > 100 (25) 171 > 136 (13)	0.9992	3.1/3.5/–0.5/7.4	10 10	62.9/96.8/104.7/53.4 13.3/5.2/1.2/10.2	63.5/91.7/93.4/54.3 1.4/18.4/1.2/5.5	52.6/85.1/87.2/50.7 4.4/11.1/5.6/3.7
63	Dicloran	14.79	176 > 148 (10) 206 > 176 (10)	0.9973	14.1/5.1/4.8/37.5	2 50	106.6/107.5/114.8/110.7 5.2/6.2/3.8/2.2	106.1/101.4/101.2/109.4 2.2/1.9/3.9/2.1	105.5/99.9/99.3/108 2.2/1.2/3/1.3
64	Dieldrin	20.43	263 > 193 (34) 277 > 241 (8)	0.9972	9.2/13.7/8.2/14.2	5 20	116.6/119.4/116/117.9 2.4/1.5/3.7/2.1	116/119.2/118.3/115.3 1.2/1.6/1.8/1.8	119.3/109.2/118.6/118.5 1.2/1.2/1.7/2.3
65	Dimethachlor	16.65	134 > 105 (13) 197 > 148 (8)	0.9988	–74.6/25.2/15/21.2	1 50	117.4/102.9/110.2/110 1.2/1.3/2.3/9.3	118.3/115.4/107.9/113 2.2/1.8/1.3/1.3	115/117.1/109.5/115.1 1.2/1.5/1.2/1.2
66	Diphenamid	18.4	239 > 72 (10) 239 > 167 (8)	0.9972	9.8/10.6/9.5/17.5	2 10	113.4/116.5/114.7/114.5 3.2/4.6/2.7/1.6	112.8/119.9/116.5/108.4 3.8/1.8/1.3/2	117.7/116.7/118.2/110.2 2.4/1.3/1.2/2.3
67	Diphenylamine	13.45	168 > 167 (14) 168 > 139 (38)	0.9979	6.4/5.2/0.8/11.1	10 50	114.3/110.2/107.3/98.3 2.1/9.5/2.8/6.4	114.9/117.6/114/106.6 1.4/7.6/1.2/1.8	115.2/116/118.1/105.7 3.5/1.1/1.8/2.7
68	Disulfoton	15.85	88 > 60 (6) 142 > 109 (6)	0.998	11994.7/11515.3/11081.7/13188.5	50 50	< LOQ	46.1/36.6/56.4/48.8 5.5/9.1/4.7/1.2	49.7/45/55.6/40.6 5.9/12.2/3.1/1.7
69	Edifenphos	21.88	109 > 65 (13) 173 > 109 (8)	0.9972	56.1/43.5/20.9/106.7	10 10	71.6/55.9/49.2/98.4 19.3/2.6/1.5/19.8	75.9/55.9/45.1/90.8 5.7/7.6/1.4/14.5	62.4/59.8/49.5/88.9 1.5/4.7/1.7/17.5
70	Endosulfan ether	16.51	239 > 204 (13) 241 > 206 (13)	0.9951	–82.2/–58.3/–22.2/–81.7	50 30000	< LOQ	31/50.7/50.1/77.7 7/1.6/1.5/3.4	31.3/50.8/50.3/59.6 1.4/1.4/1.4/19.2
71	Endosulfan I	19.81	195 > 159 (6) 241 > 206 (10)	0.9991	5.2/13/3.1/10.2	5 30000	105.3/102.1/111/107 1.5/1.4/10.6/5	118/113.7/119.9/112.8 2.3/1.2/1.2/1.3	117.5/117.6/111.9/114.5 3.6/2.8/1.6/1.8
72	Endosulfan II	21.15	195 > 125 (23) 195 > 159 (8)	0.9983	17.9/15.5/5.7/16.2	5 30000	107.7/111.8/109.6/115.5 2.1/1.6/11.3/1.4	110.6/117.8/107.1/111.9 1.3/4.6/2/1.7	110.1/111.6/110.2/110.9 2.6/1.1/1.8/3.8
73	Endosulfan sulfate	22	241 > 206 (8) 272 > 237 (10)	0.9967	–5.5/25.1/7.4/14.3	10 30000	96.2/100.7/92.8/102.8 19/9.8/4.9/12.3	89.9/88/90.6/106.3 2.6/1.2/1.3/10.8	91.1/94.9/88.1/104.7 5.1/4.5/4.7/5
74	Endrin	20.92	263 > 193 (30) 279 > 243 (8)	0.9985	21.2/19.6/11/34.1	5 10	94.6/103.3/109.6/109.6 2.6/1.2/2.6/8.6	108.9/112.3/107.1/108.6 2.4/1.1/1.4/3.5	109/113.2/107.2/105.8 1.6/1.1/3.3/3.9
75	Endrin ketone	23.09	315 > 279 (8) 317 > 281 (8)	0.9965	4.8/12.2/–3.5/15.1	5 10	107.1/104/102.6/110.5 1.1/16.1/7.3/7.7	98.8/106.1/93.8/105.1 2.8/1.6/1.4/1.2	103.5/109.7/101.2/106.4 4.8/5.2/3/1.8
76	EPN	23.11	169 > 77 (22) 169 > 141 (8)	0.9971	21.6/20.3/5.1/61.9	5 10	104/88.1/74.1/111.4 14.7/13.2/13/2.9	78.3/75.6/66.4/89.6 1.7/2.2/2.5/5	78.2/78.9/69.9/90.2 4.8/3.6/2.1/3.8
77	Ethalfluralin	13.64	276 > 202 (15) 316 > 276 (10)	0.9975	–4.1/–5.4/–6.7/18.3	1 10	105.2/113.4/111.5/100.1 7.3/2/2.9/6.8	98.5/106.6/102.7/99.9 2.9/1.5/1.1/1.1	97.9/103.6/103.8/100 1.1/1.2/1.4/1.6
78	Ethion	21.15	153 > 97 (10) 231 > 129 (24)	0.9973	21.9/13.3/7.3/40.4	1 3000	101/104/92.4/111.7 5.3/3.9/2/2.9	96.7/97.3/88.2/102 1.9/1.1/2.4/1.5	99.8/98.3/89.3/101.9 3.4/2.6/2.2/2.9
79	Ethylan	20.8	223 > 167 (12) 223 > 179 (22)	0.9984	17.9/20.2/12.6/24.5	1 10	112.7/118.8/112.8/113 3.7/2/1.3/3.2	108.8/116.9/112.9/104.9 1.2/1.8/2.1/1.2	112.9/115.5/113.5/107.2 2.6/1.4/1.2/1.6

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
80	Etofenprox	26.62	163 > 107 (18) 163 > 135 (10)	0.9967	12.7/19.8/5/31	10 50	72.5/98.9/70.6/92.8 4.3/2.6/3.3/3.8	86.3/92.4/78.7/96 2.6/3.4/3.6/1.3	90.7/94.8/84.4/97.9 5/4.4/3.1/2.6
81	Etridazole	10.88	183 > 140 (16) 211 > 183 (10)	0.996	14/6.5/–1.8/45.2	10 50	55.1/85.5/87.6/51.1 12.5/2.7/8.4/10.5	51.7/77.7/71.9/54.3 1.1/14.2/2.1/8.6	42.4/75.9/68.2/46.3 10.4/7.4/6.1/7.8
82	Fenamiphos	19.81	303 > 195 (9) 303 > 154 (8)	0.9953	245/243.5/188.3/324.9	10 50	62.3/75/60.9/75.2 1.9/10.5/14.7/8.6	60.3/69.8/61.7/71.5 10/7.9/3.6/2.3	68.2/74.1/63.7/70.7 2.5/4.2/1.9/2.1
83	Fenarimol	24.53	139 > 111 (16) 219 > 107 (12)	0.9965	9.1/7.4/–2.5/24.1	5 50	79/81.7/68.5/104.5 3.4/4.6/3.1/6	86.4/85.4/73.9/100.9 1.7/1.2/4.2/2.7	89.2/88.3/76.4/100.1 4.9/2.7/3/2.3
84	Fenchlorphos	17.16	285 > 270 (11) 287 > 272 (11)	0.9985	22.2/19.5/10.3/28.6	1 100	110.7/109.4/98.5/114 3.2/1.1/2.8/1.2	106.3/101.3/96.3/105.5 2.6/1.9/3.4/2.4	109/100.5/96.2/104.2 1.7/2.7/1.2/1.4
85	Fenitrothion	17.48	277 > 109 (18) 277 > 260 (6)	0.9968	37.1/20.2/10.7/62.9	1 50	108.4/94/74.2/108.3 5.7/7.6/3.7/9.8	94.6/82/71.7/94.4 2.4/1.4/1.3/4	98.3/82.5/73.4/93.9 1.8/1.1/3.1/1.4
86	Fenpropathrin	23.26	181 > 152 (24) 265 > 210 (8)	0.998	15.8/16.5/5.9/24.7	2 2000	101.4/107.1/98.4/110.7 4.2/5.5/4.1/5	100.6/99.2/91.4/101.9 1.6/1.3/2.1/2.1	102.2/107.3/97.4/101.9 3.5/3.2/4.6/2
87	Fenson	18.39	141 > 77 (8) 268 > 141 (8)	0.9982	13.1/13.4/9/16.9	2 10	106.5/117.9/116.8/111.4 2.8/3.3/3.8/2.3	116.6/118.2/118.6/107 2.6/2/1.6/1.9	115.6/118.6/119.2/110.2 4.1/1.2/2.1/1.8
88	Fenthion	17.97	278 > 109 (18) 278 > 169 (17)	0.9984	129.7/128.1/111.4/138.6	5 50	91.3/96.5/96.8/91.3 1.5/6.7/1.9/6.7	86.8/84/89.1/88.4 3.4/4.7/1.8/1.1	93.5/89.6/91.6/84.6 1.2/3.8/1.2/1.3
89	Fenvalerate (*)	27.3 27.54	167 > 125 (8) 169 > 127 (10)	0.9964	–1.1/5.5/–7/12.9	10 100	79/73.6/54.4/103.6 1.4/8.6/8.8/10.1	81.8/73.6/59/103.1 3.9/1.5/1.6/3.6	81.8/74.7/61.9/99.8 5.4/4.5/2.5/2.6
90	Fipronil	18.67	367 > 213 (30) 369 > 215 (30)	0.9948	1/–1.8/–10.8/12	2 5	93.4/98.3/92.3/104.1 3.4/2.7/2.5/7.8	92.1/89.9/88.3/95 1.5/1.2/5.7/4.4	93/93.2/92.2/96.3 1.1/1.9/1.7/1.7
91	Fluazifop-P-butyl	20.71	383 > 268 (8) 383 > 282 (12)	0.9974	22.1/26.9/14.1/37.7	5 50	102.4/110.1/102.9/103.1 4.5/1.6/1.9/7.3	103.2/109.4/104.1/103.2 1.2/1.2/1.4/1.7	108.6/104/105.9/104.6 3.9/1.1/2.2/2.2
92	Fluchloralin	15.55	264 > 160 (15) 306 > 264 (8)	0.9963	–1.4/9.3/–0.3/29.2	1 10	105.1/106.2/111.5/101.8 4.2/4.8/2.7/4.1	96.6/103.8/101.9/94.7 2.9/2.7/2.5/1.9	101.2/105.7/104/96.5 1.3/1.2/1.6/1.2
93	Flucythrinate (*)	26.4 26.63	157 > 107 (13) 199 > 157 (8)	0.998	2.5/12.6/–1.1/16.1	10 50	75/76.4/60.7/103.5 4.6/3.1/19.2/2.6	81.3/85.8/68.1/101.2 2.7/3.2/2.4/1.4	86.5/86.2/71.7/101 6.8/4.1/2.2/3
94	Fludioxonil	19.96	154 > 127 (8) 248 > 127 (30)	0.9955	28.6/23.3/12.2/44.2	10 50	83.5/82.3/69.6/94.5 3.5/5/1.3/1.3	93.7/93.5/82.7/95.9 2.9/3.1/1.4/1.2	95.7/96/85.3/101.7 2.8/1.4/3/3.5
95	Fluquinconazole	25.38	340 > 108 (42) 340 > 298 (14)	0.9967	11.6/18/0/29.7	2 50	86.9/86.4/65.3/105.5 2.3/2.3/1.3/4.6	89.2/81.6/69.4/99.2 2.5/4.4/3.3/1.2	90.5/86.8/75.7/100.3 5.1/3.5/3.8/3.4
96	Fluridone	26.87	328 > 189 (38) 328 > 259 (24)	0.9953	30.1/23.6/3.2/52	50 10	< LOQ	73.9/63.1/47.5/88.8 4.4/1.2/18.8/1.2	73.2/64.2/52.7/86.3 1.5/1.7/2.6/9.8
97	Flusilazole	20.33	233 > 152 (14) 233 > 165 (18)	0.9948	13.1/13.2/5/22.9	2 50	97.8/109.6/92.4/102.8 4.3/1.4/1.2/3.1	102.7/108.1/96.3/101.8 1.2/1.8/1.3/1.2	109.1/108.8/99.6/106.7 3.5/1.4/2/1.9
98	Flutolanil	19.89	173 > 145 (14) 281 > 173 (10)	0.9957	17.9/17/6.8/34	2 50	94.2/110.8/88.7/104 4.2/2.9/1.4/1.2	97.6/109.2/91.7/100.1 1.4/1.1/2/1.2	102.8/110.6/93.4/104.1 1.6/1.8/1.6/3
99	Flutriafol	19.84	123 > 95 (12) 219 > 123 (14)	0.9971	17.7/19.3/7.7/27.3	2 50	75.5/106/69.5/79.8 7.1/1.2/6.5/11.2	92.6/103.8/90.1/93.7 2/1.9/4.8/2.1	101.5/111.3/98.2/102.1 2.2/1.9/1.5/2.5
100	Fonofos	15.53	137 > 109 (6) 246 > 137 (8)	0.999	8.4/11.1/5.3/11.6	2 10	112.5/100.7/96.1/107.3 3.8/4/1.4/2	110.8/114.2/111.5/104.5 1.4/2/1.8/1.5	113.9/119.2/117.5/105.3 1.7/1.5/3.4/1.1

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							10 µg/kg	50 µg/kg	75 µg/kg
101	Heptachlor	17.16	100 > 65 (12) 272 > 237 (13)	0.998	16/16.7/8.4/26.8	1 20	107.1/117.8/117.8/108 4.9/1.2/1.2/3.3	106.9/118.8/113.5/106.3 1.7/3.2/1.9/1.7	111.1/119.6/116.4/105.1 2/3.6/2.5/2.3
102	Heptachlor epoxide	18.94	351 > 261 (11) 353 > 263 (13)	0.9974	2.6/4.3/0.1/5.4	2 20	105.5/109.7/102.1/107.5 1.3/6.9/3.5/8.2	118.1/111.1/116.4/113.7 1.3/1.4/1.4/1.9	119.4/119.3/118.6/114.1 1.1/2/1.2/1.6
103	Hexachlorobenzene	14.59	249 > 214 (14) 284 > 249 (18)	0.9993	1.6/3.5/0.9/3.1	1 20	115.9/118.5/112.7/107 5.2/1.2/6.3/4.2	111.2/116.1/108.4/97.3 2.1/2/1.2/1.2	113.7/113/109/94.5 1.3/2.1/2.9/2.8
104	Hexazinone	22.12	171 > 71 (16) 171 > 85 (16)	0.9939	41/31.7/20.7/55.1	2 10	82.9/87.4/70/95.6 5.6/1.3/1.4/1.7	98.7/96.2/86.6/106.2 1.2/1.6/3.4/1.2	103.7/98.4/90.8/109.6 4.5/2.8/2.4/3.8
105	Iodofenfos	19.98	377 > 93 (34) 377 > 362 (15)	0.994	36.8/30/14.7/62	1 10	100.5/96.9/83.8/114.8 11.9/3.4/3/1.5	90.1/90.2/67.4/93.5 4.4/3.3/9.3/2.7	88.6/85.8/72.7/96.2 9.8/7/15.9/5.8
106	Iprodione	22.85	314 > 245 (14) 314 > 271 (12)	0.9937	5.4/32.5/9.1/44.6	10 50	104.6/81.7/97.8/110.5 10.7/4.6/9.8/5.4	110.1/82.7/74/104.7 1.7/6.2/12.6/13.5	85.9/83.9/78.5/100.4 13.9/2.4/9.2/1.1
107	Isazophos	15.84	161 > 119 (8) 172 > 130 (8)	0.9987	10.5/10.4/4.6/16.2	10 10	115.3/114.2/113.1/108 1.7/6.1/4.2/3.1	112.6/118.9/115.4/113.7 1.8/1.1/4.5/2	116.1/115.5/118.3/110.5 2.6/1.1/1.3/2.5
108	Isodrin	18.74	193 > 123 (30) 193 > 157 (19)	0.9982	3/4.2/–1/8.5	2 10	117.3/117.3/118.6/111.5 1.2/2.2/1.3/2.4	116/111/118.1/107.8 2.7/1.9/1.4/1.6	119.2/116.9/119.2/110.2 2/1.2/1.4/1.2
109	Isopropalin	18.46	280 > 180 (10) 280 > 238 (8)	0.9958	6.2/2.5/–1.6/25.4	1 10	104.6/104.8/101.5/104.3 4.6/1.2/1.3/6.5	96.6/97.9/97.8/97.3 1.2/1.6/1.7/2.1	99.5/97.1/97.4/99.2 1.1/1.2/1.2/1.2
110	Lenacil	21.94	136 > 53 (18) 153 > 136 (14)	0.9906	45.3/34.1/18/69.9	5 100	62.7/79.8/55.6/78.9 4.5/4.5/2/2	87.1/90.9/80.5/95.5 2.4/3.8/2.3/1.2	90.1/95/84.6/100.7 4.6/3.6/1.2/4
111	Leptophos	23.91	171 > 77 (18) 171 > 124 (8)	0.9972	24.4/22.4/8.1/33.6	5 10	91.2/89.3/73.5/101.9 3.8/1.8/1.3/10.4	88.7/85.6/75.9/97 3.2/3/1.8/1.5	90.2/91/78.4/98.3 5.7/1.9/3.8/2.8
	Lindan-d6 (surrogate) (**)	14.39	224 > 150 (20) 224 > 187 (10)	0.9942	8.4/8.4/6/17	– 0	114.3/112.2/114.1/112 3.9/11.3/14/16.7	–	–
112	Linuron	17.62	187 > 124 (21) 248 > 61 (8)	0.9988	48/65.9/40.8/70.6	10 50	102.2/86/106.1/94.7 9.8/11.1/13.4/2.1	103/94/74.5/104.2 2.4/5/6.3/12.1	98/78.2/80.9/97.3 7.7/2.8/9.8/18.9
113	Malathion	17.67	127 > 99 (6) 173 > 127 (6)	0.9982	24.8/20.3/10/35.7	10 500	101.2/97.1/92.5/114.9 2/1.1/6.1/1.5	100.7/95.1/86.7/103.3 1.2/1.4/1.3/1.1	103.2/96.4/89.1/104 1.2/1.8/1.5/1.4
114	Metalaxyl	17.11	160 > 130 (10) 220 > 160 (16)	0.9933	7.7/10.6/4/12.4	2 50	89.9/100.2/86.6/100.9 11/12.7/2.7/20	109.4/113.9/106.4/113.2 12.4/2.1/5.1/1.3	106.3/103/97/115.7 1.9/1.5/1.1/1.1
115	Metazachlor	18.71	133 > 117 (25) 209 > 132 (15)	0.9958	21.4/19.6/10/25.7	2 100	102.3/101.6/96.4/105.8 6.1/2.1/4.3/4.2	100.7/99.6/94/100.1 1.2/1.7/2.1/2.3	104.9/101.2/97.4/102.6 1.1/1.2/1.2/2.1
116	Methacrifos	11.53	125 > 79 (6) 180 > 93 (8)	0.9982	0.3/–4.6/–1.5/7.7	2 50	78/84.2/118.2/78 11.7/3.4/1.2/8.5	88.5/94.9/118.1/87.2 1.2/6.6/1.9/2.6	82.7/94.7/117.5/85.5 1.5/3.4/1.5/3.7
117	Methoxychlor	23.25	227 > 141 (33) 227 > 169 (25)	0.9919	38/45.5/20.2/81.9	5 100	98.4/99.7/89.2/98.1 16.3/2.3/3.8/5.6	96/95.5/95.9/86.3 4.1/6.4/4/12.5	85/110/105.2/89.1 3.8/2.3/8.6/19.2
118	Methyl parathion	16.89	263 > 109 (10) 263 > 136 (8)	0.9967	55.9/29.8/17.5/81.4	10 50	111.4/89.3/81.7/110.8 2.1/7.9/1.9/4.3	102.8/78.2/73.3/100.6 1.4/2.1/2.5/1.8	98.7/80.5/74.6/101.5 1.4/3.5/1.2/5
119	Metolachlor	17.82	238 > 133 (27) 238 > 162 (10)	0.9984	14.3/12.4/4.8/16.9	1 50	118.2/116.8/114.8/116.3 2/1.5/1.5/1.1	115.6/116.3/110.2/111.9 1.8/1.2/1.4/1.2	118.8/114/111.4/113 1.5/1.3/1.2/1.4
120	Mevinphos	10.43	127 > 109 (8) 192 > 127 (10)	0.9985	17.5/–1.8/–5.8/27.6	2 20	112.3/103.1/95/113 5.2/4.3/3.4/6.8	103.3/95/87.7/100.7 1.5/2.9/2/1.5	99.1/91.4/87.1/99 2.7/2.6/1.7/1.5

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
121	MGK 264 (*)	18.44 18.74	164 > 67 (10) 164 > 98 (14)	0.9979	11.5/10.3/8/20.4	5 10	113.4/114.7/114.1/116.4 5.1/1.2/2.1/2.9	110.3/115.4/119.9/106.7 2.2/1.2/1.2/1.9	114.7/116.8/114.7/107 2/1.5/1.6/1.4
122	Mirex	24.51	272 > 237 (15) 274 > 239 (15)	0.9984	–0.1/–0.3/–3/6	1 10	110.5/118.9/108.7/117 4.5/1.1/2.6/3.2	106.2/111.3/101.9/107.9 1.8/2.2/2.7/1.4	109/111.7/104.2/108 3.1/2/2.6/1.3
123	Myclobutanil	20.29	179 > 125 (14) 179 > 152 (8)	0.9954	13.9/14.2/8/22.4	1 50	100.2/109.6/95/104.3 6.6/5.1/1.3/4	103.9/109.6/97.7/102.6 1.7/1.1/1.7/1.5	107.9/109.3/100.2/108.5 1.3/2.2/2.1/1.8
124	N-(2,4-Dimethylphenyl)formamide	11.32	120 > 77 (15) 121 > 106 (8)	0.9974	7.5/–0.8/–0.1/20.8	10 10	80.3/111.5/86.2/73.3 11.2/3.1/3.4/2.9	101.2/111.5/119.5/98.8 1.8/6.6/1.6/1.5	105.5/112.4/113.3/104.8 1.7/7.4/4.2/2.3
125	Nitralin	22.44	274 > 216 (6) 316 > 274 (8)	0.992	–10.9/20.1/–0.4/48.7	10 10	81.2/91.7/84.6/91.5 7.5/1.3/4.7/1.8	79.2/83.4/82.3/72.9 1.7/3.3/1.9/12.1	80.8/90.4/85.6/82.6 5.6/1.6/1.8/8
126	Nitrofen	20.8	202 > 139 (20) 283 > 202 (10)	0.9974	22.3/20.5/8.4/57.5	1 20	94.6/98.1/82.1/105.9 2.4/6.3/3.1/3.7	93.7/89.9/82.8/94.1 1.2/1.8/1.3/3	95.5/92.8/85.5/98.2 6.8/1.2/1.5/1.5
127	Nonachlor, cis-	21.24	409 > 300 (23) 409 > 302 (20)	0.9985	5.3/4.7/–2.8/17.1	2 10	114.5/110.2/111.5/113.2 6.1/8.5/1.2/4.1	107.2/116.3/107.4/107.6 2.4/2.3/2.9/1.4	115/114.7/109.3/110.6 2.2/2.8/2/1.1
128	Nonachlor, trans-	19.85	409 > 300 (20) 409 > 302 (22)	0.9995	9.7/9/3.1/15.4	2 10	117.4/112.7/103.6/113.4 1.7/1.2/2.8/2	113.3/113.2/113.4/111 1.7/2.9/1.5/1.8	108.2/117.2/116.5/112.9 12.5/1.6/1.1/1.1
129	Norflurazon	21.77	145 > 95 (18) 303 > 145 (17)	0.9903	54.6/37.7/24.9/71.9	5 10	78.8/76.2/57.3/83.4 2.4/1.5/5.8/3.8	95.6/84.6/75.3/94 1.3/2.2/5.6/1.9	101.7/87.5/77.2/101.3 2.5/1.7/4.3/4.4
130	Oxadiazon	20.17	175 > 112 (13) 258 > 175 (8)	0.9985	8.2/10.2/3.3/8.9	1 50	116.6/118/116.7/119.1 4.1/1.8/1.9/1.4	114.7/112.3/113.3/111.2 3.3/1.2/1.2/1.3	116.5/116.9/116.3/111.8 1.6/3.3/1.3/1.2
131	Oxyfluorfen	20.28	252 > 146 (33) 300 > 223 (15)	0.996	15.5/13.9/4.9/42.4	2 50	93.6/93.3/80.3/95.2 2.6/8.1/1.2/3.2	94.4/102.7/86.3/98.4 1.7/4/2.4/5.8	98.5/98.4/91.8/102.5 1.3/1.3/1.8/4.2
132	Paclobutrazol	19.57	236 > 125 (12) 236 > 167 (10)	0.9984	22.8/27/10/39.3	5 50	72.9/87.8/63.8/90 1.4/3.3/5.7/3.3	98.1/110.4/91.1/101.1 1.5/3.6/1.4/1.2	103.2/115.1/93.7/109.4 1.7/2.4/1.4/3.6
133	Parathion	18.04	109 > 81 (8) 139 > 109 (8)	0.9935	18.7/7.1/2.9/39.2	5 100	79.1/82.4/84.5/80.5 6.6/5.7/3.7/5.2	98.2/90.9/83.3/95.9 2.9/4.9/3.1/4.5	104.6/93.5/86.6/101.2 1.6/2.2/2.3/4.2
	Parathion-d10 (surrogate) (**)	17.94	115 > 83 (10) 301 > 115 (10)	0.9921	24.1/10.5/6.9/49.9	–	111.4/119.3/110.7/96.8 10.8/17/11.1/15.9	–	–
134	Pebulate	11.02	128 > 57 (8) 161 > 128 (6)	0.9993	–0.1/–3/–7.5/6.7	10 10	69.9/107/108/68.2 13.1/12.8/14/13.2	72.6/96.3/95.5/68.3 1.6/12.5/1.8/4.4	57.7/91.5/89.2/61.1 13.5/6.9/3.6/8.1
135	Penconazole	18.8	248 > 157 (26) 248 > 192 (16)	0.9949	13.4/9/4.2/23.9	2 50	104.2/103.9/96.6/104 3.1/1.6/4.2/2.1	105/101.9/97.7/102.4 1.5/1.3/3.1/2.5	110.1/103.1/102.2/107.1 2/1.6/1.9/2.3
136	Pendimethalin	18.63	252 > 162 (10) 252 > 191 (8)	0.9955	5.2/–0.1/–2.3/28.9	1 50	104/100.1/98.5/101.7 1.6/2.4/1.5/1.2	94.5/93/90.9/95.9 2/1.2/2.8/3.9	98/93/91.1/97.6 2.8/1.2/1.5/1.4
137	Pentachloroaniline	16.45	263 > 192 (20) 265 > 194 (22)	0.999	–73.4/–70.2/–71.8/–73.5	50 10	< LOQ	108.5/121.3/124.1/109 2/1.6/1.1/1.2	115.4/119/109.3/104.8 1.7/8.5/2.3/6.8
138	Pentachloroanisole	14.73	265 > 237 (12) 267 > 239 (10)	0.9993	4.4/5/0.6/8.3	1 10	115.4/118.1/119.7/110 3.4/1.2/1.7/7.3	115.4/112.1/118.2/102.1 1.5/2.2/1.7/1.7	113.4/119.9/118.1/101 3/1.6/1.1/1.5
139	Pentachlorobenzene	11.96	250 > 179 (30) 250 > 215 (20)	0.9993	–2.1/5.2/–1.1/1.9	2 10	84.5/112.8/114.8/80 12.4/1.6/6.6/9.1	86.6/102.7/106.3/73.7 1.4/7.9/1.4/1.4	78.6/101/102.5/70.1 7.2/4/2/2.4
140	Pentachlorobenzonitrile	15.3	273 > 238 (17) 275 > 205 (30)	0.9978	5.6/5.2/0.4/7.2	1 10	114.4/119.4/115/114.1 1.8/1.4/5.5/5.6	111.7/115.2/109.7/105 1.9/2.5/1.2/1.2	116.9/113.9/111.9/106.1 1.1/1.8/1.7/1.2

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
141	Pentachlorothioanisole	17.65	296 > 263 (12) 298 > 265 (8)	0.9994	7.9/9.9/4.2/11.9	1 10	114.2/118.5/101.8/106.8 3.8/1.1/8.4/5.5	114.5/107.6/94/99.7 1.6/1.4/1.3/1.4	116.5/104.1/95.9/96.6 3.2/3.1/4.1/3.2
142	Permethrin, cis-	25.19	163 > 127 (6) 183 > 168 (10)	0.9981	6.2/12.2/0.3/24.1	5 100	80.5/89.8/78/97.3 2.5/5.8/14/2.6	90.7/87.7/76.2/98.9 1.2/1.3/1.2/1.2	91.1/94.3/81/99.1 3.5/3.3/4.2/1.9
143	Permethrin, trans-	25.34	163 > 127 (6) 183 > 153 (14)	0.9973	6.6/16.2/–0.6/25.8	10 100	77.3/71.6/51.8/103 17.6/7.7/2.6/12.4	84.1/77.2/64.9/94.9 1.2/1.5/4.1/1.1	85.7/84.7/72.3/96.2 7.6/2.4/8/3.3
144	Phenothrin (*)	23.58 23.71	183 > 153 (14) 183 > 168 (12)	0.9975	16.1/14.6/2.3/29.1	5 50	88.8/96.9/85.5/99.2 18/5/7/13.5	95.4/95.7/82.7/103.8 1.7/5/7.6/6.8	98.7/98.6/90.7/101.4 2.5/3.5/1.9/1.4
145	Phorate	14.34	121 > 65 (10) 260 > 75 (8)	0.9981	144.8/145.3/144.9/160.7	1 50	92.1/99.7/101.3/92.9 5.4/7.7/6.5/6.3	89.7/87.7/96.7/88.3 3.1/1.3/1.2/1.3	88.3/92.2/98.3/83.3 3.8/2.1/1.3/3.1
146	Phosalone	23.87	182 > 111 (16) 182 > 138 (8)	0.9973	47.4/36.7/16.4/60.9	2 50	80.2/77.8/59.7/108 4/2.9/6.4/5.5	82.2/70/62.2/99.8 2.2/1.4/2.2/2.3	80.2/74.7/66.3/95.2 4.3/2.7/5.4/6.5
147	Phosmet	23.08	160 > 77 (24) 160 > 133 (10)	0.9952	93.2/70.4/38/105	10 100	76.7/71.5/50.7/104.6 6.6/5.4/6.3/15.1	83.4/61.3/54.9/86.6 2.3/3/3.2/2	73.5/72.5/59.9/87 2.5/5.6/11.9/10.6
148	Piperonyl butoxide	22.45	176 > 103 (26) 176 > 131 (14)	0.9969	18/16.1/9.3/33.5	2 10	98.7/103.9/94.1/105.9 5.7/6.2/2.9/2.9	98.9/102.2/94.8/100.2 1.3/1.6/3.6/1.5	103.1/105/97/103.7 3.4/2/2.4/1.8
149	Pirimiphos-ethyl	18.31	318 > 166 (12) 318 > 182 (8)	0.9986	15.3/13.1/11.1/21.3	2 10	110.7/107.5/118.3/115.8 3.5/1.9/2.1/1.7	116.5/110.4/119.2/110 1.3/1.4/1.1/1.7	119/115.4/118.3/111.6 1.2/2/1.2/1.4
150	Pirimiphos-methyl	17.39	290 > 233 (10) 305 > 180 (8)	0.9985	13.7/15.3/7.8/21.1	2 50	119.3/117.2/119.3/116.5 1.3/3.1/1.2/2.1	114/117.5/113.7/108.7 1.8/1.5/1.2/1.3	118.2/114.8/114.1/110.6 1.7/1.2/1.2/1.2
151	Pretilachlor	20.03	162 > 132 (18) 262 > 202 (8)	0.9981	20.8/24/13.3/35.9	1 10	100.1/110.1/98.6/112.1 6/4/5.6/2	100.3/108.1/95.6/103.8 1.6/1.1/2.9/1.7	103.6/107.5/96.1/105.9 1.4/2.1/2.3/2.6
152	Prochloraz	25.43	180 > 138 (12) 308 > 70 (13)	0.996	30.4/25.7/6/54.9	50 100	< LOQ	72/65.4/53.1/82.4 6/1.2/3.8/4.5	74.3/67.4/59.3/87.3 9.7/3.8/3.8/6.8
153	Procymidone	19.11	283 > 67 (28) 283 > 96 (10)	0.998	10.9/13.4/7.8/15.5	2 50	114.8/119.2/117.5/113.8 2/1.2/2.6/2	110.4/111.2/111.8/111.4 1.7/1.5/3.3/1.2	116.4/112.5/116.5/109.4 1.7/1.2/1.2/2.2
154	Prodiamine	17.41	279 > 203 (8) 321 > 279 (6)	0.9976	10.5/4.4/–1.3/31.1	1 10	103.9/108.8/91/104.1 3.9/2.8/2.1/1.3	104.1/103.5/98.5/99.1 5.2/5.3/1.4/8.4	104.8/100.3/91.9/105.2 3/1.4/1.6/2.3
155	Profenofos	20.13	337 > 267 (13) 339 > 269 (13)	0.9986	50/46.5/23.6/87.3	10 50	89.6/90.2/66.3/98.1 7.5/9.7/2.5/5.9	87.6/82.8/69/97.5 2.8/1.5/1.7/4.6	86.5/86.9/69.9/95.6 1.2/3.4/4.7/9.9
156	Profluralin	15.25	318 > 199 (17) 330 > 69 (25)	0.9953	–1/–1.5/–7.1/19.1	2 10	100.4/107.7/106.6/108.4 4.6/3.5/4/4.1	96.9/104.1/99.9/98.2 1.8/1.8/1.3/1.5	100.3/102.4/99.2/98.6 2.9/1.2/1.5/1.9
157	Propachlor	13.15	120 > 77 (19) 176 > 57 (8)	0.998	9.8/4.2/–0.6/19	1 100	111.9/112.7/105/111.4 5/1.3/3.4/6.9	106.9/106.7/100/106.6 1.6/1.4/1.9/1.2	106.5/104/101.2/106.1 1.1/1.6/1.2/1.8
158	Propanil	16.61	217 > 161 (8) 219 > 163 (8)	0.9961	44.5/37.9/33/42.6	5 50	86.2/112.8/81.3/101.4 1.1/2.8/14.6/10.8	108.8/107.6/112.2/110.7 2/5.6/2.2/2.3	113.4/104.7/101.6/115.4 3.2/2.4/2.8/2.2
159	Propargite	22.37	135 > 77 (24) 135 > 107 (14)	0.999	14.3/11.4/5.6/29.5	10 10000	97.2/91.7/103.8/87.2 7.3/1.6/3/16.4	100.6/104.3/96.3/99.5 5.1/2.4/9.1/10.5	104.9/106.2/101.1/103.9 6.4/2.7/8.2/2.5
160	Propisochlor	17.01	162 > 120 (13) 162 > 144 (10)	0.9981	18.3/14.5/6.3/17.9	1 50	107.6/103.4/110.8/104.6 1.8/7.5/1.3/4.6	114.2/113.6/109.4/112.3 1.6/1.5/1.1/2.1	118.3/112/111.4/112.4 1.3/1.2/1.2/1.4
161	Propyzamide	15.49	173 > 109 (27) 173 > 145 (13)	0.9984	12.8/12.4/7.7/21.4	1 50	112.4/118.2/118.9/116.6 1.4/1.3/1.7/3.8	113.8/113.2/119.7/108.8 1.2/1.5/1.1/2.3	117.1/119/118.6/111.5 1.7/1.1/1.5/1.4

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
162	Prothiofos	20.03	267 > 239 (8) 309 > 239 (15)	0.9973	17.4/17.5/9.9/25.5	2 10	112.7/118/113.9/117.8 6.3/3.3/1.2/2	103.1/111.5/100.7/102.3 2.8/1.3/1.2/1.3	107.3/109.7/102.5/103.9 2.5/1.7/4.1/1.7
163	Pyraclofos	24.8	194 > 138 (18) 360 > 194 (10)	0.9968	68.4/50.4/21.8/102.5	10 10	74.8/57.4/44/103.5 13/10.1/15.9/19.1	79/60.7/48.6/97.5 2.2/2.9/2.8/1.4	74.3/65.9/52.6/90.6 3.3/5.3/9.1/13
164	Pyrazophos	24.42	221 > 193 (8) 232 > 204 (8)	0.9973	30.6/22.6/6.8/51.2	10 50	85.3/80.8/60.6/100.9 13.4/1.1/3.3/4	80.3/74.9/61.3/94.8 2.1/4/3.5/1.7	78.9/77.8/65.9/92.7 3.9/1.3/4/4.3
165	Pyridaben	25.42	147 > 117 (20) 147 > 132 (13)	0.9976	10.5/10.3/–3.9/28.3	10 50	88/78.5/61.5/113.3 3.3/3.9/1.5/4	81/72.2/58.5/97.4 3.5/1.5/2.6/1.5	80.4/77.2/64.8/94.8 6.3/4.1/7.1/2.3
166	Pyridaphenthion	22.85	340 > 109 (20) 340 > 199 (8)	0.9974	50.1/31.8/14.3/78.1	10 10	79.7/73.8/56.9/97.5 7/4.8/3.4/3.9	80.5/73.1/63.2/94 3.2/1.8/6.6/2.7	80.2/76.4/65.1/94.3 3.3/1.3/1.9/5.2
167	Pyrimethanil	15.68	198 > 118 (32) 198 > 183 (16)	0.9973	9.5/10.3/5.1/17.5	1 50	109.1/107.3/110.8/99.1 2.1/2.7/2.7/1.1	110.8/113.4/112/114.6 4.5/1.2/6.9/1.5	115.9/118/118.2/113.2 1.4/1.2/1.3/1.2
168	Pyriproxyfen	24.04	136 > 78 (20) 136 > 96 (12)	0.9965	21.2/22.2/11/32	5 15000	88.7/83.9/76.9/99.5 1.3/1.9/1.2/1.1	99.5/95.9/84.5/102.4 1.2/1.5/3.4/1.4	100.5/100.1/88.8/103.5 3.5/2.5/4.1/3.6
169	Quinalphos	19.03	146 > 91 (24) 146 > 118 (10)	0.9964	29.3/19.9/12.7/40.6	2 50	105.8/98.8/89/111.1 6.1/4.1/3.4/3.7	100.4/94/89.7/101.1 3.1/1.2/2.8/1.3	102.3/93.2/91.2/101.2 1.3/1.2/1.6/1.7
170	Quintozene	15.21	235 > 141 (26) 295 > 237 (15)	0.9973	7.5/7.9/3.4/22.5	5 100	111.9/115.5/109.5/109.7 6/1.4/1.2/9.7	104.5/107.2/103.3/96.7 1.8/1.4/2.1/1.8	103.6/107/102.5/96.7 3.2/1.4/1.1/1.8
171	Resmethrin (*)	22.37 22.51	143 > 128 (10) 171 > 143 (6)	0.9995	15.6/10.1/–0.8/30.9	5 50	118.2/119.5/118.5/116 1.3/1.2/1.4/2.1	94.1/104.7/94.8/95.7 1.2/1.2/1.3/2.7	93.8/100.5/94.6/88.6 5.3/3/3.1/2.1
172	Sulfotep	14.02	202 > 146 (10) 322 > 202 (10)	0.9986	6/7.2/4.1/15.7	1 10	114.4/112.2/111.5/113.2 3.7/1.2/2.7/4.4	110.6/111.8/114.3/111.8 1.5/1.2/1.1/2.3	111.9/114.3/115.6/107.3 2/1.2/2.3/1.3
173	Sulprofos	21.53	322 > 156 (13) 322 > 97 (24)	0.9983	151.3/151/138.8/173.1	2 10	78/83.2/81.1/86.1 1.3/9.7/5.2/4.2	73.8/73.9/82.5/79.7 3.7/1.2/1.3/1.1	79.3/81/84/75.3 2.6/4.1/3.5/2.1
174	tau-Fluvalinate (*)	27.41 27.48	250 > 55 (23) 250 > 200 (19)	0.9949	–20.4/–6.8/–18.9/–2.6	10 10	86.8/76.7/61.6/106.5 1.4/3.5/3/3.3	79.9/65.9/53.9/100.2 3.1/3.1/1.8/6.8	76.3/65.8/54.6/99.7 6.2/5.9/3.7/3.9
175	Tebuconazole	22.35	125 > 89 (16) 250 > 125 (22)	0.9925	19.8/17.9/6.9/35.1	2 50	79.1/88.6/71.7/88.9 5.4/2.5/1.2/2.3	93.6/95.9/86.3/98.2 1.1/1.6/2.8/1.3	98.7/99.7/89.9/103.6 3.3/2.8/1.9/3.5
176	Tebufenpyrad	23.39	276 > 171 (10) 333 > 276 (8)	0.9974	17.7/22.9/5.3/32	1 50	94.8/98.3/89.4/104.8 5.7/2.2/2.2/8	97.5/95.2/87.3/100.4 2.5/3/3.3/1.8	100.7/101.3/94/102 4.6/2.4/6.4/1.9
177	Tecnazene	12.96	215 > 179 (8) 261 > 203 (13)	0.9982	1.9/0.2/–6.1/12.2	1 50	101.2/112.8/110.9/95.8 7.2/1.6/3.5/7	96.5/105.2/103.3/90.2 1.4/5/1.6/1.3	91.7/103.8/103/88.4 4.9/2.8/1.3/1.8
178	Tefluthrin	15.86	177 > 127 (15) 177 > 137 (15)	0.9976	7.2/6.5/3.5/14.4	2 50	117.2/117.5/116/115 3.3/1.8/1.5/2.4	113.1/118.9/117/108.8 1.3/1.2/2/1.3	114.2/117.6/116.3/107.4 1.7/1.2/1.2/1.3
179	Terbacil	15.83	160 > 117 (8) 161 > 144 (14)	0.9975	30.4/10.7/8.6/48.8	2 10	110.6/96.5/96/106.8 2.4/1.3/4.3/1.6	100.4/97.8/94.2/102.6 1.3/1.6/3.2/3.9	105.2/98.1/95/104.4 1.4/1.3/2/3.5
180	Terbufos	15.42	231 > 129 (23) 231 > 175 (12)	0.9983	161.9/160.5/148.4/175.3	1 10	102.7/114.7/117.5/100.2 4.4/4.6/2.2/4	100.2/102/110.6/93.7 1.5/2/1.1/1.2	99.9/103.5/110.2/92 2.8/2.4/1.6/2.1
181	Terbutylazine	15.4	229 > 138 (12) 229 > 173 (8)	0.9983	9.9/9.4/3.6/17.1	1 10	110.8/117/115.5/102.1 7.4/3.8/1.7/1.3	104.4/110.4/114/99.3 1.7/1.7/1.7/2	103.1/111.5/114.9/97.7 1.7/1.4/1.2/1.9
182	Tetrachloroaniline, 2,3,5,6-	13.47	231 > 158 (20) 231 > 160 (22)	0.9987	3/3.5/–0.9/5.5	1 10	113.5/114.1/116.9/108.8 6.3/2.3/2.2/6.9	109.4/116.7/113.4/102.1 1.1/3/2.3/1.4	111.5/114.5/114.2/102.8 1.8/1.5/1.2/1.2

#	Compound	RT (min)	Quantitative peak (CE) Confirm peak (CE)	R^2	ME, % (WT/GT/OT/BT)	LOQ MRL (µg/kg)	% Recovery (WT/GT/OT/BT) % RSD (WT/ GT/OT/BT) (n=5)		
							10 µg/kg	50 µg/kg	75 µg/kg
183	Tetrachlorvinphos	19.49	331 > 109 (20) 333 > 109 (17)	0.9969	51.9/65.5/27.4/88.6	10 10	78.2/76.7/48.8/110 19.7/7.8/18.1/11.6	86.6/79/66.1/103.3 5.3/6.9/6.6/5.3	76.7/79.2/63.6/102.3 7.3/3.4/2.4/10.8
184	Tetradifon	23.75	159 > 111 (20) 159 > 131 (10)	0.9972	15.9/11.9/1.6/17	2 50	79.7/83.4/75/110.6 2.5/6.3/2.4/1.3	98.3/94.3/91/117 1.7/1.1/11.4/3.3	107.6/102.4/96/112.9 5.8/2.8/4.6/5.7
185	Tetrahydrophthalimide	11.51	151 > 80 (6) 151 > 122 (10)	0.991	5.7/–0.6/–0.6/9.5	10 10	61.7/71.6/112.7/56.7 15.5/7.5/4.1/1.5	89.4/91.4/108.5/85.5 1.4/2.3/2.2/1.1	87.2/93.9/107.3/87.4 3/1.9/1.2/1.9
186	Tetramethrin (*)	22.93 23.11	164 > 77 (25) 164 > 107 (12)	0.9981	21.7/12.3/2.9/28.9	5 10	97.2/91.5/84.3/105.5 1.7/3.4/4.8/2	90/88.1/77.9/98.8 1.5/2.9/1.1/3.3	92/90.7/80.3/99.7 3.7/3/3.5/3
187	Tolclofos-methyl	16.93	265 > 250 (10) 267 > 252 (10)	0.9988	17/17.7/8/20.4	1 50	117.8/116.5/111.3/111.9 1.4/2.5/7.8/2.1	119.9/118/114.7/111 1.7/1.2/2.3/1.2	116.4/116.5/116.3/112 1.6/1.2/1.3/1.7
188	Tolylfluanid	18.87	137 > 91 (17) 238 > 137 (10)	0.9948	–4.8/5.2/–18/–16.7	2 100	103.8/97.6/83.6/112 3.5/9.3/5.8/8.5	88.5/84.7/72.4/97 5.1/2.3/1.8/9.2	92.9/88.6/76.3/106.9 1.1/1.7/1.3/1.8
189	Transfluthrin	16.94	163 > 91 (12) 163 > 143 (13)	0.9987	12.2/9.6/4.1/15.2	1 10	118.1/118.2/116.5/114.1 2.8/1.5/2.8/1.3	117.5/113.1/119.4/115 1.3/1.5/1.2/1.3	118/119.1/119.7/114 1.7/1.2/1.5/1.1
190	Triadimefon	18.12	208 > 111 (24) 208 > 181 (10)	0.9961	10.4/5.5/1/17.5	2 50	115.7/114.4/103.7/112.5 1.7/4.1/1.3/1.2	110.8/110.9/103.9/105.4 1.4/1.6/3.7/1.1	116.3/112.7/105.8/108.8 1.5/1.2/1.2/2.5
191	Triadimenol	19.11	128 > 65 (22) 168 > 70 (10)	0.9911	14.8/10.4/6.4/26.3	5 50	92.2/88.1/84.4/92.8 5.5/4.7/10.4/6.8	98.5/95.6/97.3/104.2 2.5/1.8/2.6/6	103.5/100.2/101/104.4 2.5/2.1/1.1/2.8
192	Triallate	16.03	268 > 184 (20) 268 > 226 (10)	0.9984	5.1/2.6/–0.6/12.1	1 100	115/119.6/118.8/113.8 2/1.3/1.6/2.3	114/117.8/118.3/108.6 1.1/1.3/1.7/1.5	114.9/116.1/117.9/108 1.5/1.2/1.2/1.2
193	Triazophos	21.48	161 > 134 (8) 257 > 162 (8)	0.9984	59.3/49.2/30.8/69	2 20	100.8/91.1/84.2/108.7 5.4/6.3/5.4/3.7	96/89.3/83/97.3 1.7/2.3/2.5/2.7	96.5/90.8/84.5/101.1 3/2.7/3.2/7.4
194	Tricyclazole	20.19	189 > 135 (18) 189 > 162 (12)	0.9991	109.4/76.8/54.2/112.4	10 50	105.9/96.3/85.9/115.5 2/19.4/1.3/1.1	107.1/92.7/78/99.9 2.9/1.3/5.9/6.7	108.5/91.3/82.6/104.7 7.8/1.6/3.7/12.7
195	Triflumizole	19.11	206 > 179 (14) 206 > 186 (10)	0.9959	17.7/13.6/10.1/24.5	2 100	108.8/103.7/93/105.6 8.5/3.5/7.4/6.3	100.3/105.9/101.2/103.3 3.9/4/1.8/1.4	110.6/105/103.4/107.2 1.2/1.6/1.9/1.3
196	Trifluralin	13.85	306 > 206 (12) 306 > 264 (8)	0.997	–4/–7.6/-10.1/18.4	1 50	107.4/108/104.9/108.8 4.4/1.2/2.9/5.5	98.2/101.5/97.5/100.3 1.5/1.8/1.3/1.2	98.6/100.1/97.8/100.2 2/1.1/1.4/1.8
	Trifluralin-d14 (IS) (**)	13.7	315 > 163 (25) 315 > 267 (10)	–		–	–	–	–
197	Vinclozolin	16.87	212 > 172 (12) 285 > 212 (12)	0.999	16.6/12.1/6.9/19.6	1 50	119.3/117.6/115/115.6 1.2/2.5/3.6/1.2	119.3/116.5/113.3/111.8 1.2/1.2/1.2/3.5	119.7/115.3/113.6/111.2 1.1/2/1.2/2.2

(*) Pesticides with more than one isomer, calculated all peaks together.
(**) Surrogate and internal standard compound.
(CE): Collision energy (V)
WT, GT, OT, BT: white, green, oolong and black tea, respectively
ME: matrix effect
MRL: maximum residue limit (EU MRL)

Table A-15. Summary information of tea samples (chapter 5).

#	Code	Type	Sample name	Origin(*)	Organic	Trademark	Lot number	Expiry date
1	BT001	Black tea	Organic Assam (GIJ2018171 - 17.10.18)	India	Yes	N.I.	17.10.18	17/10/21
2	BT002	Black tea	Jaipur assay (1998-2018)	India		N.I.	1998-2018	01/01/20
3	BT003	Black tea	Organic CTC classic 18H0407 (04.07.18)	India	Yes	N.I.	04.07.18	04/07/21
4	BT004	Black tea	Kanan Devan 08PP25-9 (10.2018)	India		N.I.	10.2018	01/10/21
5	BT005	Black tea	Tata tea 09PP45-1 (05.2018)	India		N.I.	09PP45-1 (05.2018)	01/05/21
6	BT006	Black tea	Oothu organic (TA081891 - 02.08.18)	India	Yes	N.I.	TA081891 - 02.08.18	02/08/21
7	BT007	Black tea	Black tea (Long Dinh)	Vietnam		Long Dinh	N.I.	01/05/19
8	BT008	Black tea	Red tea (Suoi Giang 2018)	Vietnam	Yes	N.I.	N.I.	01/05/17
9	BT009	Black tea	Black tea (Happy valley 2015 - T1024)	India	Yes	Mariage Frères	2015	N.I.
10	BT010	Black tea	Balck tea (Namring 2014 - T1018)	India		Mariage Frères	2014	N.I.
11	BT011	Black tea	Black tea (Twinings)	India, Sri Lanka and Kenya		Twinings tea	N.I.	N.I.
12	BT012	Black tea	Black tea (Yorkshire Gold)	India, Sri Lanka and Rwanda		Yorkshire tea	L6139	31/10/17
13	BT013	Black tea	Black tea (Jungpana Upper - T1111)	India	Yes	Mariage Frères	2016	N.I.
14	BT014	Black tea	Black tea (Gold Himalaya - T4302)	Nepal	Yes	Mariage Frères	2017	N.I.
15	BT015	Black tea	Black tea (T1001)	India		Mariage Frères	SGTGFOP1 - DJ1/2015	01/03/19
16	BT016	Black tea	Red tea (Nana Ding, Yunnan 2015)	China		Nana Ding	2015	N.I.
17	BT017	Black tea	Black tea (Yorkshire)	India and Africa		Yorkshire tea	L4188O27	31/12/15
18	BT018	Black tea	Black tea (Folliet, Ha Giang, Organic)	Vietnam	Yes	Folliet	07.10.2017	07/10/19
19	BT019	Black tea	Black tea (Happy valley 2017 - T1024)	India	Yes	Mariage Frères	FTGFOP1 DJ1/2017	N.I.
20	BT020	Black tea	Black tea (Brumes d'Himalaya - T1109)	India	Yes	Mariage Frères	SFTGFOP1	N.I.
21	BT021	Black tea	Black tea (Lipton yellow, 200g, France, L904331A79)	Unknown		Unilever (Netherlands)	L904331A79	01/02/21
22	BT022	Black tea	Black tea (Lipton yellow label tea, tea bag, France)	Unknown		Unilever (Netherlands)	L40220L023	01/01/18
23	BT023	Black tea	Black tea (Lipton yellow, tea bag, Vietnam)	Vietnam		Unilever (VN)	230913	23/09/15
24	BT024	Black tea	Black tea (Lipton yellow, 200g, France, L727631A79)	Unknown		Unilever (Netherlands)	L727631A79	01/09/19

#	Code	Type	Sample name	Origin(*)	Organic	Trademark	Lot number	Expiry date
25	BT025	Black tea	Black tea (Yorkshire tea for hard water, 80 tea bags)	India, Sri Lanka and Kenya		Yorkshire tea	N.I.	N.I.
26	BT026	Black tea	Black tea (Palais des thés, ref. D018AM, 70025733)	India		Palais des thés	70025733	N.I.
27	BT027	Black tea	Red tea (Springtea, Taiwan)	Taiwan		Springtea	15.04.2019	15/04/21
28	BT028	Black tea	Organic black tea (Folliet, Ha Giang)	Vietnam	Yes	Les Vergers du Mekong	02.05.19	02/05/21
29	BT029	Black tea	Lipton yellow label tea (India)	India		Unilever (Netherlands)	20201214	14/12/20
30	BT030	Black tea	Balck tea (Yung Fa tea, Taiwan)	Taiwan		Yung Fa tea	20210215	15/02/21
31	BT031	Black tea	English breakfast tea (Dilmah, Sri Lanka)	Sri Lanka		Dilmah	08.11.2017	08/11/20
32	BT032	Black tea	Black tea (Vintage Darjeeling, Twinings of London)	India		Twinings tea	07.01.2022	07/01/22
33	BT033	Black tea	Black tea with festive spices (TC921, Mariage Frères)	Unknown		Mariage Frères	1.2023	01/01/23
34	BT034	Black tea	Black tea (N6033, TWG, Singapore)	Unknown		TWG tea	N.I.	N.I.
35	BT035	Black tea	Thé noir d'Inde (T174, Mariage Frères)	India	Yes	Mariage Frères	N.I.	N.I.
36	BT036	Black tea	Superb Chinese black tea (grand Yunnan impérial, Palais des thés)	China		Palais des thés	70027803	01/10/21
37	BT037	Black tea	Fist flush Darjeeling (grand Himalaya, Palais des thés)	India		Palais des thés	70027803	01/10/21
38	BT038	Black tea	Excellent Himalayan black tea (Margaret's hope, Palais des thés)	India		Palais des thés	70027803	01/10/21
39	BT039	Black tea	Strong, full-bodied black tea (Palais des thés)	India		Palais des thés	70027803	01/10/21
40	BT040	Black tea	Delectable black tea from Sri Lanka (Saint-James, Palais des thés)	Sri Lanka		Palais des thés	70027803	01/10/21
41	BT041	Black tea	Royal ruby black tea (assamfarm, Taiwan)	Taiwan	Yes	Assamfarm	03/10/21	03/10/21
42	BT042	Black tea	Deluxe Assam black tea (assamfarm, Taiwan)	Taiwan	Yes	Assamfarm	11/10/21	11/10/21
43	GT001	Green tea	Thé vert Yunnan	China		Les 2 Marmottes	FB190225	28/02/22
44	GT002	Green tea	Green tea (Suoi Giang 2018)	Vietnam	Yes	N.I.	N.I.	01/05/19
45	GT003	Green tea	Green tea (Suoi Giang, Yen Bai, Tu Hai)	Vietnam	Yes	Tu Hai	26.08.2017	26/08/19
46	GT004	Green tea	Green tea special 1 bud 2 leafs (Suoi Giang, Yen Bai, Tu Hai)	Vietnam	Yes	Tu Hai	22.08.207	22/08/18
47	GT005	Green tea	Green tea (Phu Ho tea, Phu Tho)	Vietnam		Phu Ho Tea	N.I.	N.I.
48	GT006	Green tea	Green tea (T2202)	China		Mariage Frères	N.I.	N.I.
49	GT007	Green tea	Green tea (Mrs Hue, China)	China		N.I.	N.I.	N.I.

#	Code	Type	Sample name	Origin(*)	Organic	Trademark	Lot number	Expiry date
50	GT008	Green tea	Green tea (Folliet, Lao Cai, Organic)	Vietnam	Yes	Folliet	30.09.2017	30/09/19
51	GT009	Green tea	Green tea (Thuong Tra, 2017)	Vietnam		Thuong Tra	2017	N.I.
52	GT010	Green tea	Green tea (Hai Binh Son, Suoi Giang, Yen Bai)	Vietnam	Yes	Hai Binh Son	15.06.2016	15/06/17
53	GT011	Green tea	Green tea scent of natural jasmine flower (Tam Chau)	Vietnam		Tam Chau	18.01.2019	18/01/21
54	GT012	Green tea	Lotus tea (green tea, lotus scent, Phuc Long)	Vietnam		Phuc Long	30.10.2018	30/10/20
55	GT013	Green tea	Jasmine tea (green tea, jasmine scent, Phuc Long)	Vietnam		Phuc Long	26.10.2018	26/10/20
56	GT014	Green tea	Green tea (Lipton, France, L90153I620)	Unknown		Unilever (Netherlands)	L90153I620	01/01/21
57	GT015	Green tea	Green tea (85%) with citrus and spices	China		Palais des thés	70026357	01/05/21
58	GT016	Green tea	Green tea (Les 2 Marmottes, FB180916A)	China		Les 2 Marmottes	FB180916A	30/09/21
59	GT017	Green tea	Green tea (Long Phu)	Vietnam		Long Phu	17.01.19	17/07/20
60	GT018	Green tea	Black tea (85%) with almond, cherry and cranberry	China, India and Africa		Palais des thés	70026357	01/05/21
61	GT019	Green tea	Green tea (Phu Ho tea, Phu Tho)	Vietnam		Nomafsi	N.I.	N.I.
62	GT020	Green tea	Green tea (1 bud and 1 leaf, Suoi Giang, Yen Bai)	Vietnam	Yes	Suoi Giang - Yen Bai	15.08.2017	N.I.
63	GT021	Green tea	Green tea (T2305)	China		Mariage Frères	N.I.	N.I.
64	GT022	Green tea	Green tea (Palais des thés, ref. D809AM, 70027068)	China		Palais des thés	70027068	N.I.
65	GT023	Green tea	Green tea (flat leaf, handmade, Shanghai)	China		West lake, Longjing	May-18	N.I.
66	GT024	Green tea	Green tea (Conifer leaf, handmade, Shanghai)	China		West lake, Longjing	May-18	N.I.
67	GT025	Green tea	Organic green tea (Folliet, Lao Cai)	Vietnam	Yes	Les Vergers du Mekong	25.01.19	25/01/21
68	GT026	Green tea	Organic green tea (Fito pharma)	Vietnam	Yes	Fito Pharma	417	13/07/20
69	GT027	Green tea	Jasmine green tea (Good Young, Taiwan)	Taiwan		Good Young company	12.11.2021	12/11/21
70	GT028	Green tea	Jasmine green tea (Viet Anh, Vietnam)	Vietnam		Viet Anh tea	N.I.	N.I.
71	GT029	Green tea	Lotus green tea (Viet Anh, Vietnam)	Vietnam		Viet Anh tea	N.I.	N.I.
72	GT030	Green tea	Green tea (Gunpowder, Twinings of London)	China		Twinings tea	20.10.2020	20/10/20
73	GT031	Green tea	Sweet jasmine blossoms green tea (TC8313, Mariage Frères)	China		Mariage Frères	1.2023	01/01/23
74	GT032	Green tea	Green tea (TWG, Singapore)	Unknown		TWG tea	N.I.	27/12/21
75	GT033	Green tea	Green tea (N6036, TWG, Singapore)	Unknown		TWG tea	N.I.	N.I.

#	Code	Type	Sample name	Origin(*)	Organic	Trademark	Lot number	Expiry date
76	GT034	Green tea	Thé vert d'Inde (T1420, Mariage Frères)	India	Yes	Mariage Frères	N.I.	N.I.
77	GT035	Green tea	Remarquable Chinese green tea (longjing, Palais des thés)	China		Palais des thés	70027803	01/10/21
78	GT036	Green tea	Japanese green tea with roasted rice (Genmaicha, Palais des thés)	Japan		Palais des thés	70027803	01/10/21
79	GT037	Green tea	Delicious Japanese green tea (Sencha ariake, Palais des thés)	Japan		Palais des thés	70027803	01/10/21
80	GT038	Green tea	Lotus green tea (Ancient Shan Tuyet tea, Vietnam)	Vietnam		Sen que Bac	N.I.	01/10/21
81	OT001	Oolong tea	Oolong tea (Long Dinh 21.09.2019)	Vietnam		Long Dinh	21/09/19	21/09/21
82	OT002	Oolong tea	Oolong four seasons (Long Dinh)	Vietnam		Long Dinh	N.I.	01/05/19
83	OT003	Oolong tea	Oolong Original (Long Dinh)	Vietnam		Long Dinh	N.I.	01/05/19
84	OT004	Oolong tea	Oolong Kim Tuyen (Long Dinh)	Vietnam		Long Dinh	N.I.	01/05/19
85	OT005	Oolong tea	Oolong tea (Cau Tre, Lam Dong)	Vietnam		Cau Tre	N.I.	N.I.
86	OT006	Oolong tea	Oolong tea (Palais des thés, Ref. D896AM, 70019806)	Taiwan		Palais des thés	70019806	N.I.
87	OT007	Oolong tea	Oolong tea (Springtea, Taiwan)	Taiwan		Springtea	15.01.2019	15/01/21
88	OT008	Oolong tea	Alishan Tian tea (Spring tea, Taiwan)	Taiwan		Springtea	15.05.2019	15/05/21
89	OT009	Oolong tea	Tieguanyin tea (Spring tea, Taiwan)	Taiwan		Springtea	N.I.	N.I.
90	OT010	Oolong tea	Oriental beauty tea (Spring tea, Taiwan)	Taiwan		Springtea	15.01.2019	15/01/21
91	OT011	Oolong tea	Oolong tea (Folliet, Lai Chau)	Vietnam		Les Vergers du Mekong	25.04.19	25/04/21
92	OT012	Oolong tea	Oolong tea (Ten Ren, Taiwan)	Taiwan		Ten Ren Tea	20210221	21/02/21
93	OT013	Oolong tea	Longjing tea (Yuan Chang Tai, China)	China		Yuan ChangTai Tea	25.12.2017	25/12/19
94	OT014	Oolong tea	Oolong tea (N670, TWG, Singapore)	China		TWG tea	N.I.	N.I.
95	OT015	Oolong tea	Thé bleu de Thaïlande (T4623, Mariage Frères)	Thailand		Mariage Frères	N.I.	N.I.
96	OT016	Oolong tea	Oolong tea (Long Dinh, Vietnam)	Vietnam		Long Dinh	NT2240919	24/09/21
97	OT017	Oolong tea	Delicate oolong from Taiwan (butterfly of Taiwan, Palais des thés)	Taiwan		Palais des thés	70027803	01/10/21
98	PT001	Pu-erh tea	Pu-Erh tea (Nana Ding, Yiwu 2000)	China		Nana Ding	N.I.	N.I.
99	PT002	Pu-erh tea	Pu-Erh tea (Vietnam, spring 2017)	Vietnam		N.I.	N.I.	N.I.
100	PT003	Pu-erh tea	Dark tea from China (Pu-Erh impérial, Palais des thés)	China		Palais des thés	70027803	01/10/21
101	WT001	White tea	White tea (Suoi Giang 2018)	Vietnam	Yes	N.I.	N.I.	01/05/19

#	Code	Type	Sample name	Origin(*)	Organic	Trademark	Lot number	Expiry date
102	WT002	White tea	White tea (Himalaya, 437)	Nepal	Yes	Mariage Frères	Nepal Summer Flush	N.I.
103	WT003	White tea	White tea (Suoi Giang, Yen Bai, 1 bud)	Vietnam	Yes	Suoi Giang - Yen Bai	27.06.2017	N.I.
104	WT004	White tea	White tea (Acient tea, Tay Con Linh)	Vietnam		N.I.	N.I.	N.I.
105	WT005	White tea	White tea (N4023, TWG, Singapore)	China		TWG tea	N.I.	N.I.
106	WT006	White tea	Thé blanc de Nepal (T4370, Mariage Frères)	Nepal	Yes	Mariage Frères	N.I.	N.I.

Note: (*) Origin according to manufacturer information
N.I.: no information

Table A-16. Sumary of pesticides detected by samples (chapter 5).

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
BT001	2-Phenylphenol	50	23.57	1.76
BT002	Acetamiprid	50	9.9	12.43
	Bifenthrin	30000	10.98	3.27
	Clothianidin	700	1.32	12
	Cyhalothrin, lambda-	10	2.62	13.86
	Cypermethrin	500	11.96	1.54
	Ethion	3000	30.28	2.9
	Fenazaquin	10000	4.26	7.07
	Fenpyroximat	8000	1.25	2.38
	Imidacloprid	50	4.18	5.13
	Monocrotophos	50	1.76	7.91
	Propargite	10000	2.83	6.59
	Quinalphos	50	5.23	1.4
	Thiacloprid	10000	4.57	2.87
	Thiamethoxam	20000	8.5	10.68
BT004	Acetamiprid	50	7.02	8.04
	Clothianidin	700	1.21	0
	Cyhalothrin, lambda-	10	6	5.36
	Cypermethrin	500	41.66	1.03
	Ethion	3000	4.82	1.55
	Fenpyroximat	8000	3.75	5.5
	Hexaconazol	50	2.98	4.37
	Hexythiazox	4000	3.56	5.1
	Monocrotophos	50	3.03	8.11
	Propargite	10000	13.1	6.03
	Thiacloprid	10000	2.28	2.63
	Thiamethoxam	20000	4.61	6.67
BT005	Acetamiprid	50	7.85	5.24
	Carbendazim	100	4.92	9.22
	Clothianidin	700	1.38	5.31
	Cypermethrin	500	58.5	2.36
	Ethion	3000	11.43	2.15
	Fenpyroximat	8000	18.39	2.28
	Hexaconazol	50	1.02	1.59
	Hexythiazox	4000	2.71	4.51
	Monocrotophos	50	1.64	8.54
	Propargite	10000	24.21	7.39
	Thiacloprid	10000	2.7	6.38
	Thiamethoxam	20000	5.68	5.25
BT007	Dinotefuran	10	2.61	24.65
BT009	Ethion	3000	4.58	5.25
BT010	Dichlorobenzophenone, 4,4‘-	10	15.26	0.74
	Endosulfan II	30000	8.97	3.63
BT011	Diuron	50	2.14	13.66
	Transfluthrin	10	3.07	33.91
BT012	Bifenthrin	30000	12.84	3.25
	Hexythiazox	4000	2.64	15.42
	Propargite	10000	2.73	4.58
	Thiamethoxam	20000	1.5	4.26
BT014	2-Phenylphenol	50	10.99	2.32
BT018	Cypermethrin	500	70.23	8.96
BT021	Diuron	50	3.69	1.78
BT022	2-Phenylphenol	50	44.16	3.71
	Fenpyroximat	8000	1.52	7.33
	Transfluthrin	10	2.43	10.79
BT023	Transfluthrin	10	5.31	13.46
BT024	Diuron	50	4.11	14.05
BT025	Cyhalothrin, lambda-	10	2.23	0.63
	Dichlorobenzophenone, 4,4‘-	10	6.16	17.12

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Thiacloprid	10000	4.07	10.36
BT026	Dichlorobenzophenone, 4,4'-	10	23.92	5.2
	Propargite	10000	5.71	6.09
	Thiamethoxam	20000	1.73	0.25
BT027	Chlorpyrifos	2000	3.32	9.17
	Clothianidin	700	11.74	0.13
	Cyhalothrin, lambda-	10	197.11	2.12
	Difenoconazole	50	7.2	0.89
	Dinotefuran	10	3.62	5.9
	Thiamethoxam	20000	6.73	2.15
BT029	Acetamiprid	50	3.16	0.11
	Bifenthrin	30000	151.48	6.64
	Clothianidin	700	3.29	2.12
	Cypermethrin	500	71.65	7.59
	Ethion	3000	9.75	4.44
	Fenazaquin	10000	6.62	7.57
	Fenpropathrin	2000	28.22	3.89
	Fenpyroximat	8000	6.03	4.33
	Hexythiazox	4000	6.27	5.66
	Monocrotophos	50	1.67	0.81
	Thiacloprid	10000	19.73	1.64
	Thiamethoxam	20000	22.8	2.43
BT030	Acetamiprid	50	7.06	16.69
	Buprofezin	50	3.11	6.02
	Carbendazim	100	2.11	18.38
	Chlorpyrifos	2000	3.42	5.73
	Cyhalothrin, lambda-	10	12.62	5.74
	Cypermethrin	500	77.27	13.81
	Imidacloprid	50	6.33	13.57
	Pyridaben	50	9.56	18.1
BT031	Diuron	50	2.79	3.7
BT032	Bifenthrin	30000	106.49	1.17
BT033	Bifenthrin	30000	55.79	2.55
	Cyhalothrin, lambda-	10	4.91	9.44
	Fenpyroximat	8000	1.94	1.17
	Pyrimethanil	50	1.86	7.68
	Thiacloprid	10000	1.44	10.44
	Thiamethoxam	20000	1.89	13.93
BT034	Bifenthrin	30000	49.54	8.82
	Cyhalothrin, lambda-	10	6.32	11.36
	Ethion	3000	2.98	0.85
	Fenpropathrin	2000	11.17	3.56
	Thiacloprid	10000	5.14	3.56
	Thiamethoxam	20000	3.42	4.2
BT036	Bifenthrin	30000	8.23	2.05
	Hexythiazox	4000	5.09	6.58
BT039	Cyhalothrin, lambda-	10	10.17	12.16
	Fenpyroximat	8000	16.27	13.95
	Thiacloprid	10000	4.74	19.36
	Thiamethoxam	20000	10.04	24.95
GT003	Permethrin, cis-	100	10.72	5.41
	Permethrin, trans-	100	15.32	11.17
GT004	Permethrin, cis-	100	5.85	13.3
	Permethrin, trans-	100	13.07	5.78
GT005	Buprofezin	50	2.65	13.5
	Chlorpyrifos	2000	61.75	14.62
	Fenobucarb	10	15.74	15.89
GT007	Acetamiprid	50	1.29	1.26
	Buprofezin	50	294.74	1.75
	Chlorpyrifos	2000	261.64	2.76
	Cyhalothrin, lambda-	10	3.01	8.46

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Cypermethrin	500	41.44	2.49
	Fenpyroximat	8000	3.26	5.67
	Imidacloprid	50	2.11	2.41
GT008	2-Phenylphenol	50	10.61	5.57
GT009	Acetamiprid	50	2.53	19.4
	Carbendazim	100	4.33	17.75
	Chlorfenapyr	50000	51.1	0.19
	Cyhalothrin, lambda-	10	324.35	0.12
	Cypermethrin	500	1089.44	1.09
	Etofenprox	50	172.14	1.97
	Fipronil	5	60.95	13.89
	Imidacloprid	50	22.73	10.28
	Lufenuron	50	19.76	14.58
	Thiamethoxam	20000	12.17	11.12
	Tricyclazole	50	5.9	13.03
GT011	Acetamiprid	50	61.41	4.87
	Anthraquinone	20	16.155	1.585
	Buprofezin	50	12.08	2.07
	Carbendazim	100	254.84	2.52
	Chlorfenapyr	50000	19.22	1.51
	Chlorfluazuron	10	3.65	0.93
	Chlorpyrifos	2000	10.16	7.59
	Cyhalothrin, lambda-	10	5.39	15.1
	Cypermethrin	500	348.69	14.29
	Fenobucarb	10	4.13	0.82
	Fenpropathrin	2000	3.98	12.36
	Fenvalerate	100	123.79	14.22
	Hexaconazol	50	3.74	2.7
	Imidacloprid	50	8.77	5.74
	Permethrin, cis-	100	8.82	11.38
	Permethrin, trans-	100	13.2	9.7
	Propargite	10000	141.72	30.18
GT012	Acetamiprid	50	19.76	6.27
	Anthraquinone	20	17.91	2.01
	Bifenthrin	30000	2.61	0.27
	Buprofezin	50	20.82	1.2
	Chlorfenapyr	50000	55.43	1.61
	Chlorfluazuron	10	1.07	7.42
	Chlorpyrifos	2000	21.04	0.1
	Cyhalothrin, lambda-	10	34.11	5.99
	Cypermethrin	500	373.12	2.94
	Fenobucarb	10	5.16	0.3
	Hexaconazol	50	3.82	5.76
	Imidacloprid	50	18.49	11.11
	Indoxacarb	5000	11.15	5.04
	Permethrin, cis-	100	5.65	1.38
	Permethrin, trans-	100	11.38	4.99
	Propargite	10000	11.56	9.59
	Pyridaben	50	17.45	1.92
GT013	Acetamiprid	50	15.6	6.78
	Anthraquinone	20	14.62	7.5
	Bifenthrin	30000	2.38	0.89
	Buprofezin	50	27.66	4.61
	Carbendazim	100	3.35	18.73
	Chlorfenapyr	50000	68.27	2.88
	Chlorfluazuron	10	1.86	4.63
	Chlorpyrifos	2000	22.02	2.67
	Cyhalothrin, lambda-	10	30.57	0.3
	Cypermethrin	500	326.91	4.59
	Fenobucarb	10	5.86	4.01
	Hexaconazol	50	3.03	2.66
	Imidacloprid	50	15.51	9.01

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Indoxacarb	5000	13.47	6.46
	Permethrin, cis-	100	10.98	4.25
	Permethrin, trans-	100	11.77	6.43
	Propargite	10000	10.54	7.83
	Pyridaben	50	14.07	4.69
GT014	Bifenthrin	30000	83.39	19.88
	Chlorfenapyr	50000	50.8	17.09
	Thiacloprid	10000	3.51	21.63
	Thiamethoxam	20000	3.98	6.45
GT015	Anthraquinone	20	16.05	0.6
	Bifenthrin	30000	442.46	1
	Carbaryl	50	3.02	2.15
	Chlorfenapyr	50000	149.46	2.2
	Chlorpyrifos	2000	5.7	0.25
	Cyhalothrin, lambda-	10	2.18	5.19
	Diflubenzuron	50	8.82	1.61
	Fenbuconazole	50	1.18	0.6
	Propargite	10000	30.14	20
	Pyraclostrobin	100	5.68	2.65
	Thiacloprid	10000	52.83	0.78
	Thiamethoxam	20000	2.69	2.16
	Trifloxystrobin	50	4.52	0.31
GT016	Bifenthrin	30000	357.69	0.09
	Buprofezin	50	2.21	1.06
	Chlorfenapyr	50000	340.46	0.87
	Cyhalothrin, lambda-	10	3.1	4.11
	Hexachlorobenzene	10	5.83	1.7
	Pentachlorobenzene	10	3.32	5.96
	Piperonyl butoxide	10	5.18	3.99
GT017	Acetamiprid	50	3.38	4.06
	Carbendazim	100	2.16	5.63
	Chlorpyrifos	2000	9.67	0.22
	Cypermethrin	500	18.31	16.3
	Etofenprox	50	77.95	0.18
	Hexaconazol	50	4.59	6.32
	Permethrin, cis-	100	5.32	3.99
	Permethrin, trans-	100	10.2	1.9
	Thiamethoxam	20000	1.08	5.36
GT018	Bifenthrin	30000	12.09	1.75
	Cyhalothrin, lambda-	10	4.42	1.6
	Diuron	50	1.69	3.23
	Ethion	3000	20.16	0.11
	Fenpyroximat	8000	1.19	2.38
GT019	Buprofezin	50	10.17	2.04
	Chlorpyrifos	2000	22.96	0.06
	Cypermethrin	500	117.62	2.26
	Fenobucarb	10	2.06	3.15
	Fenpyroximat	8000	3.88	8.79
	Imidacloprid	50	118.35	2.97
	Pyridaben	50	18.64	7.44
GT022	Bifenthrin	30000	16.27	3.61
	Cyhalothrin, lambda-	10	4.04	5.08
	Cypermethrin	500	12.61	15.88
	Trifluralin	50	2.9	4.15
GT023	Acetamiprid			
	Bifenthrin	30000	31.87	1.71
	Buprofezin	50	13.48	5.88
	Carbendazim	100	4.01	0.35
	Chlorfenapyr	50000	33.85	5.83
	Cyhalothrin, lambda-	10	3.18	1.56
	Cypermethrin	500	24.34	8.11
	Difenoconazole	50	1.89	11.87

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Dinotefuran	10	15.93	1.97
	Fenpropathrin	2000	7.48	2.65
	Oxadixyl	20	2.45	5.02
	Pyridaben	50	4.25	0.66
	Tebuconazole	50	4.97	12.87
	Thiamethoxam	20000	1.14	16.14
GT024	Acetamiprid	50	7.06	15.28
	Bifenthrin	30000	100.41	5.25
	Buprofezin	50	7.14	8.99
	Carbendazim	100	6.76	1.19
	Chlorfenapyr	50000	54.03	4.92
	Chlorpyrifos	2000	4.56	6.2
	Cyhalothrin, lambda-	10	16.87	2.31
	Difenoconazole	50	5.5	7.99
	Fenpropathrin	2000	25.18	3.93
	Propiconazole	50	3.17	1.03
	Pyridaben	50	2.81	4.21
	Thiamethoxam	20000	2.85	18.58
GT027	Acetamiprid	50	1.75	8.95
	Anthraquinone	20	11.04	1.43
	Buprofezin	50	7.03	9.45
	Chlorfenapyr	50000	10.95	10.75
	Chlorpyrifos	2000	16.1	8.25
	Cypermethrin	500	28.14	5.79
	Permethrin, cis-	100	5.81	17.03
	Permethrin, trans-	100	14.36	9.28
GT028	Acetamiprid	50	3.87	2.91
	Bifenthrin	30000	13.01	0.36
	Buprofezin	50	16.96	2.04
	Carbendazim	100	10.02	0.62
	Chlorfenapyr	50000	328.06	1.17
	Chlorfluazuron	10	24.38	0.79
	Chlorpyrifos	2000	4.42	2.54
	Cyhalothrin, lambda-	10	54.39	1.44
	Cypermethrin	500	267.37	1.34
	Difenoconazole	50	2.62	2.4
	Fenobucarb	10	2.67	1.54
	Fipronil	5	4.07	14.39
	Hexaconazol	50	1.92	1.4
	Imidacloprid	50	14.48	2.75
	Indoxacarb	5000	19.23	1.46
	Lufenuron	50	8.84	5.68
	Metaflumizone	100	2.73	2.3
	Permethrin, cis-	100	5.19	0.6
	Permethrin, trans-	100	10.55	5.27
	Pyridaben	50	2.6	17.83
	Thiamethoxam	20000	1.72	8.43
GT029	Acetamiprid	50	5.98	0.65
	Bifenthrin	30000	5.54	1.72
	Buprofezin	50	14.33	0.71
	Carbendazim	100	28.99	0.83
	Chlorfenapyr	50000	272.22	1.03
	Chlorfluazuron	10	15.44	0.94
	Chlorpyrifos	2000	4.34	5.18
	Cyhalothrin, lambda-	10	31.76	0.81
	Cypermethrin	500	224.51	2.36
	Difenoconazole	50	1.15	1.23
	Fenobucarb	10	2.47	0.63
	Fipronil	5	3.4	6.49
	Imidacloprid	50	10.88	3.47
	Indoxacarb	5000	8.68	1.4
	Lufenuron	50	2.76	0.56

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Permethrin, cis-	100	7.07	0.93
	Permethrin, trans-	100	11.28	3.66
	Pyridaben	50	3.72	5.01
	Tebuconazole	50	1.19	3.46
	Thiamethoxam	20000	1.88	3.12
GT030	Bifenthrin	30000	121.57	2.52
	Cyhalothrin, lambda-	10	9.13	1.32
	Fenpropathrin	2000	4.95	0.03
	Thiacloprid	10000	2.58	2.53
	Thiamethoxam	20000	1.27	11.2
GT031	Bifenthrin	30000	52.63	13.89
	Carbendazim	100	4.45	6.32
	Chlorpyrifos	2000	4.06	15.05
	Cyhalothrin, lambda-	10	45.3	5.29
	Fenpropathrin	2000	5.15	13.46
GT032	Acetamiprid	50	2.12	2.31
	Bifenthrin	30000	171.41	6.27
	Chlorfenapyr	50000	123.67	4.85
	Cyhalothrin, lambda-	10	28.63	1.92
	Propargite	10000	3.63	25.03
	Pyridaben	50	3.88	23.65
	Thiacloprid	10000	12.26	7.35
GT033	Bifenthrin	30000	612.87	9.5
	Chlorfenapyr	50000	497.82	9.35
	Clothianidin	700	6.95	2.86
	Thiacloprid	10000	80.06	5.83
GT035	Acetamiprid	50	3.55	11.87
	Fenpropathrin	2000	5.29	2.08
	Pyrimethanil	50	2.01	8.55
	Triazophos	20	3.11	6.82
GT037	Chlorfenapyr	50000	411.94	0.72
	Tefluthrin	50	2.6	1.77
OT001	Difenoconazole	50	5.64	2.17
	Dinotefuran	10	3.86	13.92
OT002	Difenoconazole	50	1.65	3.9
OT003	Dinotefuran	10	3.87	16.18
OT004	Chlorpyrifos	2000	3.73	11.29
	Difenoconazole	50	1.72	7.05
	Dinotefuran	10	3.39	8.36
OT005	Buprofezin	50	2.84	7.81
	Chlorpyrifos	2000	21.33	5.94
	Dinotefuran	10	5.8	4.12
	Imidacloprid	50	4.28	5.73
	Permethrin, cis-	100	29.59	4.95
	Permethrin, trans-	100	35.01	5.47
	Thiamethoxam	20000	4.84	2.62
OT006	2-Phenylphenol	50	33.99	2.33
	Bifenthrin	30000	22.82	3.04
	Cyhalothrin, lambda-	10	8.9	1.35
	Ethion	3000	10.97	2.97
	Fenpropathrin	2000	2.4	12.73
	Imazalil	100	8.93	2.32
	Pyrimethanil	50	27.49	13.88
	Pyriproxyfen	15000	3.29	0.79
	Thiacloprid	10000	1.29	0.55
OT007	Anthraquinone	20	11.11	4.45
	Buprofezin	50	7.73	5.44
	Chlorpyrifos	2000	3.47	8.15
	Clothianidin	700	4.4	0.13
	Difenoconazole	50	3.17	2.03
	Dinotefuran	10	51.2	0.18

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Fenpropathrin	2000	36.2	1.5
	Imidacloprid	50	24.28	1.65
	Thiamethoxam	20000	26.27	2.92
OT008	Buprofezin	50	6.43	0.48
	Chlorfluazuron	10	6.61	0.39
	Chlorpyrifos	2000	99.43	3.28
	Clothianidin	700	5.96	4.26
	Cypermethrin	500	20.67	5.34
	Difenoconazole	50	9.09	0.05
	Dimethomorph	50	3	3.94
	Dinotefuran	10	58.45	5.28
	Fenpropathrin	2000	2080.41	2.49
	Imidacloprid	50	5.23	6.27
	Permethrin, cis-	100	23.75	2
	Permethrin, trans-	100	24.75	2.51
	Tebuconazole	50	2.2	6.39
	Thiamethoxam	20000	36.78	1.84
OT009	Ametryn	10	1.56	1.81
	Bifenthrin	30000	17.73	3.75
	Buprofezin	50	2.41	3.25
	Carbendazim	100	1.88	2.03
	Chlorfenapyr	50000	45.19	4.93
	Chlorfluazuron	10	1.65	6.09
	Chlorpyrifos	2000	14.24	2.24
	Cyhalothrin, lambda-	10	33.28	1.06
	Difenoconazole	50	3.59	6.44
	Dinotefuran	10	34.18	8.67
	Fenpropathrin	2000	44.21	2.9
	Flucythrinate	50	241.82	1.68
	Flufenoxuron	15000	1.55	0.87
	Imidacloprid	50	311.36	10.22
	Methomyl	50	5.76	6.35
	Oxadiazon	50	3.47	0.61
	Pendimethalin	50	4.08	1.21
	Permethrin, cis-	100	12.55	1.3
	Permethrin, trans-	100	14.76	2.17
	Procymidone	50	3.43	3.51
	Prothiofos	10	3.22	5.06
	Pyraclostrobin	100	2.13	5.33
OT010	Permethrin, cis-	100	12.16	1.8
	Permethrin, trans-	100	16.35	0.13
OT011	Acetamiprid	50	5.6	7.06
	Buprofezin	50	78.55	2.85
	Chlorpyrifos	2000	51.51	1.02
	Cyhalothrin, lambda-	10	2.3	2.77
	Cypermethrin	500	133.19	2.34
	Dinotefuran	10	4.63	7.53
	Fenobucarb	10	4.83	3.54
	Imidacloprid	50	2.79	10.9
	Thiamethoxam	20000	6.07	7.49
OT012	Ametryn	10	1.61	17.04
	Bifenthrin	30000	6.85	9.1
	Chlorfenapyr	50000	30.45	8.93
	Chlorpyrifos	2000	12.19	10.98
	Cyhalothrin, lambda-	10	30.48	4.51
	Difenoconazole	50	2.81	14.01
	Dinotefuran	10	9.37	1.73
	Fenpropathrin	2000	151.87	9.78
	Fenvalerate	100	11.1	5.88
	Flucythrinate	50	113.56	9.19
	Flufenoxuron	15000	187.99	15.28
	Imidacloprid	50	9.01	11.07

Sample code	Compound	MRL(*) (µg/kg)	Result (µg/kg)	RSD (%, n=3)
	Oxadiazon	50	1.47	3.65
	Pyraclostrobin	100	7.2	14.35
	Spinetoram	100	2.25	12.01
	Tebuconazole	50	23.2	14.09
OT013	Anthraquinone	20	70.42	4.38
	Bifenthrin	30000	2297.81	5.54
	Buprofezin	50	3.28	8.63
	Carbendazim	100	1996.99	2.7
	Cyhalothrin, lambda-	10	1252.89	3.14
	Cypermethrin	500	3700.77	2.94
	Diethofencarb	50	5.28	0.29
	Difenoconazole	50	64.96	3.33
	Fenpropathrin	2000	3.55	1.1
	Fenvalerate	100	13.57	3.38
	Hexaflumuron	10	2.32	0.15
	Indoxacarb	5000	7.41	0.33
	Lufenuron	50	14.16	2.05
	Methoxyfenozide	50	3.41	19.34
	Pyraclostrobin	100	269.45	3.79
	Pyriproxyfen	15000	20.72	20.11
	Thiacloprid	10000	73.44	3.98
OT014	Acetamiprid	50	1.57	0.72
	Buprofezin	50	2.02	6.59
	Clothianidin	700	1.41	6.13
	Cyhalothrin, lambda-	10	5.34	4.48
OT015	Dinotefuran	10	3.27	6.09
OT016	Chlorpyrifos	2000	18.54	3.74
	Dinotefuran	10	10.18	0.1
OT017	Bifenthrin	30000	8.23	3.44
	Chlorfenapyr	50000	35.61	2.93
	Cypermethrin	500	17.46	0.14
	Dichlorobenzophenone, 4,4‘-	10	4.81	1.12
	Imidacloprid	50	8.58	10.37
PT001	Bifenthrin	30000	279.25	1.56
	Imidacloprid	50	6.77	3.75
	Pyriproxyfen	15000	1.52	3.78
WT005	Bifenthrin	30000	6.94	2.35
	Cyhalothrin, lambda-	10	4.93	15.41
	Thiamethoxam	20000	1.47	7.96

(*): EU MRLs regulation

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Résumé de la thèse

Introduction

Le thé est la deuxième boisson la plus consommée au monde, dépassée uniquement par l'eau, en raison de ses bienfaits pour la santé. Cependant, en raison de pratiques monoculturales dans des régions au climat chaud et humide, l'utilisation de pesticides pour la culture du thé est très courante. Au fil du temps, le nombre de pesticides utilisés a fortement augmenté avec de nombreuses familles de molécules. Aussi, pour protéger la santé des consommateurs, de nombreux pays et régions ont établi des limites maximums de résidus de pesticides pour un grand nombre d'aliments et de boissons, dont le thé. C'est le cas notamment de l'Union européenne (UE) qui a fixé les limites maximums de résidus (LMR) pour plus de 480 pesticides et leurs métabolites dans les produits à base de thé, avec des valeurs variant de 0,005 (fipronil) à 70 mg/kg (ion bromure). Par conséquent, le développement de méthodes analytiques capables de détecter plusieurs centaines de résidus de pesticides dans le thé est un défi, car le thé est un produit complexe avec de nombreux composés pouvant interférer avec les résultats, tels que les polyphénols, les pigments, les acides gras, les acides organiques et la caféine.

À des fins quantitatives, l'analyse des résidus de pesticides dans le thé nécessite généralement l'extraction, la purification et/ou l'enrichissement/la dilution. De nombreux auteurs se sont concentrés sur les QuEChERS (méthode rapide, facile, bon marché, efficace, robuste et sûre) pour la préparation des échantillons en combinaison avec l'extraction dispersive en phase solide (d-SPE) (AOAC 2007.01; Cajka et al., 2012; Chen et al., 2011; Hou et al., 2016; Hou et al., 2014; Lehotay et al., 2010; Lozano et al., 2012; Rajski et al., 2013; Steiniger et al., 2010; J. Wang et al., 2011; Zhao et al., 2012). Cepoendant, l'extraction QuEChERS et la purification par d-SPE présentent des inconvénients durant l'analyse du thé, notamment du fait d'effets de matrice ainsi que d'une faible sensibilité (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rajski et al., 2013). Des études antérieures ont montré qu'il est difficile d'éliminer les interférences en utilisant uniquement l'étape d-SPE. Ce problème est d'autant plus marqué lors de l'analyse des résidus de plusieurs centaines de pesticides avec des propriétés physico-chimiques très différentes, telles que la polarisation, les groupes fonctionnels, la masse molaire et la pression de vapeur. Aussi, l'étude s'est focalisée sur l'élimination des interférences en combinant l'extraction QuEChERS et la purification par extraction en phase solide (SPE) en utilisant différents sorbants, comme que l'octadécyle (C18), le noir de carbone graphité (GCB) et les amines primaires et secondaires (PSA), pour préparer les échantillons. Ceci a permis d'analyser plusieurs centaines de pesticides avec une sensibilité, une exactitude et une précision élevées.

Par ailleurs, l'effet de matrice est un phénomène courant en LC-MS/MS et GC-MS/MS, qui peut provoquer des résultats appelés faux positifs ou faux négatifs. Ces problèmes d'erreurs deviennent plus graves si les effets de matrice (EM) ne sont pas soigneusement pris en compte lors du développement et de la validation des méthodes analytiques (Rahman, El-Aty, et al., 2013; SANTE/11945/2015; Smeraglia et al., 2002; Taylor, 2005). L'élimination ou la réduction de l'effet de matrice se fait généralement de la manière suivante : (i) amélioration de l'extraction des échantillons, (ii) modification des temps de rétention des analytes, (iii) changement de la source d'ionisation, (iv) utilisation d'étalons internes à base d'isotopes, (v) ajout de protecteurs d'analytes (pour GC uniquement), (vi) dilution, (vii) étalonnage adapté à la matrice et (viii) utilisation de l'ajout dosé d'étalon (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013;

Rutkowska et al., 2019; Taylor, 2005). Le choix de la méthode appropriée dépend de la quantité d'analyte, de la matrice de l'échantillon et de l'instrument d'analyse (GC ou LC). Par exemple, l'ajout de protecteurs d'analyte n'est utilisé que dans le cas GC mais pas pour LC.

Cette thèse comporte 6 chapitres.

Le chapitre 1 constitue un résumé de l'état de l'art sur les connaissances liées au thé et aux méthodes analytiques utilisées pour la détermination des résidus de pesticides dans le thé. Il décrit en détail le thé, la transformation du thé, les pesticides utilisés durant la culture du thé, les résidus de pesticides dans le thé, les méthodes analytiques et l'effet de matrice.

Le chapitre 2 présente le matériel et les méthodes utilisés dans toutes les expériences. Il se concentre sur les expériences de développement de méthodes, les études des effets de matrice et la validation des méthodes analytiques.

Le chapitre 3 met l'accent sur le développement de méthodes analytiques pour 400 résidus de pesticides dans des feuilles de thé vert. Cela implique des études sur différents sorbants utilisés lors de l'étape de nettoyage, le volume d'élution du procédé SPE, ainsi que l'optimisation de l'évaporation. Par la suite, ces méthodes ont été validées conformément aux exigences de SANTE/11945/2015. Ce chapitre a été publié dans la revue *Food Chemistry* (https://doi.org/10.1016/j.foodchem.2020.126928).

Le chapitre 4 montre la complexité de l'effet de matrice dans l'analyse multi-pesticides pour le thé. Plusieurs méthodes ont été étudiées pour surmonter les effets de matrice tels que la purification par SPE, en utilisant un protecteur d'analyte (pour GC uniquement), la réduction du volume d'injection et la dilution. De plus, la comparaison des effets de matrice dans différents types de thé a été réalisée.

Le chapitre 5 présente les résultats de la validation de la méthode pour la méthode UPLC-MS/MS et GC-MS/MS dans plusieurs types de thés. Par la suite, ces méthodes ont été utilisées pour évaluer les résidus de pesticides dans 106 thés provenant de différentes sources (jardins de thé) et marques de thé.

Le dernier chapitre est consacré aux conclusions et perspectives finales.

Chapitre 1. Etat de l'art

1.1 Le thé

Le thé est la deuxième boisson la plus consommée au monde, dépassée uniquement par l'eau (Banerjee et al., 2010; Biswas et al., 2007). Les variétés de thé sont produits en modifiant la forme et la chimie des feuilles, appelées « transformation » ou « procédés ». Les différents types de (noir, vert, oolong, blanc et Pu'erh) proviennent tous de la même plante, *Camellia sinensis* (il est lié aux belles fleurs de camélia vues dans les jardins botaniques et les paysages). *Camellia sinensis* est une plante subtropicale à feuilles persistantes originaire d'Asie, mais est maintenant cultivée dans le monde entier. Le théier pousse mieux dans les sols meubles, acides, riches et profonds, à haute altitude et dans les climats subtropicaux. Par la suite, le « thé » représentera tout ce qui dérive de la plante *Camellia sinensis*. La boisson « thé » est aussi appelé tisane ou liqueur pour les amateurs avertis. Ce terme de tisane est générique, désignant une infusion dans l'eau durant quelques minutes, comme c'est le cas pour les tisanes de camomille, de rooibos et des thés aromatisés aux fruits.

Jusqu'à présent, les thés sont classés en cinq catégories comprenant six types, à savoir non oxydés (thé vert et thé jaune), légèrement oxydés (thé blanc), semi oxydés (thé oolong), entièrement oxydés (thé noir) et post-oxydé (thé noir ou Pu'erh) (Kosińska & Andlauer, 2014; Xu et al., 2018). Le traitement du thé est composé de cinq étapes principales. Certains thés n'utilisent pas toutes ces étapes, tandis que d'autres thés les répètent plusieurs fois. Le traitement primaire est la cueillette, le flétrissement (permettant aux feuilles de flétrir et de ramollir), le roulage (pour façonner les feuilles et essorer les jus), l'oxydation (fermentation) et la cuisson (séchage).

Les conditions idéales pour une bonne croissance des plants de thé sont les températures froides (15-25 °C), une humidité élevée (80-90 %) et des précipitations annuelles élevées (2 000 mm). L'humidité élevée aide à assurer que les feuilles poussent à un rythme lent et restent tendres (Fung et al., 1999). Néanmoins, en raison de la pratique de la monoculture et souvent des variétés monoclonales dans les zones à forte humidité et température, le théier est facilement attaqué par les insectes, les acariens, les champignons, les virus et les maladies (Beneta et al., 2018). Au fil du temps, le nombre de pesticides utilisés dans l'agriculture a augmenté. Jusqu'à présent, plus de 800 pesticides ont été utilisés en agriculture pour lutter contre les ravageurs, les insectes, les champignons, les maladies et les mauvaises herbes (Zhang et al., 2012). Afin de protéger la santé des consommateurs, de nombreux pays et plusieurs organisations internationales ont établi des limites maximums de résidus (LMR) de pesticides pour le thé. Les réglementations sur les LMR diffèrent d'un pays à l'autre, non seulement sur le nombre de pesticides mais également sur la réglementation des LMR. Par exemple, l'Union européenne (UE) a établi la liste des LMR pour plus de 470 pesticides et leurs métabolites dans les produits à base de thé qui varient de 0,005 (fipronil) à 70 mg/kg (ion bromure) (EU MRL), alors que le Codex exige seulement la vérification de 23 d'entre eux avec des teneurs variant de 0,5 (méthidathion) à 70 mg/kg pour le méthidathion et le spiromésifène, respectivement (Codex MRLs). Par conséquent, il est nécessaire de disposer de méthodes d'analyse fiables, robustes et sensibles pour déterminer les résidus de pesticides multiples dans le thé afin de répondre aux exigences strictes de l'UE ainsi qu'à celles d'autres pays.

1.2 Utilisation des pesticides dans la culture du thé

Aujourd'hui, il existe 5 groupes de pesticides couramment utilisés dans l'agriculture, à savoir les pesticides organochlorés (OCP), les organophosphorés (OPP), les carbamates (CB), les pesticides synthétiques pyréthroïdes (PYR) et les triaziniques (TRZ) (LeDoux, 2011).

Les pesticides organochlorés, efficaces contre une variété d'insectes, ont été largement utilisés dans le monde entier dans l'agriculture et la production animale jusqu'à ce que les pays développés introduisent des restrictions à la fin des années 1970. Ces molécules sont très stables, peu volatiles, non polaires et lipophiles.

Les pesticides organophosphorés, principalement utilisés comme insecticides, sont des esters d'acide phosphorique avec différents substituants. Les OPP ont des propriétés physico-chimiques très variables. C'est le cas notamment de leur polarité et de leur solubilité dans l'eau.

Les carbamates, ou esters d'acide carbamique N-substitués (RO–C(O)–NR'R''), sont des composés à large spectre, utilisés pour la lutte contre les insectes dans le monde entier. L'exposition à des carbamates, agissant comme des inhibiteurs de l'acétyl-cholinestérase, peut entraîner des troubles neurologiques réversibles. Certains sont soupçonnés d'être cancérigènes et mutagènes.

Les pesticides à base de pyréthroïdes synthétiques sont des insecticides à large spectre, efficaces. Ils présentent une faible toxicité pour les mammifères et une persistance environnementale à court terme. Les pyréthroïdes sont des composés lipophiles non polaires à faible polarité.

Les triazines sont parmi les herbicides les plus utilisés en agriculture. La plupart d'entre eux sont dérivés de la s-triazine (1,3,5-triazine), mais quelques-uns sont basés sur la 1,2,4-triazine. Les triazines sont dégradées par des processus chimiques et biologiques dans leurs hydroxytriazines respectifs. Les s-triazines et leurs produits de dégradation sont des composés faiblement basiques, peu solubles dans l'eau, de faible polarité, stables dans l'environnement et donc persistants.

1.3 Résidus de pesticides dans le thé

Les aliments contaminés par des résidus de pesticides sont de plus en plus détectés. Parmi eux, le thé est un aliment régulièrement contrôlé. Un rapport sur les résidus de pesticides dans les aliments a montré une quantité importante d'échantillons de thé contaminés par des résidus de pesticides (EFSA, 2016). Parmi les produits alimentaires le thé constitue une matrice présentant des taux de dépassement de LMR les plus élevés (supérieurs à 10 %). Il y a 243 échantillons sur 1 016 échantillons totaux (représentant 23,9 %) de ces résidus de pesticides supérieurs à la LMR. Pour les aliments transformés, le thé figure également parmi les 3 premières matrices avec des résidus de pesticides supérieurs à la LMR (8/38 échantillons, soit 21,1 %).

Un échantillon peut être contaminé par de multiples résidus pour diverses raisons : pratiques agricoles (utilisation d'herbicides, de fongicides ou d'insecticides contre les ravageurs ou les maladies), contaminations pendant la transformation des aliments, mélange de plusieurs lots, adsorption de résidus de pesticides par le sol ou dérive lors des pulvérisations sur les surfaces agricoles alentours. Selon la réglementation européenne actuelle, un échantillon qui contamine des résidus de multi-pesticides est toujours conforme si chaque pesticide ne dépasse pas la LMR

correspondante. Cependant, le rapport UE 2016 sur les pesticides indique que le nombre d'échantillons contaminés par deux pesticides ou plus augmente. Selon ce rapport, 504 échantillons (49,7 %) et 13 échantillons (34,2 %) pour le thé non transformé et transformé, respectivement, ont été contaminés par de multiples résidus de pesticides. Une fréquence élevée de dépassements des LMR pour l'anthraquinone dans le thé a été observée. Les teneurs en résidus les plus élevées pouvaient atteindre 0,37 mg/kg bien que la LMR fût fixée à la LOQ de 0,02 mg/kg.

Huang et al. (2007) ont présenté une méthode d'analyse de multi-pesticides par GC-MS pour les résidus de pesticides dans 3 042 échantillons de thé réel, y compris 1 532 thés verts, 620 thés noirs, 727 thés oolong et 163 tisanes (Zhiqiang Huang et al., 2007). Du fenvalérate (concentration détectée de 0,05 à 0,25 mg/kg), de la cyperméthrine (0,01 à 0,05), de la fenpropathrine (0,03 à 0,30), de la buprofézine (0,06 à 0,25) et du triazophos (0,02 à 0,20) ont été fréquemment détectés. Certains pesticides dépassaient les LMR de l'UE, comme le fenvalérate (73,4 % des échantillons dans les thés oolong et 52,3 % dans tisanes), la fenpropathrine (57,6%, 30,2%, 22,7% et 16,4% dans les thés oolong, fleurs, noirs et verts, respectivement). De plus, Huang et al. (2009) ont également utilisé une méthode multi-pesticides par LC-MS/MS pour analyser 3 000 échantillons de thé, dont 1 500 thés verts, 650 thés noirs et 850 thés oolong (Huang et al., 2009). Parmi eux, l'acétamipride (0,01-0,05 mg/kg), l'imidaclopride (0,01-0,05), le paclobutrazol (0,01-0,08) et le triazophos (0,06-0,10) ont été fréquemment détectés.

1.4 Méthodes analytiques pour la détermination des résidus de pesticides dans le thé

Le développement de méthodes analytiques capables de détecter plusieurs centaines de résidus de pesticides dans le thé est un défi, car le thé est un produit complexe contenant de nombreux composés, tels que les polyphénols, les pigments, les acides gras, les acides organiques et la caféine, qui peuvent modifier les résultats (Reto et al., 2007). Généralement, les méthodes analytiques publiées pour un ou plusieurs groupes de pesticides sont composées des étapes suivantes : (i) l'utilisation de procédures d'extraction, telles que l'extraction par solvant (SE), l'extraction par fluide supercritique (SFE) ; (ii) les procédures de purification, telles que l'extraction liquide-liquide (LLE), l'extraction en phase solide (SPE) ou l'extraction en phase solide dispersive (d-SPE) ; et, enfin, (iii) la séparation suivi de la détection à l'aide d'un système chromatographique basé sur la chromatographie en phase gazeuse (GC) ou la chromatographie liquide (LC), couplé à différents détecteurs (Cao et al., 2015; Chen et al., 2014; Feng et al., 2013; Hu et al., 2005; Moinfar & Hosseini, 2009; Schurek et al., 2008).

1.4.1 Préparation des échantillons

L'extraction par solvant (SE) est l'une des techniques les plus couramment utilisées pour extraire les pesticides de la matrice. Pour l'analyse des pesticides, il est nécessaire de considérer l'équilibre entre l'efficacité d'extraction et l'effet de matrice. Des solvants à faible polarité tels que l'acétonitrile (ACN), l'acétone et le méthanol (MeOH) ont été utilisés pour l'extraction car ils permettent la dissolution de composés et produits issus de l'agriculture et, du fait de le caractère hydrophoben pénètrent aisément dans les tissus des échantillons (Picó, 2015). Dans ces solvants, ACN et l'acétate d'éthyle (EtOAc) sont souvent utilisés en combinaison avec du $MgSO_4$ anhydre non seulement dans le thé mais également dans d'autres matrices alimentaires.

L'extraction liquide-liquide (LLE) est l'une des techniques utilisées pour éliminer les interférences au cours de l'analyse de pesticides. Cette méthode est basée sur le principe qu'un soluté ou un analyte peut se répartir en un certain rapport entre deux solvants non miscibles, généralement l'eau (phase aqueuse, polaire) et le solvant organique (phase organique, apolaire). L'extraction liquide-liquide est utilisée couramment dans l'analyse des pesticides pour éliminer l'eau, les composés hydrosolubles et transférer l'analyte dans un solvant de faible polarité possédant un point d'ébullition bas.

Depuis quelques années, l'extraction à l'aide d'un fluide supercritique (SFE) - une forme de la matière existant dans des conditions de pression et de température supérieures au point critique - est utilisée pour récupérer rapidement les composés de pesticides. Dans ces conditions, ce fluide peut rapidement diffuser dans la phase solide et dissoudre certains analytes. Dans des études récentes, le CO_2 a été couramment utilisé comme fluide supercritique pour extraire les pesticides en raison des valeurs de température et de pression, de sa faible toxicité, de son ininflammabilité et de son séchage facile après extraction. De plus, le CO_2 supercritique permet l'extraction de manière efficace des composés polaires ou moyennement polaires, tout en éliminant/diminuant les interférences des composés non polaires de l'échantillon et n'extrayant pas les pesticides à forte polarité.

Depuis le milieu des années 1970, l'extraction en phase solide (SPE) est considérée comme l'une des techniques couramment utilisées pour isoler, enrichir les composés de pesticides dans l'eau, les aliments ou éliminer les composants parasites. Depuis le début des années 1990, cette technique s'est fortement généralisée en raison de sa simplicité et du facteur d'enrichissement élevé. Tout d'abord, l'échantillon subit une extraction par un solvant avant d'être isolé, puis enrichi par SPE. Durant l'étape d'enrichissement, la solution contenant l'échantillon passe à travers la colonne SPE, préalablement activée, les interférents étant retenues dans la phase stationnaire. Les substances parasites sont ensuite éliminées de la colonne SPE avec un solvant approprié. Enfin, les analytes sont élués et analysés. La SPE est considérée comme plus efficace que l'extraction liquide-liquide. Les extractions sont quantitatives, faciles à réaliser, rapides et automatisables. L'utilisation de solvants et le temps de laboratoire en sont alors réduits.

Bien que la SPE donne un rendement élevé lors du traitement simultané de plusieurs échantillons, et qu'elle prenne du temps lors du traitement d'un échantillon, son coût reste encore plus élevé. C'est pourquoi une autre forme de technique SPE a été imaginée, l'extraction dispersive en phase solide (d-SPE). Dans cette méthode, une petite quantité d'adsorbant est mise dans la solution d'extrait. Il est nécessaire ensuite de bien mélanger pour éliminer les substances « parasites ». La solution est ensuite centrifugée et le liquide analysé. La d-SPE présente de nombreux avantages, comme l'utilisation de phases moins statiques et de solvants, un gain de temps et de main-d'œuvre, sans support d'équipements telles que des pompes à vide. Comparée à la SPE, la d-SPE est un traitement d'échantillons plus simple, plus rapide, moins cher et plus productif.

QuEChERS est l'acronyme en anglais des mots : rapide, bon marché, efficace, robuste et sûr. Cette méthode QuEChERS a été publiée pour la première fois en 2003 par M. Anastassiades et al. (2003), afin de traiter des échantillons destinés à l'analyse de pesticides dans les fruits et légumes à haute teneur en eau. La méthode QuEChERS est considérée comme combinant et simplifiant nombreuses techniques différentes : (i) le processus d'extraction avec un mélange de solvant ACN/eau ; (ii) la séparation de la phase ACN/eau en ajoutant du $MgSO_4$ anhydre et du

NaCl ; et enfin (iii) l'extraction en phase solide d-SPE (avec une variété de adsorbants) pour éliminer les interférents potentiels. La combinaison de l'extraction, de l'isolement et de l'élimination des interférents se produit en une seule étape, ce qui simplifie les opérations, évite la filtration, tout en limitant ainsi l'évaporation et minimisant la quantité de solvant utilisé. De nos jours, les méthodes QuEChERS et QuEChERS modifiées sont largement utilisés dans le traitement des échantillons pour déterminer les pesticides dans les aliments, en particulier dans le criblage d'échantillons.

1.4.2 LC-MS/MS and GC-MS/MS

Actuellement, la GC couplée à la spectrométrie de masse (GC-MS) et la GC ou la LC couplées à la spectrométrie de masse en tandem (GC-MS/MS et LC-MS/MS) sont les méthodes de séparation par chromatographie les plus utilisées pour séparer et détecter les résidus de pesticides multiples dans le thé, simultanément avec de faibles limites de détection (LOD) et de limites de quantification (LOQ) ainsi qu'avec une bonne précision (Cajka et al., 2012; Fan et al., 2013; Hayward et al., 2015; Hayward et al., 2013; Hou et al., 2016; Z. Huang et al., 2007; Huang et al., 2009; Li et al., 2012; Pang et al., 2011; Y. Wang et al., 2011). Malgré ces avantages, le système dit à « *triple-quad* » (QQQ) présente certains inconvénients. La précision de masse est médiocre (résolution unitaire), ce qui rend difficile la confirmation et la quantification de l'analyte au niveau de trace, en particulier dans les échantillons complexes avec de nombreux interférents de co-élution. Aussi, le détecteur QQQ ne présente pas d'utilité pour identifier les composés non cibles (Yashin et al., 2015). En outre, comme le détecteur *triple-quad* a une faible vitesse de balayage, il est donc nécessaire de diviser plusieurs segments pour augmenter la sensibilité et le nombre de points de données obtenus pour chaque pic (Tsipi et al., 2015). Cependant, ce système de détection QQQ a été amélioré en incluant une segmentation séparée à l'aide des techniques MRM dynamiques, ce qui lui permet aujourd'hui d'analyser des centaines de pesticides en fonction de leur temps de rétention.

Plus généralement, l'analyse des résidus de pesticides dans le thé nécessite des étapes d'extraction, de purification et/ou d'enrichissement/dilution. De nombreux auteurs se sont focalisés sur la méthode QuEChERS pour la préparation d'échantillons en combinaison avec l'étape de d-SPE (AOAC 2007.01; Cajka et al., 2012; Chen et al., 2011; Hou et al., 2016; Hou et al., 2014; Lehotay et al., 2010; Lozano et al., 2012; Rajski et al., 2013; Steiniger et al., 2010; J. Wang et al., 2011; Zhao et al., 2012). Cependant l'extraction QuEChERS et la purification par d-SPE présentent des inconvénients dans l'analyse du thé, y compris des effets de matrice et une faible sensibilité (Kittlaus et al., 2011; Rahman, El-Aty, et al., 2013; Rajski et al., 2013). Des études antérieures ont montré qu'il est difficile d'éliminer les interférences en utilisant uniquement le d-SPE. Ce problème est encore plus marqué lors de l'analyse des résidus de plusieurs centaines de pesticides ayant des propriétés physico-chimiques très différentes (polarisation, groupes fonctionnels, masse molaire et pression de vapeur).

Il est important de souligner que les effets de matrice se produisent généralement en LC-MS/MS et GC-MS/MS, provoquant des erreurs quantitatives, qui peuvent être importantes.

1.5 Effet de matrice (EM)

L'UICPA définit les effets de matrice comme « l'effet combiné de tous les composés de l'échantillon autres que l'analyte sur la mesure de la quantité » (Stahnke et al., 2012). Il se

produit généralement en analyse chromatographique, en particulier avec la spectrométrie de masse. La raison de ce phénomène est difficile à expliquer même s'il a été étudié par de nombreux auteurs (Li et al., 2018). Des matrices différentes donneront une ME différente, même si elles appartiennent au même type de catégorie selon le document d'orientation SANTE/11945/2015 (Gómez-Ramos et al., 2016). Il existe trois façons d'estimer l'EM : (i) comparer le signal composé dans l'étalon de solvant avec le signal dans l'étalon matriciel (Gómez-Ramos et al., 2016; Li et al., 2018; Rutkowska et al., 2018; Stahnke et al., 2012) ; et (ii) utiliser une dérivation post-colonne (Kittlaus et al., 2011). La première méthode permet d'estimer l'EM de chaque substance avec un nombre spécifique, tandis que la seconde méthode permet de quantifier l'EM se produisant pendant toute l'étape d'analyse chromatographique (Stahnke et al., 2012).

La suppression des ions (EM < 0) et l'amélioration (EM > 0) sont les deux causes de l'effet de matrice (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Ucles et al., 2017). L'amélioration ionique se produit généralement en GC-MS (/MS), tandis que la suppression d'ions apparaît dans le cas de la LC-MS (/MS). EM est classé en : faible (< 20 %), moyen (20-50 %) et fort (> 50 %). L'EM dépend généralement non pas des composés à analyser, mais principalement des types de matrice d'échantillons, de détection des instruments et d'extraction d'échantillons. En particulier dans les feuilles de thé, la complexité de l'EM augmente, car l'EM dépend également de l'origine, de la variété et du processus de transformation des feuilles de thé (Li et al., 2018). Pour un faible EM, il est possible d'utiliser des courbes d'étalonnage dans un solvant donné pour l'étape de quantification. Sinon, il est nécessaire de minimiser ou compenser l'EM par d'autres méthodes.

Dans le cas de la GC-MS/MS, il est courant de trouver une augmentation du signal dans le thé (Beneta et al., 2018; Li et al., 2012; Li et al., 2018). Cependant, les effets de matrice peuvent également modifier les formes des pics (moins de résidus, plus symétriques et une intensité plus élevée) par rapport à ceux des solutions étalon préparées dans un solvant. Les interférents dans les solutions semblent bloquer les sites actifs de la colonne et de l'injecteur. De ce fait, davantage de pesticides pourraient atteindre rapidement le détecteur MS (Lozano et al., 2012). Certains groupes de pesticides souffrent souvent d'un EM (comme le carbamate, le phosphate, le carboxyle, l'azole, l'hydroxyle, le groupe amino, l'urée, l'imidazole et le benzimidazole) (Li et al., 2012; Rahman, Abd El-Aty, et al., 2013). Ces substances ont souvent un EM élevé car leurs groupes fonctionnels interagissent avec les groupes silanols ou ion métal des surfaces en verre (M. Anastassiades et al., 2003).

Dans la méthode LC-MS/MS, la suppression des ions est la méthode la plus couramment mise en œuvre. L'une est due aux composants de la matrice qui diminue l'efficacité de la formation des gouttelettes et du nombre d'ions (Kittlaus et al., 2011; Smeraglia et al., 2002; Taylor, 2005; Ucles et al., 2017). L'EM dépend du type de produit, de la méthode de préparation des échantillons, de la composition de la phase mobile et de la conception de la source d'ionisation par *électrospray* (Gómez-Ramos et al., 2016). Si l'EM en LC-MS n'est pas lié à la structure moléculaire du pesticide, il est fortement influencé par le temps de rétention de ce composé (Kittlaus et al., 2011). En chromatographie en phase inverse, une forte suppression apparaît généralement au début du chromatogramme du fait de la présence de composés faiblement retenus (Kittlaus et al., 2011).

Pour un EM hors domaine, ± 20 %, il est possible de le compenser par : (i) une dilution ; (ii) l'utilisation de l'addition d'étalons, *i.e.* méthode des ajouts dosés ; (iii) l'ajout d'étalons internes marqués avec des isotopes ; (iv) l'ajout d'un protecteur d'analyte (uniquement pour GC-MS/MS) ; et (v) l'étalonnage adapté à la matrice (Kittlaus et al., 2011; Ucles et al., 2017). La dilution est une méthode simple et efficace pour réduire l'EM. Cependant elle nécessite une haute sensibilité de l'équipement analytique pour atteindre les LMR de pesticides dans les aliments. L'ajout d'étalons ne convient pas à l'analyse de routine. Les étalons internes marqués sont coûteux et ne sont généralement pas disponibles pour toutes les substances. Pour l'analyse par GC-MS/MS, des protecteurs d'analyte sont ajoutés aux solutions étalons et d'échantillonnage pour bloquer les sites actifs de la colonne et de l'injecteur afin de surmonter l'EM. De plus, l'utilisation d'un solvant polaire sous forme d'eau est nocif pour la colonne GC et le détecteur MS (Li et al., 2018). Par conséquent, l'étalonnage adapté à la matrice pourrait être le meilleur moyen de surmonter le phénomène EM. Il a apporté des résultats de haute précision pour l'analyse de résidus de pesticides multiples. Cependant, une des conséquences en sera une augmentation du nombre d'impuretés dans la colonne et le détecteur, pouvant conduire à une maintenance accrue de l'équipement.

1.6 Conclusion

L'extraction QuEChERS et l'étape de purification d-SPE présentent des inconvénients dans l'analyse des résidus de pesticides dans le thé, y compris les effets de matrice et une faible sensibilité. De ce fait, il est indispensable que ces étapes soient modifiées pour augmenter la sensibilité, l'exactitude et la précision de l'analyse simultanée de centaines de pesticides dans le thé. Un autre défi est de surmonter l'EM qui se produit souvent en LC-MS/MS et GC-MS/MS. Enfin et surtout, il est nécessaire que la méthode analytique permette de détecter de façon la plus quantitative possible le maximum de résidus de pesticides dans le thé.

Divers pesticides sont fréquemment détectés dans les feuilles de thé tels que les pesticides pyréthroïdes (cyperméthrine, étofenprox, fenpropathrine et fenvalérate), les insecticides néonicotinoïdes (acétamipride, imidaclopride), les pesticides organophosphorés (triazophos), les fongicides triazoles (paclobutrazol) et d'autres groupes (anthofquinone). Ces pesticides sont parfois détectés à des niveaux plus élevés que les LMR de l'UE. Pour les aliments transformés, le thé figure également dans les 3 premières matrices avec des résidus de pesticides supérieurs à la LMR. Par conséquent, la détection et la quantification des résidus de pesticides multiples dans le thé doivent être poursuivies.

Chapitre 2. Matériel et méthodes

2.1 Matériel

L'acide acétique glacial (AA), l'acétonitrile de qualité HPLC (ACN), le méthanol (MeOH), l'hexane, l'acétate d'éthyle (EA) et l'acétone ont été obtenus auprès de Merck (Darmstadt, Allemagne). Les tubes GCB/PSA SPE (500 mg/500 mg/6 ml), PSA SPE (500 mg/6 ml) et C18 SPE (500 mg/6 ml) ont été obtenus auprès d'Agilent (Santa Clara, États-Unis). Le tube GCB SPE (500 mg/6 ml) a été obtenu auprès de CNW (Shanghai, Chine). Les kits d'extraction QuEChERS (2 g de MgSO4, 0,5 g de NaCl, 0,5 g de citrate de sodium et 0,25 g de citrate disodique sesquihydrate) ont été préparés en pesant chaque substance (obtenue auprès de Merck, Darmstadt, Allemagne) dans un tube à centrifuger de 15 mL.

Pour les analyses LC-MS/MS, 204 composés dans des kits de solution de pesticides ont été obtenus auprès de Restek (Bellefonte, États-Unis) et trois autres composés (atrazine, simazine et phoxim) ont été obtenu auprès de Sigma Aldrich (St. Louis, États-Unis). Pour les analyses GC-MS/MS, 203 composés dans des kits de pesticides ont été achetés auprès de Restek (Bellefonte, États-Unis). Pour l'atrazine, la simazine et le phoxime, des solutions mères à 100 mg/L ont été préparées pour chaque composé dans l'ACN. Pour tous les pesticides, des solutions intermédiaires de 10 mg/L ont été préparées dans ACN pour LC-MS/MS et toluène pour GC-MS/MS et stockées dans des flacons en verre à bouchon à vis ambrés dans l'obscurité à –20 °C.

Des solutions de mélange standard à des concentrations de 1 mg/L ont été préparées à partir des solutions mères pour optimiser et valider chaque méthode. Étant donné que trois des composés (alanycarbe, benfuracarbe et mésotrione) dans le mélange standard LC-MS/MS contenant 207 pesticides n'étaient pas stables, 204 pesticides ont été utilisés pour cette étude.

Pour la méthode GC-MS/MS, une solution mère de substitution (un mélange de α-BHC-d6 et de parathion-d10 à 40 µg/mL dans ACN) obtenue auprès de Restek (32571, Bellefonte, États-Unis) a été utilisée pour contrôler la validité. Une solution de substitution de travail à 1 mg/L a été préparée dans du toluène et stockée à –20 °C. La trifluraline-d14 (Dr. Ehrenstorfer, Augsburg, Allemagne) a été utilisée comme étalon interne (IS) pour l'analyse GC-MS/MS. Une solution mère IS a été préparée dans du toluène à 1 mg/L et stockée à –20 °C. Les solutions IS de travail (10 µg/L dans ACN) ont été utilisées dans la dernière étape d'extraction de l'échantillon, avant l'injection dans l'instrument GC-MS/MS. Une solution de protection d'analyte (AP) a été préparée avec du sorbitol (5 mg/ml), de l'acide d-(-) gluconique-δ-lactone (10 mg/ml), de l'acide shikimique (5 mg/ml) et du 3-éthoxy-1,2-propanediol (0,2 g/mL) dans ACN/H_2O (6/4, v/v).

2.2 Équipement

Une machine homogène (IKA, USA), un vortex (Velp, Italie), un multi-vortex (Heidolph, Allemagne), un collecteur sous vide SPE à 24 ports (Supelco, USA) et un concentrateur d'échantillons mivac Quattro (Genevac, United Uni) ont été utilisés pour préparer les échantillons.

Le système UPLC-MS/MS (Thermo Fisher Scientific, Waltham, États-Unis) était un UPLC Vanquish (équipé d'une pompe binaire, d'un échantillonneur automatique et de thermostats à colonne) reliant un spectromètre de masse quadripolaire triple TSQ Quantiva. Une colonne à extrémité polaire Accucore™ aQ C18 (100 x 2,1 mm de diamètre intérieur et 2,6 µm de taille de

particules) combinée à une cartouche filtrante de 0,5 µm a été utilisée (Thermo Fisher Scientific). La phase mobile consistait en MeOH et H_2O dans un rapport de 2/98 (v/v) pour la phase mobile A et 98/2 (v/v) pour la phase mobile B. Les deux phases mobiles ont été complétées avec du formiate d'ammonium 5 mM et 0,1% d'acide formique pour améliorer la sensibilité des signaux et la stabilité des temps de rétention. La phase mobile à gradient a été configurée de la manière suivante : 0–0,5 min, 0% B ; 0,5–2 min, 0–40% B ; 2–22 min, 40-100% B ; 22–22,1 min, 100–0% B ; 22,1–25 min, 0% B (durée totale de 25 min). Le débit a été fixé à 0,3 mL/min et le volume d'injection était de 3 µL. Le four avec la colonne a été maintenu à une température constante de 40 °C. Les paramètres MS ont été optimisés pour chaque étalon dans le spectromètre de masse en utilisant une solution à 1 mg/L en mode MRM positif et négatif. Les directives EU 657/2002/CE pour l'analyse LC-MS/MS ont été suivies de deux transitions MRM pour chaque composé (intensité plus élevée pour la quantification et intensité plus faible combinée avec le rapport MRM pour la confirmation). Pour le détecteur MS, N_2 pureté> 99,98%) a été utilisé comme gaz porteur, gaz de balayage ionique et gaz auxiliaire à des débits de 40, 1 et 12 ua (unités arbitraires), respectivement. Les températures du tube de transfert d'ions et du vaporisateur ont été fixées à 325 °C et 300 °C, respectivement ; la tension d'*électrospray* était de +3,5 kV (mode positif) et de –2,5 kV (mode négatif). Le détail des paramètres de masse, y compris le temps de rétention (RT), le mode d'ionisation par *électrospray* (ESI), le pic quantitatif, le pic de confirmation, la radiofréquence (RF) et l'énergie de collision (CE), est reporté en annexe.

L'appareil GC-MS/MS (Thermo Fisher Scientific, Waltham, États-Unis) consiste en un chromatographe en phase gazeuse Trace 1300 Thermo Scientific™ couplé à un spectromètre de masse triple quadripôle TSQ 8000. Il a été utilisé en mode d'ionisation électronique (EI, 70 eV). Les analytes ont été séparés dans une colonne capillaire en silice fondue DB-5ms (30 mx 0,25 mm de diamètre intérieur, 0,5 µm d'épaisseur de film) d'Agilent. La température du four avec la colonne a été programmée comme suit : une température initiale de 90 °C a été maintenue pendant 1 min, puis augmentée de 8,5 °C/min à 320 °C et maintenue pendant 5 min, la durée totale étant de 40 min. Le volume d'injection était de 2 µL en mode sans division, maintenu pendant 1 min à une température de 250 °C. Le débit de gaz de N_2 de purge a été fixé à 50 mL/min. En utilisant le logiciel Thermo AutoSRM, les deux transitions les plus intenses et leurs énergies de collision optimales ont été sélectionnées. Le produit le plus intense a été sélectionné comme ion quantificateur et le deuxième plus intense a été défini comme ion qualificatif. Les paramètres du détecteur de spectrométrie de masse, y compris la RT, le pic quantitatif, le pic de confirmation et le CE, sont reportés en annexe.

2.3 Préparation des échantillons

Les sous-échantillons (2 g) ont été pesés dans des tubes à centrifuger de 50 mL, puis 0,02 mL de substitut 1 µg/mL et 10 mL d'ACN (1% CH_3COOH) ont été ajoutés. La solution a ensuite été mélangée à l'aide d'un vortex pendant 30 min. Un kit d'extraction QuEChERS a été ajouté et le tube a été immédiatement mélangé. Après centrifugation, 5 mL de la couche supérieure d'ACN ont été transférés et purifiés avec SPE en mode mixte comme indiqué dans la figure 1. L'extrait d'ACN a été introduit dans la cartouche, puis un volume de 20 mL d'ACN-toluène (3/1, v/v)) a été utilisé comme solvant d'élution. La totalité de la solution d'extrait et des solvants d'éluant a été recueillie et concentrée à 1 mL en utilisant un concentrateur (40 °C, 1000 bars). Après séchage sous N_2 gazeux, le résidu a été redissous avec 1 mL de MeOH et agité à l'aide d'un

vortex pendant 1 min (solution finale). Pour la solution LC-MS/MS, 0,4 mL de solution finale a été diluée deux fois avec de l'eau. Pour GC-MS/MS, une solution finale de 0,4 ml a été séchée et redissous avec 0,8 mL de solution IS, puis un volume de 24 µL d'analyte a ajouté à la solution comportant un agent protecteur (AP). Le facteur de dilution final est de deux pour les méthodes LC-MS/MS et GC-MS/MS.

2.4 Procédures d'expérimentation

Optimisation des adsorbants SPE (chapitre 3)

Plusieurs types d'adsorbants SPE et d-SPE ont été préparés et codés comme suit : MS-A est une cartouche SPE avec seulement GCB ; MS-B est un mode mixte composé d'une cartouche SPE avec une couche GCB en haut et PSA en bas ; dans MS-C, 250 mg de l'adsorbant C18 sont ajoutés dans la solution d'extraction d'échantillon (d-SPE) et ont été agités avant chargement sur une cartouche SPE GCB/PSA en mode mixte ; MS-D est similaire à MS-C mais utilise 500 mg d'adsorbant C18 ; dans MS-E, 500 mg de l'adsorbant C18 ont été ajoutés à une cartouche SPE qui était connectée au sommet d'une cartouche SPE GCB/PSA en mode mixte par un adaptateur. Avant la procédure SPE, tous les pesticides ciblés ont été ajoutés à 50 µg/kg dans 5 mL de solution d'extraction ACN (1% AA) à partir d'un échantillon blanc de thé vert.

Volume d'élution du processus SPE (chapitre 3)

Le volume d'élution est également un facteur important affectant la récupération. Si le volume est trop faible, l'analyte ne serait pas libéré. Si le volume est trop élevé, les substances interférentes seraient co-éluées. Les expériences ont été menées avec des volumes d'élution de 10 mL (EV-A), 15 mL (EV-B), 20 mL (EV-C) et 25 mL (EV-D). Les solutions ont été enrichies de 50 µg/L d'étalons avant le chargement sur SPE en mode mixte.

Optimisation de l'évaporation (chapitre 3)

Des recherches sur l'impact de la sécheresse pour 407 pesticides ont été effectuées en ajoutant la solution étalon (50 µL, 1 mg/L) à 25 mL de solvant (5 mL ACN contenant 1% d'AA et 20 mL ACN/toluène, 3/1, v/v). Le solvant a été évaporé jusqu'à ce que le volume restant soit de 1 mL (EC-A) ou l'échantillon soit sec (EC-B). Un blanc a été préparé de la même manière, jusqu'à l'étape de concentration, et une solution de mélange étalon similaire a été ajoutée pour obtenir 25 mL de la solution d'élution finale (EC-C).

Validation de la méthode pour le thé vert (chapitre 3)

La méthode a été validée conformément à la norme SANTE (SANTE/11945/2015), où sont répertoriés les effets de matrice, la linéarité, la répétabilité, le LOD et la LOQ. Les courbes d'étalonnage ont été obtenues par ajout d'étalons, allant de 5 à 200 µg/L, dans des solutions d'extrait de matrice vierge avant l'injection. La récupération et la précision ont été déterminées sur la base d'échantillons enrichis à 10, 50 et 100 µg/kg (6 échantillons pour chaque niveau sur deux jours). Les effets de matrice ont été évalués en comparant les pentes des courbes d'étalonnage adaptées à la matrice aux courbes d'étalonnage des solvants. Les LOQ ont été évaluées en déterminant le pic de concentration le plus bas pour les échantillons où la récupération et la répétabilité étaient satisfaisantes (dans les limites de 70 à 120% et de moins de

20%, respectivement) (SANTE/11945/2015). Les limites de détection étaient estimées à un tiers des LOQ.

Évaluation de l'effet de matrice (chapitre 4)

Le thé vert a été choisi pour évaluer les effets de matrice. La réduction de l'effet de matrice a été réalisée par réduction du volume d'injection de 3 à 1 µL pour LC-MS/MS, et de 2 à 1 µL pour GC-MS/MS. En continu, la méthode de dilution a été évaluée pour compenser l'effet de matrice avec différents facteurs de dilution à 4, 10 et 20. Par conséquent, la solution de post-extraction a été diluée avec un mélange MeOH/H_2O (1/1) et une solution IS pour LC et GC , respectivement, avant de préparer des courbes d'étalonnage adaptées à la matrice.

Enfin, les effets de matrice de différents types de thés (blanc, vert, oolong et thé noir) ont été comparés pour estimer les thés. Tous les échantillons étaient considérés comme bio c'est-à-dire sans pesticides après avoir été testés avant cette étude.

Validation de la méthode pour différents types de thé (chapitre 5)

La méthode a été validée conformément à la norme SANTE/11945/2015 (détermination de la linéarité, la récupération, la précision et la LOQ). La répétabilité et la précision de la méthode ont été déterminées sur la base de 5 échantillons enrichis à des niveaux de 10, 50 et 100 µg/kg pour 4 types de thé. Les LOQ ont été évaluées en déterminant le pic de concentration le plus bas pour l'échantillon où la récupération et la répétabilité étaient toujours satisfaisantes (dans les limites de 70 à 120% et de moins de 20%, respectivement). Dans certains cas et généralement avec des méthodes multi-résidus, une récupération moyenne inférieure à 70% et RSD ≤ 20% peut être acceptable.

Résidus de pesticides dans les thés (chapitre 5)

Dans cette enquête, un total de 106 échantillons de thé a été collecté dans des magasins de thé ou des plantations de thé du Vietnam, de la Chine, de Taïwan, de Singapour, de la France et du Qatar entre octobre 2017 et mai 2019. Parmi eux, il y a 27 échantillons considérés comme bio, soit 25,5 %. En termes d'origine, 34 échantillons provenaient du Vietnam (représentant 32,1%), suivi de l'Inde (20 échantillons), de la Chine (19 échantillons) et de Taïwan (12 échantillons). Le reste des pays comme le Népal, Sri Lanka, le Japon et la Thaïlande avaient moins de 10 tailles d'échantillon. En outre, 8 échantillons sans informations d'origine ont été notés comme « inconnus », souvent des mélanges de thés de différents pays producteurs.

Chaptire 3. Détermination de 400 résidus de pesticides dans les feuilles de thé vert par UPLC-MS/MS et GC-MS/MS combinés avec une extraction QuEChERS et une méthode de nettoyage SPE en mode mixte

3.1 Extraction et optimisation du nettoyage

Plusieurs adsorbants SPE ont été étudiés pour réduire les effets de matrice pendant l'étape de nettoyage et pour obtenir des LOQ faibles et une grande précision. De plus, les conditions d'évaporation et les volumes d'élution ont également été optimisés pour obtenir des récupérations maximales.

3.1.1 Adsorbants SPE

Nos essais préliminaires sur les adsorbants C18 et PSA ont montré qu'ils éliminaient les acides organiques, les sucres, la caféine et les acides gras du thé mais pas les pesticides. Cela est probablement dû au fait que les interactions des pesticides avec l'ACN étaient plus fortes qu'avec les phases solides, même le C18, qui absorbent facilement les composés organiques. Le GCB a éliminé les composés colorés, par exemple les pigments et les chlorophylles, certains pesticides avec des structures planes, y compris les cycles aromatiques ou les chaînes de carbone conjuguées, et les substances contenant du Cl, F, O et N (Belhamdi et al., 2016). Par conséquent, en combinant plusieurs types d'adsorbants SPE, nous avons supposé qu'il serait possible d'éliminer les interférences dans l'analyse des extraits de thé (Figure 3-1).

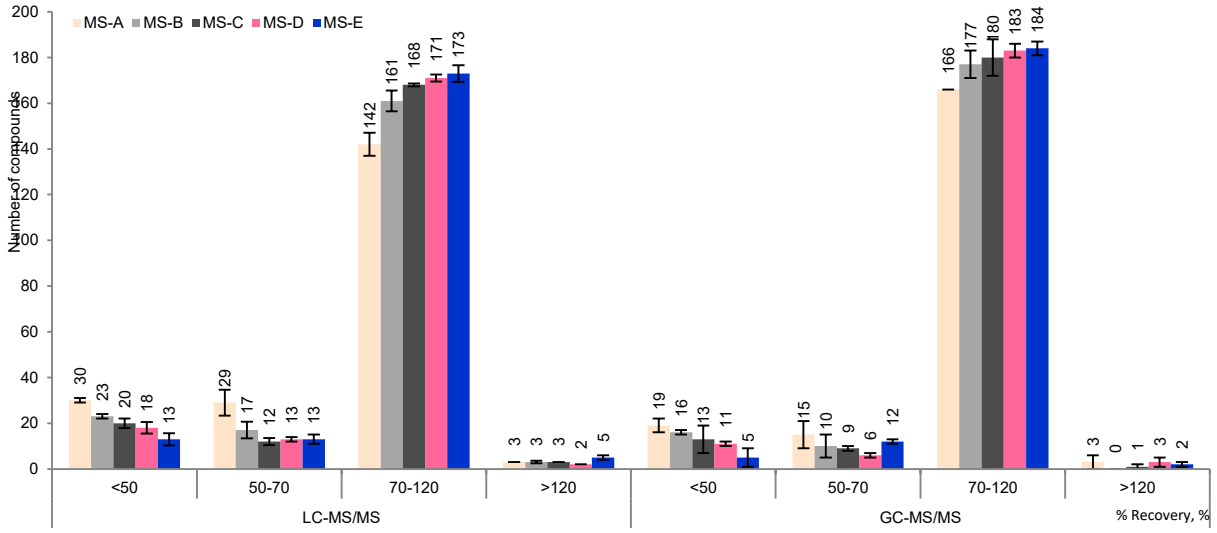

Figure 0-1. *Comparaison des récupérations obtenues par l'analyse des résidus de pesticides à l'aide de différents absorbants SPE en mode mixte (LC-MS/MS: 204 composés ; GC-MS/MS: 203 composés; n = 3). MS-A : GCB (500 mg) ; MS-B : PSA/GCB (500 mg/500 mg) ; MS-C : d-SPE (250 mg C18) + PSA/GCB (500 mg/500 mg) ; MS-D : d-SPE (500 mg C18) + PSA/GCB (500 mg/500 mg) ; MS-E : C18 (500 mg/6 mL) connecté à PSA/GCB (500 mg/500 mg/6 mL)*

La figure 3-1 montre les récupérations obtenues en mélangeant plusieurs adsorbants SPE, dont C18, GCB et PSA. Lorsque l'on compare les adsorbants GCB uniquement (MS-A) avec le PSA dans la cartouche GCB/PSA en mode mixte (MS-B), le nombre de pesticides avec des

récupérations de 70 à 120% est passé à 161 en UPLC-MS/MS (78,9 %) et 177 pesticides en GC-MS/MS (87,2%). Ainsi, le PSA semblait être capable d'éliminer les acides organiques, les acides gras et les sucres dans la matrice, réduisant la suppression des ions et augmentant les récupérations.

Lorsque 250 mg de d-SPE C18 ont été ajoutés à la solution d'extraction, avant de passer à travers la cartouche GCB/PSA SPE en mode mixte (MS-C), le nombre de composés avec des récupérations de 70 à 120% a augmenté de sept (pour LC) et trois (pour GC), respectivement, par rapport à MS-B. Il est clair que l'adsorbant C18 éliminait seulement les lipides et les stérols dans la solution de matrice sans absorber les pesticides. Lorsque la teneur en C18 est passée de 250 mg (MS-C) à 500 mg (MS-D), le nombre de pesticides a légèrement augmenté, avec trois autres composés pour LC et GC. Lors de l'utilisation de deux cartouches SPE (MS-E), le nombre de pesticides avec une récupération de 70 à 120% était le meilleur (173 composés pour UPLC-MS/MS et 184 composés pour GC-MS/MS). Ainsi, la cartouche SPE C18 associée à SPE GCB/PSA était idéale pour les matrices complexes telles que le thé.

3.1.2 Volume d'élution du procédé SPE

Le volume d'élution est également un facteur important affectant la récupération. Si le volume est trop faible, l'analyte n'est pas libéré. Si le volume est trop élevé, les substances interférentes seraient co-éluées. Les expériences ont été menées avec des volumes d'élution de 10 mL (EV-A), 15 mL (EV-B), 20 mL (EV-C) et 25 mL (EV-D). Avec 10 mL de solvant, 43 pesticides (21,1% des composés analysés par LC-MS/MS) et 45 pesticides (22,2% des composés analysés par GC-MS/MS) ont été obtenus, mais les récupérations étaient inférieures à 70%. Avec 20 mL de solvant, 172 pesticides (84,3% des composés analysés par LC-MS/MS) et 147 pesticides (72,4% des composés analysés par GC-MS/MS) ont été récupérés (70-120%). Avec 25 mL, la récupération de certains des composés a diminué, car les composés interférents ont été élués simultanément et ont provoqué une suppression ionique (UPLC-MS/MS) ou une amélioration ionique (GC-MS/MS). Par conséquent, un volume de solvant d'élution de 20 mL (ACN/toluène, 3/1, v/v) a été choisi pour le nettoyage du SPE.

3.1.3 Optimisation de l'évaporation

Les composés dans la solution d'élution peuvent se décomposer ou s'évaporer pendant l'évaporation du solvant, ce qui signifie que la température et le séchage doivent être gérés avec soin. Fan et al. (Fan et al., 2013) ont indiqué que 40 °C et une solution presque sèche (0,3 à 0,5 mL) étaient les meilleures conditions pour 201 pesticides et polluants chimiques dans un mélange de solvants (ACN/toluène, 3/1, v/v). La température utilisée dans notre étude a été fixée à 40 °C.

Pour cette étude, le solvant qui a enrichi les étalons a été évaporé jusqu'à ce que le volume restant soit de 1 mL (EC-A) ou que l'échantillon aille à sec (EC-B). En UPLC-MS/MS, EC-A était le meilleur avec 197 composés (96,5%, 70–120%), ce qui signifie qu'un volume restant de 1 mL était plus efficace que de concentrer les échantillons pour les sécher complètement. En GC-MS/MS, le nombre de composés avec des récupérations supérieures à 70% était de 109 (53,7%) et 81 (39,9%) pour les conditions EC-A et EC-B, respectivement. Sur la base de ces résultats, 1 mL de volume restant a été choisi pour l'évaporation.

3.2 Validation de la méthode

Dans l'extraction et la purification, quatre composés analysés en UPLC-MS/MS (cyromazine, thidiazuron, hydraméthylnon et pymétrozine) et trois composés analysés en GC-MS/MS (acéquinocyl, captane et aldéhyde endrine) avaient des taux de recouvrement très faibles (< 30%) en raison de la dégradation. Par conséquent, la validation de la méthode concernait 200 pesticides pour UPLC-MS/MS et 200 pesticides pour GC-MS/MS.

3.2.1 Effet de matrice

Nos résultats ont montré que 154 composés (77%) pour UPLC-MS/MS et 71 composés (35,5%) pour GC-MS/MS satisfaisaient ou dépassaient ce critère, ce qui signifie que 225 pesticides (56,25% des 400 pesticides) pouvaient être quantifiés en utilisant courbes d'étalonnage des solvants (tableau 3-1).

Table 0-1. Évaluation de l'effet de matrice sur deux méthodes analytiques

Effect de matrice (%)	UPLC-MS/MS	GC-MS/MS
	Nombre de pesticides (% proportion)	
< (–50)	12 (6,0)	3 (1,5)
(–50) ÷ (–20)	33 (16,5)	4 (2,0)
(–20) ÷ (+20)	154 (77,0)	71 (35,5)
(+20) ÷ (+50)	1 (0,5)	38 (19,0)
> (+50)	0 (0,0)	84 (42,0)

Nous avons reconnu que, pour la méthode UPLC-MS/MS, la suppression des ions était plus courante. La suppression des ions se produit lorsque les composants de la matrice diminuent la formation de gouttelettes et d'ions. En GC-MS/MS, il est plus courant de trouver une amélioration du signal (125 composés ou 61,5%). Cependant, les effets de matrice ont également amélioré les formes des pics (moins de résidus, plus de symétrie et une intensité plus élevée) par rapport aux pics de solution étaloln. Les composés interférents dans la matrice semblaient bloquer les sites actifs sur la colonne GC et l'injecteur, ce qui signifie que davantage de pesticides ont atteint le détecteur MS.

Les effets de matrice en dehors de la plage ± 20% peuvent être compensés par : (i) la dilution ; (ii) l'utilisation d'un ajout d'étalon ; (iii) l'ajout d'étalons internes marqués isotopiquement ; et/ou (iv) l'étalonnage matriciel (Kittlaus et al., 2011; Uclés et al., 2017). La dilution est une méthode simple et efficace pour réduire les effets de matrice mais nécessite un équipement analytique très sensible pour détecter ultérieurement les LMR de pesticides dans les aliments. L'utilisation de l''ajout d'étalon ne convient pas à l'analyse de routine. Les étalons internes d'isotopes sont très chers et, généralement, ne sont pas disponibles pour toutes les substances. Par conséquent, l'étalonnage adapté à la matrice peut être le meilleur moyen de surmonter les effets de matrice et de générer des résultats très précis.

3.2.2 Linéarité

L'étalonnage lié à la matrice a été réalisé dans la gamme de 1 - 200 µg/L et de 1 - 100 µg/L dans le cas de la LC-MS/MS et la GC-MS/MS, respectivement. Les réponses étaient considérées comme linéaires lorsque le coefficient de corrélation était supérieur ou égal à 0,99. Dans notre étude, tous les coefficients ont été supérieurs à 0,99, à l'exception de trois composés (biphényle, dichlobénil et captafol), bien que les coefficients de régression pour ces composés soient toujours acceptables ($R^2 > 0,97$). D'excellentes relations linéaires ont été obtenues pour tous les résidus de pesticides testés dans notre étude.

3.2.3 Récupération et reproductibilité

Les valeurs des reproductibilité et récupération dans les échantillons sont reportées dans le tableau 3-2. En utilisant les courbes d'étalonnage appropriées à la matrice, les écarts-types relatifs (RSD %) étaient inférieurs à 20% et les taux de récupération se situaient entre 70 et 120% pour la plupart des pesticides. Ces résultats indiquent que notre méthode a une précision appropriée pour la quantification des résidus multi-pesticides dans le thé, selon SANTE/11945/2015.

Table 0-2. Le nombre de pesticides qui répond à la norme SANTE/11945/2015 pour la récupération (allant de 70 à 120%), RSD (≤ 20%) et LOQ (récupération dans la plage de 70 à 120% et RSD ≤ 20%) à différents niveaux

Paramètres de validation	Concentration (µg/kg)	UPLC-MS/MS	GC-MS/MS	Total
		Nombre de pesticides (% proportion)		
Récupération (70-120%)	dix	191 (95,5)	182 (91)	373 (93)
	50	195 (97,5)	196 (98)	391 (97,75)
	100	196 (98)	196 (98)	392 (98)
RSD (< 20%)	dix	197 (98,5)	193 (96,5)	390 (97,5)
	50	199 (99,5)	199 (99,5)	398 (99,5)
	100	199 (99,5)	198 (99)	397 (99,25)
LOQ	1	0 (0)	19 (9,5)	19 (4,75)
	2	192 (96,0)	31 (15,5)	223 (55,75)
	5	7 (3,5)	137 (68,5)	144 (36,0)
	10	1 (0,5)	9 (4,5)	10 (2,5)
	25	0 (0)	3 (1,5)	3 (0,75)
	50	0 (0)	1 (0,5)	1 (0,25)

3.2.4 Détermination de la LOQ

Des quantités de pesticides à différentes concentrations ont été ajoutées aux échantillons pour déterminer les LOQ. Les résultats obtenus ont montré que les LOQ variaient entre 2 et 5 µg/kg pour la plupart des pesticides, bien que quatre pesticides aient des LOQ supérieures à 10 µg/kg (25 µg/kg pour la bioalléthrine, le carbophénothion, le chlorbenside et 50 µg/kg pour le captafol). Cependant, les LOQ de chlorbenside et de captafol étaient inférieures à 100 µg/kg, ce qui est également la LMR dans les réglementations de l'UE pour les produits à base de thé (LMR UE). Il n'y a pas de LMR réglementées pour la bioalléthrine et le carbophénothion.

3.3 Conclusions

Une méthode de préparation d'échantillons pour l'analyse des résidus de multi-pesticides dans le thé vert combinant plusieurs adsorbants pour la purification a été développée. En utilisant l'extraction QuEChERS couplée à une technique de purification SPE avec trois sorbants différents (C18, GCB et PSA), pour éliminer les effets de matrice, avant les systèmes de chromatographie liquide et gazeuse couplés à MS, les solutions finales étaient presque incolores. Les résultats ont montré une faible co-extraction. Par conséquent, 225 pesticides (154 pour UPLC-MS/MS et 71 pour GC-MS/MS) ont été quantifiés à l'aide de courbes d'étalonnage de solvant. De plus, en utilisant des courbes d'étalonnage adaptées à la matrice pour surmonter les effets de la matrice, un total de 400 composés a été quantifié avec une récupération et une répétabilité élevées et des LOQ faibles. À 10 µg/kg, 373 pesticides (93%) respectaient les normes de récupération SANTE/11945/2015 (70 à 120%) et 390 pesticides (97,5%) respectaient les réglementations pour la RSD (≤ 20%). Les LOQ pour presque tous les pesticides (386 ou 96,5%) étaient <10 µg/kg, ce qui est inférieur aux LMR pour ces pesticides dans le thé (de 5 µg/kg à 70 mg/kg). Dans de futures recherches, nous continuerons d'étudier les effets de matrice dans les thés blancs, noirs et oolong pour évaluer si cette méthode peut être appliquée à ces types de produits.

Chaptire 4. Évaluer et surmonter les effets de matrice dans plusieurs types de thé

4.1 Élimination de la matrice par le nettoyage SPE en mode mixte

Dans l'étude précédente, afin d'éliminer autant que possible les interférences dans le thé vert, une méthode de purification par SPE en mode mixte, y compris C18 SPE couplé avec une cartouche GCB/PSA, a été étudiée après extraction de QuEChERS (Ly et al., 2020). Les résultats des effets de matrice sont représentés dans la figure 4-1.

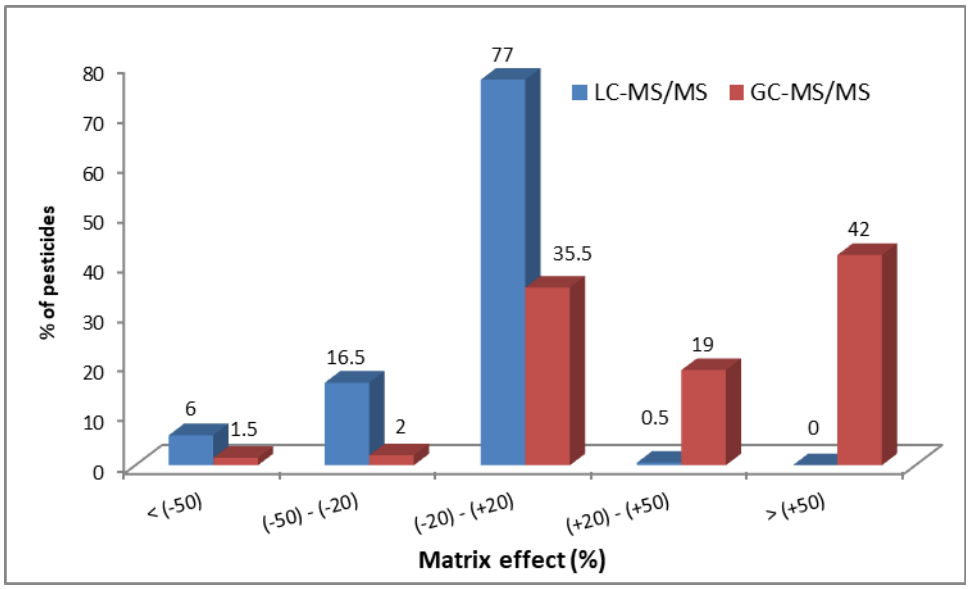

Fig. 0-1. Pourcentage de pesticides dans chaque plage d'effet de matrice (selon SANTE/11945/2015) obtenus à partir des méthodes LC-MS/MS et GC-MS/MS pour le thé vert. Extraction QuEChERS puis nettoyage avec SPE en mode mixte ; injection de 3 et 2 µL pour LC-MS/MS et GC-MS/MS, respectivement

Pour la méthode LC-MS/MS, 154 composés du thé vert (77% des 200 pesticides étudiés) ont eu des effets de matrice de l'ordre de ± 20%. Près d'un quart (16,5%) des pesticides présentaient une suppression de signal moyenne, seulement 6% des composés présentaient une forte suppression et un seul pesticide (l'ivermectine, représentant 0,5%) était une amélioration moyenne. En excluant les composés sans effet de matrice, les résultats ont montré une suppression des ions de 98% et seulement 2% de renforcement des ions pour la méthode LC-MS/MS. Ce résultat prouve que le phénomène d'EM commun en LC est la suppression des ions, conformément aux études précédentes (Uclés et al., 2017; J. Wang et al., 2011).

En outre, nous avons reconnu que la suppression ionique apparaît majoritairement au début (avant 3,6 min) et en fin (après 14 min) du chromatogramme, où les composés matriciels polaires et apolaires sont élués.

En GC-MS/MS, il est plus courant de trouver une amélioration du signal (122 composés ou 61%). De plus, il n'a présenté aucun effet de matrice pour 35,5% des pesticides et une suppression du signal pour 3,5% des composés. Après avoir éliminé les données sans effet de matrice, les résultats ont montré une amélioration de 94,5% et une suppression de 5,5%, ce qui est en accord avec l'étude précédente (Li et al., 2012; Uclés et al., 2017). L'amélioration pourrait être expliquée que les composés interférents dans la matrice semblaient bloquer les sites actifs

sur la colonne GC et l'injecteur, ce qui signifie que davantage de pesticides atteignaient le détecteur MS. Pendant ce temps, le mécanisme de suppression du signal dans GC-MS/MS, jusqu'à présent, n'a pas été clairement expliqué (Uclés et al., 2017). Il y avait 84 composés (42%) présentant une forte amélioration du signal (tableau S3 dans le SI). Parmi eux, les organophosphates (27 composés), les pyréthroïdes (16), la dinitroaniline (5) et le thiocarbamate (3) ont été les plus détectés, tandis que les autres n'avaient qu'une ou deux substances.

4.2 Surmonter l'EM en réduisant le volume d'injection

Dans cette étude, les volumes d'injection ont été réduits de 3 à 1 µL pour LC-MS/MS et de 2 à 1 µL pour GC-MS/MS, respectivement, pour surmonter EM. Le nombre de pesticides à effet de matrice faible a considérablement augmenté, passant respectivement de 154 à 194 composés (jusqu'à 26%) pour LC-MS/MS et de 71 à 140 composés (jusqu'à 97%) pour GC-MS/MS. Le pourcentage de pesticides à effet de matrice faible, moyen et fort était de 97, 2,5 et 0,5% pour LC-MS/MS, respectivement, et 70, 23 et 7% pour GC-MS/MS, respectivement. À notre connaissance, c'est la première fois qu'une réduction du volume d'injection est réalisée pour surmonter les effets de matrice. Les résultats suggèrent que la combinaison de la méthode de nettoyage SPE en mode mixte ci-dessus et du volume d'injection réduit peut être un moyen efficace de surmonter/compenser les effets de matrice, en particulier pour la méthode LC-MS/MS.

4.3 Surmonter l'EM par dilution

Bien que les effets de matrice aient été considérablement améliorés en réduisant le volume d'injection, certains composés n'atteignent pas la plage ± 20%, extrêmement en GC-MS/MS. Par conséquent, il n'est pas possible d'utiliser des courbes d'étalonnage de solvant pour la quantification (SANTE/11945/2015). Nous avons donc continué à diluer les solutions après post-extraction (le facteur de dilution était de 2 pour l'extraction de l'échantillon) pour éliminer l'EM avec différents facteurs de dilution à 4, 10 et 20 pour le thé vert.

Pour LC-MS/MS, il y avait une légère augmentation du composé dans la région EM ± 20% de 97% (194 composés) à 98,5% (197 composés) lorsque le facteur de dilution est passé de 2 à 4 et est resté le même jusqu'à 20. Pour un facteur de dilution, f = 4, presque aucun cas n'avait d'effet de matrice sauf pour la carbendazime (3,5 min, log K_{ow} 1,48), le fuberidazole (3,73 min, log K_{ow} 2,71) et le prothioconazole (12,23 min, log K_{ow} 2).

Compte tenu de la méthode GC-MS/MS, plus la dilution est importante, plus les composés se déplacent vers la région de suppression. La plupart des substances (composés de 198/200) avaient tendance à se déplacer vers la région de suppression. On pourrait expliquer que l'effet de matrice sur GC-MS/MS pourrait être la somme de l'amélioration et de la suppression (Fig. 4-10).

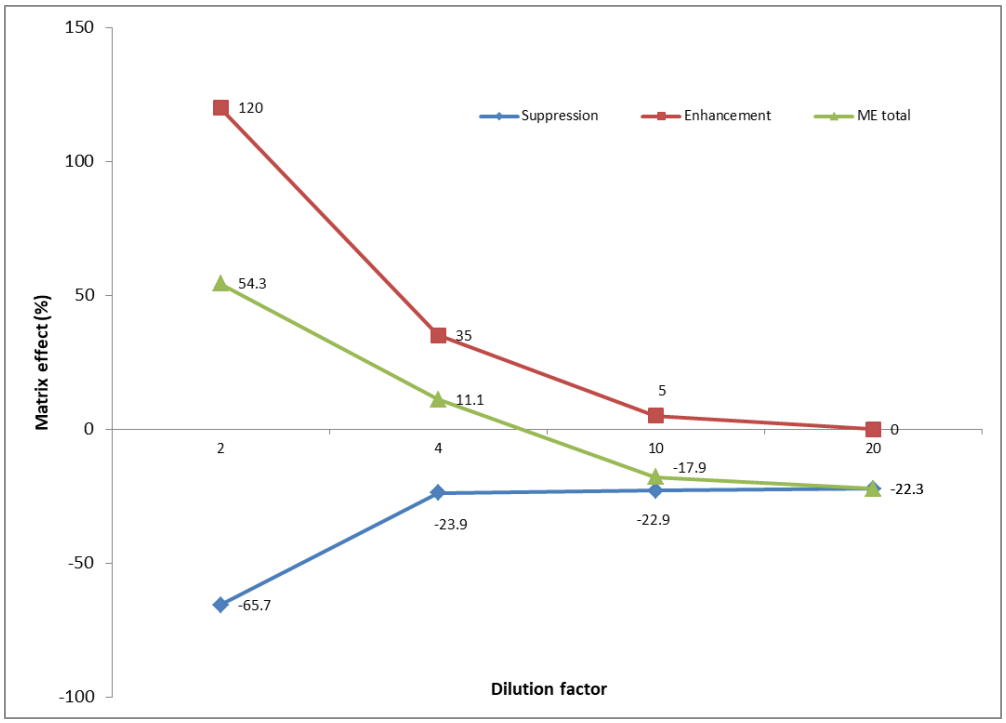

Fig. 0-2. Simulation de l'effet de matrice du p, p'-DDT en fonction du facteur de dilution dans la méthode GC-MS/MS

En général, avec un facteur de dilution de 4, les méthodes LC-MS/MS et GC-MS/MS permettent de détecter le plus grand nombre de pesticides avec un EM de ± 20%. Néanmoins, dans notre autre étude, de nombreuses substances ont des LOQ supérieures à 10 µg/kg, avec f = 4, ce qui ne respectent donc pas les limites maximales de résidus européennes pour les deux méthodes (EU MRL). Dans ces conditions, compte tenu des EM et des LOQ, la dilution ne peut pas être considérée comme nécessaire pour la méthode LC-MS/MS, puisque 97% des composés ne présentent aucun effet de matrice sans dilution. Dans le cas de la GC-MS/MS, l'effet d'amélioration du signal permet d'améliorer la taille des pics avec une meilleure qualité. Ainsi vaut-il mieux profiter de ce phénomène que de l'éliminer (Michelangelo Anastassiades et al., 2003; Cajka et al., 2005; Rahman, El-Aty, et al., 2013). En conclusion, la préparation d'échantillons d'amélioration par purification en mode mixte SPE et réduction du volume d'injection a été choisie pour la détermination de 400 résidus de pesticides dans le thé (f = 2).

4.4 Comparaison des effets de matrice dans le thé blanc, vert, oolong et noir

Des quatre produits évalués, l'OT (thé oolong) est celui qui a le moins d'effet de matrice, car 98,5 et 85,0% des pesticides ne présentent pas de valeurs pertinentes, pour LC-MS/MS et GC-MS/MS, respectivement. Par ailleurs, avec le thé noir, BT, l'amélioration du signal apparaît comme la plus élevée : seulement 91,5 (LC) et 40,5% (GC) sont dans la plage de ± 20%. Les effets de matrice correspondants étaient 193 (LC) et 132 composés (GC) pour le thé blanc, WT, et 194 (LC) et 140 unités (GC) pour le thé vert, GT, respectivement.

Il est clair que les effets de matrice en GC peuvent être divisés en trois groupes : les forts effets (BT), moyens (GT et WT) et faibles effets de matrice (OT). Ce résultat peut s'expliquer par le procédé de fabrication du BT (entièrement oxydé), du WT et du GT (légèrement oxydé) et de l'OT (semi-oxydé), conformément aux études précédentes (Li et al., 2018). En LC-MS/MS, la

plupart des composés n'avaient aucun effet de matrice, représentant de 95,5% (BT) à 98,5% (OT).

4.5 Effets de matrice : comparaison entre les méthodes LC-MS/MS et GC-MS/MS

Il ne fait aucun doute que les résultats obtenus par la LC-MS/MS ne présentent aucun effet de matrice pour les 27 composés malgré le type de thé. Au contraire, en GC-MS/MS il est nécessaire de tenir compte de l'amélioration ionique pour obtenir des résultats avec 22, 7, 6 et 2 pesticides pour BT, GT, WT et OT, respectivement. Il est important de noter que dans les deux méthodes sont injectées les mêmes solutions obtenues après extraction (dans l'étape d'extraction et de purification, avant d'ajouter un mélange de différents étalons). Par conséquent, l'EM est non seulement influencé par l'extraction, la purification et la matrice, mais aussi par les techniques analytiques. La méthode par LC-MS/MS est généralement affectée par la suppression des ions, donc par l'amélioration de l'extraction des échantillons et de l'étape de purification pouvant conduire à éliminer les EM. En revanche, les effets de matrice en GC sont beaucoup plus complexes, comme nous l'avons montré précédemment. Ce résultat indique que les substances respectueuses des deux méthodes doivent être analysées par LC-MS/MS.

4.6 Conclusions

Dans cette étude, les effets de matrice de 400 pesticides ont été estimés dans les méthodes LC-MS/MS et GC-MS/MS pour différents types de thés, y compris le thé blanc, vert, oolong et noir. En utilisant l'extraction QuEChERS, par la suite, la purification par SPE en mode mixte (y compris C18, GCB et PSA), un total de 154 (77%) et 71 (35,5%) pesticides, pour LC-MS/MS et GC-MS/MS, respectivement, répondaient à l'exigence de EM ± 20% pour le thé vert. Le phénomène matriciel commun était la suppression d'ions pour LC-MS/MS et l'amélioration du signal pour GC-MS/MS. Dans LC-MS/MS, la suppression des ions apparaît le plus au début et à la fin des régions du chromatogramme. En GC-MS/MS, les organophosphates (27 composés), les pyréthroïdes (16), la dinitroaniline (5) et le thiocarbamate (3) présentent une amélioration ionique. Par la réduction du volume d'injection, l'effet de matrice a été significativement amélioré à la fois en LC-MS/MS et GC-MS/MS. En conséquence, 194 et 140 composés sans effet de matrice ont été obtenus pour LC-MS/MS et GC-MS/MS, respectivement. À notre connaissance, c'est la première fois qu'une réduction du volume d'injection est réalisée pour surmonter les effets de matrice. De plus, la compensation par dilution a montré que les meilleurs résultats obtenus avec un facteur de dilution, f = 4, pour les deux méthodes. En ce qui concerne le type de thés, le thé noir présente un fort effet de matrice avec 128/400 composés hors plage EM ± 20%, suivis par le thé blanc (75/400), le thé vert (66/400) et le thé oolong (33/400). De plus, la LC-MS/MS n'a présenté aucun effet de matrice pour les 27 composés détectés par les deux méthodes, ce qui est un bon résultat comparé à GC-MS/MS. D'un autre côté, l'effet de matrice en GC-MS/MS pourrait être la somme de deux phénomènes liés à l'amélioration et la suppression du signal. Par conséquent, d'autres études seront nécessaires pour tester à nouveau ce phénomène.

Chaptire 5. Validation de la méthode et évaluation de 397 résidus de pesticides dans plusieurs types de thé de différents pays

5.1 Validation de la méthode pour 4 types de thés

Dans la partie précédente, 400 analyses de pesticides pour le thé vert par extraction QuEChERS, nettoyage SPE en mode mixte et détermination par spectrométrie de masse en tandem pour le thé vert ont été établies (200 composés pour chaque LC-MS/MS et GC-MS/MS). Cependant, il existe trois composés instables (captafol, chlorothalonil et folpet) suivant cette méthode d'analyse multi-résidus en raison de leur tendance à se dégrader à la fois en solution et pendant l'injection GC (EURL-SRM, 2017). Par conséquent, un total de 200 composés pour LC-MS/MS et 197 composés pour GC-MS/MS ont été sélectionnés pour la validation de la méthode en blanc (WT), vert (GT), oolong (OT) et thé noir (BT).

De plus, les résultats ont montré que pour les quatre types de thés pouvait être utilisée la courbe d'étalonnage en solvant dans le cas de la méthode par LC-MS/MS. Cependant, en raison de la forte amélioration des ions, il convient d'appliquer des courbes d'étalonnage adaptées à la matrice pour GC-MS/MS (mélanger des extraits vierges de 4 types de thés).

5.1.1 Linéarité

Dans presque 397 composés, le coefficient de détermination (R^2) était supérieur à 0,99, avec une concentration comprise entre 0,5 et 100 µg/kg. Cependant, dans des cas particuliers, les gammes de concentration de linéarité étaient supérieures à 0,5 µg/kg, mais la sensibilité est toujours acceptable.

5.1.2 Récupération et répétabilité

Des solutions étalons de pesticides ont été ajoutées à cinq échantillons de matrice vierge répliqués à des concentrations de 10, 50 et 100 µg/kg. La répétabilité pour la plupart des pesticides (> 99%) sur différents thés se situe à moins de 20%, comme l'exige SANTE.

Pour la méthode LC-MS/MS, le nombre de composés ayant atteint des taux de récupération de 70 à 120% variait de 172 (86%) à 188 (94%), pour GT, OT à 100 µg/kg et WT à 100 µg/kg, respectivement. Les résultats montrent que cette méthode donne une grande précision, même si cette méthode utilise la courbe d'étalonnage et n'utilise pas d'étalon isotopique interne.

De même, la méthode GC-MS/MS donne également une grande précision allant de 164 substances (83,2% pour OT à 10 µg/kg) à 190 (96,4% pour BT à 100 µg/kg), dont la gamme de récupération est de 70 - 120%. De plus, il n'y avait pas de composé à récupérer inférieur à 30%. Malgré la différence d'EM entre les thés, il est clair que l'utilisation de courbes adaptées à la matrice préparées à partir de différents types de thé a compensé les EM.

5.1.3 LOQ

En général, les deux méthodes sont très sensibles, avec plus de 200 (100%) et 189 substances (95,9%) pour LC-MS/MS et GC-MS/MS, respectivement, avec des LOQ de 10 µg/kg ou moins. Par conséquent, ces composés répondent à une LMR par défaut général de 10 µg/kg (CE, 396/2015). Huit composés avec une LOQ de 50 µg/kg provenaient tous de la méthode GC-

MS/MS. La plupart d'entre eux sont inférieurs aux réglementations européennes en matière de LMR, à l'exception de la bioalléthrine et de la fluridone. Il y avait 395 composés (représentant 99,5%) qui respectaient les réglementations de l'UE en matière de LMR.

De plus, la sensibilité des 27 pesticides simultanément par les deux méthodes a été comparée. Les résultats ont montré que la méthode LC-MS/MS a une sensibilité de 2 à 50 fois plus élevée que GC-MS/MS, à l'exception de six composés ayant les mêmes LOQ.

5.2 Résidus de pesticides dans le thé

Cent six échantillons de thé ont été analysés et évalués pour 397 résidus de pesticides selon les normes européennes (EC, 396/2015). Dans ce document, l'échantillon de thé est considéré suspicieux lorsque le résidu de pesticide dépasse la LMR de l'UE pour chaque composé. L'UE a fixé les LMR pour 486 pesticides et leurs métabolites dans les produits à base de thé (EU MRLs). En outre, une LMR par défaut générale de 0,01 mg/kg s'applique lorsqu'un pesticide n'est pas explicitement (EC, 396/2015).

Sur 106 échantillons, 33 (31,1%) échantillons ne contenaient aucun résidu de pesticide détectable (concentration de pesticide inférieure à la LOQ), 47 échantillons (44,3%) avaient des résidus de pesticide conformes détectables (concentration de pesticide inférieure à la LMR) et 26 échantillons (24,6%) contenait au moins un résidu unique en violation de la LMR UE.

Parmi 77 échantillons de pesticides détectés, 57 échantillons au total contenaient deux résidus de pesticides ou plus (78,1%), comparativement à 16 échantillons (21,9%) avec un seul résidu de pesticide. On peut expliquer que les pesticides sont souvent un mélange de nombreux ingrédients et/ou l'habitude d'utiliser de nombreux pesticides différents dans un champ. De plus, dix-sept échantillons (16%) contenaient plus de 10 pesticides équivalents aux études précédentes (Huang et al., 2019; Lozano et al., 2012).

En ce qui concerne les échantillons de détection de pesticides, tous ceux de thé oolong (OT) présentent des pesticides (100% ; n = 17), suivis par ceux de thé vert (GT) avec 74,1% (n = 38), de thé noir (BT) avec 64,3% (n = 42), de Pu'ehr (PT) avec 33,3% (n = 3) et enfin de thé blanc (WT) avec 16,7% (n = 6). En termes de dépassement des valeurs guides dans les échantillons (au moins un pesticide dont la concentration est supérieure à la LMR), le type de thé qui en présente le plus grand nombre est le thé vert (14 échantillons), suivi du thé oolong (7 échantillons) et du thé noir (5 échantillons). En revanche, WT et PT n'ont aucun échantillon dans ce cas, probablement en raison de la petite taille de l'échantillon.

Dans 27 échantillons de thé bio, 20 échantillons (74%) étaient exempts de pesticides, et 7 échantillons (26%) détectés des résidus de pesticides avec des concentrations allant de 4,6 (éthion) à 70,2 µg/kg (cyperméthrine). Tous les échantillons sont contaminés par un seul pesticide et sont inférieurs au seuil de LMR. Ainsi, on peut considérer que les échantillons de thé bio sont sans danger pour les consommateurs.

Sur 397 composés validés, 71 pesticides différents au total ont été détectés dans cette enquête, parmi lesquels 16 composés sont fréquemment détectés dans le thé. Lambda-cyhalothrine, avec des concentrations comprises entre 2,2 à 1252,9 µg/g, a été le plus détectés (31 échantillons) et insecticide (14 échantillons). Parmi les 71 pesticides détectés, 29 sont considérés comme approuvés et 42 non approuvés par la Commission européenne (EC No. 1107/2009). Les groupes

les plus détectés sont les néonicotinoïdes, les pyréthroïdes synthétiques et les fongicides triazolés.

Concernant l'origine des thés, ceux de Taïwan apparaissent comme étant les plus contaminés par les pesticides avec 83,3% (n = 10) suivis par ceux de Chine (73,7%, n = 19), du Vietnam (64,7%, n = 34) et de l'Inde (55%, n = 20). En termes de résidus moyens par échantillon, le chiffre le plus élevé concerne la Chine, avec 918 µg/kg suivi par Taïwan (460 µg/kg), le Vietnam (298 µg/kg) et l'Inde (82 µg/kg). Il a montré que les échantillons indiens étaient les moins contaminés par les pesticides (concernant les échantillons de pesticides détectés, la concentration moyenne de résidus et le nombre de composés détectés) car la plupart des échantillons étaient du thé noir. Avec les mêmes pratiques agricoles, la Chine et Taïwan ont un nombre comparable de composés détectés, avec respectivement 40 et 39 composés, dont 22 sont les mêmes. En raison de la petite taille de l'échantillon (n < 4, autre) ou de l'absence d'informations (inconnue), les échantillons restants (n = 21) n'ont pas suffisamment de données pour faire une comparaison par origine.

5.3 Conclusion

Au total, 395 composés (représentant 99,5%) respectaient les réglementations de l'UE en matière de LMR. Le nombre de composés qui ont atteint des taux de récupération de 70 à 120% varie de 172 (86%) à 188 (94%) pour LC-MS/MS, et de 164 (83,2%) à 190 unités (96,4%) pour GC-MS/MS respectivement. Sans EM, la LC-MS/MS peut être utilisée par étalonnage avec solvants pour la quantification. Dans le cas de la GC-MS/MS, pour surmonter les EM, des courbes d'étalonnage adaptées à la matrice sur une matrice vierge mixte (y compris WT, GT, OT et BT) ont été utilisées pour toutes sortes de thés. Les précisions intra-journalières étaient inférieures à 19,6%. De bonnes relations linéaires ont été observées avec les coefficients de corrélation R^2 ≥ 0,99 pour tous les composés.

Le taux de conformité global pour les résidus de pesticides dans les 106 échantillons de thé de cette enquête ciblée était de 75,4%. Pour les échantillons détectés de pesticides, 57 échantillons au total contenaient deux résidus de pesticides ou plus (78,1%) comparativement à 16 échantillons (21,9%) avec un seul résidu de pesticide (moyenne de 6,4 pesticides par échantillon). 26 échantillons dépassaient les valeurs autorisées avec 43 résidus de pesticides au-dessus des valeurs guides, dont aucun thé biologique. Le thé oolong possède le plus grand nombre d'échantillons de pesticides détectés, avec 100% (n = 17). Viennent ensuite le thé vert avec 74,1% (n = 38), le thé noir avec à 64,3% (n = 42), le Pu'Ehr avec 33,3% (n = 3) et enfin le thé blanc avec 16,7% (n = 6). Comparé aux thés verts et oolong, le thé noir est le moins contaminé par les pesticides, sans doute en raison des températures élevées lors de la transformation qui pourraient contribuer à la décomposition d'un grand nombre de pesticides. Les pesticides les plus fréquemment détectés appartiennent aux néonicotinoïdes, aux pyréthroïdes synthétiques et aux fongicides à base de triazole. En termes d'origine des thés dans cette étude, les échantillons de Taïwan apparaissent comme les plus contaminés par les pesticides avec 83,3% (n = 10), suivis par ceux de Chine (73,7%), du Vietnam (64,7%) et de l'Inde (55%).

Chaptire 6. Conclusions et perspectives

6.1 Conclusions

La première partie de la thèse a porté sur l'élimination des effets de matrice dans les feuilles de thé vertes en combinant l'extraction QuEChERS (rapide, facile, bon marché, efficace, robuste et sûre) et le nettoyage en mode mixte SPE (extraction en phase solide). Différents adsorbants, tels que l'octadécyle, le noir de carbone graphité (GCB) et les amines primaires et secondaires (PSA), ont été utilisés dans la préparation des échantillons de thé vert, ce qui a permis d'analyser plusieurs centaines de pesticides avec des effets de matrice faibles et des taux de récupération élevés. Quelques résultats ont été obtenus comme suit :

- Une cartouche SPE C18 couplée à SPE GCB/PSA s'est avérée être la méthode de nettoyage la plus efficace. Ceci a permis de quantifier 225 résidus de pesticides, sur la base des courbes d'étalonnage des solvants (154 résidus utilisant UPLC-MS/MS et 71 résidus utilisant GC-MS/MS).
- Un volume de solvant d'élution de 20 mL (ACN/toluène, 3/1, v/v) a été choisi pour le nettoyage du SPE.
- Un volume restant de 1 mL a été choisi pour l'évaporation.
- Les méthodes analytiques ont été entièrement validées conformément à la SANTE/11945/2015 (UE) pour le thé vert. Les LOQ pour la plupart des pesticides (386/400 ou 96,5%) étaient inférieures à 10 µg/kg, *i.e.* inférieures à la LMR de l'UE (5-70 mg/kg).
- L'étalonnage adaptée à la matrice a été réalisée dans la plage de 1 – 200 µg/L et de 1 - 100 µg/L en LC-MS/MS et GC-MS/MS, respectivement avec R^2 > 0,99 pour tous les composés.
- Les écarts-types indicatifs (RSD_R, %) étaient inférieurs à 20% et les taux de récupération se situaient entre 70 et 120% pour la plupart des pesticides (supérieurs à 93% des couches).

Dans la deuxième partie, les effets de matrice pour 400 résidus de pesticides ont été étudiés et améliorés pour l'analyse de différents types de thés (blancs, verts, oolongs et noirs). Les résultats ont montré que :

- La combinaison de l'extraction QuEChERS suivi d'une purification en mode mixte SPE, avec réduction du volume d'injection s'est révélé être la procédure la plus efficace pour surmonter les effets de matrice.
- Plus de 190 pesticides (> 95% des 200) ont un effet de matrice dans une fourchette de ± 20% dans le cas de l'UPLC-MS/MS. Par conséquent, ils peuvent être quantifiés à l'aide de courbes d'étalonnage de solvant.
- Un total de 15 à 59,5% des 200 pesticides présentaient un effet de matrice moyen et fort pour GC-MS/MS, selon le type de thés, ce qui signifie que des courbes d'étalonnage adaptées à la matrice devraient être utilisées pour surmonter les effets de matrice.
- De plus, nous avons reconnu que les effets de matrice dans GC-MS/MS n'étaient pas seulement une amélioration du signal mais aussi une suppression.

Enfin, dans la troisième partie de ce travail, la validation de la méthode a été réalisée pour 4 types de thés dont le thé blanc, vert, oolong et noir. Par la suite, la méthode a été utilisée avec succès pour déterminer des résidus de pesticides dans 106 échantillons de thé. Les résultats sont les suivants :

- Dans presque tous les cas, le coefficient de détermination (R^2) était supérieur à 0,99, avec une concentration entre 0,5 et 100 µg/kg. Certains pesticides étaient hors de cette plage linéaire, de 1 à 100 µg/kg. Cependant, la sensibilité est toujours acceptable.
- Pour la méthode LC-MS/MS, le nombre de composés ayant atteint des taux de récupération de 70 à 120% variait de 172 (86%) à 188 (94%), pour GT, OT à 100 µg/kg et WT à 100 µg/kg, respectivement. Les résultats montrent que cette méthode donne une grande précision, même si elle utilise la courbe d'étalonnage et n'utilise pas d'étalon isotopique interne. Les substances à faible récupération (< 30%) étaient le thiophanate-méthyl (toutes sortes de thé), le chlorhydrazuron (OT), la carboxine et le pirotétramate (BT). Le thiophanate-méthyle est converti en carbendazime pendant l'extraction, ce qui entraîne une faible récupération (Singh et al., 2007). Cependant, la répétabilité de ces composés était acceptable (RSD ≤ 20%).
- De même, la méthode d'analyse par GC-MS/MS donne une grande précision allant de 164 substances (83,2% pour OT à 10 µg/kg) à 190 substances (96,4% pour BT à 100 µg/kg), dans la plage de récupération de 70-120%. Par ailleurs, il n'y a pas de composé à récupérer inférieur à 30%. Il semble donc clair que l'utilisation de courbes d'étalonnage adaptées à la matrice permet de compenser les effets de matrice.
- Au total, 26 échantillons de thé (24,5%) contenaient au moins une valeur de concentration en pesticides supérieure aux valeurs autorisées, avec 43 molécules de résidus de pesticides avec des concentrations supérieures aux valeurs guides. Le thé noir est le thé possédant le plus faible nombre de pesticides détectés et le nombre de résidus. Les thés bio, avec74% des échantillons ne contenant pas de pesticides, présentent pour 26% des résidus de pesticides conformes et sans danger pour les consommateurs. Les pesticides les plus fréquemment détectés sont les néonicotinoïdes, les pyréthrinoïdes synthétiques et les fongicides triazolés. En termes d'origine dans cette étude, les thés de Taïwan sont ceux les plus contaminés par les pesticides avec 83,3%, suivi par ceux de Chine (73,7%), du Vietnam (64,7%), et de l'Inde (Darjeeling) (55,0%).

En conclusion, une méthode exacte, précise et fiable a été validée selon SANTE/11945/2015 pour déterminer 397 résidus de pesticides (captafol, chlorothalonil et folpet instable) dans plusieurs types de thé, y compris les thés blancs, verts, oolong et noirs. Les limites de quantification (LOQ) pour presque tous les composés étaient égales ou inférieures à 10 µg/kg. Au total, 395 composés (représentant 99,5%) respectaient les réglementations de l'UE en matière de LMR. Le nombre de composés qui ont atteint des taux de récupération de 70 à 120% varie de 172 (86%) à 188 (94%) en UPLC-MS/MS, et de 164 (83,2%) à 190 (96,4%) en GC-MS/MS respectivement.

6.2 Perspectives

- Pendant la validation de la méthode, certains pesticides sont instables. Dans ce cas, des méthodes pourraient être développées individuellement, y compris la cyromazine, le

thidiazuron, l'hydraméthylnon, la pymétrozine, l'acéquinocyl, le captane, l'endrine aldéhyde, le captafol, le chlorothalonil et le folpet.

- Pour les préparations d'échantillons, le toluène a été utilisé pour éluer les pesticides de la cartouche SPE. Cependant, le toluène est un solvant très toxique pour la santé humaine et l'environnement. Par conséquent, d'autres expériences sont nécessaires pour remplacer ou réduire l'utilisation de ce solvant.
- L'effet de matrice en GC-MS/MS est beaucoup plus complexe que dans le cas de la LC-MS/MS. Il est possible que l'effet de matrice soit combiné à la fois par la suppression d'ions et par l'augmentation d'ions. Par conséquent, plus d'expériences sont nécessaires pour comprendre le mécanisme de l'effet de matrice dans GC-MS/MS.
- Cette méthode sera appliquée pour contrôler les résidus de pesticides dans le thé au Vietnam, contribuant à protéger la santé des consommateurs et à soutenir les exportations.