การวิเคราะห์อย่างรวดเร็วของสารกำจัดศัตรูพืชหลายกลุ่มในหอมหัวใหญ่ด้วยแก๊สโครมาโทกราฟีแทนเดมแมสสเปกโทรเมตรี

นางสาวธนัชพร เสมาทอง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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RAPID ANALYSIS OF MULTICLASS PESTICIDES IN ONION USING GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY

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Field of Study	Chemistry
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ธนัชพร เสมาทอง : การวิเคราะห์อย่างรวดเร็วของสารกำจัดศัตรูพืชหลายกลุ่มในหอมหัวใหญ่ด้วยแก๊สโครมาโทกราฟีแทนเดมแมสสเปกโทรเมตรี. (RAPID ANALYSIS OF MULTICLASS PESTICIDES IN ONION USING GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ณัฐชนัญ ลีพิพัฒน์ไพบูลย์, 184 หน้า.

การพัฒนาวิธีการตรวจวัดอย่างรวดเร็วด้วยเทคนิคแก๊สโครมาโทกราฟีแทนเดมแมสสเปกโทรเมตรี (GC-MS/MS) เพื่อระบุชนิดและปริมาณตรวจสารกำจัดศัตรูพืชที่ตรวจด้วยวิธีการ GC จำนวน 170 ชนิด คือกลุ่มออร์กาโนคลอรีน 45 ชนิด กลุ่มออร์กาโนฟอสเฟต 45 ชนิด กลุ่มออร์กาโนไนโตรเจน 70 ชนิด และกลุ่มไพรีทรอยด์ 10 ชนิดในหอมหัวใหญ่ การเตรียมตัวอย่างใช้การดัดแปรเทคนิค QuEChERS ด้วยบัฟเฟอร์ที่เหมาะสม โดยสกัดสารกำจัดศัตรูพืชจากตัวอย่างด้วย 0.5% กรดอะซีติกในอะซิโตไนไตรล์ตามด้วยการทำความสะอาดสารละลายสกัดด้วยการกระจายวัฏภาคของแข็ง $MgSO_4$ 150 มิลลิกรัม, PSA 50 มิลลิกรัม, alumina-neutral 50 มิลลิกรัม และ GCB 5 มิลลิกรัม ต่อมิลลิลิตรของสารละลายสกัด เปรียบเทียบการตรวจวัด ด้วยเทคนิค GC-MS/MS ใช้คอลัมน์ DB5MS ขนาด30 m x 0.25 mm, 0.25 μm กับเทคนิค LP-GC-MS/MS ที่ใช้คอลัมน์วิเคราะห์ชนิด DB5MS ขนาด10 m x 0.53 mm, 0.1 μm ต่อกับคอลัมน์ที่ไม่มีสารเคลือบ ขนาด 3 m x 0.15 mm ที่ปลายทางเข้า ภายใต้ภาวะที่เหมาะสมเทคนิค LP-GC-MS/MS จะใช้เวลาตรวจวัดเพียง 9 นาที เร็วกว่า GC-MS/MS มากกว่า 4 เท่า (33 นาที) ค่าร้อยละการคืนกลับเฉลี่ยของสารทุกชนิดอยู่ระหว่าง 70-120 และค่าเบี่ยงเบนมาตรฐานสัมพัทธ์ของการทำซ้ำ 5 ครั้งน้อยกว่า 20% ที่ระดับความเข้มข้นที่เติมลงไป 0.01, 0.05 และ 0.1 มิลลิกรัมต่อกิโลกรัม ความเข้มข้นต่ำสุดที่สามารถตรวจวัดได้และขีดจำกัดต่ำสุดของการตรวจวัดเชิงปริมาณที่ 0.003-0.005 มิลลิกรัมต่อกิโลกรัมและ 0.01 มิลลิกรัมต่อกิโลกรัมตามลำดับ วึ่งค่าเหล่านี้ต่ำกว่าค่า MRLs ที่สหภาพยุโรปกำหนด ที่ 0.01 มิลลิกรัมต่อกิโลกรัม ผลการวิเคราะห์ทั้งสองวิธีไม่มีความแตกต่างกัน แต่เทคนิค LP-GC-MS/MS ได้ปริมาณงานมากขึ้น (ความเร็วมากกว่า 4 เท่าเมื่อเทียบกับ GC-MS/MS) และลดค่าใช้จ่าย เมื่อนำมาใช้ในการตรวจวัดตัวอย่างหอมหัวใหญ่จริงจำนวน 40 ตัวอย่างโดยใช้วิธี GC-MS/MS และ LP-GC-MS/MS ผลสอดคล้องกันโดยตรวจพบสารกำจัดศัตรูพืช 3 ชนิดใน 4 ตัวอย่าง

ภาควิชา……...เคมี…….. ลายมือชื่อนิสิต……..
สาขาวิชา…….เคมี…….. ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....
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THANUTCHAPORN SEMATHONGANG: RAPID ANALYSIS OF MULTICLASS PESTICIDES IN ONION USING GAS CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY. ADVISOR: ASST. PROF. NATCHANUN LEEPIPATPIBOON, Dr.,rer.nat, 184 pp.

A rapid method using gas chromatography–tandem mass spectrometry (GC-MS/MS) for simultaneous identification and quantification of 170 amenable-GC pesticides including 45 of organochlorines, 45 of organophosphates, 70 of organonitrogens and 10 of pyrethroids in onion was developed. The modified buffered-QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) approach was optimized for sample preparation. Pesticides were extracted/partitioned from the samples with acetonitrile containing 0.5% acetic acid, followed by cleanup using dispersive solid phase extraction (d-SPE) with 150 mg $MgSO_4$, 50 mg primary secondary amine (PSA), and 50 mg alumina neutral (Al-N) and 5 mg graphitize carbon black (GCB) per mL of extract. For comparison purposes conventional GC-MS/MS experiments were performed on a DB-5 30m×0.25mm×0.25µm analytical column. LP-GC-MS/MS analysis was performed on a DB-5 10m×0.53mm×1µm analytical column connected to a 3m×0.15mm non-coated restriction capillary at the inlet end. Under the optimized conditions the analysis time was reduced to 9 min with the LP-GC-MS/MS approach which corresponds to an almost threefold gain in speed versus the conventional GC-MS/MS (33 min). The average recoveries of all analytes were between 70 and 120% with relative standard deviations (RSDs) lower than 20% (n=5) at 0.01, 0.05, and 0.1 mg kg^{-1} spiking levels. The limits of detections (LODs) and limits of quantitation (LOQs) of all analytes were 0.003-0.005 mg kg^{-1} and 0.01 mg kg^{-1}, respectively. These values were far below the MRLs established by the European Union (at 0.01 mg kg^{-1}), apparent from the results, the overall analytical performances were comparable for the two GC–MS/MS methods, but the LP-GC-MS/MS was high sample throughput (approximately 4-fold gain in speed *vs.* tradition GC-MS/MS) and cost-effective. In order to assess its applicability to the analysis of real samples, 40 onion samples previously determined using conventional GC-MS/MS and LP-GC-MS/MS. The results obtained with the compared techniques showed that 3 pesticides were detected in 4 samples.

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LIST OF ABBREVIATIONS

%CV	percent coefficient of variation
%Re	percentage recovery
%RSD	percentage of relative standard deviation
%RSDr	percent of relative standard deviation for repeatability
$\%RSD_R$	percent of relative standard deviation for reproducibility
mg L^{-1}	milligram per liter
mg kg^{-1}	milligram per kilograms
1° ion	primary product ion or quantitative ion
2° ion	secondary product ion or qualitative ion
MeCN	acetonitrile
Al-N	alumina-neutral
AOAC	Association of Official Analytical Chemists
C18	octadecyl
°C	degree Celsius
cal	calculation
Conc.	concentration
crit	critical
d-SPE	dispersive solid phase extraction
EI	electron ionization
FAPAS	The Food and Environment Research Agency
GCB	graphitized carbon black
GC	gas chromatography
GC-MS	gas chromatography with mass spectrometry

GC-MS/MS	gas chromatography with tandem mass spectrometry
LLE	liquid -liquid extraction
LODs	limit of detections
LOQs	limit of quantifications
LP-GC-MS/MS	low pressure gas chromatography coupled with tandem mass spectrometry
m/z	mass per charge ratio
MRM	multiple reaction monitoring
MRLs	Maximum residue limits
%ME	%matrix effect
MW.	molecular weight
NaoAc	sodium acetate
NH_2	aminopropyl
OCs	organochlorine
OPs	organophosphate
ONs	organonitrogen
PSA	primary secondary amine
PT	proficiency testing
QuEChERS, QuE	Quick Easy Cheap Effective Robust Safe
R^2	coefficient of determination
t_R	retention time
sig	significant difference
SD	standard deviation
SD_r	standard deviation for repeatability
SD_R	standard deviation for reproducibility

S/N	signal to noise ratio
SPE	solid phase extraction
TIC	total ion chromatogram
V	volt

CHAPTER I

INTRODUCTION

1.1 Problem definitions. [1, 2, 3]

Pesticides are widely used during the production of food products to prevent diseases in plants, the damage caused by insects and pests, or to control the growth of weeds and fungi. Pesticides are frequently applied before and after harvesting to prolong storage life and improve quality of food produce. Besides their positive effect, they also pose various health risks to consumers. Therefore, the concentrations of pesticide residues have to be monitored in food commodities, this includes vegetable and fruit produce.

Onion is rich in sulfur compounds and other sulfur derivative. These are the most difficult types of matrix to influence the detection of pesticides in onion. The use of GC sepaetions, flame photometric detection (FPD), electron-capture detection (ECD) and mass spectrometry (MSD) may not be selective enough to trace all levels of residues in this matrix.

Due to food safety reasons, the European Union (EU) established the maximum residues levels (MRLs) for most pesticide residues in onion at 0.01 mg kg^{-1}. Therefore, the research activities of pesticide residue analysis lead towards the development of more efficient multiresidue analytical methods. [1]

QuEChERS is a sample preparation approach that provides high sample throughput and high quality results for wide range of GC-amenable pesticides. Theses approaches have been used and modified in many laboratories to provide high-quality of results, save time, cost, and labor, and other beneficial features. In the other hand, not only a stringent sample preparation method, but also a high selective and sensitive determination method becomes necessary in order to meet all regulatory requirements.

Gas chromatography tandem mass spectrometry (GC-MS/MS) is a powerful tool for analysis of various pesticides at low level. Triple quadrupole mass spectrometry allows for operating in multiple reaction monitoring (MRM) mode, resulting in reduction or elimination of matrix interferences that limit the accuracy and detection limit of the result, especially in complicated matrices. Therefore, to

meet the requirement of MRLs, this necessitates developing and evaluating a simple, rapid, reliable and accurate method for the analysis of multiclass pesticide residues in onion matrices, including a wide range of pesticide families by using GC–MS/MS.

1.2 Pesticides [2]

A pesticide is any chemical which is used in the production of crops by man to eliminate the threat of infection. The pests may be insects, plant diseases, fungi, weeds, snails or any other organisms that hinder the growth of crop productivity. Pesticides are often referred to according to the type of pest they control, because all pesticides are toxic or poisonous, they are potentially hazardous to humans (mutagenic, carcinogenic, etc.), animals, other organisms, and the environment. Pesticides include a wide range of products. There are many types of pesticides that are listed here such as:

Insecticides are chemicals used to control insects.

Miticides and Acaricides are chemicals used to control mites and ticks.

Fungicides are chemicals used to control fungi which cause molds, rots and plant diseases.

Herbicides are chemicals used to control weeds or unwanted plants.

Rodenticides are chemicals used to control rats, mice, bats, and other vermin.

Nematicides are chemicals used to control nematodes.

Molluscicides are chemicals used to control snails and slugs.

On the other hand, pesticides are often grouped into "families" because they share similar chemical properties, or they act as pest control in the same way. A pesticide product may have active ingredients from more than one chemical family. There are several types of pesticides in this family, depending on the exact chemicals used.

Organochlorines

Organochlorines are controls pests by disrupting nerve-impulse transmission. They are persistent in soil, food, and in human and animal bodies and does not breakdown quickly. They can accumulate in fatty tissues. Traditionally used for insect and mite control, but many are no longer used due to their ability to remain in the environment for a long time. Organochlorines were used in the past, but many have been removed from the market due to their health and environmental effects and their persistence e.g. DDT, chlordane, aldrin, endrin, lindane.

Organophosphates

Organophosphates usually made from phosphoric acid. Most of organophosphates are insecticides. They are control pests by acting on the nervous system with a few exceptions, most are highly toxic. Organophosphates are used because they are less persistent (breakdown faster) in soil, food or feed for animals than other families, such as organochlorine pesticides e.g. chlorpyrifos, pirimiphos methyl, parathion.

Carbamates

Introduced in the 1950s, and similar to organophosphate pesticides, includes insecticides, herbicides and fungicides but they are control pests by acting on the nervous system (interfere with nerve-impulse transmission by disrupting the enzyme (cholinesterase) that regulates acetylcholine (a neurotransmitter). In general, are less persistent in the environment than the organochlorine family. The health hazard to humans and animals are mild with herbicides and fungicides, while greater with insecticides e.g. carmaryl, methomyl, carbofuran, propham.

Pyrethroids (synthetic)

Pyrethroids were developed as a synthetic version of the naturally occurring pesticide pyrethrin, which is found in chrysanthemums. They are stable in sunlight, but do not degrade quickly. The health hazard to humans and animals are stimulates

nerve cells and eventually causes paralysis e.g. Cyhalothrin, cypermethrin, permethrin.

1.3 Onion [3]

The onion (Allium cepa Linn.) is a member of the pungent *Allium* genus of the lily family, and includes garlic, leeks, shallots, scallions, and chives (Fig 1.3). Onion is a good source of nutrients consisting of protein, carbohydrates, sugar, soluble and insoluble fiber, fatty acids, essential amino acids, flavonoids, quercetin, vitamins, and various minerals (Table 1.1). For all varieties of the onion family, the more quercetin and flavonoids they contain are shown to be an antioxidant and anticancer, anti-inflammatory, reduce the risk of heart disease, lower blood cholesterol level, diabetes, osteoporosis, and other diseases. Thus, these health-promoting effects are originated from nutrients containing compositions in onions. For these possible reasons, onions are being used as diet ingredients in various foods.

Table 1.1 Medical properties and health effects [4]

Raw Onions **Nutritional value per 100 g (3.5 oz)**	
Energy	**166 kJ (40 kcal)**
Carbohydrates	9.34 g
Sugars	4.24 g
Dietary fiber	1.7 g
Fat	0.1 g
saturated	0.042 g
monounsaturated	0.013 g
polyunsaturated	0.017 g
Protein	1.1 g
Water	89.11 g
Vitamin A equiv.	0 μg (0%)
Thiamine (Vit. B1)	0.046 mg (4%)
Riboflavin (Vit. B2)	0.027 mg (2%)
Niacin (Vit. B3)	0.116 mg (1%)
Vitamin B6	0.12 mg (9%)
Folate (Vit. B9)	19 μg (5%)
Vitamin B12	0 μg (0%)

Vitamin C	7.4 mg (12%)
Vitamin E	0.02 mg (0%)
Vitamin K	0.4 µg (0%)
Calcium	23 mg (2%)
Iron	0.21 mg (2%)
Magnesium	0.129 mg (0%)
Phosphorus	29 mg (4%)
Potassium	146 mg (3%)
Sodium	4 mg (0%)
Zinc	0.17 mg (2%)

Source: USDA Nutrient database

Major components in onion are sulfur-compounds, when the bulb is crushed the sulfur matricies strongly interfere with the determination of pesticide residues. Onions have volatile compounds such as thiosulfonates and organosulfur compounds (Fig 1.1). The thiosulfinates, volatile sulfur compounds, which are responsible for their characteristic pungent aroma and strong flavour of the onion. However, these compounds are very unstable and give rise to transformation within the product. Other non - volatile compounds are sapogenins and flavonol glucoside (Fig 1.2).

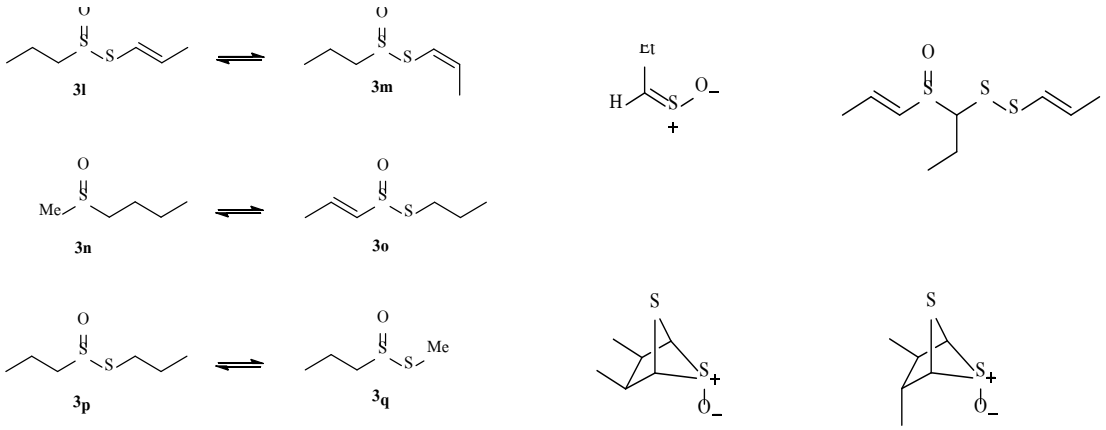
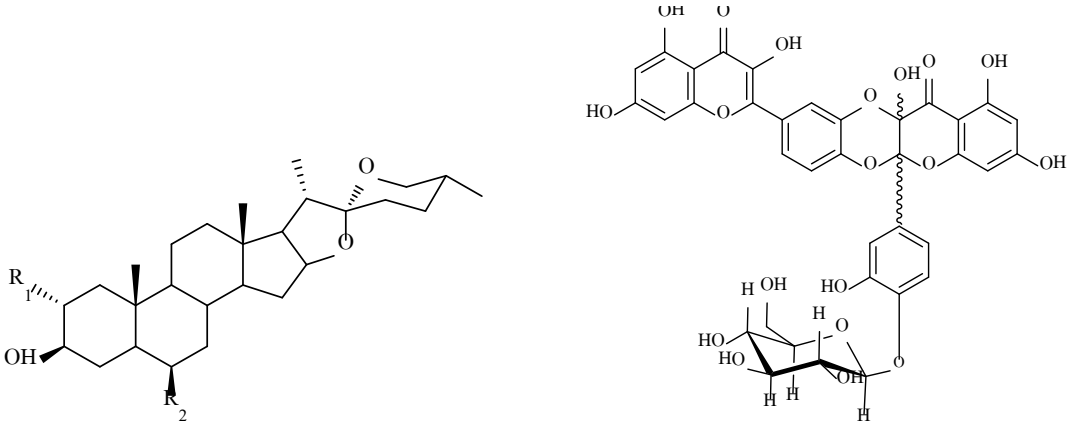


Figure 1.1 Volatile compounds (a) thiosulfonates, (b) organosulfur compounds [5]



(a) (b)

Figure 1.2 Non-volatile compounds (a) sapogenins, (b) flavonol glucoside [5]

Figure 1.3 Onion [4, 6]

1.4 Regulation

MRLs are commonly set by individual countries, such as United States, the European Union, Japan, and China. In Europe, recent EU legislation has been approved banning the use of highly toxic pesticides including those that are carcinogenic, mutagenic or toxic to reproduction. Reducing the use of pesticides and choosing less toxic pesticides may reduce risks placed on society and the environment from pesticide use. New pesticides are being developed, including biological and botanical derivatives and alternatives that are thought to reduce health and environmental risks. Though pesticide regulations differ from country to country, pesticides and products on which they were used are traded across international borders. Several European Union (EU) directives have set different MRLs for pesticide residues in vegetables and fruits at a low microgram per kilo level. The aim is to protect consumer and animal health, and the environment. These help to increase consumer confidence in the health, safety and quality of foods. However, Regulation EC/396/2005 [1], brought into force on the 1st Semtember 2008, defines a new harmonized set of rules for pesticide residues. The new regulation requires sensitive and high selective methods for the measurement of pesticide residues.

Table 1.2 shows the specified maximum levels which apply to the edible part of onion with Commission Regulation (EC) No. 396/2005.

Table 1.2 The maximum levels of certain contaminants in onion that comply with Commission Regulation (EC) No. 396/2005. [7]

Compound	**MRL (mg/kg)**
Alachlor	0.1
Aldrin and Dieldrin	0.01
Atrazine	0.05
Azoxystrobin	10
Benalaxyl	0.2
Benfluralin	0.05
Bifenthrin	0.05
Bromophos-ethyl	0.05

Bromopropylate	0.05
Bupirimate	0.05
Buprofezin	0.05
Carfentrazone-ethyl	0.01
Chlordane	0.01
Chlorfenson	0.01
Chlorpropham	0.05
Chlorpyrifos	0.2
Chlorpyrifos-methyl	0.05
Chlorthal-dimethyl	1.0
Clomazone	0.01
Cyfluthrin	0.02
Cyhalofop-butyl	0.02
Cypermethrin	0.1
DDT	0.05
Deltamethrin	0.1
Diazinon	0.05
Dichlobenil	0.05
Dichlorprop	0.05
Dichlorvos	0.01
Diclofop	0.1
Difenoconazole	0.05
Diniconazole	0.05
Disulfoton	0.02
Endrin	0.01
Ethalfluralin	0.02
Ethoprophos	0.02
Etofenprox	0.5
Fenbuconazole	0.05
Fenoxaprop	0.1
Fenpropathrin	0.01
Fenpropimorph	0.05
Fenvalerate	0.02
Fipronil	0.02
Flusilazole	0.02
Flutolanil	0.05
Heptachlor	0.01
Hexachlorobenzene	0.01
Hexaconazole	0.02
Imazalil	0.05
Iprodione	0.2
Kresoxim-methyl	0.05

Lambda-Cyhalothrin	0.2
Malathion	0.02
Mepronil	0.05
Metalaxyl	0.5
Methacrifos	0.05
Metholachlor	0.05
Methoxychlor	0.01
Metribuzin	0.1
Molinate	0.05
Oxadiazon	0.05
Oxadixyl	0.01
Oxyfluorfen	0.05
Paclobutrazol	0.02
Parathion	0.05
Parathion-methyl	0.02
Penconazole	0.05
Pendimethalin	0.05
Permethrin	0.05
Phorate	0.05
Picolinafen	0.05
Pirimicarb	0.5
Pirimiphos-methyl	0.05
Prochloraz	0.05
Procymidone	0.2
Profenofos	0.05
Propachlor	2.0
Propham	0.05
Propiconazole	0.05
Pyraflufen-ethyl	0.02
Pyrazophos	0.05
Pyriproxyfen	0.05
Quinalphos	0.05
Resmethrin	0.1
Tebuconazole	0.05
Tecnazene	0.05
Terbufos	0.01
Thiobencarb	0.1
Tolclofos-methyl	0.05
Tri-allate	0.1
Triadimefon and triadimenol	0.5
Triazophos	0.01
Trifloxystrobin	0.02

Trifluralin	0.5
Vinclozolin	1.0

Pesticides Web Version - EU MRLs

If pesticides are not included in any mentioned, the European Union (EU) established that the default MRLs for most pesticide residues is 0.01 mg kg^{-1}.

1.5 Literature Review (Table 1.3)

The analytical methods for determining pesticides in fruits and vegetables require extraction of pesticide residues from the matrix. This frequently involves the use of conventional techniques, such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Typical disadvantages of LLE include its large consumption of solvents which are laborious and time consuming. SPE needs less solvent than does LLE and has proved to be an important tool for the isolation and preconcentration.

Original QuEChERS (quick, easy, cheap, effective, rugged and safe) [8] and two versions of buffered-QuEChERS [9, 10, 11] sample preparation approaches have been introduced for the analysis of pesticide residues in fruits and vegetables and further extended in other foods. Since the development and publication of the method by Anastassiades and Lehotay, et al in 2003, QuEChERS has been gaining significant popularity in terms of sample preparation and a large number of validation and recovery experiments have also showed that QuEChERS is a reliable method. Consequently, the method has already been accepted by the international community of pesticide residues analysis and it has appeared as the AOAC office method in 2007, [12] has analyzed 20 pesticides in grapes, orange and lettuce by chromatographic separation, followed by mass selective detector (GC-MSD) and liquid chromatography tandem mass spectrometry (LC-MS/MS) were all applied for the analysis. The limits of quantification (LOQ) were lower than 0.01 mg/kg. Therefore, many scientists used QuEChERS extraction method for estimating pesticide residues, Nguyen et al. 2008 [13] determined 107 pesticides in cabbage, Mezoue et al. 2009 [14] estimated 2 pesticide residues in pepper by using gas chromatography mass mass spectrometry and gas chromatography tandem mass spectrometry (GC-MS/MS), respectively.

Chromatographic methods are widely used for analytical separation, identification and quantification of pesticides such as a flame photometric detector (FPD), electron capture detector (ECD), GC-MS, GC-MS/MS, liquid chromatography (LC-MS), and LC-MS/MS. [15, 16, 17]

In terms of GC-analysis, typical GC-MS analyses for pesticides with long analytical column (30 m), generally take >30 min runtime per sample. In recent years, the development of GC has focused on faster analysis in routine monitoring within laboratories. With respect to fast GC, the main focus is on the use of low pressure (LP), commercially known as rapid-MS, which is an interesting approach to speed up the analysis by a relatively short (10 m) mega bore (0.53 mm i.d.) column is used as the analytical column. Arrebola et al. [18] developed and evaluated for the fast analysis of 72 pesticide residues in cucumber, tomato and pepper by method based on LLE using GC separation between conventional GC-MS/MS and LP-GC-MS/MS. The different pesticides were recovered at rate of 70.3-126.9% with an LOD value ranging from 0.1 to 10 µg/kg. LOQ values of the method were found to be 0.2-22.0 µg/kg. Moreno et al. [19] showed applicability of the LP-GC-ITMS/MS method for analysis 65 pesticide residues in fat matrices (avocado) at diffent spiking levels, where recoveries were found to be between 70 and 110% with RSD values lower than 19%. The limit of quantification ranged from 0.04 to 8.33µg/kg.

Recently, Koesukwiwat et al. [20] developed a method of fast GC using the sample throughput of the combination of QuEChERS sample preparation technique followed by LP-GC/MS-TOF in fruits and vegetables (Orange, tomato, strawberry, lettuce and potato). The recovery rates ranged from 70 to 120% with limit of detection (LOD) value of the method were <5 ng/g.

There are several techniques to isolate pesticides from onion matrices, Ueno et al. [21] developed a method for determining 41 organophosphorus pesticide residues by extracting and cleaning up with Gel permeation chromatography (GPC) technique followed by pulsed-FPD. Zhang et al. [22] developed 16 herbicides in onion based on preventing formation of sulfur-compounds by microwave-assisted heating and cleaning up with by SPE analysed by GC-MS. Rodrigues et al. [23] evalulated 5

pesticides from onion by matrix solid phase dispersion (MSPD) with the determination by LC-ESI-MS/MS, However, these methods are time and labor consuming, and require a lot of disposable materials (solvent, SPE materials, etc.), which reduce laboratory productivity.

1.6 Purpose of the study

To meet the demand of a quick, easy, reliable, effective and safe sample preparation for complex samples like onion, a QuEChERS method was the most frequently used sample preparation approach for fruits and vegetables in pesticide residue analysis worldwide, as reviewed and described in many internation texts and articles providing high recoveries of pesticides. On the other hand, tandem mass spectrometry detection was used because of the high separation power, sensitivity, selectivity, identification and improved the detection limit.

The aim of this study was to devise and validate a simple and efficient method for the analysis of 170 pesticides including organochlorines, organophosphates, organonitrogens and pyrethroids in onion extracts. These pesticides were commonly found in routine analysis and were chosen from the list of controlled pesticides. The acetate-buffered QuEChERS method was modified to efficiently remove sulfur interferences and to obtain acceptable analytical results for the majority of analytes in the method validation. GC–triple quadrupole mass spectrometry (QQQ) conditions were optimized to accommodate a variety of pesticides and provide reliable quantitation and identification results. In addition the aim to obtain LOQs significantly lowers in comparison to MRL values.

Therefore, speeding-up analysis in gas chromatography is required to reduce analysis time and improves detection limits in routine analytical laboratories by using LP-GC. There are possibilities to shorten time by improving analysis times and sensitivity. The results obtained by this approach were compared to those obtained using conventional capillary columns of GC-MS/MS and LP-GC-MS/MS.

Table 1.4 Literature of extraction method and detection methods for pesticides analysis in onion.

Matrix	Analyte	Column	Sample preparation	Detection	Sensitivity	Reference
Grape Orange Lettuce	20	DB-5MS 30 m × 0.25 mm, 0.25 µm C-18 15 cm x 3 m, 3 µm	AOAC QuEChERS	GC-MS LC-MS/MS	LOQ < 0.01 mg/kg	[12]
Cabbage	107	DB-5MS 30 m × 0.25 mm, 0.25 µm	QuEChERS	GC-MS	LOD = 0.002-0.1 mg/kg	[13]
Pepper	2	HP-5MS 30 m × 0.25 mm, 0.25 µm	QuEChERS	GC-MS/MS	LOD = 0.1-0.3 µg/kg	[14]
Cucumber Tomato Pepper	72	CP-sil 8 CB 10 m × 0.53 mm, 0.25 µm	LLE, Dichloromethane	GC-MS/MS LP-GC-MS/MS	LOD = 0.1-10 µg/kg	[18]
Avocado	65	CP-sil 8 CB 10 m × 0.53 mm, 0.25 µm	PLE GPC SPE	LP-GC-MS/MS	LOQ = 0.04-8.33 µg/kg	[19]
Orange Tomato Strawberry Lettuce Potato	150	Restex 10 m × 0.53 mm, 1.0 µm	QuEChERS	LP-GC-MS-TOF	LOD = 10-1000 ng/g	[20]

Table 1.4 Literature of extraction method and detection methods for pesticides analysis in onion.

Matrix	**Analyte**	**Column**	**Sample preparation**	**Detection**	**Sensitivity**	**Reference**
Onion Welsh onion	41	Rtx-OP 30 m × 0.32 mm, 0.5 µm	GPC	Plused-FPD	LOD = 0.002-0.01 mg/kg	[21]
Onion	16	DB-5MS 30 m × 0.25 mm, 0.25 µm	Microwave Acetonitrile/SPE	GC-MS	LOQ = 0.003-0.015 mg/kg	[22]
Onion	5	XTerra 50 x 3 mm, 3.5 µm	MSPD	LC-MS/MS	LOQ = 0.01-0.1 mg/kg	[23]
Onion	**170**	DB-5MS 30 m × 0.25 mm, 0.25 µm DB-5MS 10 m × 0.53 mm, 1.0 µm	**QuEChERS**	**GC-MS/MS** **LP-GC-MS/MS**	**LOQ = 0.005-0.01 mg/kg** **LOQ = 0.003-0.01 mg/kg**	**This work**

CHAPTER II

THEORY

2.1 QuEChERS method [24, 25, 26]

QuEChERS, which stands for Quick, Easy, Cheap, Effective, Rugged and Safe. The method is a fast, simple and effective alternative to conventional sample preparation for multiresidue pesticide analysis. QuEChERS employs a very short shake-extraction step, making it fast and less labor intensive. To reduce costs and speed up sample preparation, dSPE technique was developed. The Method for this analysis incorporates a simple acetonitrile water extraction facilitated by the addition of $MgSO_4$, which remove water from the sample and includes a liquid/liquid extraction with solvents. The extraction step is followed by a dispersive solid phase extraction that combines both a primary and secondary amine (PSA), and anhydrous $MgSO_4$ to remove fatty acids and reduce the remaining water in the extract. This method has already been widely accepted by the international community of pesticide residues analysis, it appeared as the AOAC official method in 2007.

Using QuEChERS, samples are prepared in 3 simple steps. Samples are first homogenized, then, extracted and portioned with an organic solvent typically acetonitriles are used as the extraction solvents, which are compatible with both GC and LC-MS analyses, and salt solution. The extracts are finally cleaned using the dSPE technique, the sorbent is added to an aliquot of the extract and a smaller amount of sorbent is used because only an aliquot of the sample is subjected to the clean up. This takes less time and uses less labor and lower amounts of solvent than the matrix solid-phase extraction. Often, the sample aliquot can be injected directly into a GC or HPLC system without further work up. For LC–MS analysis, it might be necessary to add formic acid to provide better MS sensitivity or for GC–MS analysis. If the instrument is not equipped with a programmable temperature vaporizer, evaporation of the supernatant with reconstitution in toluene might be needed.

2.2 Dispersive solid-phase sorbent (dSPE) [27]

Using the dSPE approach, the quantity and type of sorbent, can easily be optimized for different matrix interferences and difficult analytes, which effectively remove sugar, organic acid, lipids, proteins, pigment, sterols and excess water. The method now is widely accepted for many types of pesticide residue samples

2.2.1 Primary Secondary Amine (PSA)

PSA is a polymeric base sorbent that contains both primary and secondary amines as a weak anion exchanger sorbent with pKa 10.1-10.9. PSA has higher carbon content making it a more non-polar sorbent than NH_2 and thus a better choice for very polar compounds that retain strongly in NH_2 sorbent. It has a strong affinity and high capacity for removing fatty acids, sugars, organic acids and some polar pigments. The structure of PSA is show in figure 2.1.

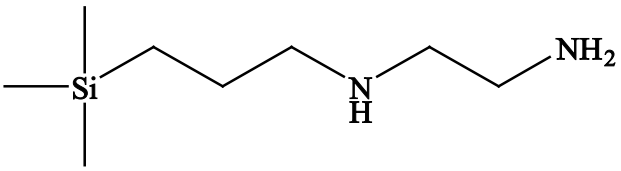


Figure 2.1 The chemical structure of PSA.

2.2.2 Aminopropyl (NH_2)

NH_2 is a polar sorbent, like silica, it can utilize both hydrogen bonding and anion exchange with different selectivity for acidic or basic analytes. The pH range is 2-8, the majority of functional groups are positively charged (shown in Figure 2.2). NH_2 is a weak anion exchanger because it is a quaternary amine sorbent that is always charged and it is therefore a better sorbent choice for the retention of very strong anions, such as sulfonic acids and it can be used for non-polar isolations from polar samples.

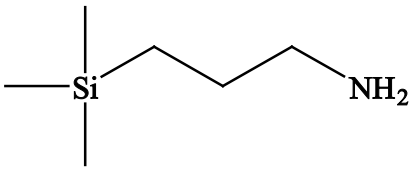


Figure 2.2 The chemical structure of NH_2

2.2.3 Octadecyl (C18)

C18 is the most common hydrophobic silica-based bonded phase, with the long hydrocarbon chain. It is the most popular dSPE sorbent because of; its extremely retentive nature for non-polar compounds, which suggests its use for removing of non polar interferences such as fat, whilst it retains most organic analytes from aqueous matrices (shown in figure 2.20).

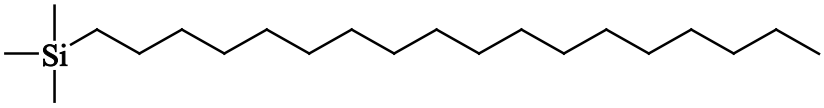


Figure 2.3 The chemical structure of C18

2.2.4 Alumina-neutral (Al-N)

Al-N sorbents are a highly surface active, neutral (with 40 μm particle size) that can adsorb molecules by interaction with the aluminum metal center, hydrogen bonding with the surface hydroxyl groups, surface allows interaction with heteroatoms compounds (e.g. N, O, P, S), with an electron-rich and interaction the π-electrons of aromatic hydrocarbon.

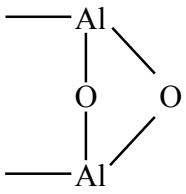


Figure 2.4 The chemical structure of Al-N.

2.2.5 Graphitized carbon black (GCB)

GCB sorbents have a strong affinity towards planar molecules and can isolate and remove pigments such as chlorophyll, carotinoids and sterols commonly present in foods and natural products.

2.3 Mass spectrometry

Mass spectrometers can be divided into three fundamental parts (Figure 2.5), an ion source that produces a beam of particles that is characteristic for the sample, an analyzer or mass filter that separates particles based on their mass, and a detector which collects and characterizes the separated ion components, useable signals are generated and recorded by a computer system.

The computer displays the signals graphically as a mass spectrum showing the relative abundance of the signals according to their m/z ratio. MS technique can provide both qualitative (structure) and quantitative (molecular mass or concentration) information on analyte molecules after their conversion to ions.

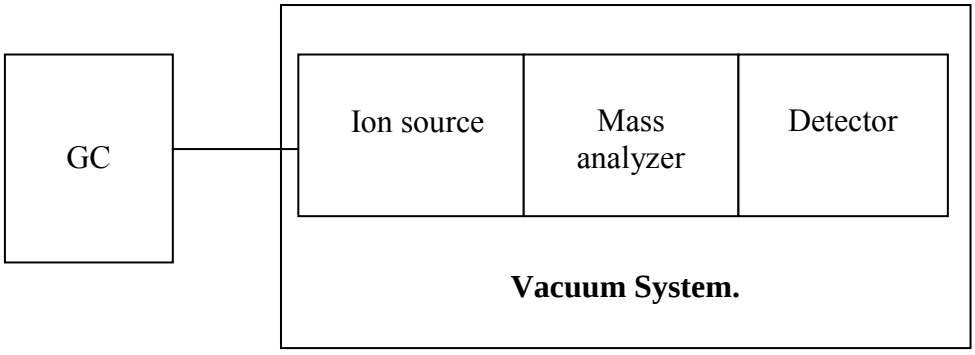


Figure 2.5 Schematic diagram of MS system.

2.3.1 Ion sources for gas chromatography [28]

2.3.1.1 Electron Ionization (El)

EI (electron impact) has been the most widely used ionization technique in mass spectrometry because of its extensive ion fragmentation for structural analysis of analytes and its reproducibility. In this common ionization method, atoms or molecules in the gas phase are ionized by a beam of electrons generated by a tungsten or rhenium wire. The ions are created as a result of collisions between the electrons in the electron beam and the molecules present in the sample

$$\mathbf{M + e^- \rightarrow M^+ + 2e^-}$$

Where: M is the molecule being analyzed

M^+ is the corresponding ionized molecule.

Positive ions are accelerated in an electrical field and made to traverse a magnetic field. Ions with a specific mass/charge ratio can be collected and characterized by changing the acceleration voltage (the actual speed of the ions) or the strength of the magnetic field.

Standard mass spectra are obtained typically at 70 eV because maximum ion intensity is observed at this value, and mass spectra are reproducible and characteristicly independent on this type of instrument. EI is therefore preferred for the identification of unknowns, determination of molecular structure, and confirmation of target analyte identity through consistent ion abundance ratios and library spectra matching.

2.3.1.2 Chemical Ionization (CI)

CI represents a low energy or ‘‘soft’’ ionization technique and is therefore very suitable for those less volatile or thermally labile molecules that do not yield to molecular ions by EI. For CI, a suitable reagent gas (e.g. methane, ammonia or in

some cases solvent molecules) is introduced into the ion source at a concentration that largely exceeds the amount of analytes.

Positive chemical ionization (PCI), the ion source is filled with a reagent gas (e.g., methane), at a relatively high pressure (0.1–100 Pa), producing an excess of reagent ions. Sample molecules are subsequently ionized by the reagent gas ions via proton transfer, producing pseudomolecular ions and depending on the choice of reagent gas, adduct ions may be formed. PCI is less suitable for confirmation. In other words, PCI can offer both increased sensitivity and improved detectability due to reduced chemical noise from background or co-eluting analytes, resulting in increased signal to noise ratio (S/N).

Negative chemical ionization (NCI), that maybe called electron capture, or negative ionization (ECNI) or negative ion chemical ionization (NICI), is the basic mechanism of this technique. It is similar to that of an electron capture detector: a low-energy electron that is captured by an electronegative sample molecule, forming the molecular anion (by the resonance capture, dissociative capture, or ion-pair formation mechanisms), which may undergo fragmentation, depending on its structure.

The main advantages of NCI compared to EI and PCI include the possibility of up to 100-fold improvement in sensitivity, and higher degree of selectivity, since only a limited number of analytes, such as those containing a halogen atom, a nitro group, or an extended aromatic ring system, are prone to efficient electron capture.

2.3.2 Mass Analyzer [29]

The main function of the mass analyser is to separate, or resolve, the ions formed in the ionisation source of the mass spectrometer according to their mass-to-charge (m/z) ratios. There are a number of mass analysers currently available, the better known of which include quadrupoles , time-of-flight (TOF) analysers, magnetic sectors , and both Fourier transform and quadrupole ion traps . These mass analyzers have different features, including the m/z range that can be covered in the mass accuracy, and the achievable resolution. The compatibility of different analysers with different ionisation methods varies.

2.3.2.1. Quadrupole

A quadrupole represents the most popular mass analyzer mainly due to its relatively low cost, ruggedness, reliability, and the simplicity of operation. The quadrupole mass analyzer (or called “mass filter”) is made up of four parallel conducting rods (hyperbolic or cylindrical), the four rods are arranged at the corners of a square and placed in a radial array (Figure 2.6). Opposite rods are charged by positive direct-current (DC) voltage, while adjacent rods have the opposite (negative) charge applied. Ions are introduced into the quadrupole field by means of a low accelerating potential. An appropriate combination of DC and radio frequency (RF) fields on the quadrupole rods allows passing only the ions of one particular m/z at a time. Ions with a nonstable trajectory through the quadrupole collide with the quadrupole rods, thus are not detected using the given DC and RF potential settings. The mass filter, sorts these ions based upon their mass-to-change ratio (*m/z*). There are two types of single quadrupole mass spectrometric analysis:

(1) Full scan of a selected mass range (e.g., m/z 50–550), at the beginning of a scan, the quadrupole mass filter is ready and waiting at the top of the specified scan range. To acquire a mass spectrum, the mass filter moves in consecutive, discrete steps of 0.1 amu from the top of the scan range to the bottom. The number of times the abundance of each mass is measured or sampled during a scan is the sampling rate.

(2) Selected ion monitoring (SIM), allows the mass spectrometer to detect specific compounds with very high sensitivity, the instrument is set to acquire data at masses of interest, instead of stepping the mass filter over a wide range of masses. Because the mass spectrometer collects data at only the masses of interest, it responds only to those compounds that possess the selected mass fragments. In essence, the instrument is focused on only the compounds of interest. Also, because only a few masses are monitored, much more time may be spent looking at these masses, with the abundant increase in sensitivity, accuracy, and precision. SIM mode is roughly 30 times more sensitive than scan mode. In practice, improvements are possible, depending on instrument, background, and sample matrix.

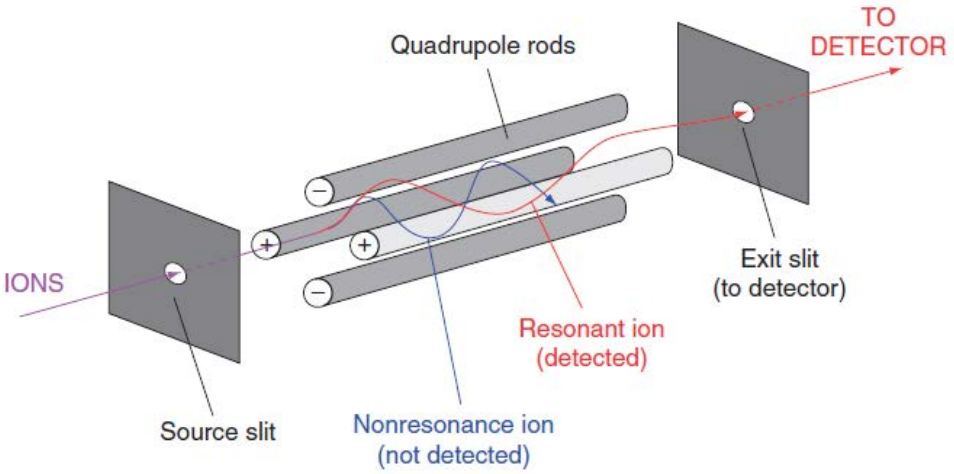


Figure 2.6 Schematic of a quadrupole mass analyzer [29]

2.4 Tandem Mass Spectrometry (MS/MS) [30]

Tandem mass spectrometer, which is a method involving at least two stages of mass analysis, either in conjunction with a dissociation process or a chemical react ion that causes a change in the mass or charge of particular ion. MS-MS methods involve activation of selected ions (called precursor or parent ions), typically by collision with an inert gas, sufficient to induce fragmentation (resulting in ions called product or daughter ions). Basically, two different approaches in MS-MS exist: in space by coupling of two physically distinct parts of the instrument (e.g., in triple quadrupole, or in time by performing a sequence of events in an ion storage device (e.g., in an ion trap).

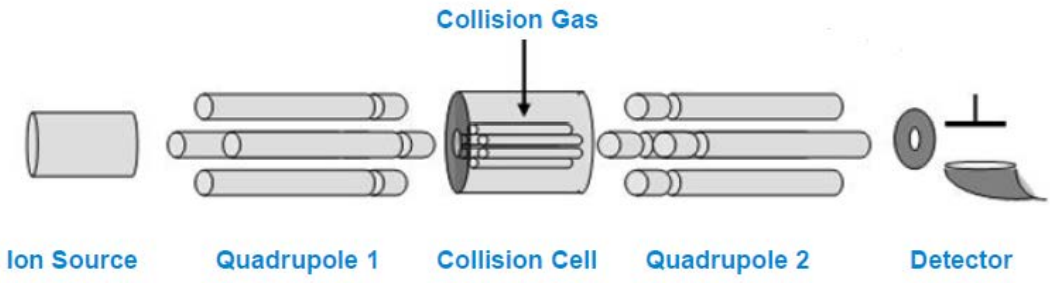


Figure 2.7 Schematic overview of triple quadrupole mass spectrometer [30]

The basic components of the GC-MS/MS are shown above (Figure 2.7), and consist of an ion source, a quadrupole, a collision cell, a second quadrupole and a detector. The ion source creates ions. Q1 is the first quadrupole filter that allows separation of ions either through the function of scan or selected ion monitoring (SIM). The ions exiting Q1 are called “precursor” ions (formerly called “parent” ions). The collision cell is the area after Q1 where selected ions are allowed to collide with a gas (nitrogen, argon or helium) to create product ions (formerly called “daughter” ions). The second quadrupole (Q3) filter allows for the passage of the selected product ions to the detector. There are five main scan experiments possible using MS/MS, (1) production scan , which involves selection of an ion of interest, its activation, and mass analysis of the product ions in full scan mode, (2) precursor ion scan represents opposite process compared to the product ion scan, providing information about all precursor ions that react to produce a selected product ion, (3) neutral loss scan is a scan that deter mines all precursor ions that react to the loss of a selected neutral mass, (4) multiple reaction monitoring (MRM) is used if several different react ions are monitored in a one time window, as described in section 2.4.1 to 2.4.4 below.

2.4.1 Precursor ion scan mode

In a precursor ion scan, the MS1 Scan is equivalent to a scan experiment on a single quadrupole instrument. The sample is ionized at the ion source. Quadrupole one operates in scan mode. No collision energy is applied, so no fragmentation caused by CID occurs. Q3 is held to measure the occurrence of a particular fragment ion and Q1 is scanned from the high range to the *m/z* of the monitored product ion. This result is a spectrum of precursor ions that result in that particular product ion. In addition, these spectra may be slightly different than a scan on a single quadrupole due to the ‘time of flight’ with the collision cell and second quadrupole. The usual fragments may not be stable during the entire flight time.

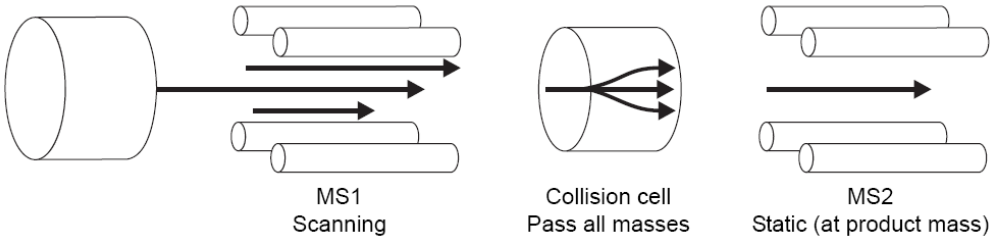


Figure 2.8 Schematic of precursor ion scan mode [30]

2.4.2 Product ion scan mode

The precursor ion is selected in Q1 and transferred into Q2, the collision cell, where it interacts with a collision gas, nitrogen, and fragments. The fragments are measured and then all resultant masses are scanned in the second mass analyzer and detected in the detector that is positioned after the second mass analyzer. This experiment is commonly performed to identify transitions used for quantification by tandem MS.

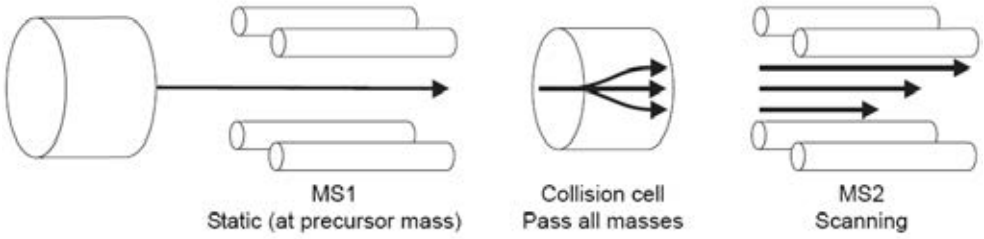


Figure 2.9 Schematic of product ion scan mode [30]

2.4.3 Neutral loss scan

A neutral loss scan can be used to monitor the occurrence of a particular class of compounds. Both quadrupoles are operated in the scanning mode the first mass analyzer scans all the masses. The second mass analyzer also scans, but they are offset from the first mass analyzer by the mass of the expected neutral loss and collision cells operating in CID mode. The detector will only see a signal when the neutral loss is realized. Neutral loss scans cannot be done with time based MS instruments. In a

constant-neutral-loss scan, all precursors that undergo the loss of a specified common neutral are monitored. To obtain this information, both mass analyzers are scanned simultaneously, but with a mass offset that correlates with the mass of the specified neutral. Similar to the precursor-ion scan, this technique is also useful in the selective identification of closely related class of compounds in a mixture.

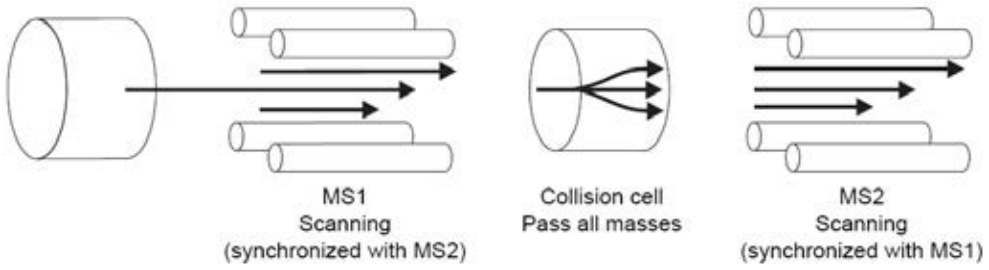


Figure 2.10 Schematic of Neutral loss scan [30]

2.4.4 Multiple Reactions Monitoring (MRM)

This is most commonly accomplished by setting Q1 to pass a single *m/z* and then having Q3 alternate between two, or more, *m/z*s from product ions produced by the fragmentation of the ion passed through Q1. MRM is the most selective and sensitive mode because only a specific ion which fragments can produce the specific product ion, these are monitored for the whole of the scan time cycle, rather than just part of it. Moreover, a greater dwell time on the ions of interest is possible and therefore better sensitivity is achieved. A ratio can be established between the abundance of these different transitions and a highly specific determination can be made when both a quantification and qualifier ion are detected. MRM is often viewed as the ultimate target compound analysis tool that does not produce a full spectrum. It can produce highly specific and exquisitely sensitive results.

The main benefit of MRM (Multiple Reaction Monitoring) over the classical single quadrupole SIM (Selected Ion Monitoring) is the specificity and therefore the reduction of interferences of matrix in the samples and background. In SIM analysis, the ions being monitored may be composed of the target and interference. With united mass resolution instruments, there is no way to distinguish the two species. In MRM

analysis, it is very unlikely that the interference will produce the same product ion as the target.

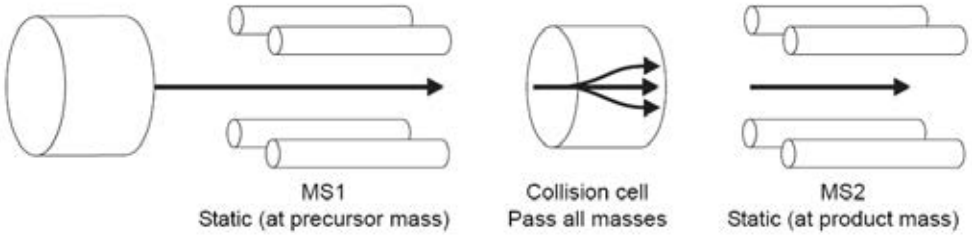


Figure 2.11 Schematic of Multiple Reactions Monitoring [30]

Triple quadrupole provides superior sensitivity and selectivity. This is due to the tandem MS specificity, low detection limits are common for quantification due to the elimination of background interferences, able to meet stricter regulatory guidelines for certain applications, especially those in more complex matrices. More popular tandem mass spectrometers include those of the quadrupole-quadrupole, magnetic sector-quadrupole, and more recently, the quadrupole-time-of-flight geometries.

2.5 Detector [31,32]

The detector monitors the ion current and amplifies it. The signal is then transmitted to the data system, where it is recorded in the form of mass spectra. The m/z values of the ions are plotted against their intensities to show the number of components in the sample, the molecular mass of each component, and the relative abundance of the various components in the sample. The type of detector is supplied to suit the type of analyser; the more common ones are the electron multiplier or the photomultiplier. The electron multiplier and photon multiplier are detectors typically used for quadrupole, ion trap, and sector instruments.

2.5.1 With the Electron Multiplier (EM) and High Energy Dynode (HED), the ions reach the first plate (dynode) of an electron multiplier and then the ejected electrons are accelerated through an electric potential to a second dynode (Figure 2.9).

This process is typically repeated 10–12 times (according the number of used dynodes). Positive ions are attracted to the HED from the quadrupole and cause electrons to be emitted. Electrons are then attracted into the more positive EM horn (Figure 2.10). Once the electrons hit the side of the horn more electrons are emitted from the surface, every electron impact releases even more electrons, causing a cascade. A signal current is generated by the detector proportional to the number of ions striking it. The detector and mass filter operate under high vacuum (10^{-6} Torr) to allow the ions to travel unimpeded to the detector. The final flow of electrons provides an electric current that can be further increased by electronic amplification.

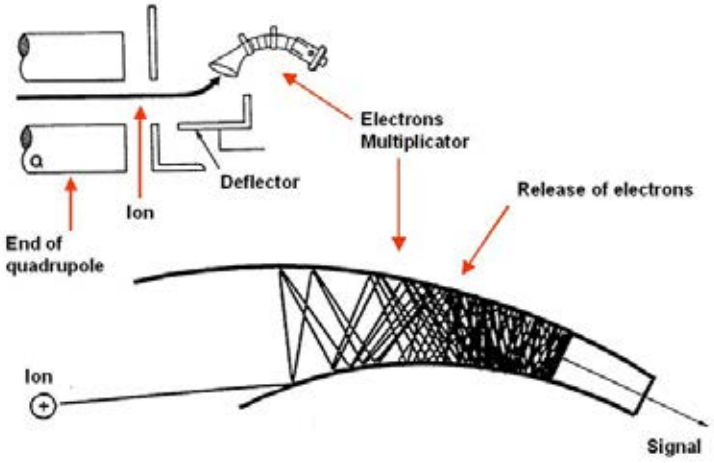


Figure 2.9 Schematic of signal generation by EM detector [31]

Figure 2.10 HED and EM horn by Agilent Technologies [32]

2.5.2 The photon multiplier is made up of two conversion dynodes, a phosphorescent screen, and a photomultiplier. Considering the positive mode, secondary ions are accelerated towards the dynode that holds the negative potential. Secondary electrons that are generated are accelerated towards the phosphorescent screen, where conversion into photons occurs, followed by their detection by the photomultiplier. The photomultiplier detector reduces detector noise for both positive and negative ion modes, and improved sensitivity in negative ion mode.

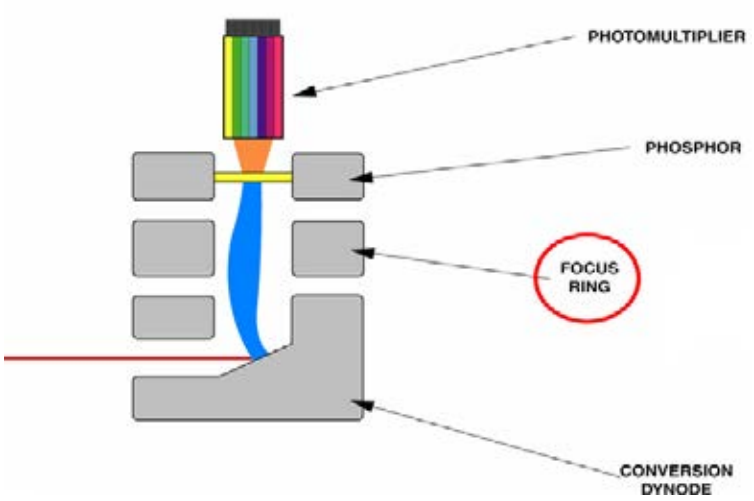


Figure 2.13 Schematic of Whisper Dynolite photomultiplier detector design on MS/MS [32]

The photomultiplier tube is commonly used as a detector. It consists of a photo emissive cathode (a cathode which emits electrons when struck by photons of radiation), several dynodes (which emit several electrons for each electron striking them) and an anode. A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. By this time, each original photon has produced 10^6 - 10^7 electrons. The resulting current is amplified and measured. Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers and they are limited to measuring low power radiation. The photomultiplier tube is very sensitive and has very fast response times.

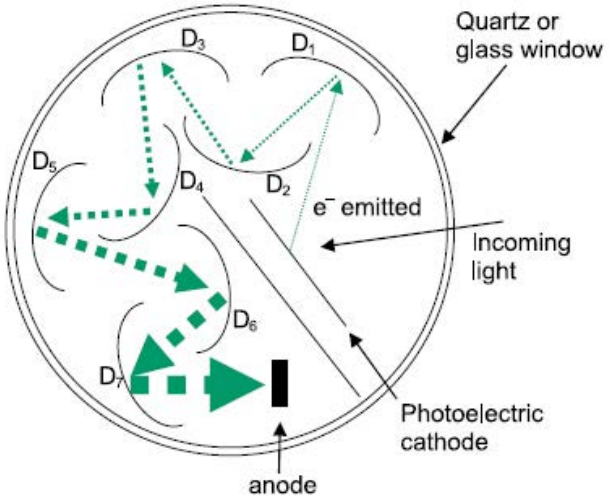


Figure 2.14 Cross section of a photomultiplier tube [32]

2.6 Low pressure gas chromatography (LP-GC) [33, 34, 35, 36, 37, 38, 39]

LP-GC is a fast chromatography approach to speed up analysis time, provide higher throughput and reduce cost. The method involves the use a relatively short (10 m) mega-bore (0.53 mm I.D.) column that is used as the analytical column connected with an uncoated restriction capillary (0.1-0.25 mm I.D.), with optimal length (e.g. 3 m), is connected at the inlet end and in front part of mega-bore analytical column, eliminating the problem of vacuum from the MS extends to inlet injection. The restriction capillary serves as guard column in the analysis of dirty sample extracts and acceptable ruggedness of the method after many injections. The mega-bore column is connected to the MS detector, in which vacuum from the MS provides low pressure along the column. The LP-GC column set-up used in this study is shown in Figure 2.3.

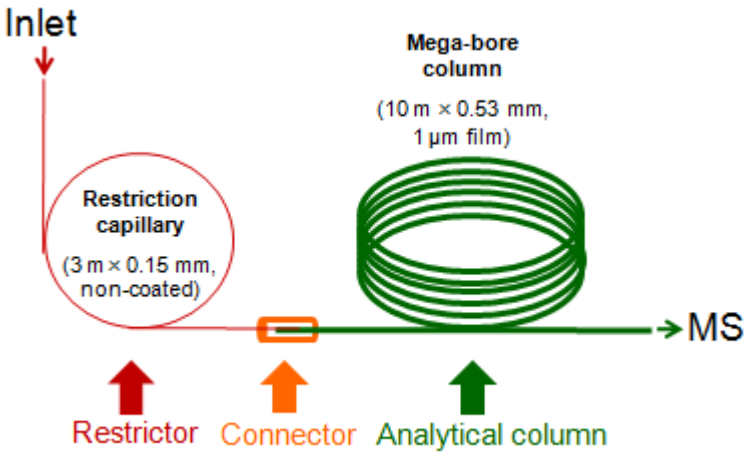


Figure 2.15 LP-GC column set up [40]

The mega-bore analytical column is operated under low pressure conditions, while inlet and injector are at atmospheric conditions, which the same conventional GC injection method. Using helium (He) carier gas under low pressure conditions, which leads to decause viscosity and increase in diffusion of the analysis in gas phase. When the column operates at a low pressure, gas phase diffusion coefficient increases and the optimum carrier gas velocity (μ_{opt}) incrases to a high value and allows the use of high flow rate. The speed of analysis is increased and analyte peaks become narrower. On the other hand, the main drawback of LP-GC technique is the loss of separation efficiency. But the latter case can be compensated by the features of MS/MSMS, which can resolve and separate co-eluting analytes by their differences in mass spectra. Many types of mass analyzers commonly used for pesticide analysis include TOF, MS, ion trap, and hybrid MS (MSMS, QTOF, etc.). [20,40]

Therefore, the advantages of LP-GC are; (1) higher flow rate can be used which may help in faster analysis (3-fold gain in speed), (2) narrow peak width compared to conventional GC separation, (3) sample capacity and injection volumes are increased with mega-bore column, (4) peak height is increased which can lead to higher *S/N* ratios and LOQ maybe lower, (5) better peak shape (reduced tailing) for relatively polar compounds, (6) thermal degradation of thermally-labile analytes is reduced and (7) no change in GC instrument.

CHAPTER III

EXPERIMENTAL

3.1 Instrument and apparatus

3.1.1 Gas Chromatography (GC) model 7890: auto sampler and multimode injection (MMI), Agilent Technologies, Wilmington, DE, USA.

3.1.2 Triple quadrupole tandem mass spectrometry (MS/MS) model 7000B, Agilent Technologies, Wilmington, DE, USA.

3.1.3 Agilent MassHunter Data Acquisition Software (version B.04.00), Agilent Technologies, Wilmington, DE, USA.

3.1.4 MassHunter Workstation Software for Qualitative Analysis (version B.04.01), Agilent Technologies, Wilmington, DE, USA.

3.1.5 MassHunter Workstation Software for Quantitative Analysis (version B.04.01), Agilent Technologies, Wilmington, DE, USA.

3.1.6 GC column: DB-5MS (Phenyl arylene polymer virtually equivalent to a 5%phenyl methyl siloxane, 30 m × 0.25 mm i.d. × 0.25 μm film thickness), J&W, Folsom, CA, USA.

3.1.7 GC column: DB-5MS (Phenyl arylene polymer virtually equivalent to a 5%phenyl methyl siloxane, 10 m × 0.53 mm i.d. × 1.0 μm film thickness), J&W, Folsom, CA, USA.

3.1.8 Deactivated non-coated capillary column (3 m × 0.15 mm i.d.), J&W, Folsom, CA, USA.

3.1.9 Mini-union 0.8 mm, SGE analytical science, UK

3.1.10 High-purity nitrogen (N_2) gas, pressure 100 psi, TIG, Bangplee, Samutplakarn, Thailand.

3.1.11 Ultra-high purity helium (He) gas, pressure 20 psi, Lab Gas, Bangkok, Thailand.

3.1.12 Vortex mixer, model GENIE 2, Scientific Industries, Bohemia, NY, USA.

3.1.13 Centrifuge model Allegra^{TM} X-12, Beckman Coulter Inc., Brea, CA, USA.

3.1.14 Electronic balance 2 digits and 4 digits, Mettler Toledo, Prague, Czech Republic.

3.1.15 Ultra sonic bath model 8200, Branson Ultrasonic Corporation, Danbury, CT, USA.

3.1.16 Freezer, Sanyo, Japan.

3.1.17 Refrigerator, Haier, China.

3.1.18 Incubator, Eyela, Japan.

3.1.19 Micropipetts: volume 0.1-10, 10-100, 25-200, 100-1000 µL, and 1-5 mL with tips from Eppendorf, Hamburg, Germany.

3.1.20 Nylon syringe filter (13 mm, 0.2 µm) from Chrom Tech Inc., AppleValley, MN, USA.

3.1.21 GC autosampler glass vial 2 mL with PTFE cap, La-Pha-Pack, Germany.

3.1.22 Volumetric flask volume class A 25 mL, Witeg Duran, Germany

3.1.23 Polypropylene centrifuge tube 50 mL, LP Italy, Italy

3.1.24 Beaker 50, 100 mL, Pyrex, Germany

3.1.25 Graduated cylinder 100 mL, Witeg Duran, Germany

3.1.26 Glass syringe 10 mL, Mira, Bangkok, Thailand

3.1.27 Microcentrifuge tube 1.5 mL, Axygen scientific, CA, USA.

All glasswares were cleaned with detergents, rinsed with acetone, and dried before used in order to prevent possible contamination.

3.2 Chemicals

3.2.1 Pesticide standards

The 170 standard pesticides as listed in APPNDIX-A including organochlorines, organophosphates, organonitrogens, and pyrethroids (≥98.0% or highest purity) were purchased from Dr.Ehrenstorfer (Augsburg, Germany), Sigma-

Aldrich (St.Louis, MO, USA), Supelco (Bellefonate, PA, USA), and WAKO (Richmond, VA, USA).

Isotopically-labeled internal standard (I.S.), chlorpyrifos-methyl d_6, was supplied from Dr.Ehrenstorfer (Augsburg, Germany).

3.2.2 Organic solvents

Acetonitrile (MeCN), methanol (MeOH), toluene, and acetone of pesticide grade were purchased from Kanto (Tokyo, Japan). Glacial acetic acid (HOAc) was analytical grade obtained from J.T. Baker (Phillipsburg, NJ, USA).

3.2.3 Reagents and sorbents

Anhydrous magnesium sulphate (anh. $MgSO_4$) was purchased from Panreac (Barcelona, Spain). Anhydrous sodium acetate (anh. NaOAc) was purchased from Ajax (Finechem Pty Ltd, Australia). Primary secondary amine sorbent (PSA) 40-60 μm was obtained from Agela technologies Inc. (DE, USA). Aminopropyl (NH_2) powder 40 μm was purchased from Agilent technologies (DE, USA). Octadecyl (C_{18}) powder 40 μm was purchased from Merck (Darmstadt, Germany). Alumina-neutral (Al-N) was purchased from Macherey-nagel GnbH &Co. KG (Düren, Germany). Graphitized carbon black (GCB) was purchased from Supelco (Bellefonate, PA, USA).

3.3 Preparation of standard solutions

3.3.1 The primary standard solutions, 1000 mg L^{-1}

The primary standard solution was prepared by weighing 0.0250 g (to nearest 0.0005 g) each of the individual standards into a 25 mL- volumetric flask, disloving, and diluting to the mark with MeCN, acetone, MeOH, or toluene. Each of standard solutions was transferred to an amber glass bottle with a screw cap and kept in a freezer at -10°C.

3.3.2 The standard solution for MS scanning, 5 mg L^{-1}

The individual standard solution was prepared by pipetting 5 μL of primary standard solution (1000 mg L^{-1}) into a GC autosampler vial, and diluting to 1 ml with acetone.

3.3.3 The working standard solutions, 10 mg L^{-1}

The 170 pesticide standards were classified into 4 groups (APPENDIX-A);

Group A: organocholrine pesticides

A mixture of 45 organocholrine pesticides was prepared by pipetting 250 μL of primary standard solution (1000 mg L^{-1}) into a 25 mL- volumetric flask and making up the volume with MeCN.

Group B: organophosphate pesticides

A mixture of 45 organophosphate pesticides was prepared by pipetting 250 μL of primary standard solution (1000 mg L^{-1}) into a 25 mL- volumetric flask and making up the volume with MeOH.

Group C: organonitrogen pesticides

A mixture of 70 organonitrogen pesticides was prepared by pipetting 250 μL of primary standard solution (1000 mg L^{-1}) into a 25 mL- volumetric flask and making up the volume with acetone.

Group D: pyrethroid pesticides

A mixture of 10 pyrethroid pesticides was prepared by pipetting 250 μL of primary standard solution (1000 mg L^{-1}) into a 25 mL- volumetric flask and making up the volume with toluene.

I.S.: chlorpyrifos-methyl d_6

I.S. solution was prepared by pipetting 250 μL of primary I.S. solution (1000 mg L^{-1}) into a 25 mL- volumetric flask and making up the volume with MeOH.

The working standard and I.S. solutions were transferred into amber glass bottles with screw cap and stored in the freezer at -10°C. These standard solutions were used for preparation of calibration standards and spiked samples.

3.4 Preparation of onion sample

Different onion samples were purchased from a local organic food store. The onion samples were chopped into small pieces and homogenized to a consistent texture. Each of homogenized onion samples were extracted and injected into GC-MS/MS under conditions to check that samples were free of pesticides. The well homogenized onions, which were not found any targeted pesticides, were mixed and kept at -10°C prior to the analysis.

3.5 Development and Optimization of traditional GC-MS/MS conditions

3.5.1 GC conditions

GC analysis was performed on an Agilent 7890 GC, which was equipped with a multimode inlet, interfaced to an Agilent 7000B triple quadrupole mass spectrometer. The injection volume was 5 μL into a sinter glass liner operated in a programmable temperature vaporizer (PTV) solvent vent mode. GC separation was conducted on a DB-5MS 30 m × 0.25 mm i.d. × 0.25 μm flim thicknesses. Ultra-high purity helium (He) was used as the carrier gas at 1.0 mL/min constant flow rate controlled by electronic pressure control.

MS transfer line and ion source temperature were set at 280 and 300°C, respectively. Electron ionization (EI) energy was 70 eV with a filament-multiplier delay of 4.5 min. The filament current was 35 μA. Quadrupole temperatures were 150°C. Collision gas flow of N_2 and He were default instrument setting at 1.5 and 2.25 mL min^{-1}, respectively.

For the GC separation part, important parameters involved initial inlet temperature, inlet temperature programming, solvent venting time, initial oven

temperature, and oven temperature programming. These parameter were developed by varying temperature in order to obtain he optimum GC conditions.

3.5.2 MS/MS conditions

For the MS/MS optimization, the optimum GC conditions were used. Standard solution for MS scanning (5 mg L^{-1}) of each analyte was individually injected and a quadrupole mass analyzer acquired full scan ion in the range of m/z 50-500. The most intense ion or molecular ion of each analyte was selected as a precursor ion.

For multiple reactions monitoring (MRM) optimization, the collision energies were applied to the selected precursor ion in the collision cell for breaking up the ion. The collision energies were experimentally optimized by running individual standard solution for product ion scans at different collision energies in the range of 5-60 V with a step of 2-5 V.

3.5 Development and Optimization of sample preparation procedure

The sample preparation based on an acetate-buffered QuEChERS method (Official Method 2007.01) was used as a template in this study. Spiked blank samples at 0.1 mg kg^{-1} concentration level were used for the entire method development and optimization. The extractions were conducted in 5 replicates.

3.5.1 The acidity of extraction solvent

The optimization of %acidity of extraction solvent was studied by comparing different amounts of HOAc in MeCN, as shown in Table 3.1. Sample preparation procedures are described in **Procedure I.**

Table 3.1 Different amounts of HOAc in MeCN.

Method no.	**x**% HOAc in MeCN
M 1	0.1%
M 2	0.3%
M 3	0.5%
M 4	0.7%
M 5	1.0%

Precedure I Sample preparation procedures for the optimization of %HOAc in MeCN.

Step 1 weigh 10±0.05 g homogenized blank sample (used 10 mL water for reagent blank) into 50 mL polypropylene centrifuge tube.

Step 2 add standard solutions group A-D and I.S. (section 3.3.3) into the sample, (use MeCN for blank extract), and vortex the tube for 1 min.

Step 3 add 10 mL of **x% HOAc in MeCN** (Table 3.1) into the sample and vortex the tube for 1 minutes.

Step 4 add 4 g anh. $MgSO_4$ + 1 g anh. NaOAc, shake the tube vigorously by hand for 1 minutes to avoid the formation of lumps, and centrifuge the tube at 3400 rpm for 2 min.

Step 5 transfer 1 mL of the MeCN extract into a microcentrifuge tube containing 0.15 g anh. $MgSO_4$ + 0.05 g PSA, cap the tube well, shake the tube for 1 min, and then centrifuge the tube at 10000 rpm for 5 min.

Step 6 filter the supernatant through 0.2 µm nylon syringe filter into a GC autosampler vial.

Step 7 perform the analysis using the optimal GC-MS/MS conditions.

The peak area responses of each anlyte were normalized to the peak areas of I.S. in all cases. The final concentration was calculated using matrix one-point calibration at 0.1 mg kg^{-1} and reported as percentage average recovery for each analyte.

3.5.2 The optimization of d-SPE sorbent

The optimization of d-SPE clean-up was studied by comparing different types of d-SPE sorbent and their amounts, as shown in Table 3.2. Sample preparation procedures are described in **Procedure II**.

Table 3.2 Types and amounts of d-SPE sorbent.

Method no.	d-SPE sorbent
M 1	no clean-up
M 2	0.15 g anh. $MgSO_4$ + 0.05 g PSA
M 3	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N
M 4	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g NH_2
M 5	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g C_{18}
M 6	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.005 g GCB
M 7	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N + 0.005 g GCB
M 8	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g NH_2 + 0.005 g GCB
M 9	0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g C_{18} + 0.005 g GCB

Precedure II Sample preparation procedures for the optimization of d-SPE clean-up.

Step 1 weigh 10±0.05 g homogenized blank sample (used 10 mL water for reagent blank) into 50 mL polypropylene centrifuge tube.

Step 2 add standard solutions group A-D and I.S. (section 3.3.3) into the sample, (use MeCN for blank extract), and vortex the tube for 1 min.

Step 3 add 10 mL of **0.5%HOAc in MeCN** into the sample and vortex the tube for 1 minutes.

Step 4 add 4 g anh. $MgSO_4$ + 1 g anh. NaOAc, shake the tube vigorously by hand for 1 minutes to avoid the formation of lumps, and centrifuge the tube at 3400 rpm for 2 min.

Step 5 transfer 1 mL of the MeCN extract into a microcentrifuge tube containing **d-SPE sorbents** (Table 3.2), cap the tube well, shake the tube for 1 min, and then centrifuge the tube at 10000 rpm for 5 min.

Step 6 filter the supernatant through 0.2 μm nylon syringe filter into a GC autosampler vial.

Step 7 perform the analysis using the optimal GC-MS/MS conditions.

The peak area responses of each anlyte were normalized to the peak areas of I.S. in all cases. The final concentration was calculated using matrix one-point calibration at 0.1 mg kg^{-1} and reported as percentage average recovery for each analyte.

3.6 Method validation for traditional GC-MS/MS

In this study, method validation was carried out in accordance with the Document No.SANCO/12495/2011 *(Method Validation and Quality Control Procedure for Pesticide Residues Analysis in Food and Feed*), Commission Regulation No.657/2002 (The performance of analytical methods and the interpretation of results), and AOAC Guidelines for Single Laboratory Validation of Chemical Methods for DietarySupplements and Botanicals. The validation parameters included selectivity, linearity, matrix effects, accuracy, precision, limit of detection (LOD), and limit of quantitation (LOQ).

The optimum sample preparation procedures (final method) used throughout the validation experiments are described in **Procedure III.**

Precedure III The optimum sample preparation procedures for the method validation studies.

Step 1 weigh 10±0.05 g homogenized blank sample (used 10 mL water for reagent blank) into 50 mL polypropylene centrifuge tube.

Step 2 add standard solutions group A-D and I.S. (section 3.3.3) into the sample, (use MeCN for blank extract), and vortex the tube for 1 min.

Step 3 add 10 mL of 0.5%HOAc in MeCN into the sample and vortex the tube for 1 minutes.

Step 4 add 4 g anh. $MgSO_4$ + 1 g anh. NaOAc, shake the tube vigorously by hand for 1 minutes to avoid the formation of lumps, and centrifuge the tube at 3400 rpm for 2 min.

Step 5 transfer 1 mL of the MeCN extract into a microcentrifuge tube containing 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N + 0.005 g GCB, cap the tube well and shake for 1 min, and then centrifuge the tube at 10000 rpm for 5 min.

Step 6 filter the supernatant through 0.2 μm nylon syringe filter into a GC autosampler vial.

Step 7 perform the analysis using the optimal GC-MS/MS conditions.

3.6.1 Selectivity

Different 20 onion samples were purchased from different local organic food stores. The well homogenized onion samples were extracted separately. System blank (0 μL injection), reagent blank, 0.01 mg L^{-1} standards in MeCN, each of final extracts (including matrix blank and 0.01 mg kg^{-1} spiked matrix blank) were injected into GC-MS/MS under the optimum conditions and determined t_R, ion ratios and chromatographic peak shapes. Ion ratio is the area of qualifier ion divided by the area of quantifier ion.

3.6.2 Linearity

Linearity of the method was demonstrated using standard calibrations. The solvent-based standards were prepared by diluting 10 mg L^{-1} of mixed standards group A-D and I.S. solutions (section 3.3.3) in MeCN to 10-concentration levels as described in Table 3.3. Calibration standards were injected (3 replicate injections at each concentration) into GC-MS/MS under the optimum conditions. The standard calibration curve of each analyte was constructed by plotting concentration versus peak area which was normalized to the peak area of I.S.

Matrix-matched calibrations were prepared in the same way as solvent-based standards calibrations but using blank onion extract as diluting solvent instead of MeCN.

Table 3.3 Concentration levels of standard calibrations.

Level	Concentration (mg L^{-1})*
1	0.01
2	0.03
3	0.06
4	0.09
5	0.12
6	0.15
7	0.18
8	0.21
9	0.24
10	0.27

*corresponding to mg kg^{-1} matrix-matched calibrations

3.6.3 Matrix effects

Matrix effects were accessed using solvent-based standard calibartions. In this study, matrix effect of each analyte was calculated from difference of best-fit slope between solvent-based calibration and matrix-matched calibrations and divided by best-fit slope of solvent-based calibration.

3.6.4 Accuracy

Accuracy of the method was performed in 5 replicates extractions of each 3 concentration levels: 0.01 (low), 0.05 (middle), and 0.10 (high) mg kg^{-1}. The 10 mg L^{-1} of mixed standards group A-D and I.S. solutions (section 3.3.3) were spiked into the homogenized blank samples prior to the addition of extraction solvent.

The peak area responses of each analyte were normalized to the peak areas of I.S. Matrix-matched calibration were used to calculate the concentration of spiked samples. Accuracy of the method was expressed as percentage average recovery for each analyte.

3.6.5 Precision

In this study, precision of the method was demonstrated in terms of repeatability (intra-day precision) and intermediate precision (with in-laboratory reproducibility). The peak area responses of each analyte were normalized to the peak areas of I.S. Matrix-matched calibration were used to calculate the concentration of spiked samples. Precision of the method was expressed as relative standard deviation (RSD) for each pesticide.

3.6.5.1 Repeatability

Repeatability of the method was carried out in 5 replicates extrations of each 3 spiking levels: 0.01 (low), 0.05 (middle), and 0.10 (high) mg kg^{-1}. The 10 mg L^{-1} of mixed standards group A-D and I.S. solutions (section 3.3.3) were spiked into the homogenized blank samples prior to the addition of extraction solvent.

3.6.5.2 Intermediate precision

Reproducibility of the method was conducted in 5 replicates at 3 spiking levels: 0.01 (low), 0.05 (middle), and 0.10 (high) mg/kg for 3 separate days analyses. The 10 mg/L of mixed standards group A-D and I.S. solutions (section 3.3.3) were spiked into the homogenized blank samples prior to the addition of extraction solvent.

3.6.5 Limit of detection (LODs) and limit of quantitation (LOQs)

LODs and LOQs were estimated by injecting spiked onion blank extract at 0.01 mg kg^{-1} and calculating the concentration of each analyte that gave signal (S/N) equal to 3 and 10 times above the background noises, respectively.

In this study, ion transition of each analyte that gave the highest signal intensity and less of matrix interferences was chosen for calculation.

3.7 Application to real samples

To evaluate the applicability of the proposed method (sample preparation and traditional GC-MS/MS), different 40 onion samples obtained from the export companies in Thailand were tested. The samples were prepared as the follows:

Step 1 weigh 10±0.05 g well homogenized onion sample into a 50 mL polypropylene centrifuge tube.

Step 2 add 10 mL of 0.5% acetic acid in MeCN into the sample and vortex the tube for a 1 minutes.

Step 3 add 4 g anh. $MgSO_4$ + 1 g anh. NaOAc, shake the tube vigorously by hand for a 1 minutes to avoid the formation of lumps, and centrifuge the tube at 3400 rpm for 2 min.

Step 4 transfer 1 mL of the MeCN extract into a microcentrifuge tube containing 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N + 0.005 g GCB, cap the tube well and shake for 1 min, and then centrifuge the tube at 10000 rpm for 5 min.

Step 5 filter the supernatant through 0.2 μm nylon syringe filter into a GC autosampler vial.

Step 6 perform the analysis using the optimal GC-MS/MS conditions.

Each of final extracts was split into two portions: the first portion was analzed using traditional GC-MS/MS method and the other portion was used for LP-GC-MS/MS analysis. The peak area responses of each analyte were normalized to the

peak areas of I.S. Matrix-matched calibrations were used for calculating the final concentrations.

3.8 Development and Optimization of LP-GC-MS/MS conditions

3.8.1 LP-GC-MS/MS conditions

LP-GC-MS/MS analysis was perfomed on the same instrument using for traditional GC-MS/MS experiments (3.5.1 and 3.5.2). The injection volume was 5 μL into a sinter glass liner operated in the PTV solvent vent mode. The inlet temperature was started at 70ºC (held for 1.1 min) and then ramped to 300ºC at 700ºC min^{-1} (held for the entire GC run). GC separation was conducted on a 10 m × 0.53 mm i.d. × 1.0 μm flim thickness DB-5MS analytical column coupled to a 3 m × 0.15 mm i.d. non-coated restriction capillary at the inlet end. He-carrier gas was 2.0 mL min^{-1} constant flow rate controlled by electronic pressure control. A range of oven temperature programming was experimentally optimized in order to obtain the overall best sensitivities.

The MS transfer line and ion source temperature were 280 and 300°C, respectively. EI energy was 70 eV with a filament-multiplier delay of 2.4 min. The filament current was 35 μA. Collision gas flow of N_2 and He were 1.5 and 2.25 mL min^{-1}, respectively. Quadrupole temperatures were 150°C. The optimized 2 MRM transitions were monitored for each analyte.

3.9 Method validation for LP-GC/MS-MS

For LP-GC-MS/MS, validation parameters involving selectivity, linearity, matrix effects, accuracy, precision, and analytical limits were evaluated as same way as the traditional GC-MS/MS (section 3.6). Sample extracts were injected into LP-GC-MS/MS and analyzed under the optimum conditions.

3.10 Application to real samples

To evaluate the applicability of the proposed approach, the portion of onion extracts (as described in the Section 3.7) were analyzed under the optimum LP-GC-MS/MS conditions.

The peak area responses of each analyte were normalized to the peak areas of I.S. Matrix-matched calibration were used for calculating the final concentrations. These results were compared with obtained when using the traditional GC-MS/MS method.

CHAPTER IV

RESULTS AND DISCUSSION

This study presents a new method for simultaneous determination of 170 pesticides including organochlorines, organophosphates, organonitrogens, and pyrethoids in onion using QuEChERS based-approach and GC-MS/MS technique.

We divided the study into 5 parts: *(1)* development and optimization of traditional GC-MS/MS, *(2)* development of sample preparation method, *(3)* validation of traditional GC-MS/MS method, *(4)* development and validation of LP-GC-MS/MS, and *(5)* comparison of traditional GC-MS/MS and LP-GC-MS/MS.

4.1 Development and optimization of traditional GC-MS/MS method

As for the injection part, the program temperature vaporization (PTV) solvent vent mode was used in this study. The solvent venting and analyte transfer conditions were carefully optimized. The starting of 80°C inlet temperature at 100 mL min^{-1} split flow for 1.1 min was effective for evaporating 5 μL of MeCN (b.p. 82°C) solvent without losing sensitivities of early eluting analytes (dichlorvos) and preventing column bleed. Then the analytes, which were trapped in the liner, were quantitatively transferred to the column by increasing inlet temperature from 80 to 300°C at 700°C min^{-1} and column flow of 1.0 mL min^{-1}. During the inlet heating, GC oven temperature was subsequently programmed to obtain maximum signal intensities and acceptable analyte separation time. Low initial oven temperature of 70°C helped to focus the early eluting analytes by using the temperature effect. Table 4.1, Table 4.2, and Figure 4.1 detail the optimized GC conditions for the analysis of 170 pesticides. Under these conditions, good analyte peak shapes and sensitivities were achieved.

Table 4.1 The optimum injector temperature program for traditional GC-MS/MS conditions.

	Rate (°C/min)	Value (°C)	Hold time (min)
Initial		80	1.1
Ramp 1	700	300	entire the GC run

Table 4.2 The optimum oven temperature program for traditional GC-MS/MS conditions.

	Rate (°C/min)	Value (°C)	Hold time (min)	Run time (min)
Initial		70	2	2
Ramp 1	30	180	0	5.67
Ramp 2	5	260	0	21.67
Ramp 3	10	290	0	24.67
Ramp 4	3	300	3	31

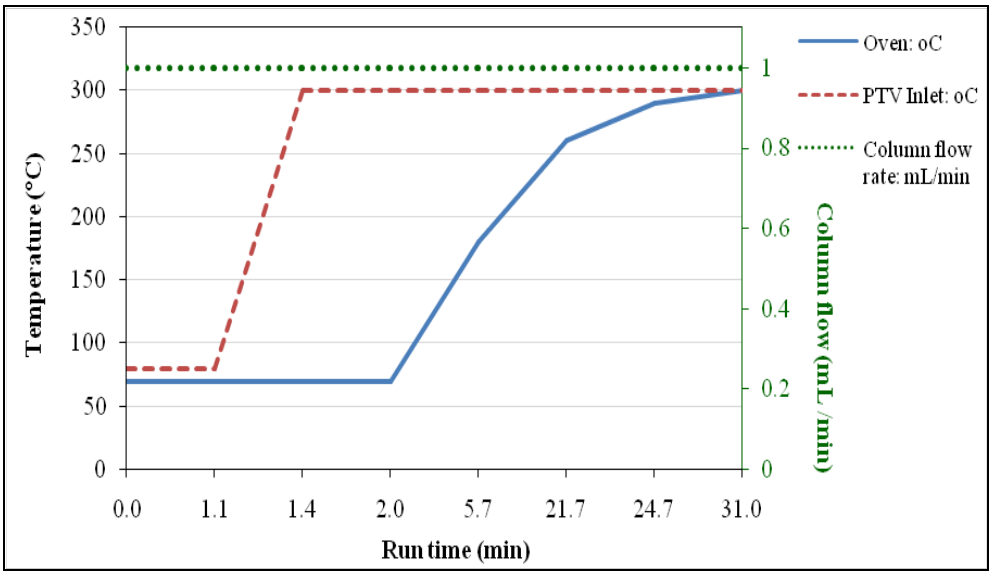


Figure 4.1 Schematic diagram of the optimum traditional GC separation conditions.

Unlike full-scan MS, in which one set of conditions is used to detect all analytes in the GC run, triple-quadrupole MS can detect specific ions/conditions for targeted analytes within time segments during the entire GC run. To develop the optimal presetting MS/MS conditions for each analyte, the initial step was to choose precursor ions. The full-scan mass spectrum (m/z 50-500) of each analyte was used for choosing the best precursor ion. In this study, the choice of precursor ion was based on a compromise between selectivity and sensitivity. The most intense ion was selected as a precursor ion to increase signal sensitivity. However, in some cases, less intense of molecular ion, which is unique to the compound structure and less of possible interferences from sample matrices and other co-eluting analytes, were necessary chosen for some pesticides to increase S/N ratios in high background noises (improving selectivity of the method).

The next step involved selecting of selective product ions with optimal collision energy for each compound. The chosen precursor ion of each analyte in collision cell was applied with energies to generate product ions. The collision energy (CE) settings in the range of 2-60 V (with a step of 2 V) were experimentally optimized by running individual analyte standard with different values of this parameter. The choice of product ion was based on the most abundant ion with the CE that showed mostly complete dissociation of the precursor ion. In this study, 2 ion transitions of each pesticide (340 transitions/170 pesticides) were selected for quantification and identification purposes. The most intense ion was served as quantification mass while another ion was used for identification purpose. Finally, the chosen MRM conditions were tested with spiked onion extracts to demonstrate the selectivity and sensitivity of the MRM method with less of matrix interferences.

To divide chromatographic separation into multiple time segments where the number of concurrent transitions was monitored in each segment, a conventional-MRM method was used to produce time-segments and grouping ion transitions according to their elution orders. By considering distribution of analyte elution times in the chromatogram and keeping constant cycle time throughout the analytical run, the MRM method acquisition was divided into 19 time segments. A group of transition ions those eluted within the time segment during the GC run was monitored, thus improving sensitivity and selectivity of the analytes.

Dwell time is the time spent for monitoring a single ion. It relates to the scan cycle time and the number of data points across a peak which is indicated by the peak width. Using longer dwell time causes in reducing number of data points collecting per peak and negatively impacts on chromatographic peak shape of the analyte. In multiple compounds analysis, each compound has different peak widths and signal intensities; therefore, data acquisition should be fast enough to collect many data points across a peak to meet the needs for quantitative purpose. This study sought out to use the possible fastest ion monitoring to obtain adequate number of points across a peak and to compromise between signal sensitivity and peak shape. By keeping constant cycle time of each segment, 2 MRM transitions of each analyte were monitored with dwell time in the range of 10-15 ms for each transition to achieve the maximum number of data points across a peak and good chromatographic peak shape, with sensitivity and selectivity of analytes.

The MRM transitions with optimal CE for each analyte are listed in Table 4.3. Using the optimum traditional GC-MS/MS conditions, total run time was 33.33 min which included ≈6 min post run. The last eluting analyte was azoxystrobin at 27.31 min. The GC-MS/MS chromatogram in MRM mode of 170 standard pesticides at 0.1 mg L^{-1} prepared in onion extract is shown in Figure 4.2. The MRM extracted ion chromatograms of 170 standard pesticides are shown in APPENDIX B.

Table 4.3 The t_R (min), MRM transitions (m/z), collision energy (CE, V), and dwell time (ms) of 170 pesticides using the optimum traditional GC-MS/MS conditions.

No.	Compound	Quantification transition	CE	Identification transition	CE	GC-MS/MS		LP-GC-MS/MS	
						t_R	Dwell time	t_R	Dwell time
1	Dichlorvos	109 → 79	5	109 → 47	15	5.852	20	2.533	2.5
2	EPTC	188.9 → 128	2	188.9 → 85.9	12	6.434	12	2.729	2.5
3	Dichlobenil	171 → 136	15	171 → 100	25	6.463	20	2.742	2.5
4	Propham	179 → 137	4	179 → 93	10	7.020	15	2.922	2.5
5	Thiometon	246 → 88	6	88 → 60	6	7.309	15	3.451	2.5

6	Methacrifos	240 → 180	8	208 → 180	4	7.310	15	2.986	2.5
7	Chloroneb	191 → 141	10	191 → 113	15	7.404	15	3.010	2.5
8	Molinate	187 → 126	4	126 → 55	14	7.656	15	3.096	2.5
9	Tecnazene	202.9 → 142.9	20	202.9 → 83	25	8.232	12	3.188	2.5
10	Propachlor	176.2 → 120.1	20	120.1 → 77.1	20	8.235	12	3.211	2.5
11	Chlorpropham	213 → 171	6	213 → 127	12	8.505	12	3.308	2.5
12	Ethafluralin	276.1 → 202	20	276.1 → 105.1	35	8.532	12	3.273	2.5
13	Triflulalin	306.1 → 264	5	306.1 → 160	30	8.665	12	3.302	2.5
14	Benfluralin	292.1 → 264	10	292.1 → 160.1	20	8.704	12	3.314	2.5
15	Cadusafos	159 → 97	12	158 → 114	4	8.869	12	3.372	2.5
16	Ethoprophos	200 → 158	10	158 → 130	10	8.869	12	3.266	2.5
17	Bromobutide metabolite	233.5 → 118.1	10	177.4 → 119.1	5	8.902	12	3.384	2.5
18	Phorate	260 → 75	8	231 → 203	4	8.962	12	3.392	2.5
19	Fenclorim	223.8 → 188.9	14	223.8 → 104	34	9.103	12	3.427	2.5
20	*alpha*-Lindane	181 → 145	15	181 → 109	30	9.124	12	3.428	2.5
21	Demeton-S-methyl	88.1 → 60	5	88.1 → 59	15	9.180	12	3.241	2.5
22	HCB	283.9 → 248.8	25	283.9 → 213.9	35	9.300	12	3.444	2.5
23	Simazine	201 → 173	4	201 → 138	10	9.390	12	3.499	2.5
24	Atrazine	215 → 200	4	200 → 122	8	9.479	10	3.517	2.5
25	Clomazole	204 → 107	16	125 → 89	12	9.575	10	3.538	2.5
26	*beta*-Lindane	181 → 145	15	181 → 109	30	9.671	10	3.537	2.5
27	Propetamphos	138 → 110	5	138 → 64	15	9.740	10	3.563	2.5
28	*gamma*-Lindane	181 → 145	15	181 → 109	30	9.775	10	3.705	2.5
29	Terbufos	288 → 231	4	231 → 174.9	10	9.804	10	3.583	2.5
30	Cyanophos	243 → 109	10	243 → 79	30	9.822	10	3.582	2.5
31	Fonophos	246.1 → 137	5	246.1 → 109	15	9.920	10	3.607	2.5
32	Pyroquilon	173 → 144	15	173 → 130	15	9.961	10	3.628	2.5

33	Diazinon	179.1 → 137.2	20	179.1 → 121.1	40	9.997	10	3.596	2.5
34	Disulfoton	186 → 153	5	142 → 109	5	10.165	10	3.662	2.5
35	*delta*-Lindane	219 → 183	6	181 → 145	12	10.310	10	3.574	2.5
36	Isazophos	257 → 162	4	257 → 119	16	10.318	10	3.660	2.5
37	Triallate	268 → 226	15	268 → 183.9	25	10.362	10	3.697	2.5
38	Iprobenfos	204 → 121	40	204 → 91.1	10	10.530	10	3.736	2.5
39	Pirimicarb	238 → 166	6	166 → 96	12	10.615	10	3.717	2.5
40	Benoxacor	261 → 120	10	259 → 120	12	10.663	10	3.760	2.5
41	Benflurasate	256 → 163	8	163 → 121	4	10.842	10	3.806	2.5
42	Dichlorfen-thion	279 → 223	15	279 → 205	30	10.929	10	3.808	2.5
43	Bromobutide	232 → 176	8	232 → 114	6	11.024	10	3.844	2.5
44	Vinclozolin	212 → 145	25	212 → 109	40	11.148	10	3.856	2.5
45	Chlorpyrifos methyl	286 → 270.9	20	286 → 93	25	11.181	10	3.840	2.5
46	Parathion methyl	263 → 109	10	263 → 79	35	11.189	10	3.876	2.5
47	Simetryn	213 → 170	8	213 → 155	20	11.252	10	3.898	2.5
48	Simiconazole	211 → 121	12	195 → 75	10	11.254	10	3.877	2.5
49	Tolclofos methyl	265 → 250	15	265 → 93	25	11.300	10	3.881	2.5
50	Alachlor	188.1 → 160.1	10	188.1 → 130.1	40	11.352	10	3.875	2.5
51	Ametryn	227 → 185	4	227 → 170	8	11.357	10	3.914	2.5
52	Heptachlor	274 → 239	14	272 → 237	12	11.417	10	3.930	2.5
53	Prometryn	241 → 184	8	226 → 184	6	11.431	10	3.926	2.5
54	Cinmethylin	168.9 → 123.1	3	168.9 → 107	3	11.451	10	3.929	2.5
55	Metalaxyl	206 → 162	6	206 → 132	14	11.475	10	3.910	2.5
56	Fenchlorfos	284.9 → 269.9	15	284.9 → 239.9	35	11.539	10	3.927	2.5
57	Dithopyr	354 → 306	6	354 → 286	12	11.726	10	3.929	2.5
58	Terbutryn	241 → 185	15	241 → 170	20	11.770	10	3.994	2.5
59	Pirimiphos methyl	290.1 → 233	10	290.1 → 125	25	11.879	10	3.974	2.5

60	Esprocarb	222 → 91	12	162 → 91	6	11.962	10	4.049	2.5
61	Malathion	173.1 → 117	10	173.1 → 99	15	12.108	10	4.039	2.5
62	Thiobencarb	125 → 89	12	100 → 72	4	12.155	10	4.096	2.5
63	Aldrin	262.9 → 192.9	40	262.9 → 190.9	40	12.309	10	4.119	2.5
64	Metalachlor	238 → 162	10	238 → 133	24	12.315	10	4.073	2.5
65	Thiazopyr	381 → 361	6	327 → 277	24	12.336	10	4.046	2.5
66	Fenpropimorph	128 → 110	6	128 → 70	8	12.369	10	4.120	2.5
67	Fenthion	278 → 169	14	278 → 109	16	12.372	10	4.107	2.5
68	Chlorpyrifos	196.9 → 168.9	15	196.9 → 107	40	12.426	10	4.081	2.5
69	Parathion	291 → 137	4	291 → 109	10	12.458	10	4.127	2.5
70	Triadimefon	208 → 181	6	208 → 127	10	12.513	10	4.142	2.5
71	Chlorthal dimethyl	301 → 223	18	299 → 221	18	12.574	10	4.109	2.5
72	Bromophos methyl	331 → 316	10	329 → 314	12	12.93	10	4.205	2.5
73	Pirimiphos ethyl	318.1 → 182.1	15	318.1 → 166.1	15	13.009	10	4.191	2.5
74	Dimethame-tryn	212 → 122	8	212 → 94	18	13.311	10	4.298	2.5
75	Pendimethalin	252 → 191	8	252 → 162	8	13.335	10	4.261	2.5
76	Penconazole	248 → 192	10	248 → 157	18	13.381	10	4.302	2.5
77	Heptachlor epoxide	355 → 265	12	353 → 263	12	13.392	10	4.326	2.5
78	Chlorfenvin-phos	325 → 269	12	323 → 267	12	13.575	10	4.318	2.5
79	Isofenfos	213.1 → 185	5	213.1 → 121	20	13.584	10	4.308	2.5
80	Fipronil	367 → 255	18	367 → 213	22	13.639	10	4.282	2.5
81	Dimepiperate	145 → 112	6	145 → 69	12	13.671	10	4.385	2.5
82	Phethoate	274 → 125	20	274 → 121	10	13.680	10	4.350	2.5
83	Quinalphos	146.1 → 118.1	10	146.1 → 91.1	22	13.683	10	4.357	2.5
84	Triadimenol	168 → 70	8	128 → 65	18	13.689	10	4.379	2.5
85	Procymidone	283 → 96	6	283 → 68	16	13.856	10	4.373	2.5
86	Chlordane-*cis*	372.9 → 265.9	40	372.9 → 263.9	30	14.078	15	4.458	2.5

87	Bromophos ethyl	358.9 → 302.9	15	358.9 → 284.8	35	14.156	15	4.432	2.5
88	Pyrifenox	262 → 200	14	262 → 91	14	14.219	15	4.465	2.5
89	Paclobutazole	236 → 167	8	236 → 125	10	14.249	15	4.493	2.5
90	*alpha*-Endosulfan	240.9 → 205.9	15	240.9 → 136	40	14.443	15	4.532	2.5
91	Butachlor	237 → 160	8	176 → 146	20	14.491	15	4.482	2.5
92	Chlordane-*trans*	372.9 → 265.9	20	372.9 → 263.9	25	14.517	15	4.530	2.5
93	Chlorfenson	302 → 175	5	302 → 111	20	14.729	10	4.590	2.5
94	Fenamiphos	303.1 → 154	20	303.1 → 80	40	14.734	10	4.557	2.5
95	Butamifos	286 → 202	12	286 → 185	22	14.765	10	4.531	2.5
96	Hexaconazole	213.9 → 172	20	213.9 → 159	20	14.842	10	4.596	2.5
97	Flutolanil	281 → 173	10	173 → 145	14	14.861	10	4.574	2.5
98	Prothiophos	162 → 98	20	162 → 63.1	40	14.954	10	4.596	2.5
99	Imazalil	214.9 → 173	5	214.9 → 145	25	14.964	10	4.599	2.5
100	Isoprothiolane	290 → 204	2	290 → 118	10	14.978	10	4.605	2.5
101	Metominostro-bin	238 → 210	10	191 → 160	8	15.040	10	4.585	2.5
102	Profenofos	339 → 269	12	337 → 267	12	15.047	10	4.623	2.5
103	Pretilachlor	262 → 202	10	162 → 147	10	15.127	10	4.600	2.5
104	Tribufos	202 → 147	4	202 → 113	12	15.138	10	4.666	2.5
105	*p,p'*-DDE	246 → 176.1	40	246 → 175.1	40	15.154	10	4.650	2.5
106	Uniconazole	234 → 165	6	234 → 137	12	15.16	10	4.658	2.5
107	Dieldrin	262.9 → 192.9	40	262.9 → 190.9	35	15.217	10	4.686	2.5
108	Oxadiazon	258 → 175	4	175 → 112	8	15.272	10	4.640	2.5
109	Oxyfluorfen	361 → 300	10	300 → 223	12	15.450	15	4.674	2.5
110	Buprofezin	172 → 57	10	105 → 104	8	15.463	15	4.689	2.5
111	Flusilazole	233 → 165	16	233 → 152	14	15.490	15	4.684	2.5
112	Azaconazole	219 → 175.1	20	217 → 173.1	10	15.552	15	4.717	2.5
113	Bupirimate	273 → 193	10	273 → 108	14	15.569	15	4.682	2.5

114	Kresoxim-methyl	206 → 131	10	206 → 116	4	15.605	15	4.684	2.5
115	Isoxathion	313 → 177	6	177 → 130	6	15.763	15	4.758	2.5
116	Endrin	262.9 → 193	35	262.9 → 190.9	35	15.880	15	4.808	2.5
117	*beta*-Endosulfan	195 → 159	10	195 → 125	25	16.186	15	4.871	2.5
118	Diniconazole	270 → 234	15	268 → 232	15	16.371	15	4.870	2.5
119	*p,p'*-DDD	235 → 199.1	20	235 → 165.1	25	16.470	15	4.893	2.5
120	Oxadixyl	233 → 146	10	163 → 132	8	16.624	15	4.887	2.5
121	Ethion	231 → 174.9	10	231 → 128.9	18	16.628	15	4.888	2.5
122	Mepronil	269 → 210	6	269 → 119	10	16.894	15	4.973	2.5
123	Iprodione	187 → 159	15	187 → 124	25	16.903	15	4.889	2.5
124	Sulprofos	322 → 156	5	322 → 97	30	16.992	15	4.984	2.5
125	Triazophos	257 → 162	4	161 → 134	6	17.061	15	4.979	2.5
126	Carbopheno-thion	157 → 121	25	157 → 75.1	40	17.296	10	5.048	2.5
127	Benalaxyl	266 → 148	8	204 → 176	4	17.366	10	5.028	2.5
128	Cafentrazole ethyl	340 → 312	8	330 → 310	8	17.409	10	5.017	2.5
129	Endosulfan sulfate	271.9 → 236.9	20	271.9 → 116.9	40	17.542	10	5.094	2.5
130	*p,p'*-DDT	235 → 199.1	20	235 → 165.1	25	17.645	10	5.113	2.5
131	Trifloxystrobin	222 → 130	8	190 → 130	6	17.717	10	5.048	2.5
132	Propiconazole-*trans*	259 → 173	12	259 → 69	8	17.736	10	5.103	2.5
133	Pyrafulfen-ethyl	412 → 349	8	349 → 307	10	17.866	10	5.096	2.5
134	Tebuconazole	252 → 127	14	250 → 125	14	18.102	10	5.198	2.5
135	Diclofop-methyl	340 → 253	8	253 → 162	12	18.214	10	5.198	2.5
136	Piperonyl butoxide	175.9 → 161.2	5	175.9 → 117.1	20	18.434	10	5.239	2.5
137	Resmethrin	171 → 143	3	171 → 115	20	18.505	10	5.254	2.5
138	Mefenpyr diethyl	301 → 255.1	10	299 → 253.1	10	18.835	12	5.282	2.5
139	Pyributicarb	181 → 108	8	181 → 93	20	18.914	12	5.303	2.5

140	Bromopropy-late	183 → 155	15	183 → 76	35	19.314	12	5.412	2.5
141	EPN	157 → 110	15	157 → 77.1	25	19.352	12	5.403	2.5
142	Bifenthrin	181.1 → 166.1	15	181.1 → 165.1	30	19.449	12	5.393	2.5
143	Picolinafen	376 → 239	10	376 → 238	16	19.461	12	5.416	2.5
144	Piperophos	320 → 122	8	140 → 98	8	19.517	12	5.415	2.5
145	Methoxychlor	227.1 → 169.1	30	227.1 → 141.1	40	19.561	12	5.440	2.5
146	Fenpropathrin	181.1 → 152.1	30	181.1 → 127.1	35	19.655	12	5.453	2.5
147	Clomeprop	323 → 288	4	288 → 169	12	20.043	10	5.525	2.5
148	Tetradifon	356 → 159	8	354 → 159	8	20.21	10	5.558	2.5
149	Oryzastrobin	205.2 → 116.1	7	116.1 → 89.1	18	20.28	10	5.464	2.5
150	Furametpyr	298 → 123	16	157 → 76	18	20.312	10	5.523	2.5
151	Triticonazole	235 → 217.2	5	235 → 182.2	15	20.413	10	5.597	2.5
152	Oryzastrobin 5 *Z* isomer	205.2 → 116.1	7	116.1 → 89.1	18	20.574	10	5.514	2.5
153	Pyriproxyfen	136 → 96	8	136 → 78	18	20.714	10	5.640	2.5
154	Mirex	271.9 → 236.9	15	271.9 → 116.9	40	20.798	10	5.715	2.5
155	Cyhalofop-butyl	357 → 256	8	256 → 120	6	20.912	10	5.651	2.5
156	Hydroxy Furametpyr	296.2 → 278.1	12	296.2 → 262.8	28	21.178	10	5.668	2.5
157	Cyhalothrin	181.1 → 152.1	30	181.1 → 127.1	35	21.316	10	5.685	2.5
158	Fenoxaprop-ethyl	361.2 → 288.1	18	361.2 → 261.1	12	22.085	15	5.829	2.5
159	Permethrin-*cis*	183.1 → 168.1	12	183.1 → 153.1	12	22.56	20	5.893	2.5
160	Permethrin-*trans*	183.1 → 168.1	12	183.1 → 153.1	12	22.779	20	5.925	2.5
161	Prochloraz	310 → 70	14	308 → 70	14	23.035	20	5.945	2.5
162	Fenbuconazole	198 → 129	8	129 → 102	12	23.522	12	6.033	2.5
163	Cyfluthrin	163 → 127.1	5	163 → 91.1	15	23.538	12	6.028	2.5
164	Cypermethrin	181.1 → 152.1	25	181.1 → 127.1	30	24.002	12	6.116	2.5
165	Etofenprox	163 → 135	8	163 → 107	30	24.45	12	6.208	2.5

166	Silafluofen	286 → 258	10	286 → 207	12	24.699	12	6.249	2.5
167	Fenvalerate	167.1 → 125	6	167.1 → 89.1	35	25.473	15	6.383	2.5
168	Difenocona-zole-*trans*	325 → 267	12	323 → 265	12	26.294	15	6.550	2.5
169	Deltamethrin	181.1 → 152.1	25	181.1 → 127.1	25	26.394	15	6.565	2.5
170	Azoxystrobin	388 → 345	14	344 → 329	10	27.311	15	6.696	2.5

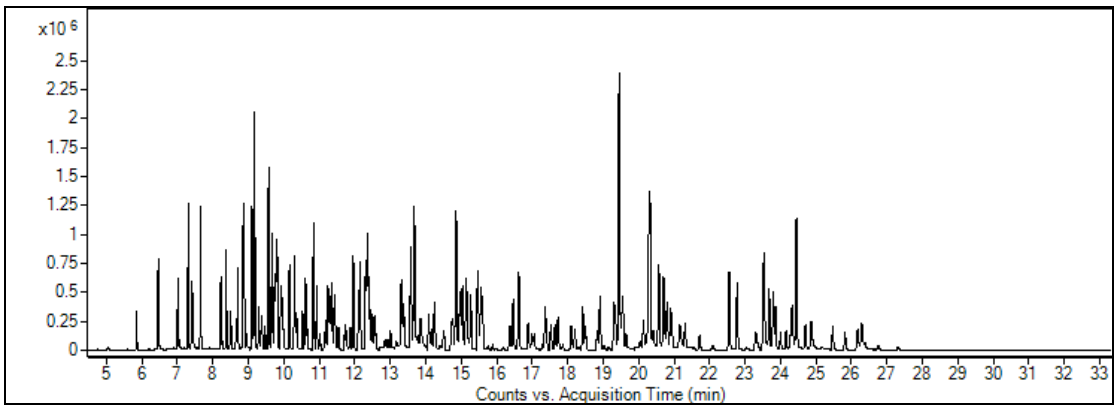


Figure 4.2 GC-MS/MS chromatogram in MRM mode of 170 standard pesticides at 0.1 mg L^{-1} in onion extract obtained using the optimum traditional GC-MS/MS conditions.

4.2 Development and optimization of sample preparation method

The great advances made in separation and detection of GC-MS/MS instrument permitted analysis of contaminants and residues in foods at desired detection limits without intensive sample preparation. However, sample clean-up is often an unavoidable step in an analytical method to reduce co-extracted components, especially in complex matrices. A proper sample preparation method is still needed to maintain long-term system performance.

As previously mentioned in the Introduction, the goal of this study was also to develop a fast and efficient sample preparation method for the analysis a number of pesticides those are required to monitor in onion. To achieve this, the QuEChERS method with an acetate buffer, which has been successfully used to analyze hundreds of pesticides in various foods, was used as a template in this study. Two important

parameters, which included acidity of extraction solvent and combination of sorbents in d-SPE clean-up, were optimized to accommodate a wide range of pesticides and provide overall good analytical results.

4.2.1 The results of the acidity of extracted solvent

As described in many literatures, the use of an acetate buffer helps to stabilize some difficult pesticides those are sensitive to acidic or basic condition into their neutral forms during matrix extracting and partitioning process. However, in this study, we also wanted to reduce the influence of matrix interferences to obtain quantitative accuracy and meet all analytical needs with method/instrument ruggedness. To achieve this, the sample size was decreased to 10 g and extracted with 10 mL of acidified MeCN (sample to solvent ratio, 1:1). %HOAc in MeCN was optimized in order to keep control pH range at about 4.6-5.6 as in the original method. The experiments were conducted by varying 0.1, 0.3, 0.5, 0.7, and 1% of HOAc in MeCN. The extraction procedures were described in the Experimental Section 3.5.1.

The obtained results were demonstrated in terms of average %recoveries (n=5) as shown in Table C-1 (APPENDIX C). Figure 4.3 shows distribution of average recoveries and RSDs for each extraction condition. The results indicated that 10 mL of 0.5% HOAc in MeCN was found to be suitable to extract 10 g onion sample. All analytes gave acceptable recoveries of 70-120% with small variation <10% RSD.

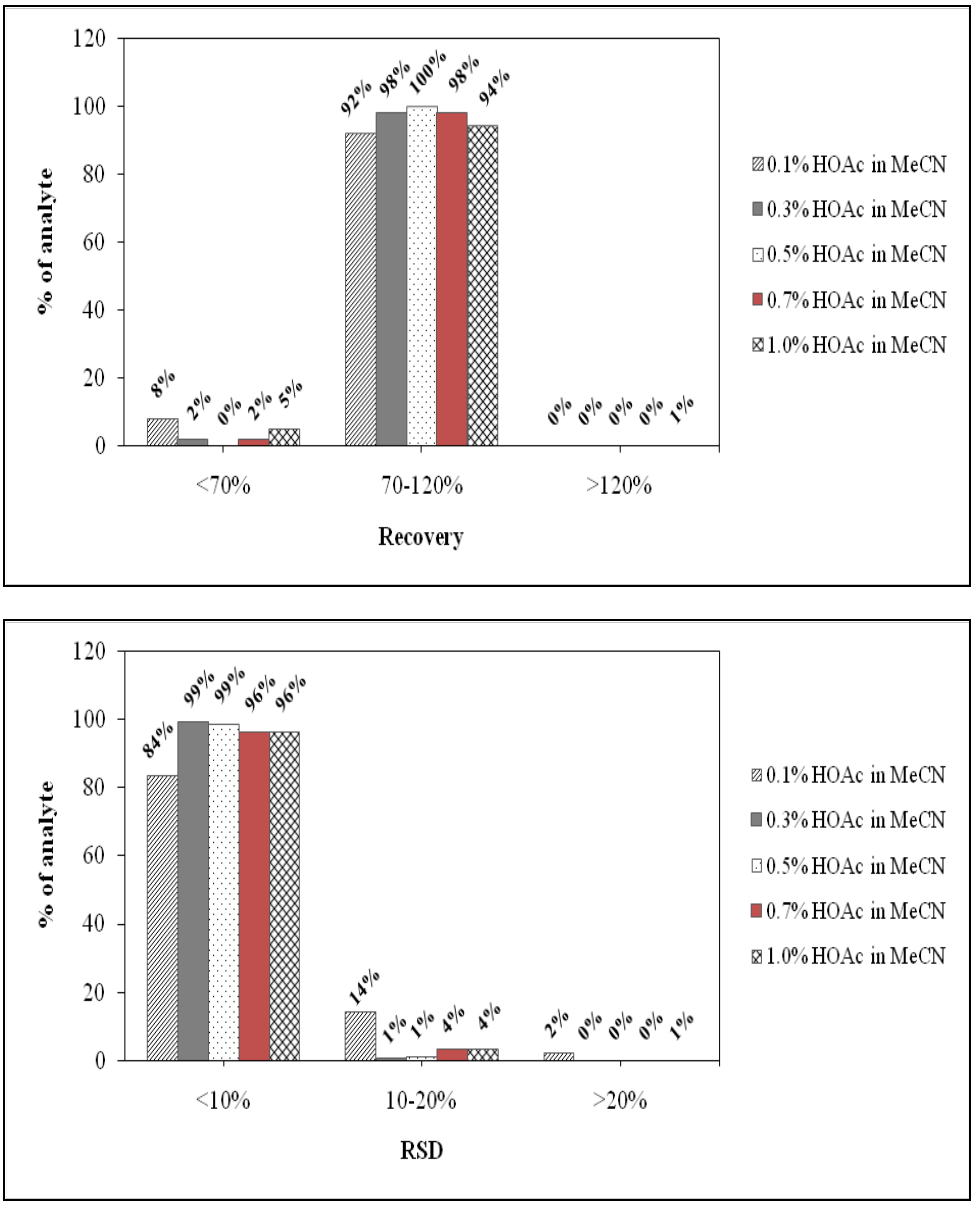


Figure 4.3 Distribution of average recoveries and RSDs obtained in the optimization of extraction solvent (**x**% HOAc in MeCN) for 170 pesticides spiked at 0.1 mg kg^{-1} in onion.

4.2.3 The study of dispersive solid phase extraction (d-SPE) sorbent

As previously mentioned in the Introduction, onion contains protein (amino acids), flavonoids, and numerous sulfur compounds (thiosulfinates, thiosulfonates, cepaenes, S-oxides, S,S-dioxides, mono-, di-, and tri-sulfides, and sulfoxides), which

are the most difficult matrix interferences for trace analysis. Moreover, the presence of faint yellow color (λ_{max} = 396 nm) in onion extract was a result of thiosulfinate components and free amino acids interaction. Therefore, clean-up step to get rid of these components or other co-extractives is necessary to protect the instruments becoming dirty and to reduce background of chromatographic responses.

As traditionally acetate buffer QuEChERS conducted, anh. $MgSO_4$ and PSA were typically used for effective clean-up co-extracted components in fruits and vegetables. anh. $MgSO_4$ was useful in removing the residual water. PSA (is a weak anion exchange sorbent) was found to effectively retain carboxylic acid molecule (fatty acids, sugars, organic acids) from the MeCN extract and provide adsorption properties for some hydrocarbons similar to C_{18}. However, the use of PSA alone may not effective enough to remove matrix interferences in onion. Therefore, additional NH_2, C_{18}, Al-N, and GCB were investigated.

Using the same onion extract (0.10 mg kg^{-1}), clean-up experiments were performed by keeping 0.15 g anh. $MgSO_4$ + 0.05 g PSA in the d-SPE format, and comparing 0.05 g each of NH_2, C_{18}, Al-N, (0.005 g) GCB, and combination of them (as described in the Experimental Section 3.5.2). In each case, recovery study (n=3) was conducted by analyzing spiked onion samples, whereas blank (without spiking pesticides) extracts were measured UV-Vis absorption (180-500 nm) for the remaining pigments and/or other matrix interferences.

Average recoveries are summarized in Table C-2 (APPENDIX-C) and depicted in Figure 4.4. The injection of M1 extract (without clean-up) into GC-MS/MS was omitted to prevent the system contamination from a large amount of pigments (strong color) in the extract. Detector saturation with the pigments was observed in the UV-Vis spectrum as shown in Figure 4.6.

- M2 (PSA): gave good recoveries for nearly all analytes, but it was not effective to remove amino acids and thiosulfinate, thus showing strong absorption in the dotted region. In this case, PSA behave like C_{18} to retain small amount of non-polar interferences.

- M5 (PSA + C_{18}): showed a similar UV spectrum to M2. C_{18} is a non-polar sorbent that removes mainly lipophilic compounds from the extract. The addition of C_{18} was found to be unsuitable in this case because it also retained a portion of non-

polar analytes like PSA, resulting in low recovery for some analytes. This was evident in low recovery of analytes in the method M9.

- M3 (PSA + Al-N): showed 2-fold lower UV-Vis abundance than M2 and M5. For Al-N, the metal clusters of aluminium can interact with compound that contains N, O, P, and S in the molecule. It was found to be very selective to remove precursors in the formation of yellow color.

- M4 (PSA + NH_2): showed a similar UV spectrum to M3 but stronger in color of the extract. Due to NH_2 has a smaller size, it can interact well with a large molecule of quercetin (flavonoids) or other phenolic pigments, leading to reduce color of the extract.

- M6 (PSA + GCB): showed the lowest UV absorbance compared to M3 and M4. GCB highly retains structurally planar molecules (pigments) and gave cleaner extract, but it removed some planar pesticides in the method.

Although the remaining pigments was not directly affecting in chromatographic separation but it gradually accumulated in the GC liner after injections, leading to reduce ruggedness of the method (t_R shift and peak broadening). Method M3, M4, and M6 provided acceptable results in terms of recovery, but they had strong color of the extract. However, the further clean-up experiments found that combination of GCB with Al-N or NH_2 provided much cleaner extracts as shown in Figure 4.5 and 4.6.

Ultimately, the combination of 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N + 0.005 g GCB was chosen as the most efficient d-SPE clean-up for onion with acceptable recoveries (≥70%) and RSD (≤20%) for all analytes with minimizing in pigments and other matrix interferences.

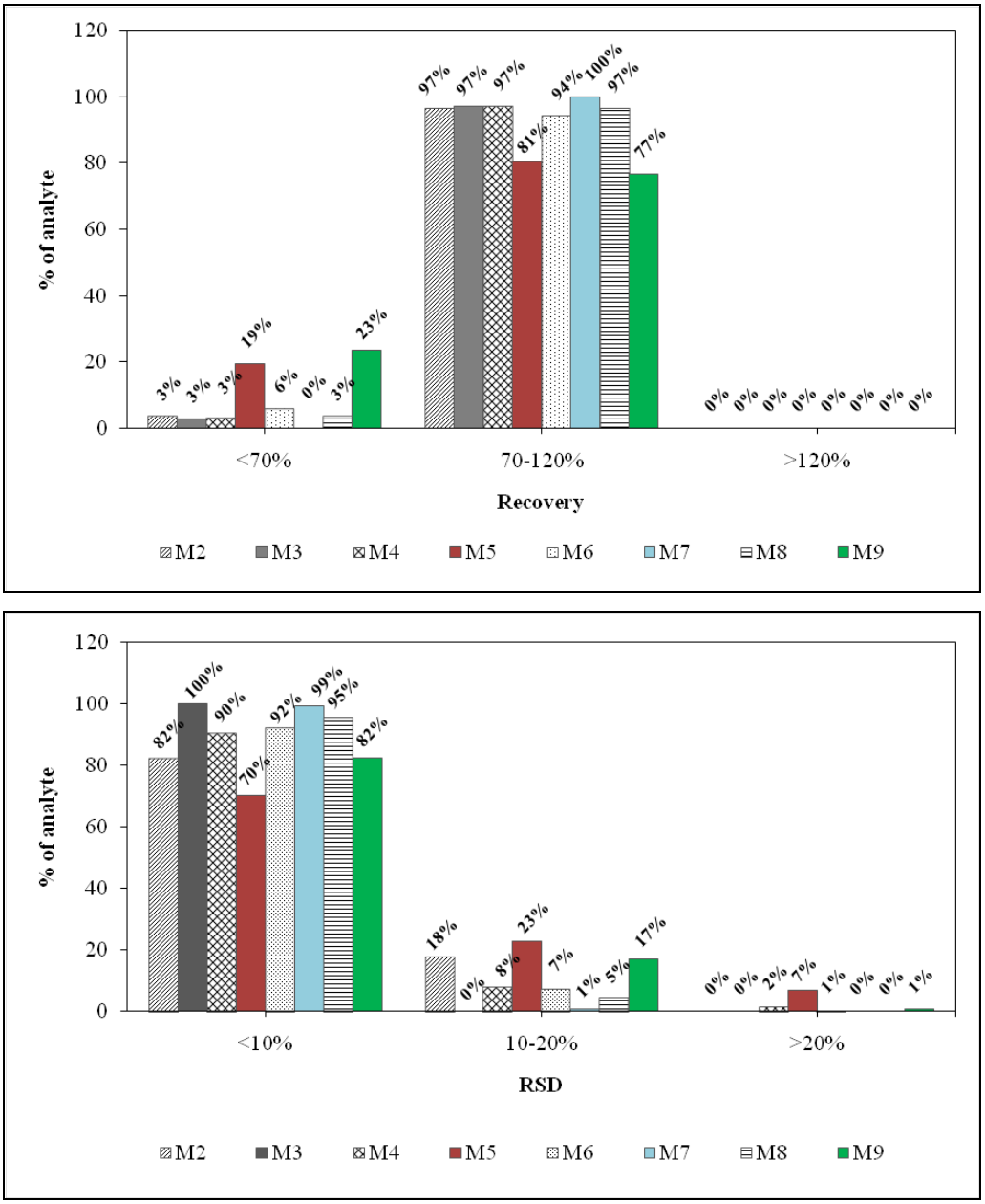


Figure 4.4 Distribution of average recoveries and RSDs obtained in the optimization of d-SPE clean-up for 170 pesticides at 0.1 mg kg^{-1} in onion.

M2**:** 0.15 g anh. $MgSO_4$ + 0.05 g PSA

M3: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N

M4: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g NH_2

M5: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g C_{18}

M6: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.005 g GCB

M7: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g Al-N + 0.005 g GCB

M8: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g NH_2 + 0.005 g GCB

M9: 0.15 g anh. $MgSO_4$ + 0.05 g PSA + 0.05 g C_{18} + 0.005 g GCB

[M1] [M2] [M3] [M4] [M5] [M6] [M7] [M8] [M9]

Figure 4.5 Color of blank onion extracts based on different combinations of d-SPE sorbents.

Figure 4.6 UV-Vis spectra (180-500 nm) of blank onion extracts obtained from different d-SPE clean-up.

4.3 Method validation for traditional GC-MS/MS

The purpose of method validation is to confirm that the developed analytical procedure is suitable for routine residues monitoring. In this study, important parameters for validation included selectivity, linearity, matrix effects, accuracy, precision, limit of detection (LOD), limit of quantitation (LOQ) and lowest calibrated level (LCL).

4.3.1 Selectivity

In this study, selectivity was performed by the analysis of different 20 blank onion samples in order to verify the absence of interferences. The results showed no interfering peaks co-eluted at the same retention time of interest for analytes in any onion extracts. Pesticide standards spiked in each onion extracts were injected and identified by their retention times (t_R) and ion ratios.

According to the 2002/657/EC, common performance criteria and requirements for mass spectrometric detection were included for identification purpose in this study. Monitoring of 2 ion transitions (1 precursor ion and 2 product ions) for each analyte provided 4 identification points, which fulfilled the minimum requirement for MS/MS. Tolerance window of t_R ± 0.5% and ion ratio ± %permitted tolerances (as demonstrated in Table 4.4) were also made into consideration. The t_R, ion ratios, and their tolerance windows are summarized in Table 4.5. The acceptable ion ratios of MRM transitions for each analyte were able to clearly distinguish between co-eluters.

Table 4.4 Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques [42].

Releative intensitiy (% of base peak)	$GC\text{-}MS^n$ (relative)
> 50%	± 20%
> 20% to 50%	± 25%
> 10% to 20%	± 30%
≤ 10%	± 50%

Table 4.5 Retention time (t_R), ion ratio, and method validation results.

No.	Compound	Traditional GC-MS/MS								LP-GC-MS/MS							
				R^2			Analytical limit					R^2			Analytical limit		
		t_R (min)	Ion ratio	in MeCN	in matrix	% ME	LOD	LOQ	LCL	t_R (min)	Ion ratio	in MeCN	in matrix	% ME	LOD	LOQ	LCL
1	Dichlorvos	5.852 ± 0.029	12.8 ± 3.8	0.990	0.990	-16	0.005	0.01	0.01	2.536 ± 0.013	11.6 ± 3.5	0.995	0.991	-22	0.003	0.01	0.01
2	EPTC	6.434 ± 0.032	48.8 ± 12.2	0.983	0.997	-11	0.005	0.01	0.01	2.747 ± 0.014	20.3 ± 5.1	0.990	0.992	12	0.003	0.01	0.01
3	Dichlobenil	6.463 ± 0.032	47.8 ± 12.0	0.993	0.999	-9	0.005	0.01	0.01	2.734 ± 0.014	69.6 ± 13.9	0.990	0.993	101	0.003	0.01	0.01
4	Propham	7.020 ± 0.035	73.7 ±14.7	0.992	0.993	139	0.005	0.01	0.01	2.929 ± 0.015	70.8 ± 14.2	0.999	0.994	79	0.003	0.01	0.01
5	Thiometon	7.309 ± 0.037	60.9 ±12.2	0.991	0.991	8	0.005	0.01	0.01	3.457 ± 0.017	4.3 ± 2.2	0.999	0.996	-83	0.003	0.01	0.01
6	Methacrifos	7.310 ± 0.037	17.0 ± 5.1	0.990	0.991	19	0.005	0.01	0.01	2.993 ± 0.015	21.6 ± 5.4	0.999	0.991	29	0.003	0.01	0.01
7	Chloroneb	7.404 ± 0.037	63.0 ± 12.6	0.995	0.995	20	0.005	0.01	0.01	3.017 ± 0.015	91.0 ± 18.2	0.996	0.992	34	0.003	0.01	0.01
8	Molinate	7.656 ± 0.038	12.7 ± 3.8	0.997	0.994	52	0.005	0.01	0.01	3.104 ± 0.016	27.6 ± 6.9	0.995	0.994	58	0.003	0.01	0.01
9	Tecnazene	8.232 ± 0.041	48.4 ± 12.1	0.995	0.995	21	0.005	0.01	0.01	3.195 ± 0.016	72.5 ± 14.5	0.997	0.990	32	0.003	0.01	0.01
10	Propachlor	8.235 ± 0.041	4.1 ± 2.1	0.999	0.996	-25	0.005	0.01	0.01	3.219 ± 0.016	6.1 ± 3.1	0.996	0.992	4	0.003	0.01	0.01
11	Chlorpropham	8.505 ± 0.043	92.7 ± 18.5	0.990	0.993	106	0.005	0.01	0.01	3.314 ± 0.017	68.1 ± 13.6	0.996	0.999	71	0.003	0.01	0.01

12	Ethafluralin	8.532 ± 0.043	70.7 ± 14.1	0.994	0.992	47	0.005	0.01	0.01	3.279 ± 0.016	48.1 ± 12.0	0.999	0.992	75	0.003	0.01	0.01
13	Triflulalin	8.665 ± 0.043	18.0 ± 5.4	0.996	0.994	38	0.005	0.01	0.01	3.308 ± 0.017	13.3 ± 4.0	0.999	0.992	62	0.003	0.01	0.01
14	Benfluralin	8.704 ± 0.044	69.2 ± 13.8	0.996	0.994	19	0.005	0.01	0.01	3.320 ± 0.017	38.6 ± 9.7	0.999	0.992	58	0.003	0.01	0.01
15	Cadusafos	8.869 ± 0.044	79.5 ± 15.9	0.990	0.994	50	0.005	0.01	0.01	3.380 ± 0.017	45.1 ± 11.3	1.000	0.997	34	0.003	0.01	0.01
16	Ethoprophos	8.869 ± 0.044	85.3 ± 17.1	0.991	0.994	30	0.005	0.01	0.01	3.273 ± 0.016	65.8 ± 13.2	0.999	0.990	34	0.003	0.01	0.01
17	Bromobutide metabolite	8.902 ± 0.045	36.2 ± 9.1	0.996	0.994	60	0.005	0.01	0.01	3.391 ± 0.017	58.1 ± 11.6	0.998	0.997	73	0.003	0.01	0.01
18	Phorate	8.962 ± 0.045	68.6 ± 13.7	0.991	0.992	64	0.005	0.01	0.01	3.400 ± 0.017	65.3 ± 13.1	0.998	0.994	54	0.003	0.01	0.01
19	Fenclorim	9.103 ± 0.046	54.6 ± 10.9	0.995	0.992	28	0.005	0.01	0.01	3.431 ± 0.017	43.5 ± 10.9	0.998	0.997	79	0.003	0.01	0.01
20	*alpha*-Lindane	9.124 ± 0.046	80.5 ± 16.1	0.990	0.993	-3	0.005	0.01	0.01	3.434 ± 0.017	49.7 ± 12.4	0.990	0.991	29	0.003	0.01	0.01
21	Demeton-S-methyl	9.180 ± 0.046	15.4 ± 4.6	0.991	0.993	17	0.005	0.01	0.01	3.248 ± 0.016	57.2 ± 11.4	0.999	0.991	72	0.003	0.01	0.01
22	HCB	9.300 ± 0.047	67.6 ± 13.5	0.993	0.993	29	0.005	0.01	0.01	3.451 ± 0.017	69.3 ± 13.9	0.992	0.991	33	0.003	0.01	0.01
23	Simazine	9.390 ± 0.047	28.4 ± 7.1	0.924	0.993	43	0.005	0.01	0.01	3.505 ± 0.018	15.6 ± 4.7	0.997	0.990	81	0.003	0.01	0.01
24	Atrazine	9.479 ± 0.047	76.0 ± 15.2	0.991	0.993	44	0.005	0.01	0.01	3.523 ± 0.018	95.8 ± 19.2	0.999	0.990	34	0.003	0.01	0.01
25	Clomazole	9.575 ± 0.048	43.0 ± 10.8	0.995	0.993	29	0.005	0.01	0.01	3.545 ± 0.018	52.9 ± 10.6	0.999	0.998	54	0.003	0.01	0.01
26	*beta*-Lindane	9.671 ± 0.048	53.9 ± 10.8	0.995	0.993	10	0.005	0.01	0.01	3.543 ± 0.018	116.1 ± 23.2	0.994	0.996	86	0.003	0.01	0.01
27	Propetamphos	9.740 ± 0.049	71.6 ± 14.3	0.978	0.994	89	0.005	0.01	0.01	3.569 ± 0.018	57.2 ± 11.4	0.999	0.998	54	0.003	0.01	0.01

28	*gamma*-Lindane	9.775 ± 0.049	34.7 ± 8.7	0.992	0.994	-7	0.005	0.01	0.01	3.582 ± 0.018	94.7 ± 18.9	0.993	0.995	218	0.003	0.01	0.01
29	Terbufos	9.804 ± 0.049	68.3 ± 13.7	0.992	0.991	49	0.005	0.01	0.01	3.589 ± 0.018	5.6 ± 2.8	0.999	0.998	52	0.003	0.01	0.01
30	Cyanophos	9.822 ± 0.049	22.1 ± 5.5	0.976	0.994	-6	0.005	0.01	0.01	3.589 ± 0.018	13.4 ± 4.0	0.999	0.991	48	0.003	0.01	0.01
31	Fonophos	9.920 ± 0.050	54.0 ± 10.8	0.997	0.992	30	0.005	0.01	0.01	3.613 ± 0.018	96.3 ± 19.3	0.998	0.996	58	0.003	0.01	0.01
32	Pyroquilon	9.961 ± 0.050	32.9 ± 8.2	0.991	0.995	89	0.005	0.01	0.01	3.634 ± 0.018	36.3 ± 9.1	0.994	0.990	68	0.003	0.01	0.01
33	Diazinon	9.997 ± 0.050	97.9 ± 19.6	0.994	0.995	36	0.005	0.01	0.01	3.604 ± 0.018	70.2 ± 14.0	0.999	0.997	38	0.003	0.01	0.01
34	Disulfoton	10.165 ± 0.051	12.9 ± 3.9	0.992	0.994	78	0.005	0.01	0.01	3.669 ± 0.018	27.8 ± 7.0	0.998	0.998	72	0.003	0.01	0.01
35	*delta*-Lindane	10.310 ± 0.052	53.3 ± 10.7	0.998	0.994	1	0.005	0.01	0.01	3.711 ± 0.019	30.6 ± 7.7	0.990	0.993	12	0.003	0.01	0.01
36	Isazophos	10.318 ± 0.052	17.3 ± 5.2	0.991	0.994	23	0.005	0.01	0.01	3.666 ± 0.018	46.5 ± 11.6	0.999	0.997	35	0.003	0.01	0.01
37	Triallate	10.362 ± 0.052	39.3 ± 9.8	0.997	0.994	25	0.005	0.01	0.01	3.705 ± 0.019	41.0 ± 10.3	0.998	0.998	53	0.003	0.01	0.01
38	Iprobenfos	10.530 ± 0.053	25.0 ± 6.3	0.971	0.997	306	0.005	0.01	0.01	3.741 ± 0.019	29.4 ± 7.4	0.999	0.996	55	0.003	0.01	0.01
39	Pirimicarb	10.615 ± 0.053	73.0 ± 14.6	0.991	0.995	62	0.005	0.01	0.01	3.724 ± 0.019	48.0 ± 12.0	0.999	0.994	48	0.003	0.01	0.01
40	Benoxacor	10.663 ± 0.053	54.7 ± 10.9	0.990	0.996	12	0.005	0.01	0.01	3.765 ± 0.019	53.5 ± 10.7	0.999	0.996	36	0.003	0.01	0.01
41	Benflurasate	10.842 ± 0.054	98.8 ± 19.8	0.995	0.994	32	0.005	0.01	0.01	3.811 ± 0.019	68.3 ± 13.7	0.999	0.998	67	0.003	0.01	0.01
42	Dichlorfenthion	10.929 ± 0.055	56.7 ± 11.3	0.994	0.994	24	0.005	0.01	0.01	3.812 ± 0.019	49.1 ± 12.3	0.999	0.998	59	0.003	0.01	0.01
43	Bromobutide	11.024 ± 0.055	58.9 ± 11.8	0.995	0.995	53	0.005	0.01	0.01	3.849 ± 0.019	68.0 ± 13.6	0.999	0.998	54	0.003	0.01	0.01

44	Vinclozolin	11.148 ± 0.056	76.3 ± 15.3	0.995	0.995	20	0.005	0.01	0.01	3.862 ± 0.019	60.0 ± 12.0	0.999	0.998	54	0.003	0.01	0.01
45	Chlorpyrifos methyl	11.181 ± 0.056	23.4 ± 5.9	0.990	0.994	25	0.005	0.01	0.01	3.880 ± 0.019	13.9 ± 4.2	0.999	0.991	34	0.003	0.01	0.01
46	Parathion methyl	11.189 ± 0.056	38.4 ± 9.6	0.913	0.994	34	0.005	0.01	0.01	3.846 ± 0.019	73.8 ± 14.8	0.989	0.992	92	0.003	0.01	0.01
47	Simetryn	11.252 ± 0.056	45.6 ± 11.4	0.978	0.997	79	0.005	0.01	0.01	3.903 ± 0.020	35.5 ± 8.9	0.998	0.997	75	0.003	0.01	0.01
48	Simiconazole	11.254 ± 0.056	40.2 ± 10.1	0.974	0.995	386	0.005	0.01	0.01	3.882 ± 0.019	70.3 ± 14.1	0.999	0.992	53	0.003	0.01	0.01
49	Tolclofos methyl	11.300 ± 0.057	70.9 ± 14.2	0.995	0.995	6	0.005	0.01	0.01	3.886 ± 0.019	44.5 ± 11.1	0.999	0.996	35	0.003	0.01	0.01
50	Alachlor	11.352 ± 0.057	60.3 ± 12.1	0.997	0.996	-7	0.005	0.01	0.01	3.881 ± 0.019	33.0 ± 8.3	0.999	0.990	21	0.003	0.01	0.01
51	Ametryn	11.357 ± 0.057	75.8 ± 15.2	0.980	0.996	53	0.005	0.01	0.01	3.921 ± 0.020	62.7 ± 12.5	0.999	0.998	60	0.003	0.01	0.01
52	Heptachlor	11.417 ± 0.057	65.7 ± 13.1	0.992	0.996	10	0.005	0.01	0.01	3.936 ± 0.020	65.0 ± 13.0	0.998	0.990	-3	0.003	0.01	0.01
53	Prometryn	11.431 ± 0.057	82.1 ± 16.4	0.993	0.995	40	0.005	0.01	0.01	3.932 ± 0.020	89.3 ± 17.9	0.999	0.997	55	0.003	0.01	0.01
54	Cinmethylin	11.451 ± 0.057	84.0 ± 16.8	0.997	0.994	7	0.005	0.01	0.01	3.934 ± 0.020	86.3 ± 17.3	0.998	0.998	51	0.003	0.01	0.01
55	Metalaxyl	11.475 ± 0.057	77.6 ± 15.5	0.994	0.996	32	0.005	0.01	0.01	3.916 ± 0.020	89.0 ± 17.8	0.998	0.990	27	0.003	0.01	0.01
56	Fenchlorfos	11.539 ± 0.058	53.3 ± 10.7	0.984	0.994	2	0.005	0.01	0.01	3.934 ± 0.020	51.1 ± 10.2	0.999	0.993	33	0.003	0.01	0.01
57	Dithopyr	11.726 ± 0.059	85.6 ± 17.1	0.998	0.996	15	0.005	0.01	0.01	3.935 ± 0.020	61.8 ± 12.4	0.999	0.998	44	0.003	0.01	0.01
58	Terbutryn	11.770 ± 0.059	31.1 ± 7.8	0.992	0.997	66	0.005	0.01	0.01	4.000 ± 0.020	41.1 ± 10.3	0.999	0.998	56	0.003	0.01	0.01
59	Pirimiphos methyl	11.879 ± 0.059	46.8 ± 11.7	0.990	0.993	44	0.005	0.01	0.01	3.981 ± 0.020	78.1 ± 15.6	0.999	0.993	25	0.003	0.01	0.01

60	Esprocarb	11.962 ± 0.060	63.6 ± 12.7	0.993	0.996	56	0.005	0.01	0.01	4.053 ± 0.020	57.0 ± 11.4	0.999	0.999	57	0.003	0.01	0.01
61	Malathion	12.108 ± 0.061	27.4 ± 6.9	0.968	0.994	38	0.005	0.01	0.01	4.045 ± 0.020	40.0 ± 10.0	0.999	0.990	46	0.003	0.01	0.01
62	Thiobencarb	12.155 ± 0.061	12.5 ± 3.8	0.994	0.995	117	0.005	0.01	0.01	4.102 ± 0.021	13.1 ± 3.9	0.997	0.999	82	0.003	0.01	0.01
63	Aldrin	12.309 ± 0.062	81.9 ± 16.4	0.991	0.994	-8	0.005	0.01	0.01	4.125 ± 0.021	84.2 ± 16.8	0.992	0.991	23	0.003	0.01	0.01
64	Metolachlor	12.315 ± 0.062	25.1 ± 6.3	0.995	0.996	36	0.005	0.01	0.01	4.078 ± 0.020	18.8 ± 5.6	0.999	0.997	49	0.003	0.01	0.01
65	Thiazopyr	12.336 ± 0.062	32.4 ± 8.1	0.995	0.997	46	0.005	0.01	0.01	4.050 ± 0.020	36.6 ± 9.2	0.999	0.997	45	0.003	0.01	0.01
66	Fenpropimorph	12.369 ± 0.062	45.9 ± 11.5	0.990	0.993	98	0.005	0.01	0.01	4.125 ± 0.021	71.0 ± 14.2	0.999	0.998	61	0.003	0.01	0.01
67	Fenthion	12.372 ± 0.062	32.8 ± 8.2	0.990	0.993	21	0.005	0.01	0.01	4.112 ± 0.021	49.8 ± 12.5	0.999	0.992	42	0.003	0.01	0.01
68	Chlorpyrifos	12.426 ± 0.062	46.3 ± 11.6	0.993	0.994	12	0.005	0.01	0.01	4.086 ± 0.020	25.5 ± 6.4	0.999	0.997	38	0.003	0.01	0.01
69	Parathion	12.458 ± 0.062	17.2 ± 5.2	0.948	0.995	63	0.005	0.01	0.01	4.130 ± 0.021	36.8 ± 9.2	0.996	0.995	64	0.003	0.01	0.01
70	Triadimefon	12.513 ± 0.063	53.5 ± 10.7	0.992	0.994	30	0.005	0.01	0.01	4.147 ± 0.021	30.3 ± 7.6	0.999	0.996	45	0.003	0.01	0.01
71	Chlorthal dimethyl	12.574 ± 0.063	94.6 ± 18.9	0.998	0.996	23	0.005	0.01	0.01	4.112 ± 0.021	94.1 ± 18.8	0.999	0.998	44	0.003	0.01	0.01
72	Bromophos methyl	12.930 ± 0.065	87.5 ± 17.5	0.970	0.995	14	0.005	0.01	0.01	4.210 ± 0.021	90.0 ± 18.0	0.998	0.992	69	0.003	0.01	0.01
73	Pirimiphos ethyl	13.009 ± 0.065	73.6 ± 14.7	0.992	0.994	65	0.005	0.01	0.01	4.195 ± 0.021	80.3 ± 16.1	0.999	0.998	47	0.003	0.01	0.01
74	Dimethametryn	13.311 ± 0.067	64.3 ± 12.9	0.990	0.996	85	0.005	0.01	0.01	4.302 ± 0.022	89.3 ± 17.9	0.998	0.997	68	0.003	0.01	0.01
75	Pendimethalin	13.335 ± 0.067	59.3 ± 11.9	0.963	0.996	95	0.005	0.01	0.01	4.265 ± 0.021	62.4 ± 12.5	0.998	0.998	55	0.003	0.01	0.01

76	Penconazole	13.381 ± 0.067	92.4 ± 18.5	0.992	0.994	65	0.005	0.01	0.01	4.305 ± 0.022	92.8 ± 18.6	0.998	0.992	57	0.003	0.01	0.01
77	Heptachlor epoxide	13.392 ± 0.067	62.2 ± 12.4	0.995	0.993	25	0.005	0.01	0.01	4.331 ± 0.022	62.8 ± 12.6	0.997	0.991	57	0.003	0.01	0.01
78	Chlorfenvinphos	13.575 ± 0.068	63.8±12.8	0.978	0.994	27	0.005	0.01	0.01	4.322 ± 0.022	64.6 ± 12.9	0.999	0.990	42	0.003	0.01	0.01
79	Isofenfos	13.584 ± 0.068	65.7±13.1	0.968	0.995	57	0.005	0.01	0.01	4.312 ± 0.022	102.8 ± 20.6	0.999	0.998	51	0.003	0.01	0.01
80	Fipronil	13.639 ± 0.068	30.1 ± 7.5	0.955	0.994	226	0.005	0.01	0.01	4.285 ± 0.021	31.1 ± 7.8	0.990	0.998	162	0.003	0.01	0.01
81	Dimepiperate	13.671 ± 0.068	39.4± 9.9	0.992	0.996	129	0.005	0.01	0.01	4.389 ± 0.022	17.3 ± 5.2	0.999	0.998	48	0.003	0.01	0.01
82	Phethoate	13.680 ± 0.068	62.5 ± 12.5	0.992	0.996	8	0.005	0.01	0.01	4.353 ± 0.022	71.0 ± 14.2	0.999	0.996	39	0.003	0.01	0.01
83	Quinalphos	13.683 ± 0.068	47.9 ± 12.0	0.990	0.996	9	0.005	0.01	0.01	4.361 ± 0.022	39.2 ± 9.8	0.999	0.993	47	0.003	0.01	0.01
84	Triadimenol	13.689 ± 0.068	55.2 ± 11.0	0.972	0.995	291	0.005	0.01	0.01	4.382 ± 0.022	43.8 ± 11.0	0.997	0.991	108	0.003	0.01	0.01
85	Procymidone	13.856 ± 0.069	21.7 ± 5.4	0.994	0.996	17	0.005	0.01	0.01	4.377 ± 0.022	13.7 ± 4.1	0.998	0.998	54	0.003	0.01	0.01
86	Chlordane-*cis*	14.078 ± 0.070	87.5 ± 17.5	0.998	0.996	31	0.005	0.01	0.01	4.461 ± 0.022	90.0 ± 18.0	0.998	0.999	54	0.003	0.01	0.01
87	Bromophos ethyl	14.156 ± 0.071	20.6 ± 5.2	0.990	0.996	19	0.005	0.01	0.01	4.436 ± 0.022	16.1 ± 4.8	0.999	0.997	44	0.003	0.01	0.01
88	Pyrifenox	14.219 ± 0.071	53.1 ± 10.6	0.961	0.997	81	0.005	0.01	0.01	4.469 ± 0.022	66.6 ± 13.3	0.998	0.994	55	0.003	0.01	0.01
89	Paclobutazole	14.249 ± 0.071	35.5 ± 8.9	0.947	0.994	284	0.005	0.01	0.01	4.494 ± 0.022	59.0 ± 11.8	0.998	0.993	70	0.003	0.01	0.01
90	*alpha*-Endosulfan	14.443 ± 0.072	22.2 ± 5.6	0.998	0.994	3	0.005	0.01	0.01	4.537 ± 0.023	14.4 ± 4.3	0.995	0.998	52	0.003	0.01	0.01
91	Butachlor	14.491 ± 0.072	97.3 ± 19.5	0.992	0.992	-6	0.005	0.01	0.01	4.487 ± 0.022	86.8 ± 17.4	0.998	0.996	39	0.003	0.01	0.01

92	Chlordane-*trans*	14.517 ± 0.072	86.9 ± 17.4	0.998	0.994	29	0.005	0.01	0.01	4.534 ± 0.023	83.2 ± 16.6	0.998	0.996	46	0.003	0.01	0.01
93	Chlorfenson	14.729 ± 0.074	93.9 ± 18.8	0.965	0.994	63	0.005	0.01	0.01	4.594 ± 0.023	64.7 ± 12.9	0.991	0.997	114	0.003	0.01	0.01
94	Fenamiphos	14.734 ± 0.074	68.4 ± 13.7	0.916	0.992	293	0.005	0.01	0.01	4.560 (0.023	57.8 (11.6	0.993	0.991	141	0.003	0.01	0.01
95	Butamifos	14.765 (0.074	94.4 (18.9	0.932	0.994	160	0.005	0.01	0.01	4.533 ± 0.023	73.2 ± 14.6	0.998	0.998	85	0.003	0.01	0.01
96	Hexaconazole	14.842 ± 0.074	84.8 ± 17.0	0.966	0.997	133	0.005	0.01	0.01	4.601 (0.023	93.7 (18.7	0.995	0.994	61	0.003	0.01	0.01
97	Flutolanil	14.861 ± 0.074	26.6 ± 6.7	0.992	0.995	70	0.005	0.01	0.01	4.577 ± 0.023	36.0 ± 9.0	0.993	0.999	67	0.003	0.01	0.01
98	Prothiophos	14.954 ± 0.075	49.7 ± 12.4	0.993	0.992	15	0.005	0.01	0.01	4.601 ± 0.023	30.5 ± 7.6	0.999	0.997	45	0.003	0.01	0.01
99	Imazalil	14.964 ± 0.075	13.1 ± 3.9	0.876	0.996	281	0.005	0.01	0.01	4.601 ± 0.023	9.7 ± 4.9	0.997	0.995	107	0.003	0.01	0.01
100	Isoprothiolane	14.978 ± 0.075	57.1 ± 11.4	0.993	0.997	50	0.005	0.01	0.01	4.609 ± 0.023	99.8 ± 20.0	0.997	0.996	51	0.003	0.01	0.01
101	Metominostrobin	15.040 ± 0.075	43.0 ± 10.8	0.990	0.996	100	0.005	0.01	0.01	4.589 ± 0.023	26.5 ± 6.6	0.994	0.991	72	0.003	0.01	0.01
102	Profenofos	15.047 ± 0.075	99.3 ± 19.9	0.991	0.991	-7	0.005	0.01	0.01	4.629 ± 0.023	100.7 ± 20.1	0.998	0.990	29	0.003	0.01	0.01
103	Pretilachlor	15.127 ± 0.076	38.6 ± 9.7	0.992	0.991	-42	0.005	0.01	0.01	4.604 ± 0.023	29.6 ± 7.4	0.998	0.993	37	0.003	0.01	0.01
104	Tribufos	15.138 ± 0.076	61.3 ± 12.3	0.994	0.993	17	0.005	0.01	0.01	4.666 ± 0.023	43.8 ± 11.0	0.999	0.997	49	0.003	0.01	0.01
105	*p,p'*-DDE	15.154 ± 0.076	15.6 ± 4.7	0.996	0.992	19	0.005	0.01	0.01	4.651 ± 0.023	13.2 ± 4.0	0.998	0.999	57	0.003	0.01	0.01
106	Uniconazole	15.160 ± 0.076	85.7 ± 17.1	0.954	0.996	331	0.005	0.01	0.01	4.661 ± 0.023	60.6 ± 12.1	0.997	0.991	96	0.003	0.01	0.01
107	Dieldrin	15.217 ± 0.076	80.8 ± 16.2	0.998	0.992	16	0.005	0.01	0.01	4.691 ± 0.023	67.5 ± 13.5	0.999	0.997	24	0.003	0.01	0.01

108	Oxadiazon	15.272 ± 0.076	46.9 ± 11.7	0.994	0.994	19	0.005	0.01	0.01	4.645 (0.023	72.0 ± 14.4	0.996	0.997	62	0.003	0.01	0.01
109	Oxyfluorfen	15.450 ± 0.077	93.1 ± 18.6	0.945	0.992	12	0.005	0.01	0.01	4.675 (0.023	65.1 ± 13.0	0.996	0.997	121	0.003	0.01	0.01
110	Buprofezin	15.463 ± 0.077	17.9 ± 5.4	0.995	0.991	51	0.005	0.01	0.01	4.689 ± 0.023	15.9 ± 4.8	0.997	0.997	53	0.003	0.01	0.01
111	Flusilazole	15.490 ± 0.077	70.5 ± 14.1	0.998	0.982	77	0.005	0.01	0.01	4.684 ± 0.023	60.6 ± 12.1	0.992	0.991	70	0.003	0.01	0.01
112	Azaconazole	15.552 ± 0.078	71.8 ± 14.4	0.993	0.995	54	0.005	0.01	0.01	4.719 ± 0.024	71.5 ± 14.3	0.990	0.997	82	0.003	0.01	0.01
113	Bupirimate	15.569 ± 0.078	86.2 ± 17.2	0.992	0.997	80	0.005	0.01	0.01	4.683 ± 0.023	69.2 ± 13.8	0.995	0.997	77	0.003	0.01	0.01
114	Kresoxim-methyl	15.605 ± 0.078	55.3 ± 11.1	0.992	0.995	144	0.005	0.01	0.01	4.688 ± 0.023	69.1 ± 13.8	0.995	0.996	56	0.003	0.01	0.01
115	Isoxathion	15.763 ± 0.079	24.6 ± 6.2	0.946	0.990	189	0.005	0.01	0.01	4.759 ± 0.024	45.2 ± 11.3	0.996	0.990	117	0.003	0.01	0.01
116	Endrin	15.880 ± 0.079	73.3 ± 14.7	0.992	0.992	87	0.005	0.01	0.01	4.811 ± 0.024	67.7 ± 13.5	0.999	0.997	50	0.003	0.01	0.01
117	*beta*-Endosulfan	16.186 ± 0.081	96.4 ± 19.3	0.995	0.994	-9	0.005	0.01	0.01	4.875 ± 0.024	79.8 ± 16.0	0.998	0.993	54	0.003	0.01	0.01
118	Diniconazole	16.371 ± 0.082	32.2 ± 8.1	0.904	0.994	271	0.005	0.01	0.01	4.873 ± 0.024	33.1 ± 8.3	0.998	0.993	99	0.003	0.01	0.01
119	*p,p'*-DDD	16.470 ± 0.082	20.5 ± 5.1	0.990	0.991	19	0.005	0.01	0.01	4.896 ± 0.024	21.8 ± 5.5	0.997	0.997	60	0.003	0.01	0.01
120	Oxadixyl	16.624 ± 0.083	19.9 ± 6.0	0.990	0.994	-42	0.005	0.01	0.01	4.887 ± 0.024	18.8 ± 5.6	0.985	0.990	22	0.003	0.01	0.01
121	Ethion	16.628 ± 0.083	70.9 ± 14.2	0.949	0.991	58	0.005	0.01	0.01	4.891 ± 0.024	71.5 ± 14.3	0.999	0.993	-85	0.003	0.01	0.01
122	Mepronil	16.894 ± 0.084	20.7 ± 5.2	0.975	0.990	47	0.005	0.01	0.01	4.974 ± 0.025	21.2 ± 5.3	0.993	0.993	128	0.003	0.01	0.01
123	Iprodione	16.903 ± 0.085	31.7 ± 7.9	0.977	0.994	95	0.005	0.01	0.01	4.892 ± 0.024	52.1 ± 10.4	0.990	0.991	164	0.003	0.01	0.01

124	Sulprofos	16.992 ± 0.085	63.4 ± 12.7	0.966	0.996	56	0.005	0.01	0.01	4.987 ± 0.025	91.0 ± 18.2	0.998	0.994	74	0.003	0.01	0.01
125	Triazophos	17.061 ± 0.085	61.7 ± 12.3	0.800	0.990	41	0.005	0.01	0.01	4.982 ± 0.025	73.7 ± 14.7	0.993	0.990	67	0.003	0.01	0.01
126	Carbophenothion	17.296 ± 0.086	59.0 ± 11.8	0.972	0.997	99	0.005	0.01	0.01	5.050 ± 0.025	63.5 ± 12.7	0.994	0.995	75	0.003	0.01	0.01
127	Benalaxyl	17.366 ± 0.087	44.9 ± 9.0	0.992	0.990	52	0.005	0.01	0.01	5.031 ± 0.025	53.9 ± 10.8	0.993	0.990	58	0.003	0.01	0.01
128	Cafentrazole ethyl	17.409 ± 0.087	88.7 ± 17.7	0.981	0.993	13	0.005	0.01	0.01	5.021 ± 0.025	84.5 ± 16.9	0.993	0.994	99	0.003	0.01	0.01
129	Endosulfan sulfate	17.542 ± 0.088	15.9 ± 4.8	0.996	0.996	49	0.005	0.01	0.01	5.097 ± 0.025	12.2 ± 3.7	0.992	0.990	31	0.003	0.01	0.01
130	*p,p'*-DDT	17.645 ± 0.088	20.1 ± 5.0	0.990	0.994	25	0.005	0.01	0.01	5.115 ± 0.026	21.7 ± 5.4	0.997	0.993	-85	0.003	0.01	0.01
131	Trifloxystrobin	17.717 ± 0.089	50.6 ± 10.1	0.984	0.995	71	0.005	0.01	0.01	5.049 ± 0.025	59.4 ± 11.9	0.992	0.994	89	0.003	0.01	0.01
132	Propiconazole-trans	17.736 ± 0.089	72.6 ± 14.5	0.986	0.991	71	0.005	0.01	0.01	5.106 ± 0.026	84.4 ± 16.9	0.994	0.998	77	0.003	0.01	0.01
133	Pyrafulfen-ethyl	17.866 ± 0.089	80.1 ± 16.0	0.951	0.994	57	0.005	0.01	0.01	5.097 ± 0.025	80.3 ± 16.1	0.993	0.995	109	0.003	0.01	0.01
134	Tebuconazole	18.102 ± 0.091	32.4 ± 8.1	0.927	0.993	234	0.005	0.01	0.01	5.200 ± 0.026	30.3 ± 7.6	0.995	0.993	105	0.003	0.01	0.01
135	Diclofop-methyl	18.214 ± 0.091	56.3 ± 11.3	0.968	0.992	46	0.005	0.01	0.01	5.200 ± 0.026	57.2 ± 11.4	0.993	0.997	99	0.003	0.01	0.01
136	Piperonyl butoxide	18.434 ± 0.092	44.7 ± 11.2	0.939	0.994	288	0.005	0.01	0.01	5.241 ± 0.026	74.8 ± 15.0	0.994	0.998	131	0.003	0.01	0.01
137	Resmethrin	18.505 ± 0.093	8.7 ± 4.4	0.951	0.996	162	0.005	0.01	0.01	5.257 ± 0.026	10.6 ± 3.2	0.996	0.998	179	0.003	0.01	0.01
138	Mefenpyr diethyl	18.835 ± 0.094	64.0 ± 12.8	0.979	0.996	54	0.005	0.01	0.01	5.284 ± 0.026	65.5 ± 13.1	0.991	0.993	87	0.003	0.01	0.01
139	Pyributicarb	18.914 ± 0.095	50.4 ± 10.1	0.966	0.991	74	0.005	0.01	0.01	5.305 ± 0.027	30.6 ± 7.7	0.996	0.997	101	0.003	0.01	0.01

140	Bromopropylate	19.314 ± 0.097	74.9 ± 15.0	0.986	0.994	84	0.005	0.01	0.01	5.414 ± 0.027	46.8 ± 11.7	0.994	0.994	90	0.003	0.01	0.01
141	EPN	19.352 ± 0.097	58.0 ± 11.6	0.862	0.994	107	0.005	0.01	0.01	5.405 ± 0.027	62.2 ± 12.4	0.996	0.993	136	0.003	0.01	0.01
142	Bifenthrin	19.449 ± 0.097	72.3 ± 14.5	0.991	0.991	46	0.005	0.01	0.01	5.417 ± 0.027	58.3 ± 11.7	0.993	0.996	94	0.003	0.01	0.01
143	Picolinafen	19.461 ± 0.097	77.8 ± 15.6	0.951	0.993	80	0.005	0.01	0.01	5.395 ± 0.027	94.3 ± 18.9	0.996	0.994	115	0.003	0.01	0.01
144	Piperophos	19.517 ± 0.098	75.4 ± 15.1	0.925	0.994	92	0.005	0.01	0.01	5.416 ± 0.027	84.8 ± 17.0	0.993	0.993	98	0.003	0.01	0.01
145	Methoxychlor	19.561 ± 0.098	98.7 ± 19.7	0.965	0.995	27	0.005	0.01	0.01	5.442 ± 0.027	72.7 ± 14.5	0.990	0.994	67	0.003	0.01	0.01
146	Fenpropathrin	19.655 ± 0.098	25.5 ± 6.4	0.973	0.994	33	0.005	0.01	0.01	5.455 ± 0.027	26.7 ± 6.7	0.992	0.995	95	0.003	0.01	0.01
147	Clomeprop	20.043 ± 0.100	25.3 ± 6.3	0.862	0.994	170	0.005	0.01	0.01	5.527 ± 0.028	47.6 ± 11.9	0.990	0.994	123	0.003	0.01	0.01
148	Tetradifon	20.210 ± 0.101	96.8 ± 19.4	0.970	0.992	-13	0.005	0.01	0.01	5.560 ± 0.028	94.5 ± 18.9	0.990	0.992	81	0.003	0.01	0.01
149	Oryzastrobin	20.280 ± 0.101	20.7 ± 5.2	0.949	0.993	235	0.005	0.01	0.01	5.465 ± 0.027	31.6 ± 7.9	0.993	0.991	156	0.003	0.01	0.01
150	Furametpyr	20.312 ± 0.102	7.2 ± 3.6	0.947	0.996	70	0.005	0.01	0.01	5.525 ± 0.028	13.3 ± 4.0	0.994	0.996	103	0.003	0.01	0.01
151	Triticonazole	20.413 ± 0.102	94.3 ± 18.9	0.897	0.993	788	0.005	0.01	0.01	5.598 ± 0.028	80.9 ± 16.2	0.994	0.995	150	0.003	0.01	0.01
152	Oryzastrobin 5 *Z* isomer	20.574 ± 0.103	24.1 ± 6.0	0.936	0.992	202	0.005	0.01	0.01	5.516 ± 0.028	37.2 ± 9.3	0.994	0.993	137	0.003	0.01	0.01
153	Pyriproxyfen	20.714 ± 0.104	78.3 ± 15.7	0.909	0.994	238	0.005	0.01	0.01	5.642 ± 0.028	95.2 ± 19.0	0.992	0.998	144	0.003	0.01	0.01
154	Mirex	20.798 ± 0.104	13.2 ± 4.0	0.996	0.992	18	0.005	0.01	0.01	5.717 ± 0.029	8.8 ± 4.4	0.998	0.997	51	0.003	0.01	0.01
155	Cyhalofop-butyl	20.912 ± 0.105	32.8 ± 8.2	0.890	0.992	178	0.005	0.01	0.01	5.653 ± 0.028	37.3 ± 9.3	0.994	0.996	154	0.003	0.01	0.01

156	Hydroxy Furametpyr	21.178 ± 0.106	25.4 ± 6.4	0.890	0.995	295	0.005	0.01	0.01	5.669 ± 0.028	18.7 ± 5.6	0.996	0.993	79	0.003	0.01	0.01
157	Cyhalothrin	21.316 ± 0.107	28.9 ± 7.2	0.949	0.994	108	0.005	0.01	0.01	5.686 ± 0.028	23.8 ± 6.0	0.994	0.992	157	0.003	0.01	0.01
158	Fenoxaprop-ethyl	22.085 ± 0.110	49.6 ± 12.4	0.870	0.994	319	0.005	0.01	0.01	5.831 ± 0.029	40.2 ± 10.1	0.996	0.993	153	0.003	0.01	0.01
159	Permethrin-cis	22.560 ± 0.113	78.1 ± 15.6	0.936	0.993	99	0.005	0.01	0.01	5.896 ± 0.029	69.8 ± 14.0	0.990	0.999	129	0.003	0.01	0.01
160	Permethrin-*trans*	22.779 ± 0.114	78.2 ± 15.6	0.926	0.992	116	0.005	0.01	0.01	5.928 ± 0.030	67.5 ± 13.5	0.992	0.997	117	0.003	0.01	0.01
161	Prochloraz	23.035 ± 0.115	95.8 ± 19.2	0.860	0.993	578	0.005	0.01	0.01	5.946 ± 0.030	100.0 ± 20.0	0.993	0.990	61	0.003	0.01	0.01
162	Fenbuconazole	23.522 ± 0.118	80.2 ± 16.0	0.923	0.995	407	0.005	0.01	0.01	6.034 ± 0.030	80.7 ± 16.1	0.994	0.993	130	0.003	0.01	0.01
163	Cyfluthrin	23.538 ± 0.118	63.1 ± 12.6	0.980	0.991	117	0.005	0.01	0.01	6.030 ± 0.030	87.0 ± 17.4	0.993	0.991	139	0.003	0.01	0.01
164	Cypermethrin	24.002 ± 0.120	27.2 ± 6.8	0.986	0.991	130	0.005	0.01	0.01	6.117 ± 0.031	24.8 ± 6.2	0.990	0.991	134	0.003	0.01	0.01
165	Etofenprox	24.450 ± 0.122	98.4 ± 19.7	0.942	0.994	244	0.005	0.01	0.01	6.211 ± 0.031	59.4 ± 11.9	0.992	0.996	184	0.003	0.01	0.01
166	Silafluofen	24.699 ± 0.123	27.2 ± 6.8	0.949	0.995	177	0.005	0.01	0.01	6.251 ± 0.031	25.4 ± 6.4	0.994	0.996	156	0.003	0.01	0.01
167	Fenvalerate	25.473 ± 0.127	29.2 ± 7.3	0.894	0.994	142	0.005	0.01	0.01	6.384 ± 0.032	22.1 ± 5.5	0.994	0.995	171	0.003	0.01	0.01
168	Difenoconazole-trans	26.294 ± 0.131	65.0 ± 13.0	0.945	0.995	39	0.005	0.01	0.01	6.553 ± 0.033	67.1 ± 13.4	0.994	0.994	182	0.003	0.01	0.01
169	Deltamethrin	26.394 ± 0.132	24.4 ± 6.1	0.863	0.990	129	0.005	0.01	0.01	6.566 ± 0.033	24.9 ± 6.2	0.993	0.991	148	0.003	0.01	0.01
170	Azoxystrobin	27.311 ± 0.137	23.2 ± 5.8	0.868	0.991	435	0.005	0.01	0.01	6.698 ± 0.033	19.4 ± 5.8	0.994	0.990	186	0.003	0.01	0.01

4.3.2 Linearity

Linearity of the method is the ability to provide signal responses that are directly proportional to the concentration of analytes in solvent or in matrix. In this study, linearity of the method was demonstrated using standard calibrations. Peak areas of the analytes were plotted as a function of concentrations and then evaluated using mathematical linear model.

4.3.2.1 Standard calibration curve

The standard calibration curves were prepared at 10 concentration levels in MeCN (triplicate injections at each level) ranging from 0.01-0.27 mg L^{-1}. Good linearities with coefficients of determnation (R^2) greater than or equal to 0.990 were obtained for 56% of analytes. A small number of the analytes (44%) gave R^2 lower than 0.990. This is probably due to the adsorption of susceptible analytes with active sites (especially solvent-based standards), which resulted in low sensitivity, deterioration of peak, or degradation of analytes in the heated GC inlet. The linear regression results are detailed in Table 4.5 and shown in Figure 4.7.

4.3.2.2 Matrix-matched calibration curve

The matrix-matched calibration curves were prepared at 10 concentration levels in onion extract (the same concentration as in standard calibration curves) ranging from 0.01-0.27 mg kg^{-1}. All analytes gave excellent linearities with R^2 greater than 0.990 as reported in Table 4.5 and in Figure 4.7. None of analytes showed R^2 less than 0.990, indicating that matrix helps to protect the analytes from the loss in GC system and improve analyte responses.

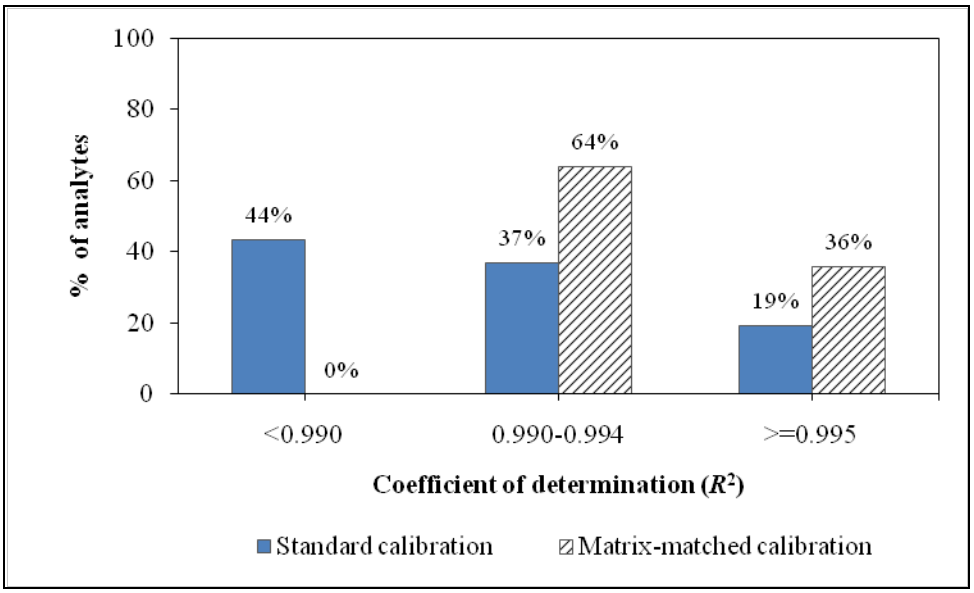
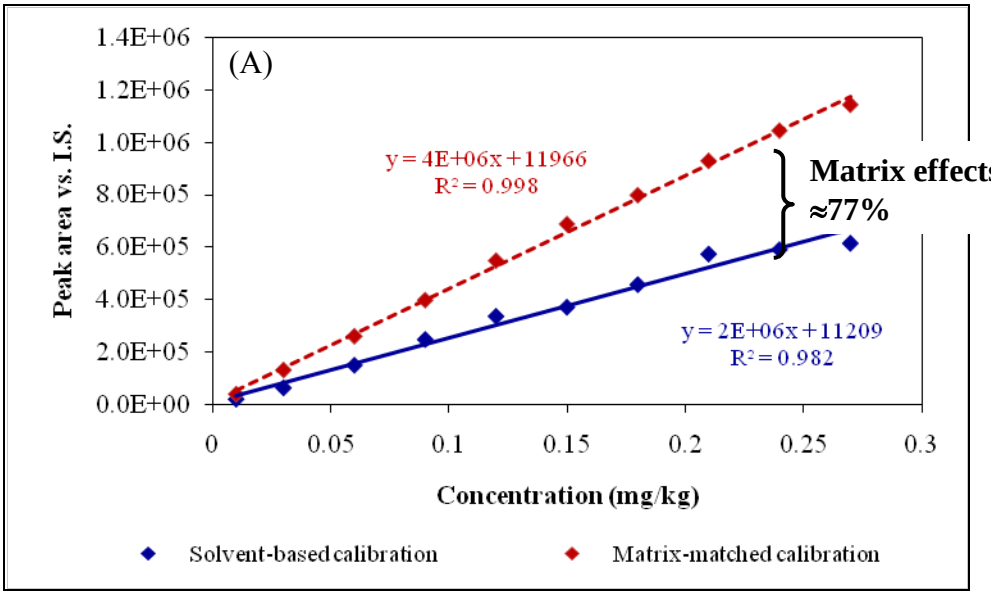


Figure 4.7 Distribution of coefficients of determination (R^2) obtained from standard calibrations and matrix-matched standard calibrations in the range of 0.01-0.27 mg kg^{-1} for 170 pesticides using the optimum traditional GC-MS/MS conditions.

4.3.3 Matrix effects

In GC analysis, injection of sample extracts may cause negatively impacting for determination accuracy of analytes, detection ability, and method ruggedness. Matrix effects (%ME) in GC can be described into two phenomenons. Firstly, matrix-induced signal enhancement is normally occurred when injected matrix extracts fill mostly the active sites in the part of injection port and column instead of analyte. This leads to reducing interaction of analyte with active sites and thus increasing efficiency of analyte transfer from the GC system to the detector. Figure 4.8 (A) shows an example of a matrix-induced signal enhancement for flusilazole observed in spiked onion extract. In this case, overestimate result would be observed if solvent-based standard calibration is used for calculation. Secondly, matrix-induced signal diminishment happens due to less volatile matrix components in the GC system formed new layers and new active surfaces which those interact with

analyte molecules. This case adversely affects the analyte responses involving signal intensities (see Figure 4.8 (B)), t_R shift, and peak shapes.



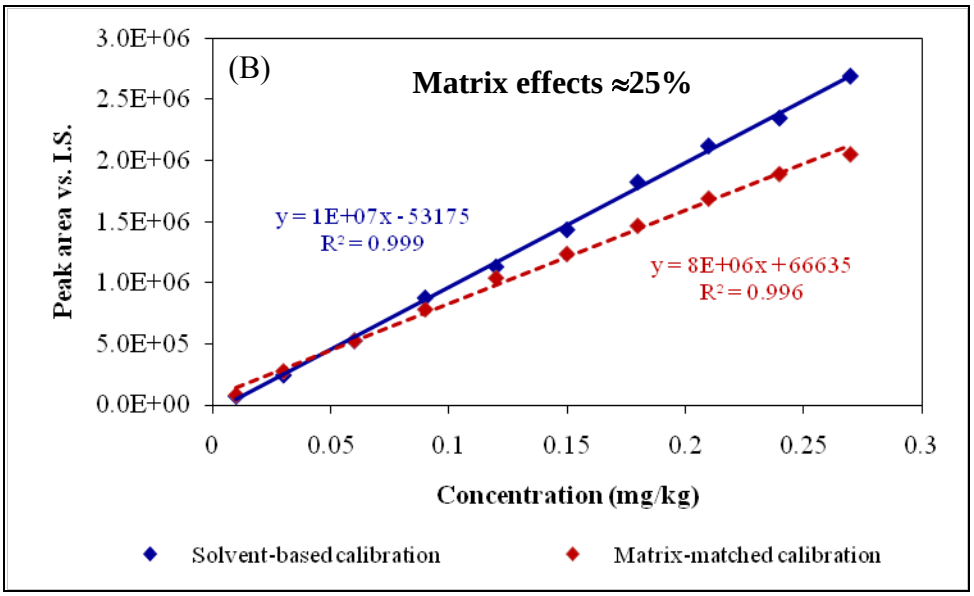


Figure 4.8 An example of matrix effects for some pesticides demonstrated using standard calibrations: (A) signal enhancement (deviation of matrix calibration above standard calibration) of flusilazole and (B) signal diminishment (deviation of matrix calibration below standard calibration) of propachlor.

To estimate the potential of matrix effects, slope of the calibrations obtained from solvent-based standards and matrix-matched standards were compared. Figure 4.9 shows distribution of the amount of matrix effects, demonstrating signal enhancements in the range of 2-788% were obtained for 91% of the analytes, whereas the rest of them (9%) provided signal diminishments.

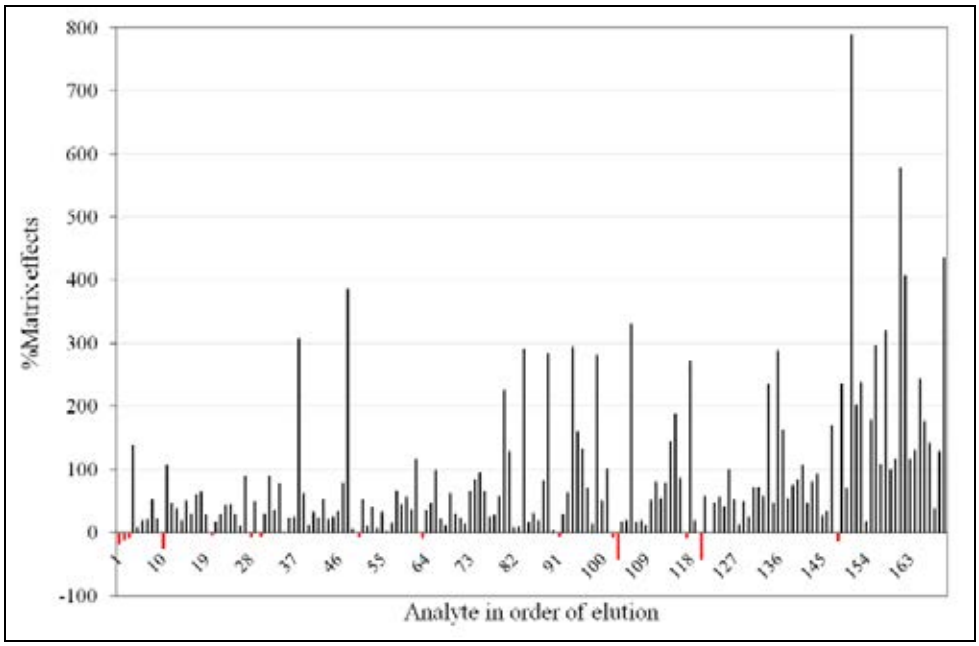


Figure 4.9 Distribution of matrix effects obtained from the difference of solvent-based standards and matrix-matched standards for 170 pesticides in the range of 0.01-0.27 mg kg^{-1} using the optimum traditional GC-MS/MS conditions.

As clearly demonstrated in Figure 4.9, matrix effects were variable and could not be measured precisely depending on the chemical properties of analytes, concentrations, and co-extracted components. For these reasons, matrix-matched calibrations were used to compensate any indirect matrix effect in the quantification of 170 pesticides throughout the study.

4.3.4 Accuracy

Accuracy of the method is described as the closeness of agreement between the measured value and ture or accepted value. In this study, accuracy was assessed by analyzing spiked samples with known concentrations and comparing the measured value with the true value. The accuracy was demonstrated in terms of percent recovery for each analyte at 0.01 (low), 0.05 (middle), and 0.10 (high) mg kg^{-1} spiking levels using the optimized sample preparation method as previously described in the Experimental Section 3.6. Percent recovery was calculated by comparing response of the analyte in spiked sample extract with the response of matrix-matched standard calibrations.

The results of accuracy experiments for all analytes are shown in Table C-3. All analytes provided excellent average recoveries in all cases over 3 days analyses entailing the recovery of 70-111% for low, 70-104% for middle, and 70-103% for high spiking levels. None of the analytes give recovery <70% or >120%. The obtained values meet the EU validation requirement with recovery value in the range of 70-120% at trace level [41], indicating the acceptable accuracy of the method for analysis of onion. Figure 4.10 depicts distribution of the obtained recoveries for the 170 tested pesticides in onion extracts on the basis of (A) each day of analysis and (B) each spiking level over 3 days experiment as described above.

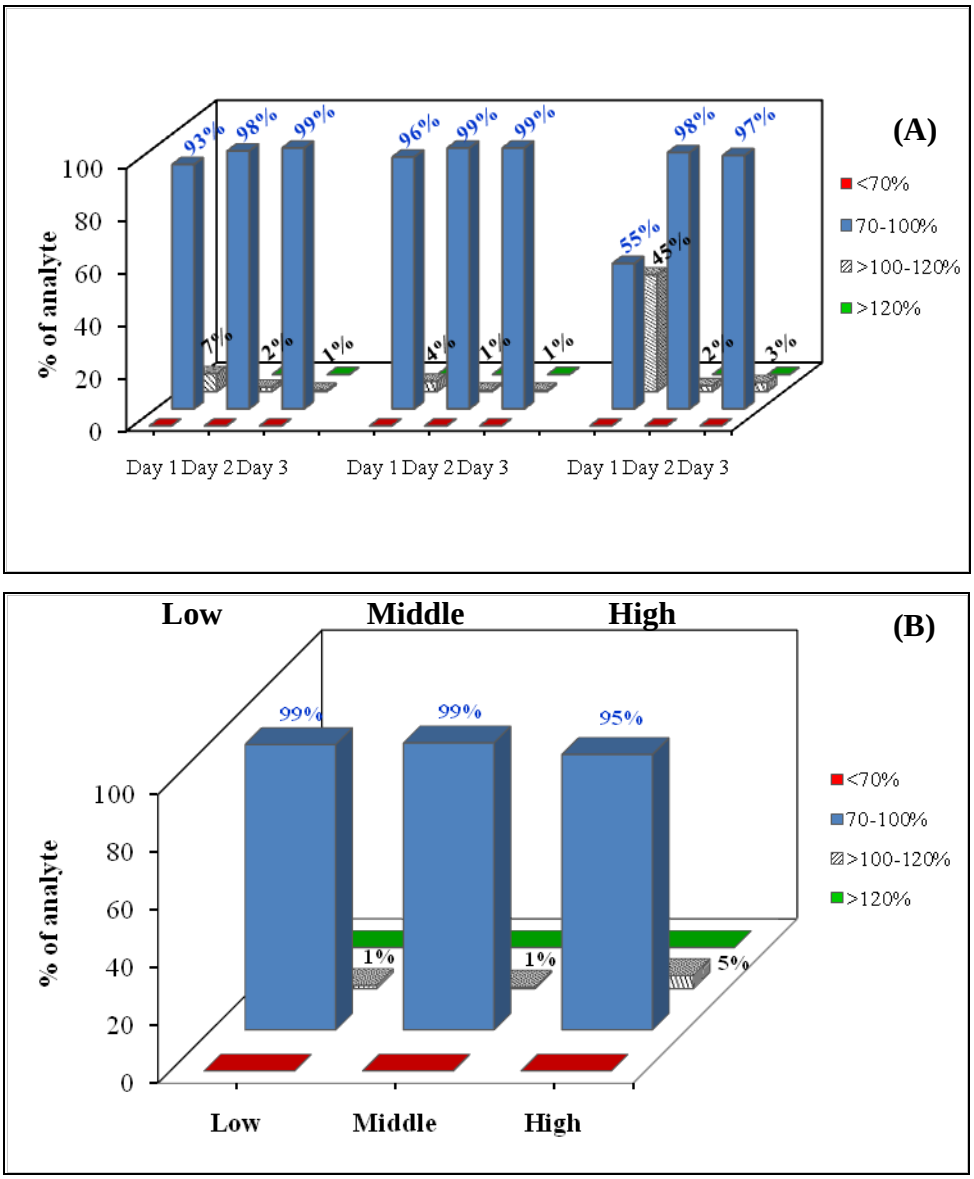


Figure 4.10 Distribution of recoveries obtained from the method validation for the 170 pesticides at 0.01, 0.05, and 0.10 mg kg^{-1} spiked in onion over 3 days extraction, (A) each day of analysis and (B) each spiking level over 3 days experiment.

4.3.5 Precision

Precision of the method is the amount of scatter in the test results obtained from multiple analyses of spiked samples. Precision can be divided into 3 categories including repeatability (or intra-assay precision), intermediate precision (or within-

laboratory reproducibility), and inter-laboratory reproducibility. The deviation of the measured values is usually expressed as standard deviation or relative standard deviation (RSD).

In this study, precision of the proposed method was studied in terms of repeatability and intermediate precision. The experiments were performed by 5 replicates extraction each of the 3 spiking levels: 0.01 (low), 0.05 (middle), and 0.10 (high) mg kg^{-1} for 3 different days.

4.3.5.1 Repeatability

Repeatabilty is obtained when a method is performed repeatedly by an operator using the same equipment over a short period of time. According to the AOAC Peer review, precision is generally dependent on analyte concentration and should be determined at a number of concentrations and if relevant. The relationship between precision and analyte concentration should be establish. As for repeatability, theoretical relative standard deviations (or acceptable RSD_r) can be calculated from the Horwitz equation.

$$RSD_r = 0.66 \times 2^{(1 - 0.5 \log C)} \quad (4.1)$$

where RSD_r = the relative standard deviation calculated from the results obtained from repeatability conditions (within laboratory)

C = the mass fraction of analyte in sample (g/g)

For analyses conducted under repeatability conditions, the acceptance limitations for RSD_r are shown in Table 4.6.

Table 4.6 Acceptance limitation for RSD_r calculated from the Horwitz equation (4.1).

Concentration level (mg kg^{-1})	Acceptable RSD_r
0.01	21%
0.05	17%
0.10	15%

$\%RSD_r$ obtained from individual day experiment are summarized in Table C-3. Figure 4.11 shows distribution of $\%RSD_r$ for the 170 pesticides at different concentrations in onion matrix.

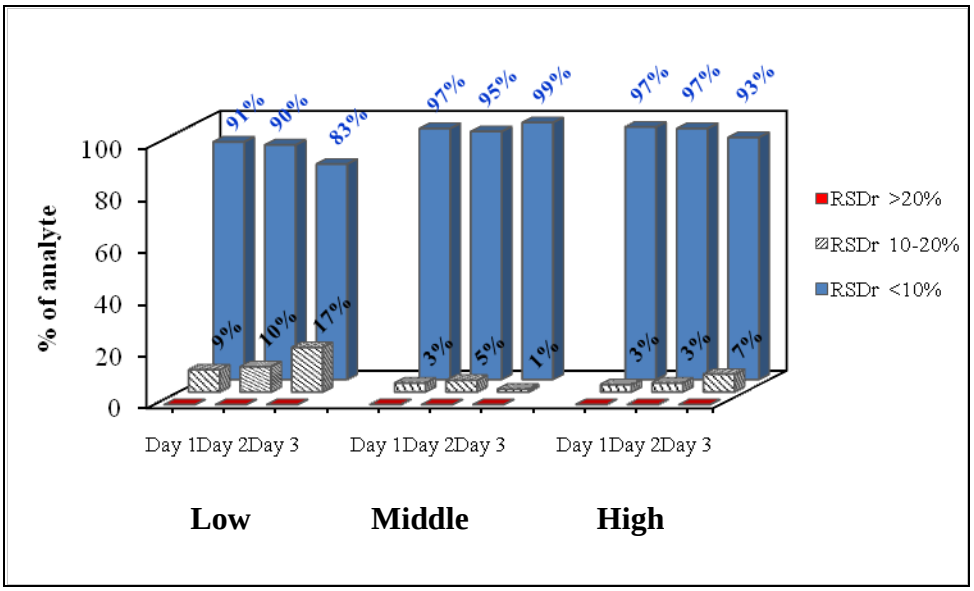


Figure 4.11 Distribution of RSD_r obtained from the method validation for 170 pesticides in the method at 0.01, 0.05, and 0.10 mg kg^{-1} in onion extracts.

RSD_r <10% was obtained for 83-99% of the analytes, whereas RSD_r values in the range of 10-20% were found for 1-17% of the compounds. None of the analytes has RSD_r >20%. These results were within the acceptable limits based on the AOAC

standard (Table 4.6) and met the EU validation criteria (RSD≤20%), indicating reliability of the method to provide acceptable results under repeatability conditions.

4.3.5.2 Intermediate precision

Intermediate precision is defined as the long-term variability of analyses. It usually refers to the standard deviation (SD_I) or the percentage of relative reproducibility standard deviation ($\%RSD_I$) of results on the same test samples by single laboratory.

Because precision is generally dependent on analyte concentration [42], acceptable RSD for intermediate precision (RSD_I) can be calculated from the Horwitz equation.

$$RSD_R = 2^{(1- 0.5 \log C)} \quad (4.2)$$

where RSD_R = the relative standard deviation calculated from the results obtained from repeatability conditions (within laboratory)

C = the mass fraction of analyte in sample (g/g)

For analyses conducted under reproducibility conditions, the acceptable RSD_I was 23% at 0.10 mg kg^{-1}. However, for mass fraction lower than 0.1 mg kg^{-1}, the application of the Horwitz Equation gives unacceptable high values. Therefore, the RSD_R for those concentrations must be lower than 23% or as low as possible [42].

In this study, intermediate precision was determined by comparing the results which were done by a single analyst using the same equipment within a single laboratory over 3 separate days of analysis. To evaluate the intermediate precision, the difference of recovery results obtained from individual day of analysis (as shown in Table C-3) were examined using analysis of variances (ANOVA).

If *P*-value is greater than 0.05 at 95% confidence limit, indicating "insignificant difference" of results over 3 days of analysis. Therefore, those data are considered as a single set and RSD_I can be calculated using the equation below:

$$SD_R = \sqrt{\text{within group mean square}} \quad (4.2)$$

$$\%\ RSD_I = \frac{SD_R}{\text{mean}} \times 100 \quad (4.3)$$

In contrast, if ANOVA shows "significant difference" of results among 3 days of analysis (P <0.05), RSD_R can be calculated using the equation below:

$$SD_{within} = \sqrt{\text{within group mean square}} \quad (4.4)$$

$$SD_{between} = \sqrt{\frac{\text{between group MS - within group MS}}{n}} \quad (4.5)$$

$$SD_R = \sqrt{S^2_{within} + S^2_{between}} \quad (4.6)$$

$$\%\ RSD_R = \frac{SD_R}{\text{mean}} \times 100 \quad (4.7)$$

From the experiment, ANOVA showed that the recovery results obtained from 3 days analyses were significantly difference (P <0.05) at 95% confidence level for all concentration levels. Therefore, intermediate precision of the proposed method was calculated using equation (4.4)-(4.7). As shown in Table C-3, RSD_R<10% was obtained for the majority of analytes (77-92%), whereas the rest of them felt in the range of 10-20% RSD_R. These results did not exceed the acceptance limitation RSD_R (≤23%), and EU validation criteria (RSD≤20%) at 0.01 0.05, and 0.10 mg kg^{-1} spiking levels. Figure 4.12 shows distribution of RSD_R for the 170 tested pesticides in onion extracts as described above.

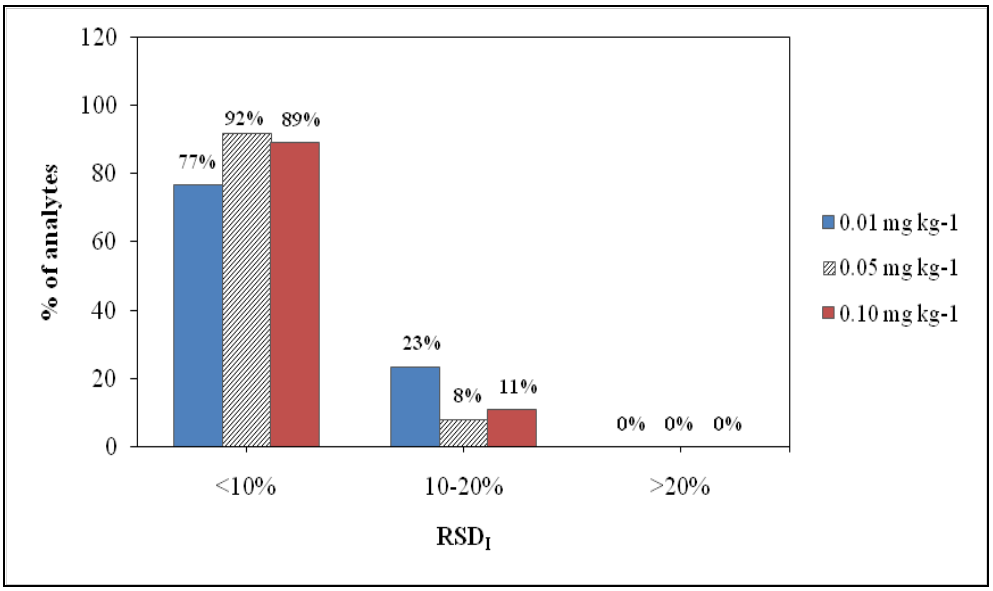


Figure 4.12 Distribution of RSD_I obtained from the method validation for the 170 pesticides at 0.01, 0.05, and 0.10 mg kg^{-1} spiked in onion over 3 days extraction.

4.3.6 Limit of detection (LOD) and limit of quantitation (LOQ)

LOD is defined as the lowest amount of analytes that can be detected with acceptable reliability at a signal-to-noise ratio of 3 above the background noises. In a similar to LOD, LOQ is the lowest amount of analytes that can be quantified with acceptable accuracy at signal-to-noise ratio of 10. Lowest calibrated level (LCL) is the lowest concentration of analyte at which the determination system is successfully calibrated throughout the analysis batch [41]. In this study, we used ion transition of each analyte which showed the greatest signal intensity with less of matrix interferences for the calculation.

Table 4.5 summarizes the LOD, LOQ, and LCL values obtained from the proposed method using the optimum traditional GC-MS/MS conditions. The analytical limits of 0.005, 0.01, and 0.01 mg kg^{-1} were observed for LODs, LOQs, and LCLs, respectively, for all analytes. These values were lower than the regulated MRLs, indicating high efficiency of the method for trace residue analysis.

4.4 Application of modified-QuEChERS and traditional GC-MS/MS in real samples

To test capability of the method in real-world application, the proposed method was evaluated using 40 different onion samples (unknown residues of pesticides to the analyst) which were obtained from the export companies in Thailand. The homogenized onion samples were extracted following the optimized QuEChERS method and determined using traditional GC-MS/MS method. Matrix-matched calibrations were used for quantitative calculations. Table 4.7 shows the results of onion samples investigated in the study.

Table 4.7 Concentration of pesticides found in onion samples obtained using the optimum traditional GC-MS/MS condtions

Code	Pesticide	Class	Detected concentration ($mg\ kg^{-1}$)
O-1	Flusilazole	Fungicide	0.19
O-7	Flusilazole	Fungicide	0.11
O-15	Difenoconazole	Fungicide	0.026
O-21	Cypermethrin	Pyrethroid	0.070

The incidence of pesticide residues was found in 4 out of 40 samples. Two samples contained flusilazole fungicide in the range between 0.114-0.188 mg kg^{-1} and another 2 samples found difenoconazole and cypermethrin at low levels of 0.026 and 0.070 mg kg^{-1}, respectively. These detected compounds met all identification criteria (t_R, ion ratio, and chromatographic peak shape) set up in this study.

4.5 Development and optimization of LP-GC-MS/MS conditions

In terms of analysis, although the traditional GC-MS/MS (30 m × 0.25 mm i.d., 0.25 μm analytical column) provided good results for the analysis of 170 pesticides in onion; however, major limiting factor of the method was the analysis

time. It took 33 min long plus time for system equilibration per analysis, resulting in decrease sample throughput.

LP-GC-MS/MS was employed using a mega bore 10 m × 0.53 mm i.d., 1 μm analytical column coupling with 3 m × 0.15 mm i.d. capillary at the inlet end. A vacuum generated under MS(/MS) system reduces the viscosity of the He carrier gas, thus allowing the use of higher carrier gas flow rate. By taking this advantage in combination of great selectivity and sensitivity of MS/MS, LP-GC-MS/MS is an alternative approach providing speed of analysis and increasing sample capacity. This approach also provides other beneficial features, such as high signal sensitivity, reduced analyte degradation, and less peak tailing. Recently, this approach has been demonstrated to analyze a hundreds of pesticides in fruits and vegetables in 10 min run time with satisfactory results and desired detection limits.

For these reasons, an LP-GC-MS/MS approach was adapted in this application with respect to reduce analysis time (increase sample throughput). The study was focused on the comparison of a traditional GC-MS/MS method with the LP-GC-MS/MS approach that would provide much faster and more sensitive analysis for 170 pesticides in onion sample. The PTV injection conditions were the same as in the traditional GC-MS/MS method. The optimum column flow rate of 2.0 mL min^{-1} and dwell time of 2.5 ms for all ion transitions, which were proved to provide overall best selectivity and sensitivity, were the same as reported in [40]. The method development involved testing the usefulness of analyte-specific MS/MS conditions (shown in Table 4.3) and optimizing analyte separation (oven temperature program).

The experiments were first conductied with 0.10 mg L^{-1} of standards in MeCN and then tested them for selectivity and sensitivity in sample extract. Table 4.5 lists chromatographic factors and MS/MS conditions for the analytes using the optimized LP-GC-MS/MS approach. APPENDIX D demonstrates selectivity of the promising MS/MS transitions of targeted analytes in onion extract. The selected MRM transitions showed high selectivity and no matrix peaks co-eluted at the same retention time of interest for analytes in sample extract. Ion ratio between two MRM transitions met all of the acceptable identification ranges. Under the optimum LP-GC-MS/MS conditions (Table 4.8-4.9 and Figure 4.13), MS acquisition was divided into 14 time windows to provide maximum number of data points across a peak, good

chromatographic peak shape, and improve sensitivity and selectivity of analytes. As shown in Figure 4.14, the last eluting analyte was azoxystrobin at 6.83 min. Total run time was 9.88 min which included ≈3 min post run.

Table 4.8 The optimum injector temperature program for LP-GC-MS/MS conditions.

	Rate (°C/min)	Value (°C)	Hold time (min)
Initial		80	1.0
Ramp 1	700	300	entire the GC run

Table 4.9 The optimum oven temperature program for LP-GC-MS/MS conditions.

	Rate (°C/min)	Value (°C)	Hold time (min)	Run time (min)
Initial		70	1.5	1.5
Ramp 1	90	180	0	2.72
Ramp 2	30	260	0	5.39
Ramp 3	60	290	0	5.89
Ramp 4	10	300	3	9.88

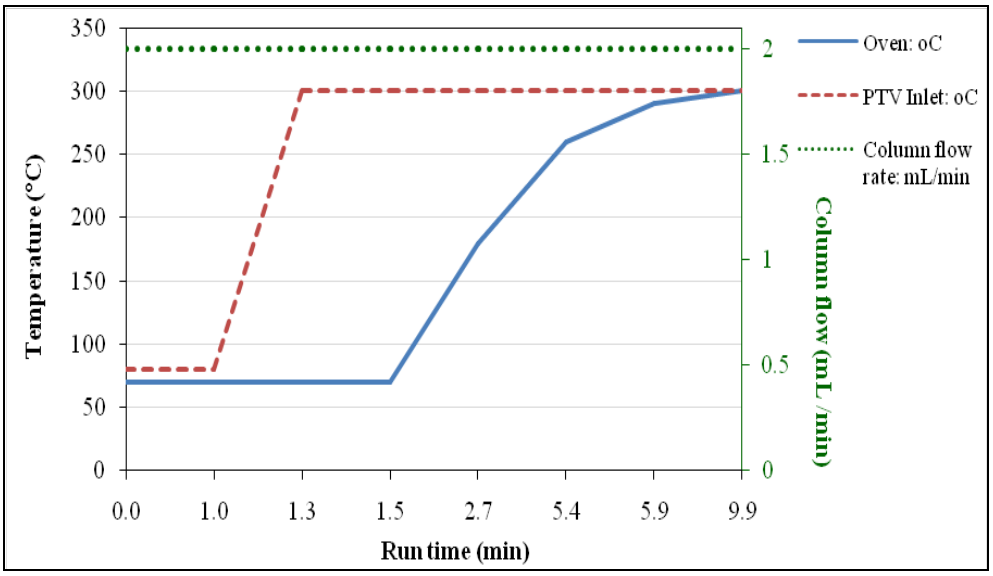


Figure 4.13 Schematic diagram of the optimum LP-GC separation conditions.

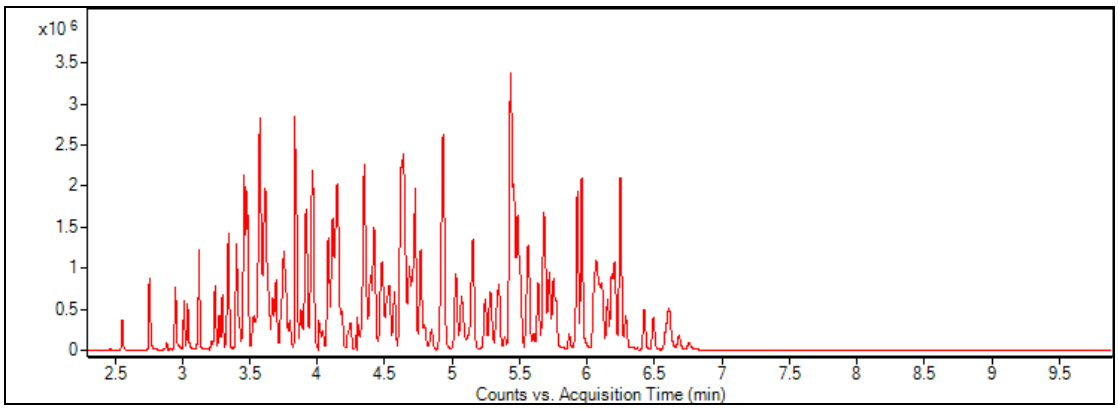


Figure 4.14 LP-GC-MS/MS chromatogram in MRM mode of 170 pesticides at 0.1 mg L^{-1} in onion extract using the optimum LP-GC-MS/MS conditions.

4.6 Method validation for LP-GC-MS/MS

To evaluate the effectiveness of LP-GC-MS/MS for routine monitoring, we performed the validation of this approach as same as the traditional GC-MS/MS method. The validation parameters include linearity, matrix effects, accuracy, precision, and analytical limits (LOD, LOQ, and LCL).

4.6.1 Linearity

Linearity was evaluated through standard calibrations for 170 pesticides in the method at 10 concentration levels in the range of 0.01-0.27 mg kg^{-1}. The relationship of average peak areas (triplicate injections at each level) versus their concentrations were plotted and fitted to linear curves. Good linearities with R^2 ≥0.990 were achieved for nearly all analytes both of solvent-based and matrix-matched standard calibrations as listed in Table 4.5. Figure 4.15 shows the distribution of R^2 values under the optimum LP-GC-MS/MS conditions.

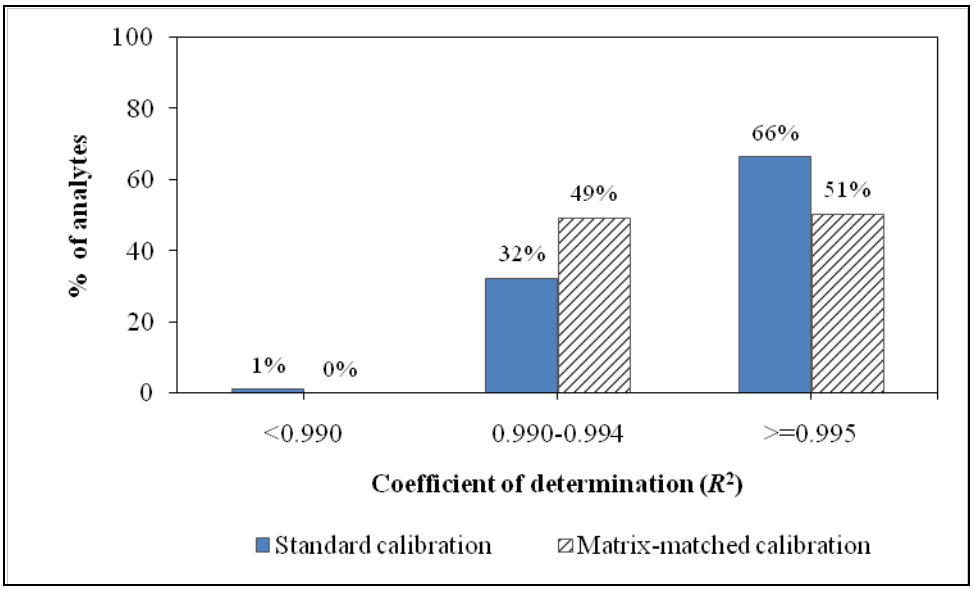


Figure 4.15 Distribution of coefficient of determination (R^2) values obtained from standard calibration and matrix-matched calibrations in the range of 0.01-0.27 mg kg^{-1} for 170 tested pesticides in onion using the optimum LP-GC-MS/MS conditions.

4.6.2 Matrix effects

As explained in the Section 4.3.3, matrix effects was calculated from the difference of calibration slopes obtained from solvent-based standards and matrix-matched standards. Figure 4.16 displays amount of matrix effects for all analytes obtained using LP-GC-MS/MS approach. Signal enhancements in the range of 4-218% were obtained for 97% of the analytes, whereas the rest of them (3%) provided signal diminishments.

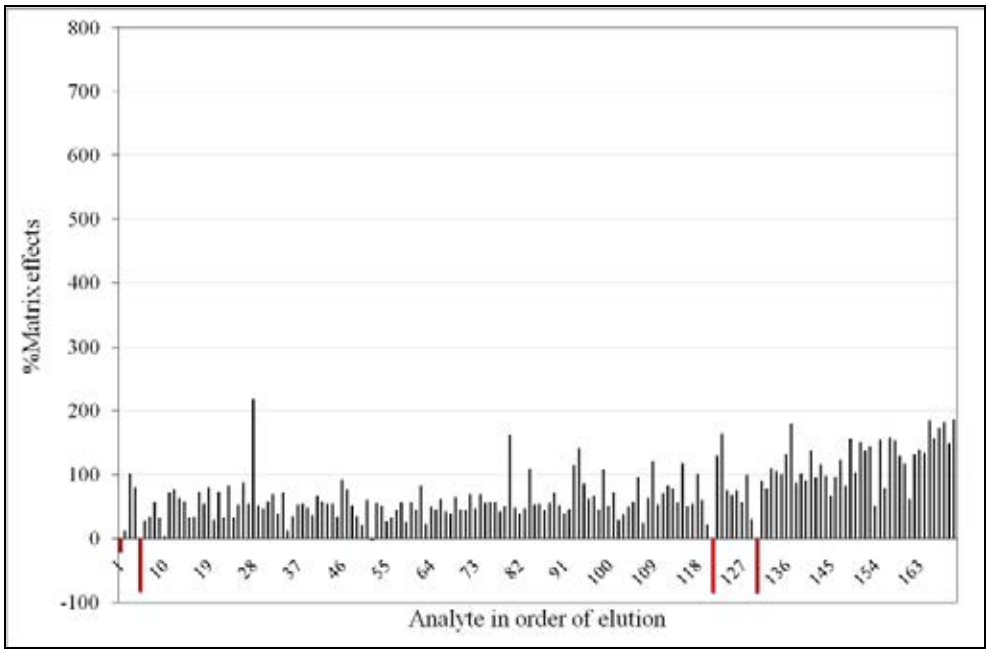


Figure 4.16 Distribution of matrix effects obtained from the difference of solvent-based standards and matrix-matched standard calibrations for 170 pesticides in the range of 0.01-0.27 mg kg^{-1} using the optimum LP-GC-MS/MS conditions.

As shown in the figure 4.16, the degree of signal enhancements was smaller than that obtained from the traditional GC-MS/MS (Figure 4.9). This is due to the use of high carrier gas flow rate (2 mL min^{-1}), analytes spent less time in the GC inlet and column, thus reducing possible interactions with active sites and/or thermal degradation of thermally labile analytes (particularly in solvent-based standards). This resulted in sharper peaks, less tailing, and reduction of degree of signal enhancements. Also, the signal diminishments were reduced as shown for 4 out of 170 analytes.

4.6.3 Accuracy

Accuracy of the method was assessed by analyzing onion samples at 0.01 (low), 0.05 (middle), and 0.10 (high) mg kg^{-1} spiking levels. Average recoveries obtained from 5 replicate extractions at each spiking level in 3 separate days are

summarized in Table D-1 (APPENDIX D). According to the SANCO/12495/2011 guidelines, the obtained results were satisfactory in the range of 70-120% for all analytes in all cases none of the analytes were outside the acceptable range.

Figure 4.17 presents distribution of recoveries for the 170 tested pesticides in onion extracts on the basis of (A) each day of analysis and (B) each spiking level over 3 days of analysis as described above.

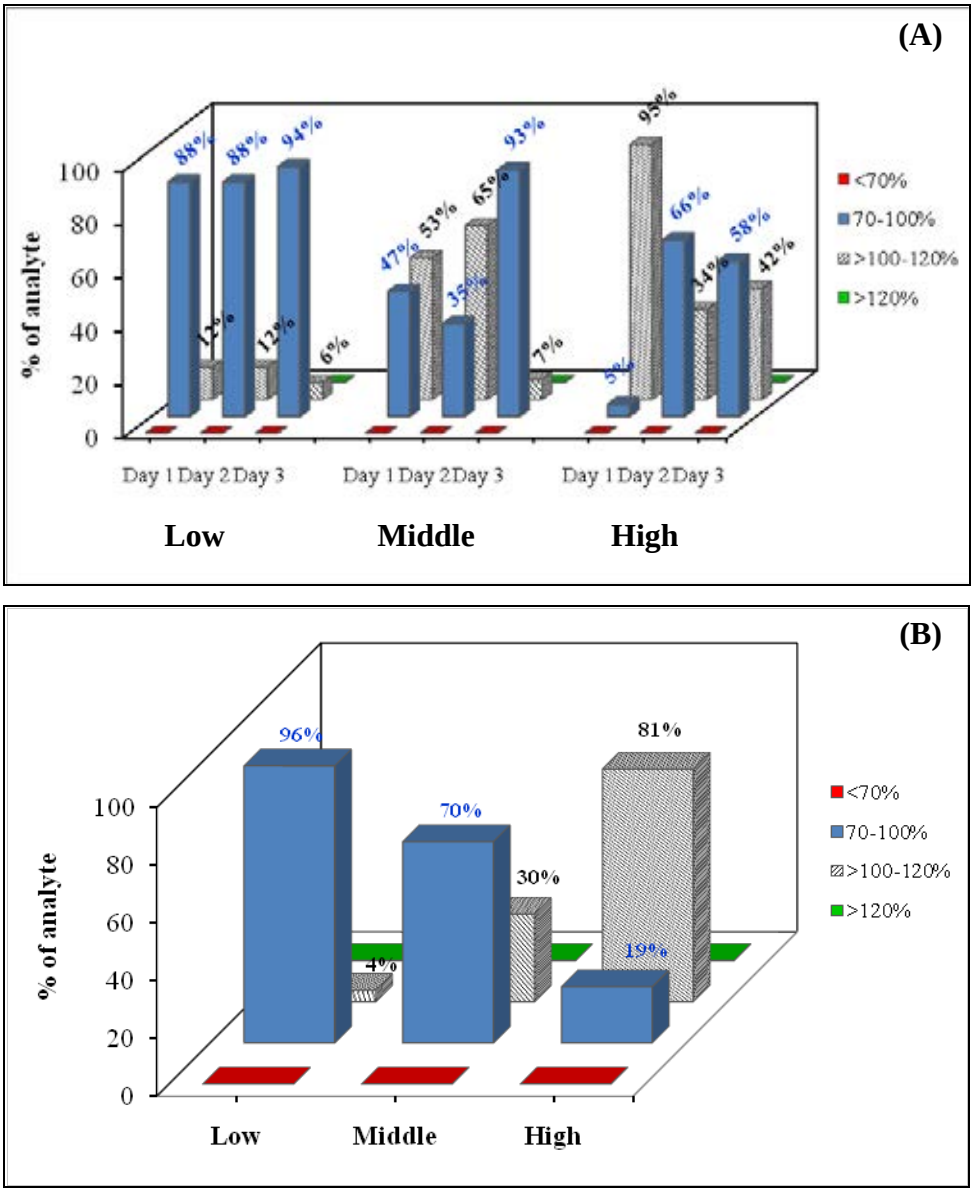


Figure 4.17 Distribution of recoveries obtained from the method validation for the 170 pesticides at 0.01, 0.05, and 0.10 mg kg^{-1} in onion (A) each day of

analysis and (B) each spiking level over 3 days of analysis using LP-GC-MS/MS approach.

4.6.4 Precision

Precision of the LP-GC-MS/MS approach was presented in terms of repeatability and intermediate precision as previously explained in the Section 4.3.5. To evaluate these parameters, we used the same set of results which were obtained from the recovery experiments over 3 days of analysis as displayed in Table D-1 (APPENDIX D).

In terms of repeatability, the results (Figure 4.18 (A)) obtained from individual day at each spiking level were within the acceptance RSD_r limitations (Table 4.6) and did not exceed the EU recommendation of RSD ≤20%. RSD_r <10% were found for the majority of analytes (77-100%). RSD_r 10-20% were observed for the rest of compounds. None of them had RSD_r >20%.

For intermediate precision (Figure 4.18 (B)), 77-94% of the analytes provided RSD_R <10% and 6-23% of the analytes had RSD_R of 10-20%. These results were all lower than 23% for concentrations <0.1 mg kg^{-1} [42].

These results demonstrated the reliability of the LP-GC-MS/MS approach for quantification.

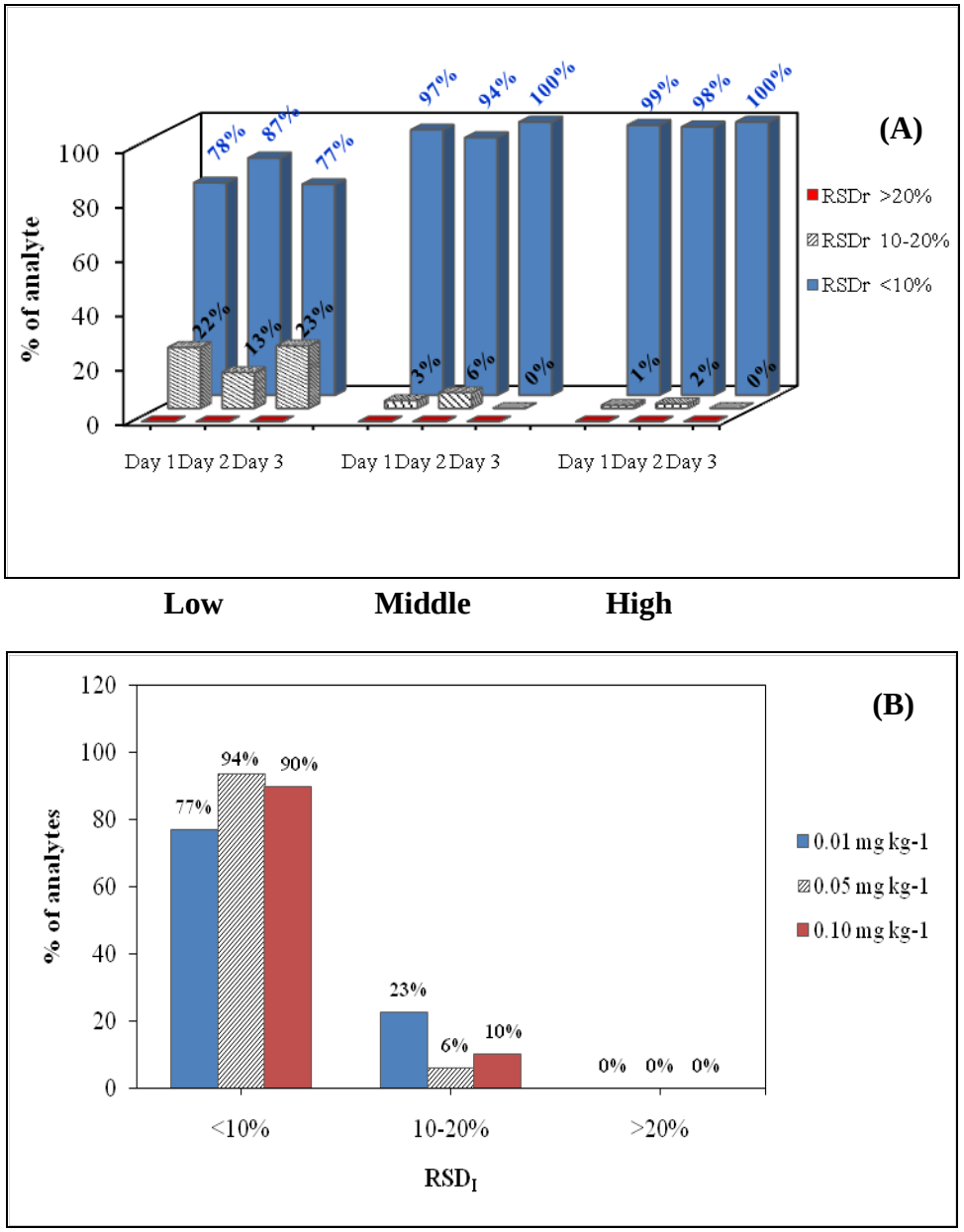


Figure 4.18 Distribution of RSDs obtained from the method validation for the 170 pesticides at 0.01, 0.05, and 0.10 mg kg^{-1} in onion (A) each day of analysis and (B) each spiking level over 3 days of analysis using the LP-GC-MS/MS approach.

4.6.5 Limit of detection (LOD) and limit of quantitation (LOQ)

The LODs and LOQs of all analytes obtained using the optimum LP-GC-MS/MS conditions are listed in Table 4.5. The LOD and LOQ values were 0.003 and 0.01 mg kg^{-1}, respectively. The LCLs were 0.01 mg kg^{-1} for all analytes. These values were well below the MRLs for pesticide residues in onion [6].

4.7 Application of modified-QuEChERS and LP-GC-MS/MS in real samples

To test the applicability of the LP-GC-MS/MS approach for routine monitoring of targeted pesticide in incurred onion samples, another portion of the onion QuEChERS extracts (which were kept from the Section 4.4) were analyzed. Matrix-matched standards were used for quantitation purpose. All identification criteria were taken into consideration for reporting the possible residues.

From the results, 3 pesticides were detected in 4 out of 40 onion samples as summarized in Table 4.6. The results were identical to those observed using traditional GC-MS/MS method, demonstrating the capability of the LP-GC-MS/MS for residues monitoring but in shorter analysis time.

Table 4.10 Concentration of pesticides found in onion samples obtained using the LP-GC-MS/MS approach.

Code	Pesticide	Class	Detected concentration (mg kg^{-1})
O-1	Flusilazole	Fungicide	0.18
O-7	Flusilazole	Fungicide	0.11
O-15	Difenoconazole	Fungicide	0.024
O-21	Cypermethrin	Pyrethroid	0.071

4.8 Comparison of the traditional GC-MSMS with the LP-GC-MSMS

The goal of this study was to develop and validate a fast and efficient method for multiresidue analysis of 170 pesticides in onion both of sample preparation and determinative analysis. As demonstrated in the previous sections, LP-GC-MS(/MS) is not only compatible with a common GC-MS(/MS) instrument (no complicated change), but this approach also provided major beneficial features as compared to the traditional GC-MS/MS method as follows:

(1) Reduced analysis time

At least 3-fold gain in speed resulted in high sample throughput as shown in Figure 4.19.

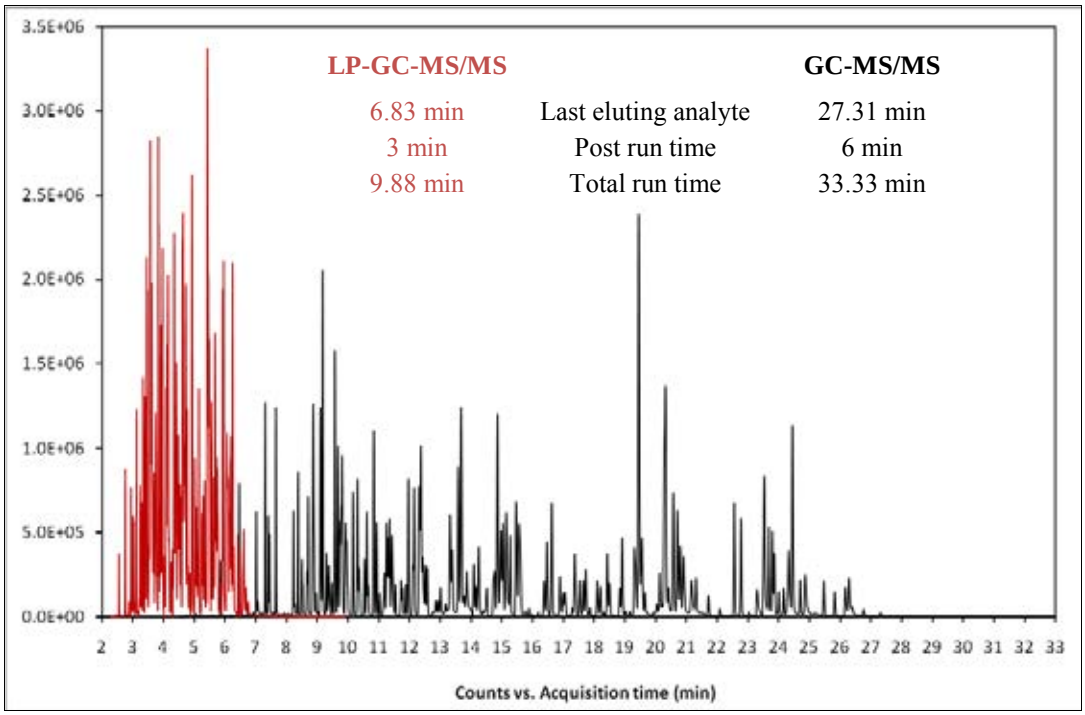


Figure 4.19 Overlays of GC-MS/MS chromatogram in MRM mode of traditional GC-MS/MS (black line) and LP-GC-MS/MS (red line) for the 170 pesticides at 0.10 mg kg^{-1} in onion extract.

(2) Improved chromatographic signal response

Figure 4.20 compares peak shapes and intensities of the selected pesticides in onion extracts obtained by traditional GC-MS/MS and LP-GC-MS/MS. The 4 pesticides were selected to represent different problematic analytes in the GC-MS. Dichlorvos was the first eluting analyte which was affected from high volatile matrix interferences. Procymidone and fenbuconazole is an example of polar pesticide prone to interact with active sites in the GC system, resulting in tailing of the peak. Azoxystrobin is a less volatile compound (last analytes eluted in the chromatogram) which usually provide low signal intensity and broad peak shape.

As a result of reducing in matrix effects, the figure clearly demonstrated the beneficial effect of the LP-GC-MS/MS approach, improving in peak shapes (FWHM) and signal responses (peak height), thus lowering detection limits of the method (0.003 mg kg^{-1}).

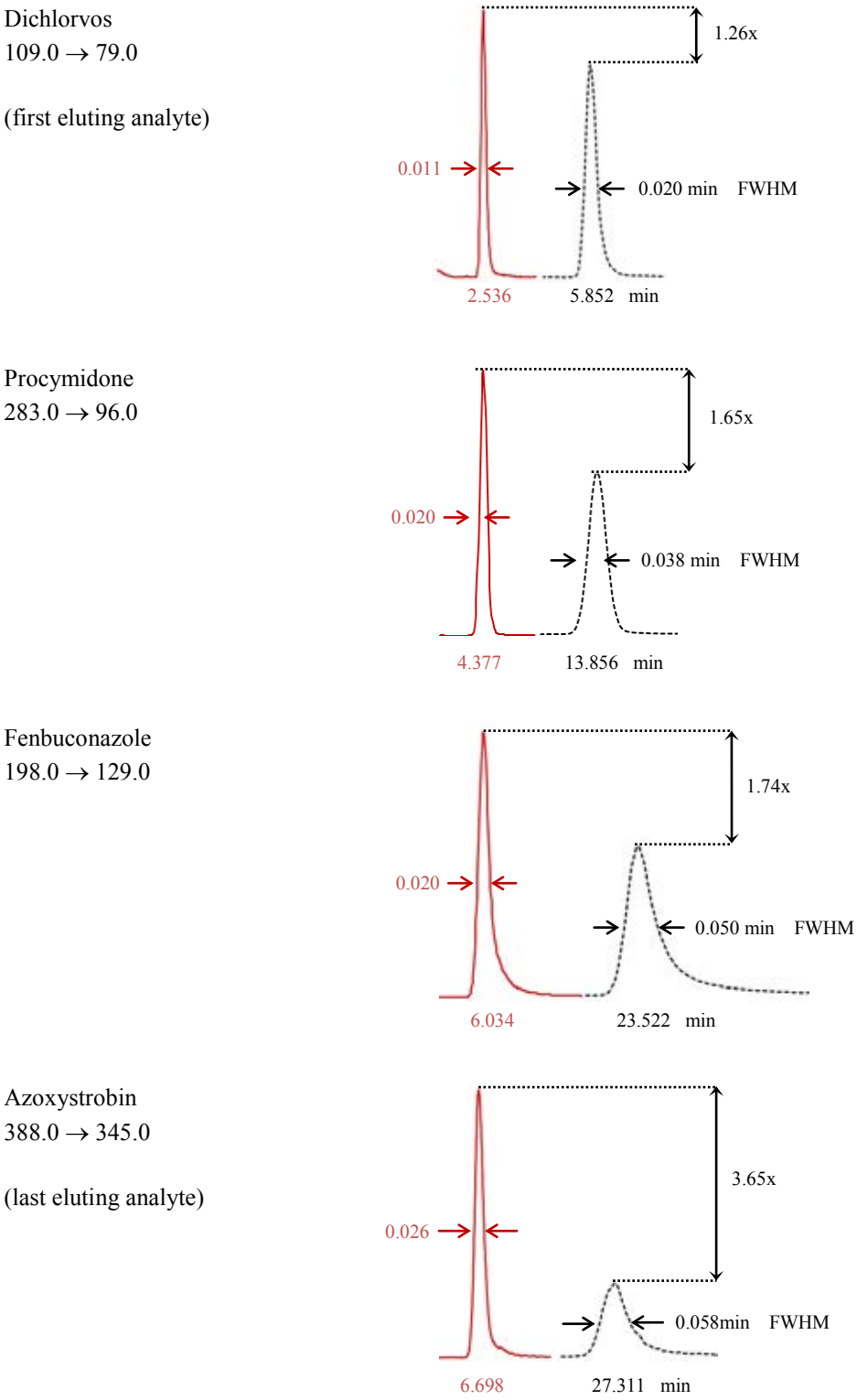


Figure 4.20 Comparison of peak shapes and intensities of 0.1 mg kg^{-1} of dichlorvos, procymidone, fenbuconazole, and azoxystrobin obtained by injection onion matrix under traditional GC-MS/MS (dotted trace) and LP-GC-MS/MS (red line) conditions.

(3) Improved analytical performance

As a result of reducing in matrix effects in LP-GC, accuracy and precision of the method were also improved. In this study, although both methods gave acceptable recoveries (70-120%) for all analytes (see Figure 4.21), but the LP-GC-MS/MS approach showed greater precision of results, which is more important for trace analysis.

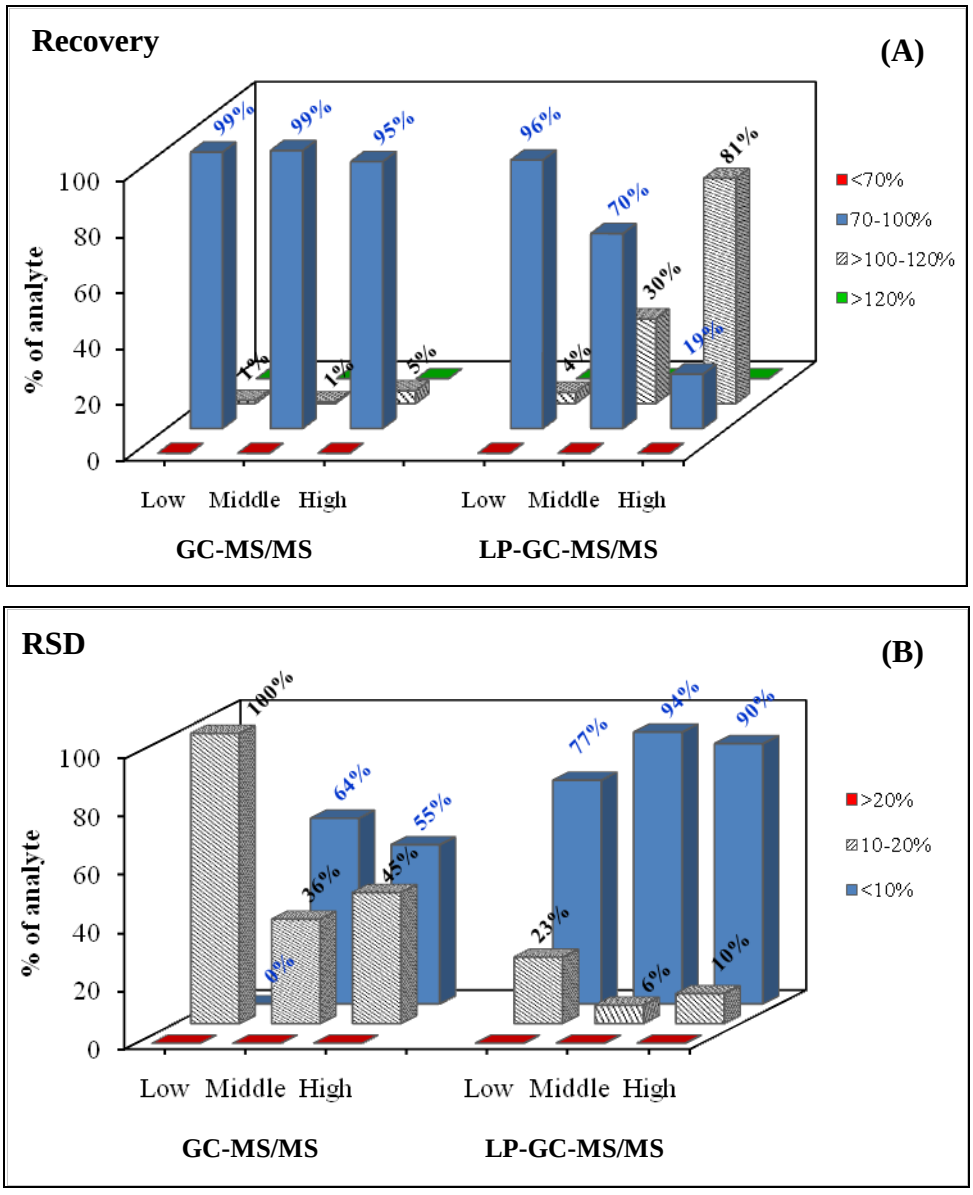


Figure 4.21 Distribution of overall recoveries (A) and RSDs (B) obtained from 3 days experiment using traditional GC-MS/MS and LP-GC-MS/MS.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

In this study, efficient methods for simultaneous identification and quantification of 170 amenable-GC pesticides including 45 of organochlorines, 45 of organophosphates, 70 of organonitrogens, and 10 of pyrethroids in onion were developed. This work covered the development and optimization of traditional GC–MS/MS method followed by modification of the acetate buffered QuEChERS based method for onion, and evaluation of a new LP-GC–MS/MS approach for multiple pesticide residues in onion.

The first part of this work, the instrumental method was done by optimizing each component to obtain a good overall working system. The injection conditions were optimized for removing the injected solvent and effective analyte transfer into the column. The oven temperature programs were tested to separate all analytes along the column (30 m × 0.25 mm i.d., 0.25 μm film thickness) with a suitable chromatographic run time. The two MRM transitions of each analyte with specific MS/MS conditions (see Table 4.3) were monitored in the MS/MS program. After complete the evaluation, the method is capable to analyze 170 targeted pesticides in 33 min with high selectivity and sensitivity.

Relying on the unique features of MS/MS that is capable of only detecting targeted analytes, the simple QuEChERS sample preparation approach was adapted for the analysis of onion. The modification of acetate buffered QuEChERS was done by optimizing the acidity of extraction solvent to keep the sensitive analytes in their neutral forms. The d-SPE clean-up step was optimized for effective removing co-extracted components (mainly amino acids, sulfur compounds, and color) with minimizing the loss of targeted analytes. The optimized procedure (Figure 5.1) provided good results in terms of overall recoveries for the majority of analytes and cleaner extracts.

Weigh 10 ± 0.05 g of the onion sample into a 50 mL centrifuge tube
(add I.S. and spiking standard solution at this stage)
↓
Add 10 mL of **0.5% acetic acid in MeCN** and vortex the tube for 1 min
↓
Add 4 g anh. $MgSO_4$ + **1 g sodium acetate** into the sample and
shake the tube vigorously by hand for 1 min
↓
Centrifuge the tube at 3400 rpm for 5 min
↓
Transfer 1 mL of the extract into the d-SPE tube containing
0.15 g anh. $MgSO_4$ + **0.05 g PSA + 0.05 g alumina-N + 0.005 g GCB**
↓
Shake the tube for 1 min and centrifuge at 10000 rpm for 5 min
↓
Filter the extract using 0.2 μm nylon syringe filter into a vial
↓
Analyze using GC–MS/MS

Figure 5.1 Schematic diagram of the modified QuEChERS method for the extraction of 170 pesticides in onion matrix.

The method accuracy and precision were studied at three spiking levels (0.01, 0.05, and 0.10 mg kg^{-1}). The method precisions were investigated for repeatability (intra-day precision) and intermediate precision. The method showed good results for the majority of analytes in the range of 70-120% recovery with less than 20% RSD which met the AOAC standard and the EU requirement (SANCO/12495/2011). Lowest calibrated levels (LCLs) which can be used as acceptable reporting limits with reliability were 0.01 mg kg^{-1} for all analytes and met the EU regulation levels.

Although the use of the modified QuEChERS method in combination with the traditional GC–MS/MS method produced overall good results; however, a major limitation factor is that the former requires long chromatographic run time.

Therefore, in the last part of this study, the LP-GC–MS/MS approach was evaluated using with respect to reduce analysis time and provide a quality of results. The LP-GC–MS/MS employed a 3 m × 0.15 mm i.d. capillary column at the inlet end coupled to a megabore column of 10 m × 0.25 mm i.d. × 1 μm film thickness which was connected to the MS vacuum system. The MS creates a vacuum in the 10 m analytical column, which reduces the viscosity of the He carrier gas and shifts the optimal flow rate to greater velocity. Thus, this allows using high column flow rate. By taking advantages of He-properties under vacuum, short analytical column, and rapid oven temperature ramp rate, total analysis time was 9.8 min (approximately 3-fold gain in speed *vs.* tradition GC–MS/MS). Other major benefits included increased sample capacity (lower detection limit), sharp peak and narrow peak width, good peak shape (reduce peak tailing) for relatively polar compounds, more accurate peak integration, and no special GC instrument needs.

To ensure the selectivity of the method, sample blank with spiked sample were injected and compared, it was found that there is no matrices interference signals appeared the analyte peaks, indicating high selectivity of the rapid LP-GC–MS/MS method. The validation results showed excellent analytical performances (in terms of linearity, recovery, precision, and analytical limits) for nearly all targeted pesticides and method ruggedness.

As apparent from the results, the overall analytical performances were comparable for the two GC–MS/MS methods, but the LP-GC–MS/MS was more time- and cost-effective. The proposed QuEChERS sample preparation and LP-GC–MS/MS method was successfully applied for testing of pesticide residues in agricultural products which contain sulfur components such as shallots, scallions, spring onion, and chives. These demonstrated the potential and suitability of the developed method for applying in routine multiresidue analysis of pesticides in onion and other related matrices.

Futher work should be expanded to the proposed method to cover more agricultural matrices.

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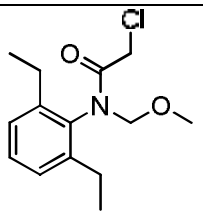
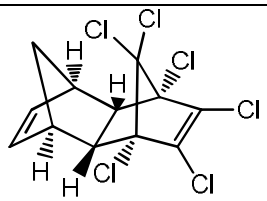
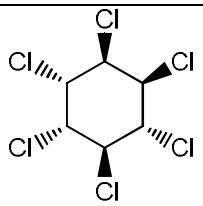
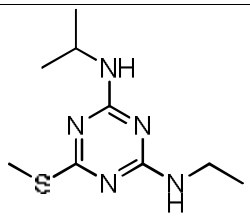
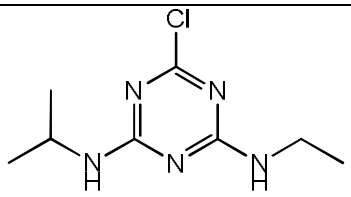
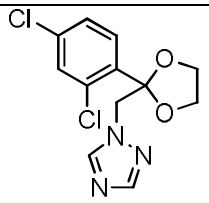
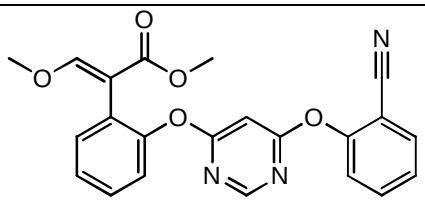
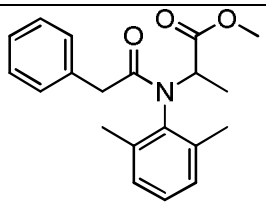
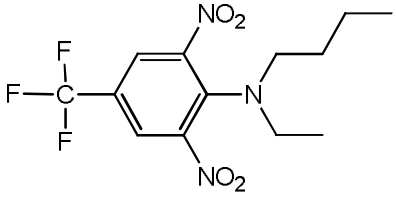
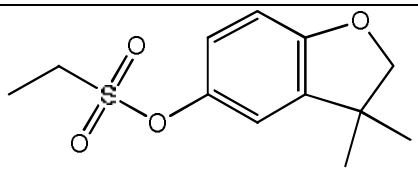
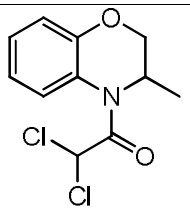
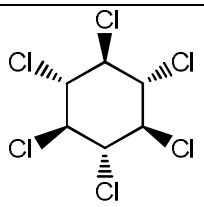
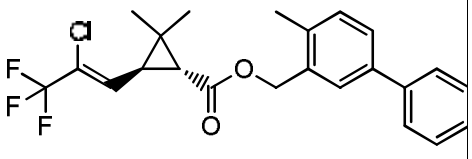
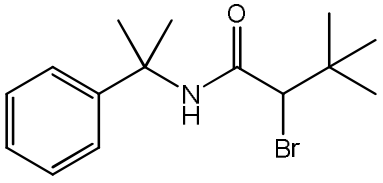
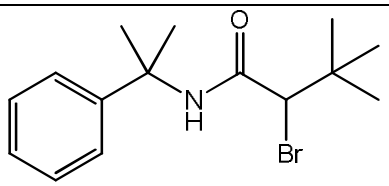
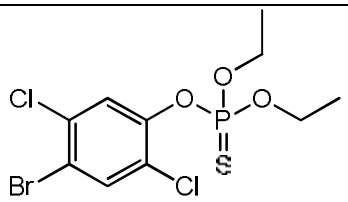
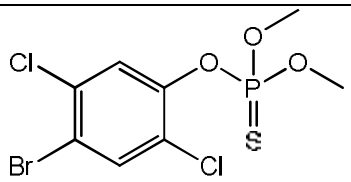
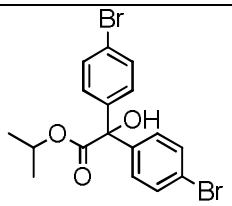
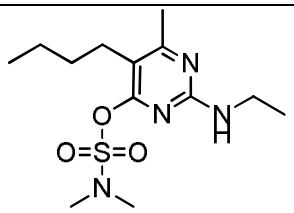
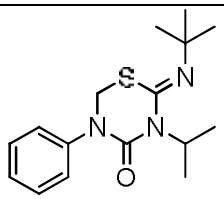
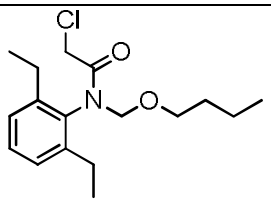
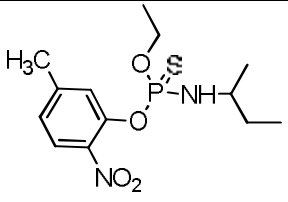
APPENDICES

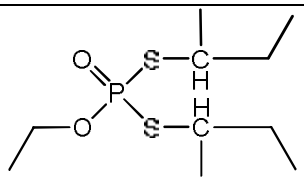
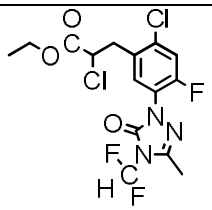
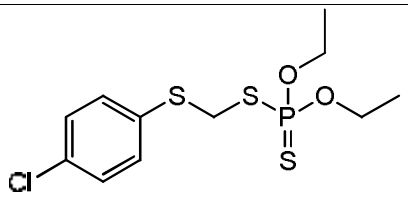
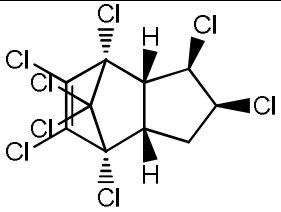
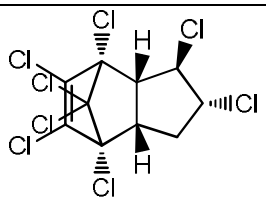
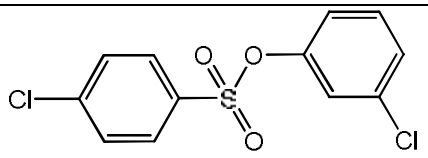
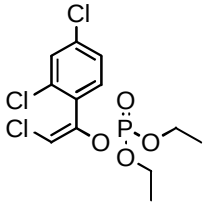
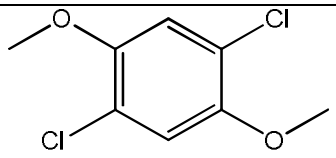
APPENDIX A

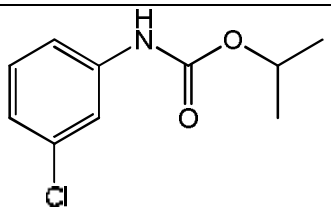
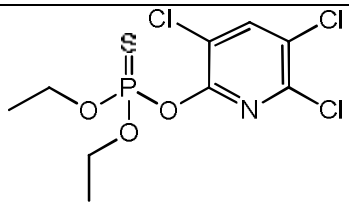
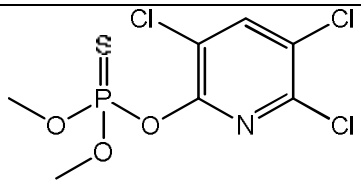
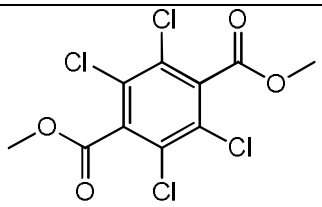
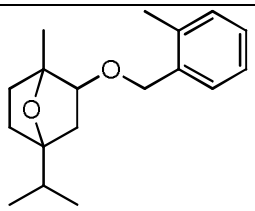
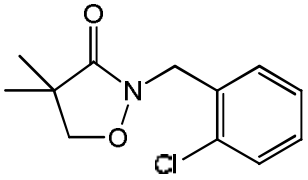
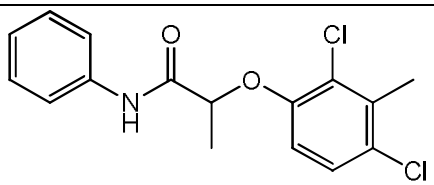
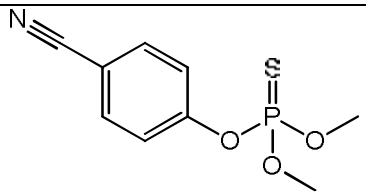
Table A-1 Name, structure, formula, and molecular weight (MW) of 170 pesticides**.**

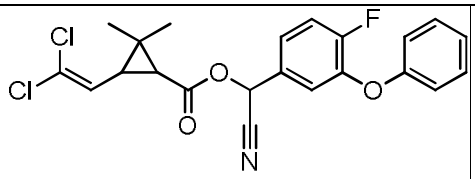
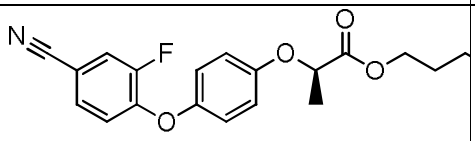
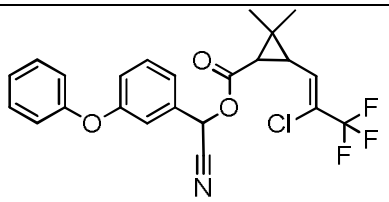
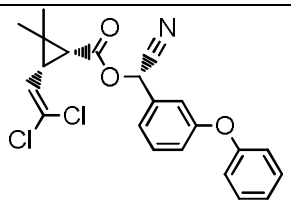
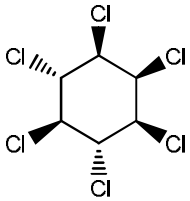
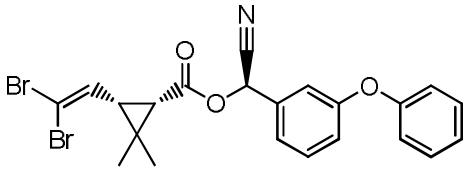
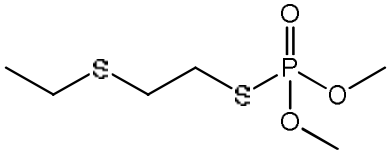
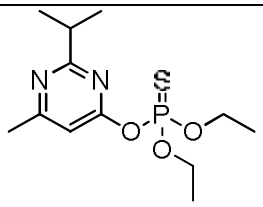
Compound	Structure	Formula	MW
Alachlor		$C_{14}H_{20}ClNO_2$	269.77
Aldrin		$C_{12}H_8Cl_6$	364.93
alpha-Lindane		$C_6H_6Cl_6$	288.00
Ametryn		$C_9H_{17}N_5S$	227.33
Atrazine		$C_8H_{14}ClN_5$	215.69
Azaconazole		$C_{12}H_{11}Cl_2N_3O_2$	300.10

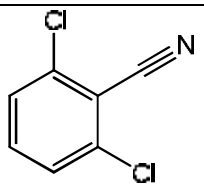
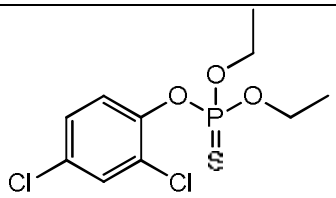
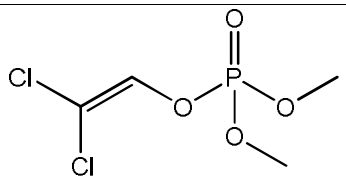
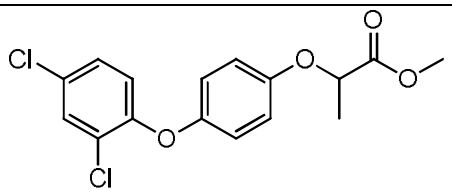
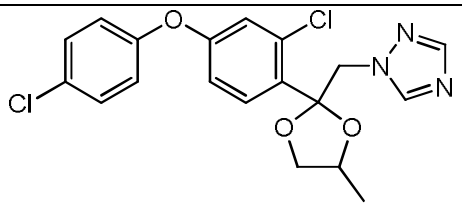
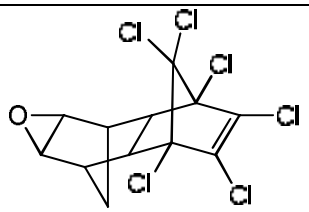
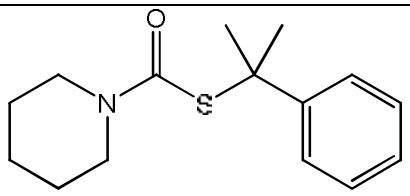
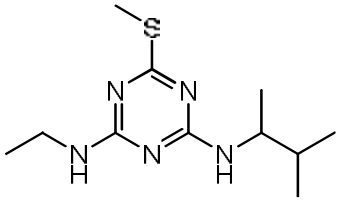
Azoxystrobin		$C_{22}H_{17}N_3O_5$	403.4
Benalaxyl		$C_{20}H_{23}NO_3$	325.4
Benfluralin		$C_{13}H_{16}F_3N_3O_4$	335.28
Benfuresate		$C_{12}H_{16}O_4S$	256.3
Benoxacor		$C_{11}H_{11}Cl_2NO_2$	260.10
beta-Lindane		$C_6H_6Cl_6$	288.00
Bifenthrin		$C_{23}H_{22}ClF_3O_2$	422.88
Bromobutide		$C_{15}H_{22}BrNO$	312.20

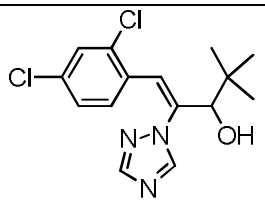
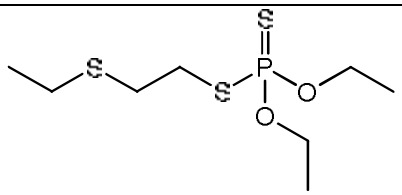
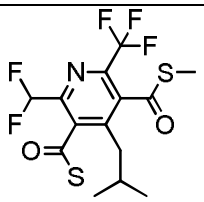
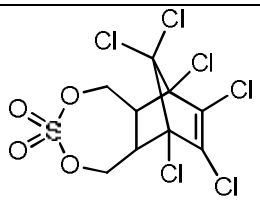
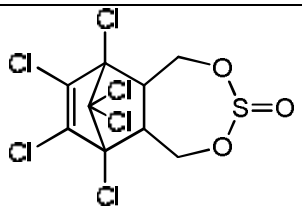
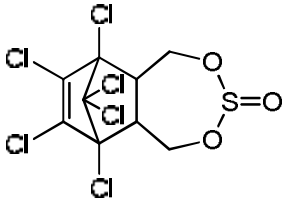
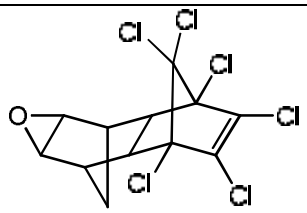
Bromobutide Metabolite		$C_{15}H_{22}BrNO$	312.2
Bromophos-ethyl		$C_{10}H_{12}BrCl_2O_3PS$	394.00
Bromophos-methyl		$C_8H_8BrCl_2O_3PS$	366.00
Bromopropylate		$C_{17}H_{16}Br_2O_3$	428.10
Bupirimate		$C_{13}H_{24}N_4O_3S$	316.43
Buprofezin		$C_{16}H_{23}N_3OS$	305.5
Butachlor		$C_{17}H_{26}ClNO_2$	311.90
Butamifos		$C_{13}H_{21}N_2O_4PS$	332.40

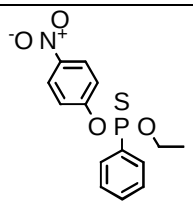
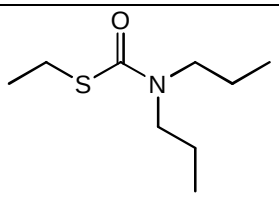
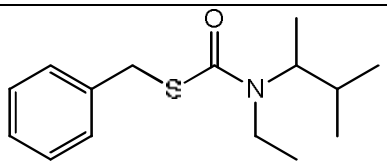
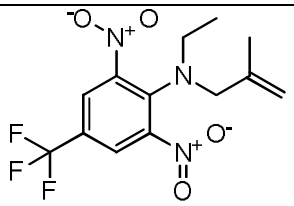
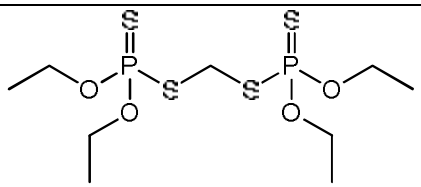
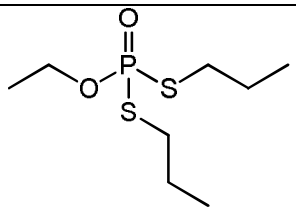
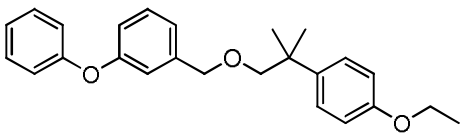
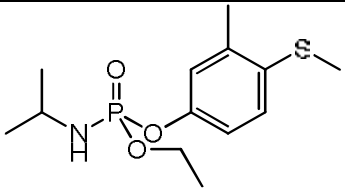
Cadusaphos		$C_{10}H_{23}O_2PS_2$	270.40
Cafentrazone-ethyl		$C_{15}H_{14}Cl_2F_3N_3O_3$	414.2
Carbophenothion		$C_{11}H_{16}ClO_2PS_3$	342.96
Chlordane-cis		$C_{10}H_6Cl_8$	409.78
Chlordane-trans		$C_{10}H_6Cl_8$	409.78
Chlorfenson		$C_{12}H_8Cl_2O_3S$	303.16
Chlorfenvinphos		$C_{12}H_{14}Cl_3O_4P$	359.60
Chloroneb		$C_8H_8Cl_2O_2$	207.10

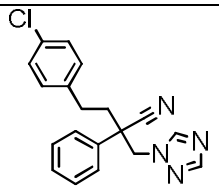
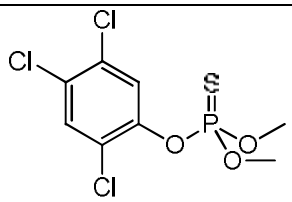
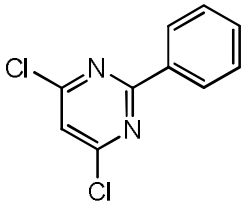
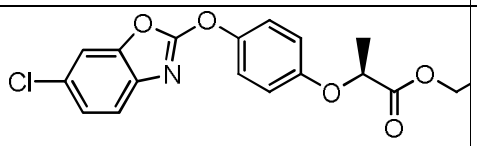
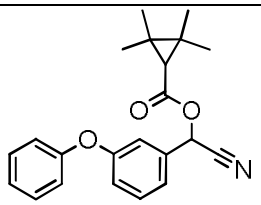
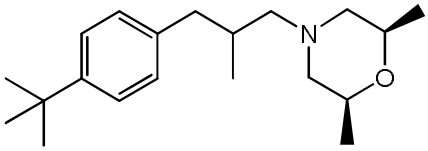
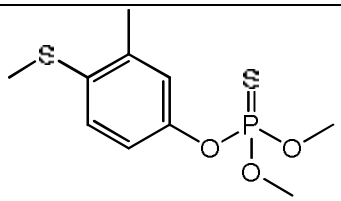
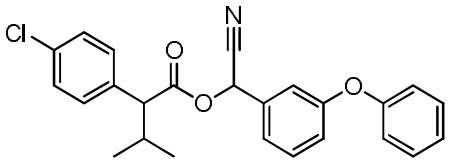
Chlorpropam		$C_{10}H_{12}ClNO_2$	213.66
Chlorpyrifos		$C_9H_{11}Cl_3NO_3PS$	350.60
Chlorpyrifos-methyl		$C_7H_7Cl_3NO_3PS$	322.50
Chlorthal-dimethyl		$C_{10}H_6Cl_4O_4$	332.00
Cimmethylin		$C_{18}H_{26}O_2$	274.4
Clomazole		$C_{12}H_{14}ClNO_2$	239.7
Clomeprop		$C_{16}H_{15}Cl_2NO_2$	324.20
Cyanophos		$C_9H_{10}NO_3PS$	243.21

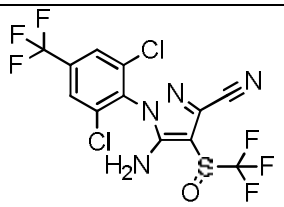
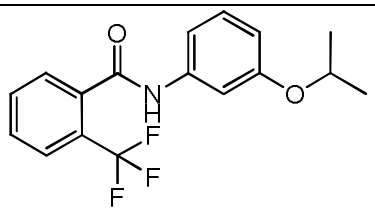
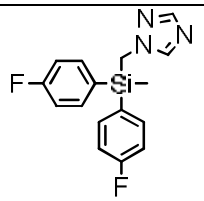
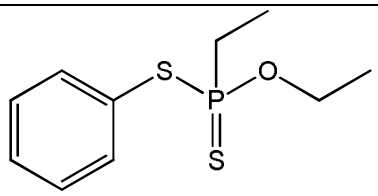
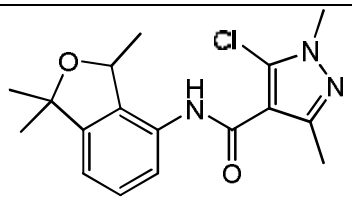
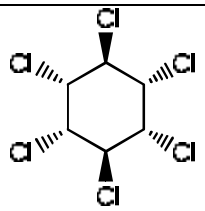
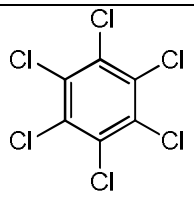
Cyfluthrin		$C_{22}H_{18}Cl_2FNO_3$	434.30
Cyhalofop-butyl		$C_{20}H_{20}FNO_4$	357.4
Cyhalothrin		$C_{23}H_{19}ClF_3NO_3$	449.90
Cypermethrin		$C_{22}H_{19}Cl_2NO_3$	416.30
delta-Lindane		$C_6H_6Cl_6$	288.00
Deltamethrin		$C_{22}H_{19}Br_2NO_3$	505.21
Demeton-S-methyl		$C_6H_{15}O_3PS_2$	230.30
Diazinon		$C_{12}H_{21}N_2O_3PS$	304.35

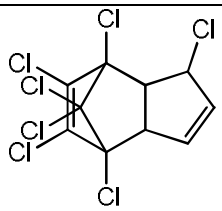
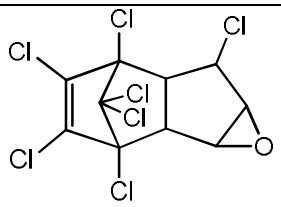
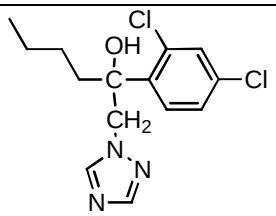
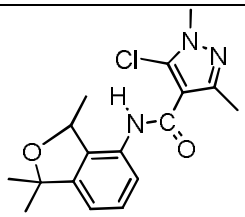
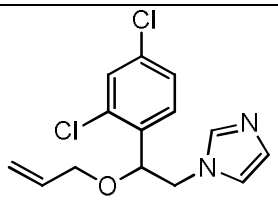
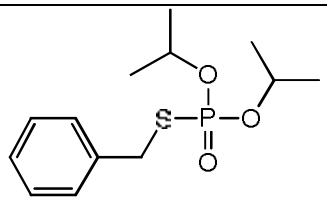
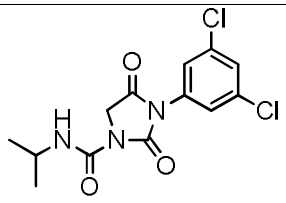
Dichlobenil		$C_7H_3Cl_2N$	172.02
Dichlorfenthion		$C_{10}H_{13}Cl_2O_3PS$	315.20
Dichlorvos		$C_4H_7Cl_2O_4P$	220.98
Diclofop-methyl		$C_{16}H_{14}Cl_2O_4$	341.2
Difenoconazole		$C_{19}H_{17}Cl_2N_3O_3$	406.27
Dieldrin		$C_{12}H_8Cl_6O$	380.93
Dimepiperate		$C_{15}H_{21}NOS$	263.00
Dimethametryn		$C_{11}H_{21}N_5S$	255.39

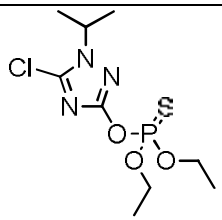
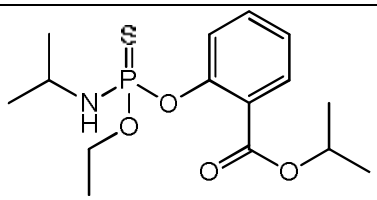
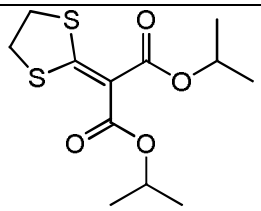
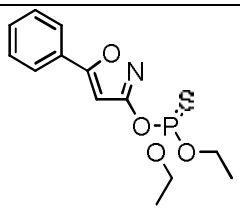
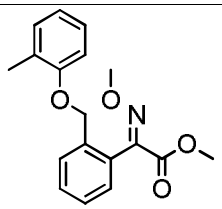
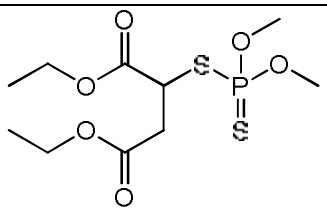
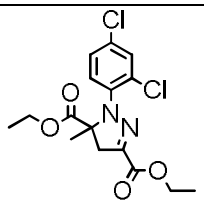
Diniconazole		$C_{15}H_{17}ClN_2O$	326.23
Disulfoton		$C_8H_{19}O_2PS_3$	274.40
Dithiopyr		$C_{15}H_{16}F_5NO_2S_2$	401.4
Endosulfan sulphate		$C_9H_6Cl_6O_4S$	422.93
alpha-Endosulfan		$C_9H_6Cl_6O_3S$	406.93
beta-Endosulfan		$C_9H_6Cl_6O_3S$	406.93
Endrin		$C_{12}H_8Cl_6O$	381.93

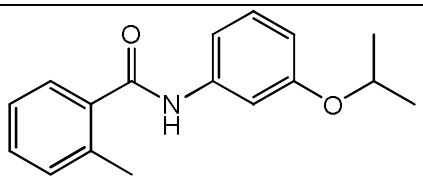
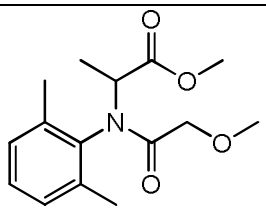
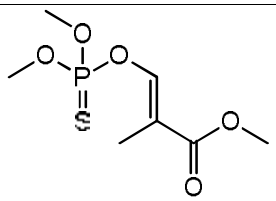
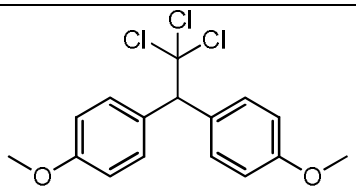
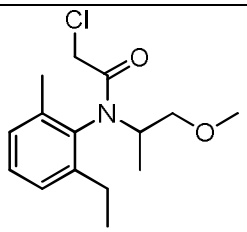
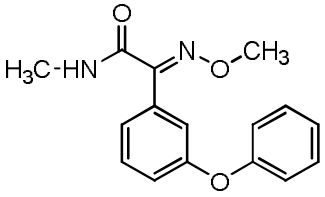
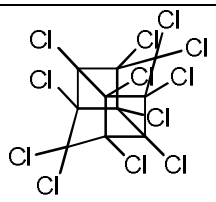
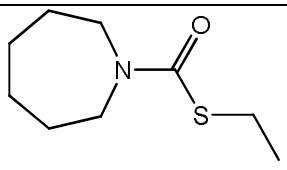
EPN		$C_{14}H_{14}NO_4PS$	323.30
EPTC		$C_9H_{19}NOS$	189.3
Esprocarb		$C_{15}H_{23}NOS$	265.4
Ethalfluralin		$C_{13}H_{14}F_3N_3O_4$	333.30
Ethion		$C_9H_{22}O_4P_2S_4$	384.48
Ethoprophos		$C_8H_{19}O_2PS_2$	242.30
Etofenprox		$C_{25}H_{28}O_3$	376.5
Fenamiphos		$C_{13}H_{22}NO_3PS$	303.30

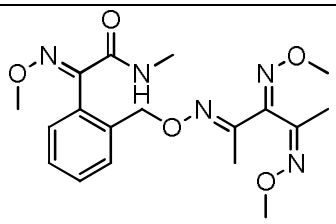
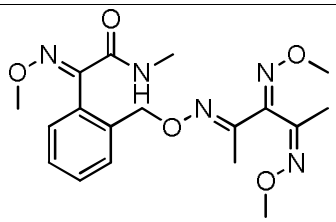
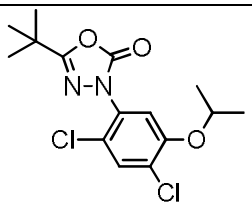
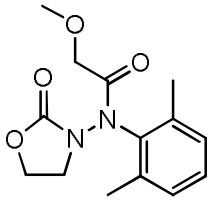
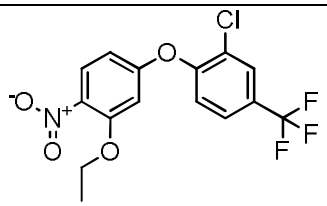
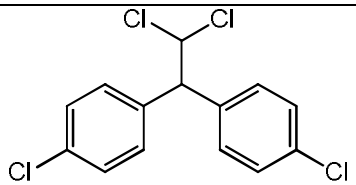
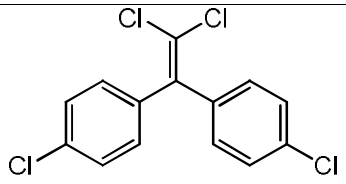
Fenbuconazole		$C_{19}H_{17}ClN_4$	336.8
Fenchlorphos		$C_8H_8Cl_3O_3PS$	321.56
Fenclorim		$C_{10}H_6Cl_2N_2$	225.1
Fenoxaprop-ethyl		$C_{18}H_{16}ClNO_5$	361.8
Fenpropathrin		$C_{22}H_{23}NO_3$	349.40
Fenpropimorh		$C_{20}H_{33}NO$	303.5
Fenthion		$C_{10}H_{15}O_3PS_2$	278.33
Fenvalelate		$C_{25}H_{22}ClNO_3$	419.91

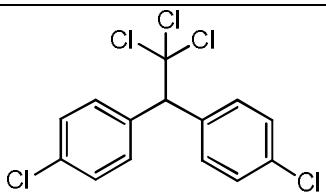
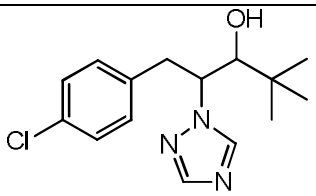
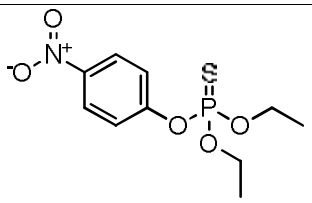
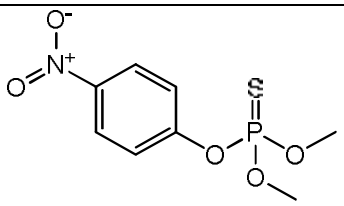
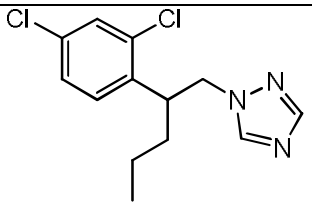
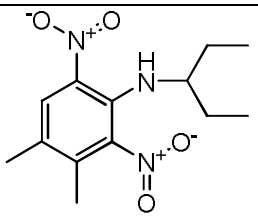
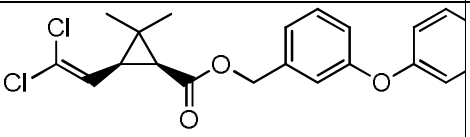
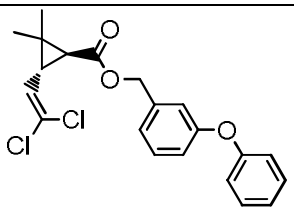
Fipronil		$C_{12}H_4Cl_2F_6N_4OS$	437.20
Flutolanil		$C_{17}H_{16}F_3NO_2$	323.3
Flusilazole		$C_{16}H_{15}F_2N_3Si$	315.39
Fonofos		$C_{10}H_{15}OPS_2$	246.34
Furametpyr		$C_{17}H_{20}ClN_3O_2$	333.81
gamma-Lindane		$C_6H_6Cl_6$	288.00
HCB		C_6Cl_6	284.81

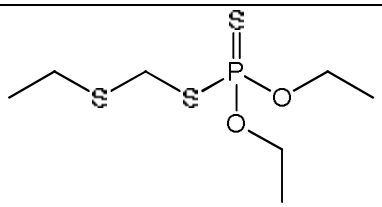
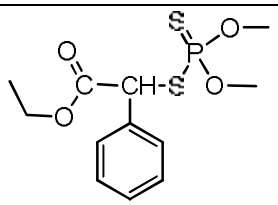
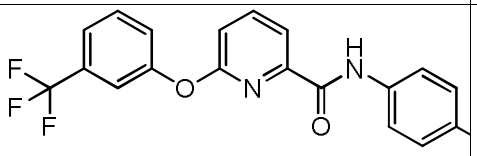
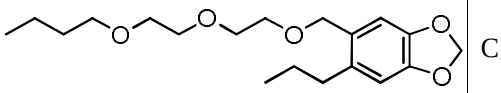
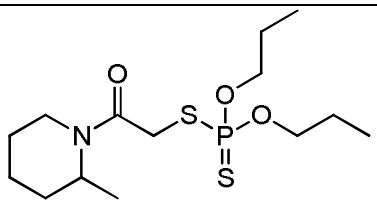
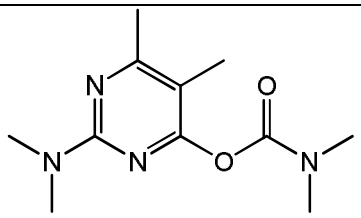
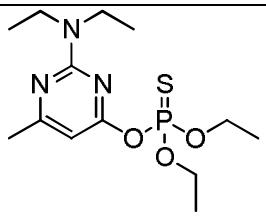
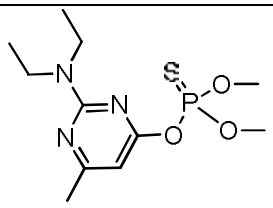
Heptachlor		$C_{10}H_5Cl_7$	373.34
Heptachlor-epoxide		$C_{10}H_5Cl_7O$	389.32
Hexaconazole		$C_{14}H_{17}Cl_2N_3O$	314.2
Hydroxy Furametpyr		$C_{17}H_{20}ClN_3O_2$	333.81
Imazalil		$C_{14}H_{14}Cl_2N_2O$	297.18
Iprobenfos		$C_{13}H_{21}O_3PS$	288.30
Iprodione		$C_{13}H_{13}Cl_2N_3O_3$	330.17

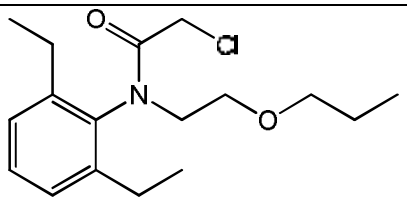
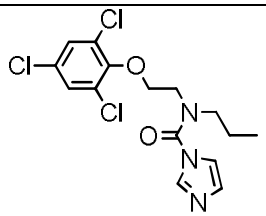
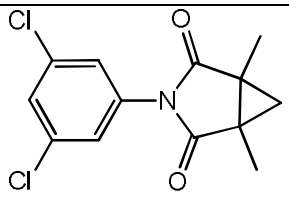
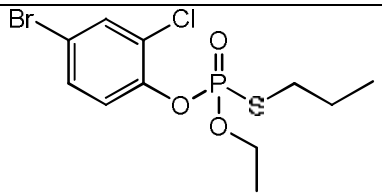
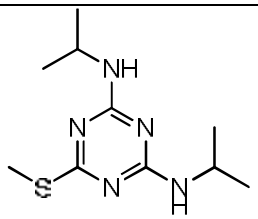
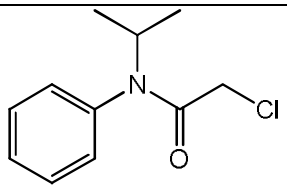
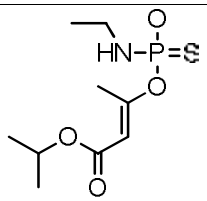
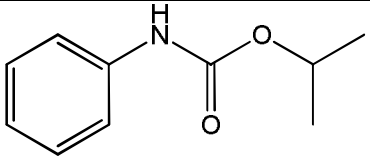
Isazofos		$C_9H_{17}ClN_3O_3PS$	313.70
Isofenfos		$C_{15}H_{24}NO_4PS$	345.40
Isoprothiolane		$C_{12}H_{18}O_4S_2$	290.4
Isoxathion		$C_{13}H_{16}NO_4PS$	313.80
Kresoxim-methyl		$C_{18}H_{19}NO_4$	313.36
Malathion		$C_{10}H_{19}O_6PS_2$	330.36
Mefenpyr-diethyl		$C_{16}H_{18}Cl_2N_2O_4$	373.20

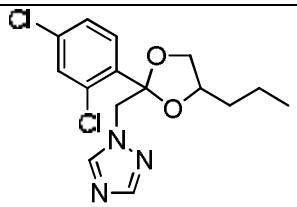
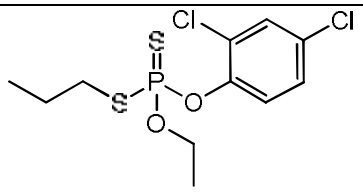
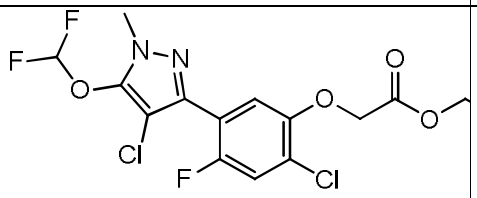
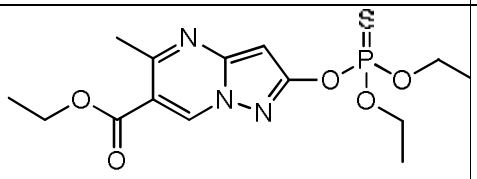
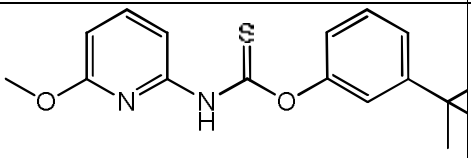
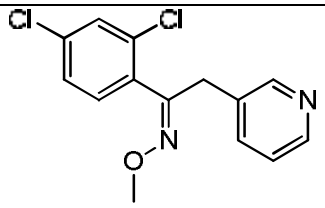
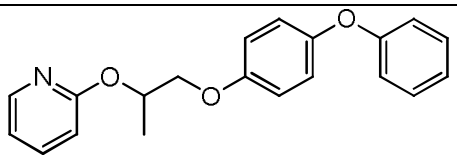
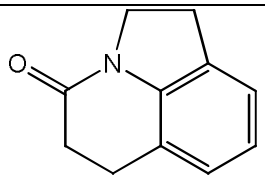
Mepronil		$C_{17}H_{19}NO_2$	269.34
Metalaxyl		$C_{15}H_{21}NO_4$	279.34
Methacrifos		$C_7H_{13}O_5PS$	240.21
Methoxychlor		$C_{16}H_{15}Cl_3O_2$	345.65
Metolachlor		$C_{15}H_{22}ClNO_2$	283.8
Metominostrobin		$C_{16}H_{16}N_2O_3$	284.3
Mirex		$C_{10}Cl_{12}$	545.55
Molinate		$C_9H_{17}NOS$	187.3

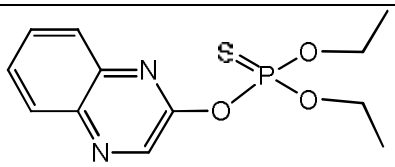
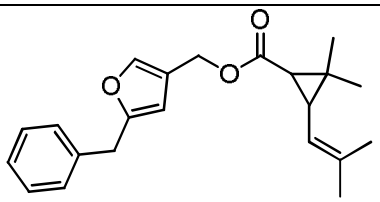
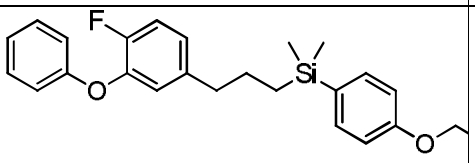
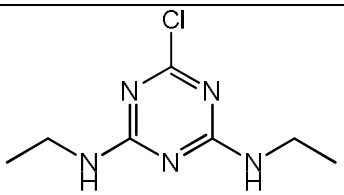
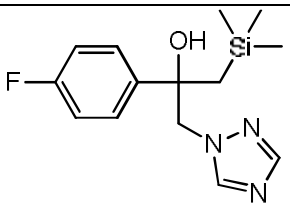
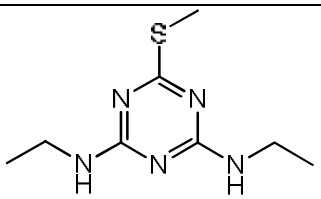
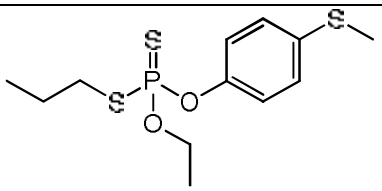
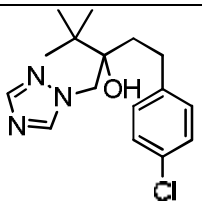
Oryzastrobin		$C_{18}H_{25}N_5O_5$	407
Oryzastrobin metabolite		$C_{18}H_{25}N_5O_5$	407
Oxadiazon		$C_{15}H_{18}Cl_2N_2O_3$	345.23
Oxadixyl		$C_{14}H_{18}N_2O_4$	278.3
Oxyfluorfen		$C_{15}H_{11}ClF_3NO_4$	361.7
p,p'-DDD		$C_{14}H_{10}Cl_4$	320.05
p,p'-DDE		$C_{14}H_8Cl_4$	318.03

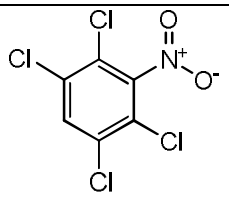
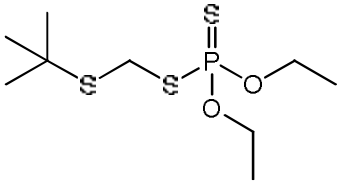
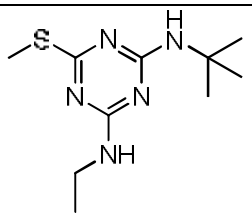
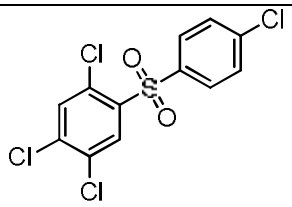
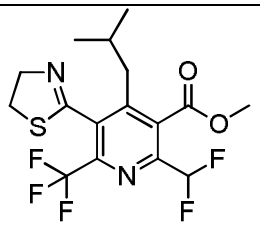
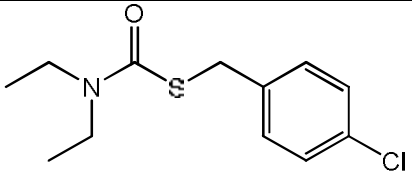
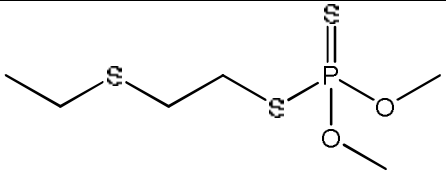
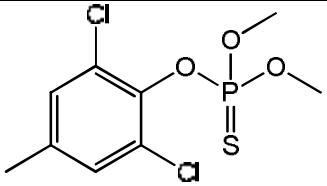
p,p'-DDT		$C_{14}H_9Cl_5$	354.51
Paclobutrazol		$C_{15}H_{20}ClN_3O$	293.8
Parathion-ethyl		$C_{10}H_{14}NO_5PS$	291.27
Parathion-methyl		$C_8H_{10}NO_5PS$	263.21
Penconazole		$C_{13}H_{15}Cl_2N_3$	284.19
Pendimethalin		$C_{13}H_{19}N_3O_4$	281.31
Permethrin-cis		$C_{21}H_{20}Cl_2O_3$	391.29
Permethrin-trans		$C_{21}H_{20}Cl_2O_3$	391.29

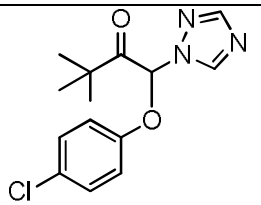
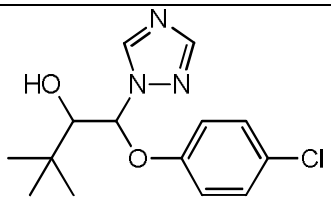
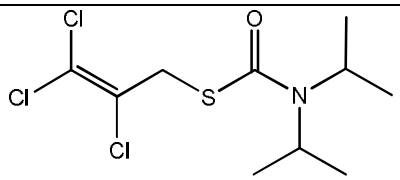
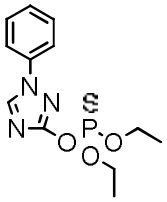
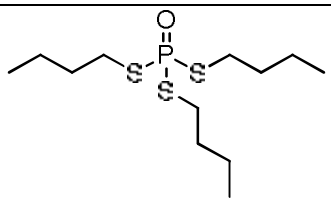
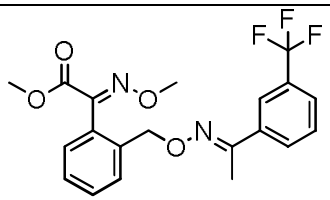
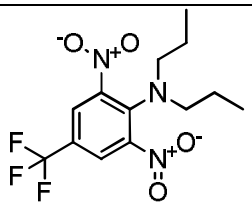
Phorate		$C_7H_{17}O_2\ PS_3$	260.38
Phenthoate		$C_{12}H_{17}O_4PS_2$	320.37
Picolinafen		$C_{19}H_{12}F_4N_2O_2$	376.3
Piperonyl butoxide		$C_{19}H_{30}O_5$	338.43
Piperophos		$C_{14}H_{28}NO_3PS_2$	353.50
Pirimicarb		$C_{11}H_{18}N_4O_2$	238.3
Pirimiphos-ethyl		$C_{13}H_{24}N_3O_3PS$	333.40
Pirimiphos-methyl		$C_{11}H_{20}N_3O_3PS$	305.30

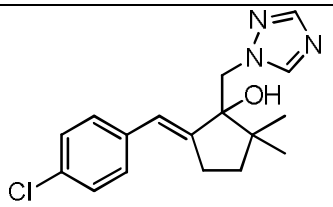
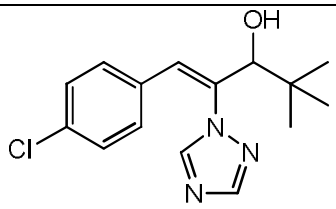
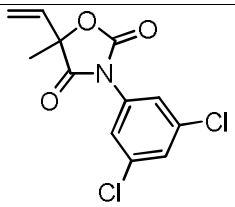
Pretilachlor		$C_{17}H_{26}ClNO_2$	311.9
Prochloraz		$C_{15}H_{16}Cl_3N_3O_2$	376.67
Procymidone		$C_{13}H_{11}Cl_2NO_2$	284.1
Profenofos		$C_{11}H_{15}BrClO_3PS$	373.60
Prometryn		$C_{10}H_{19}N_5S$	241.37
Propachlor		$C_{11}H_{14}ClNO$	211.69
Propetamphos		$C_{10}H_{20}NO_4PS$	281.30
Propham		$C_{10}H_{13}NO_2$	179.22

Propiconazole-trans		$C_{15}H_{17}Cl_2N_3O_2$	342.2
Prothiophos		$C_{11}H_{15}Cl_2O_2PS_2$	345.25
Pyraflufen-ethyl		$C_{15}H_{13}Cl_2F_3N_2O_4$	413.2
Pyrazophos		$C_{14}H_{20}N_3O_5PS$	373.37
Pyributicarb		$C_{18}H_{22}N_2O_2S$	330.4
Pyrifenox		$C_{14}H_{12}Cl_2N_2O$	295.17
Pypiproxyfen		$C_{20}H_{19}NO_3$	321.5
Pyroquilon		$C_{11}H_{11}NO$	173.2

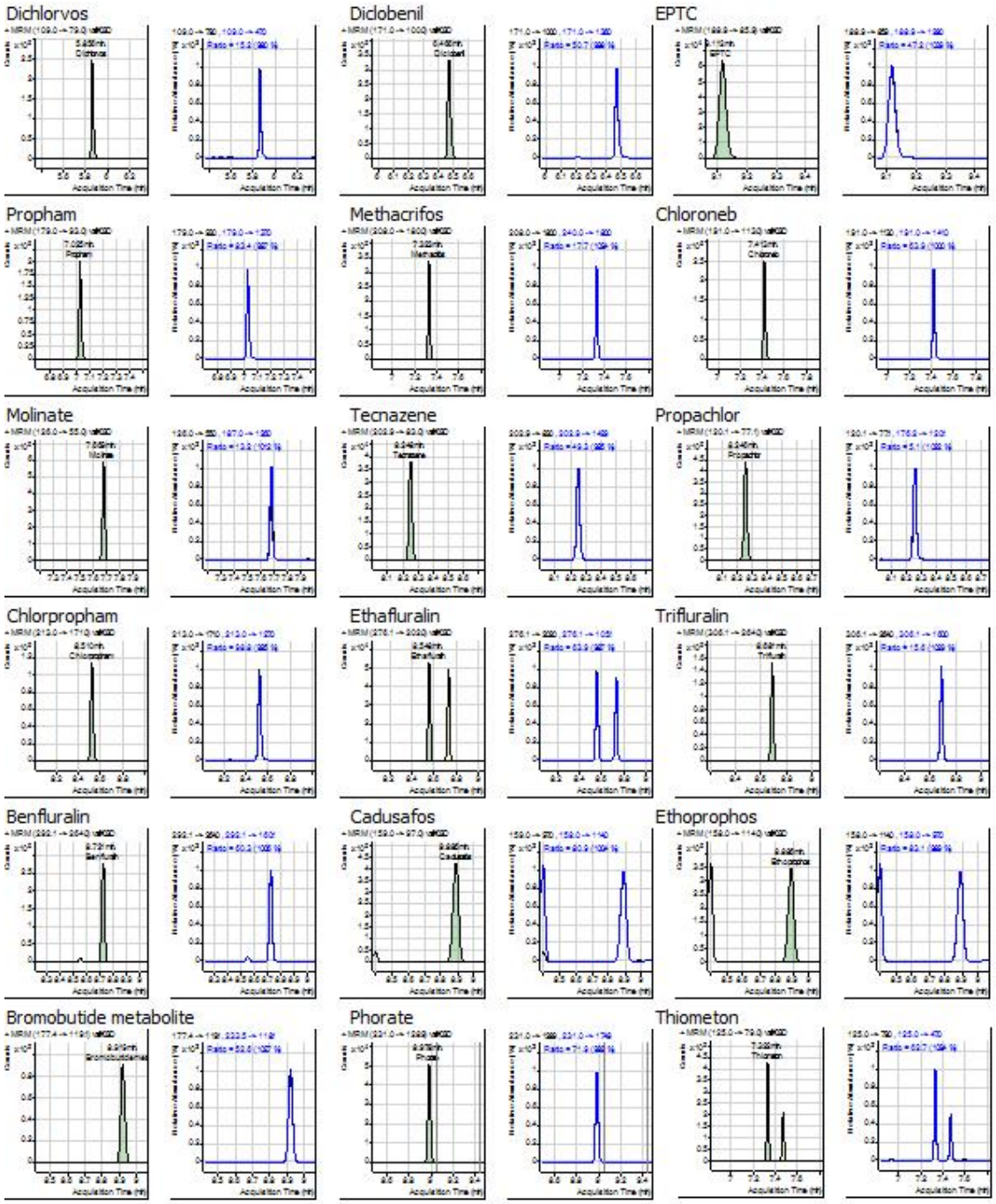
Quinalphos		$C_{12}H_{15}N_2O_3PS$	298.30
Resmethrin		$C_{22}H_{26}O_3$	338.45
Silafluofen		$C_{25}H_{29}FO_2Si$	408.6
Simazine		$C_7H_{12}ClN_5$	201.66
Simeconazole		$C_{14}H_{20}FN_3OSi$	293.4
Simetryn		$C_8H_{15}N_5S$	213.3
Sulprofos		$C_{12}H_{19}O_2PS_3$	322.42
Tebuconazole		$C_{16}H_{22}ClN_3O$	307.8

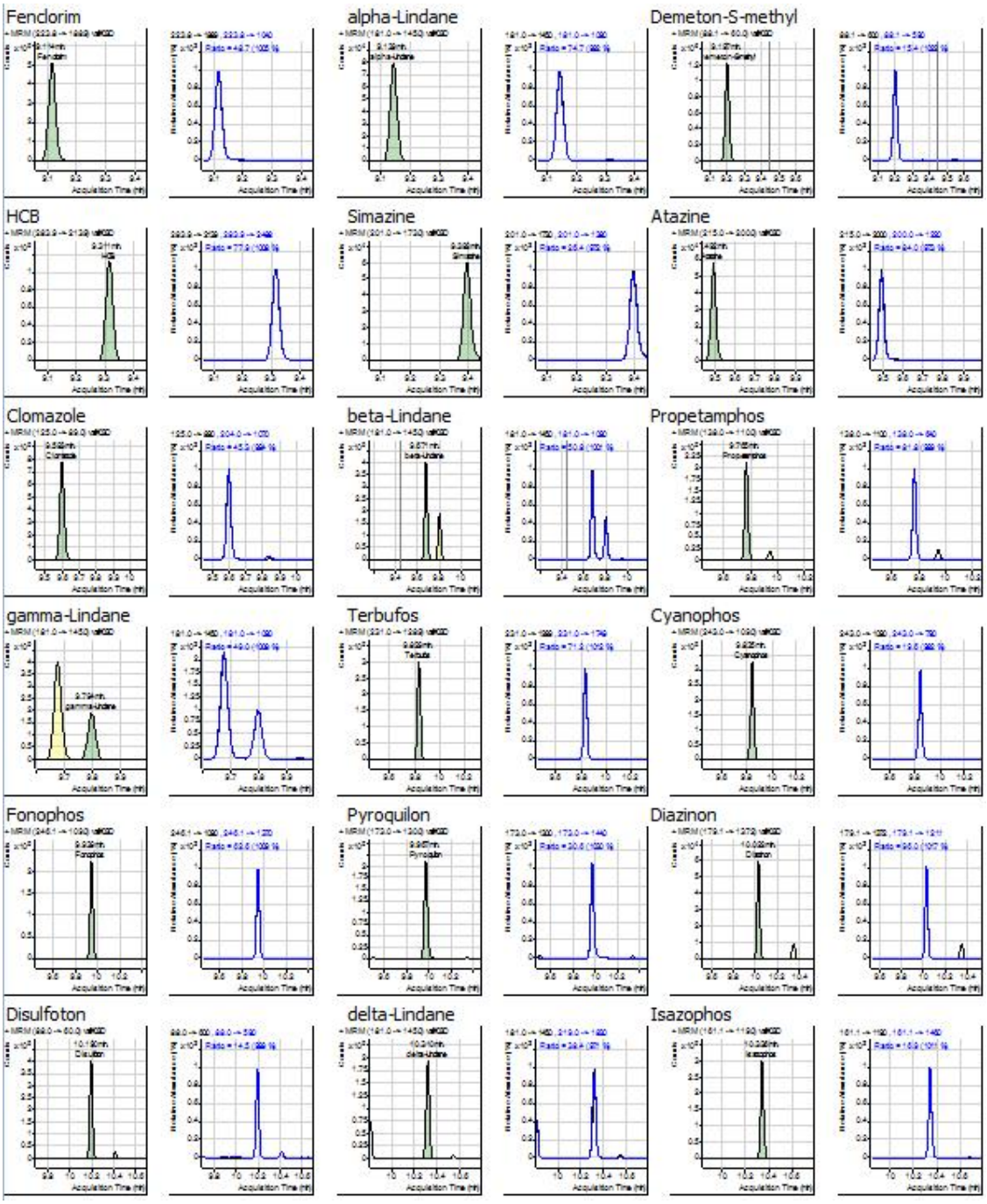
Tecnazene		$C_6HCl_4NO_2$	260.89
Terbufos		$C_9H_{21}O_2PS_3$	288.43
Terbutryn		$C_{10}H_{19}N_5S$	241.4
Tetradifon		$C_{12}H_6Cl_4O_2S$	356.06
Thiazopyr		$C_{16}H_{17}F_5N_2O_2S$	396.40
Thiobencarb		$C_{12}H_{16}ClNOS$	257.78
Thiometon		$C_6H_{15}O_2PS_3$	246.30
Tolclofos-Methyl		$C_9H_{11}Cl_2O_3PS$	301.10

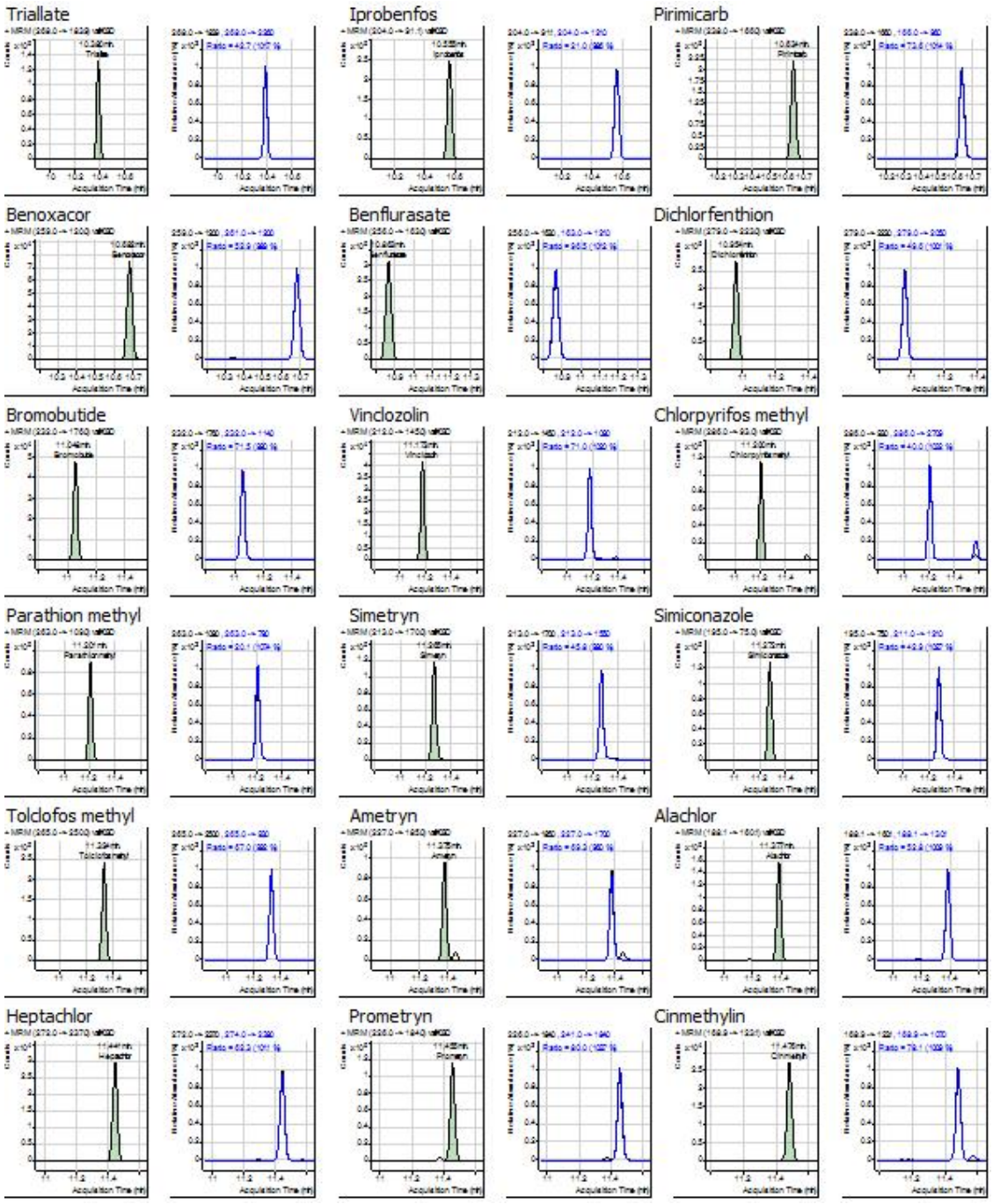
Triadimefon		$C_{14}H_{16}ClN_3O_2$	293.8
Triadimenol		$C_{14}H_{18}ClN_3O_2$	295.8
Triallate		$C_{10}H_{16}Cl_3NOS$	304.66
Triazophos		$C_{12}H_{16}N_3O_3PS$	313.30
Tribufos		$C_{12}H_{27}OPS_3$	314.52
Trifloxystrobin		$C_{20}H_{19}F_3N_2O_4$	408.4
Trifluralin		$C_{13}H_{16}F_3N_3O_4$	335.28

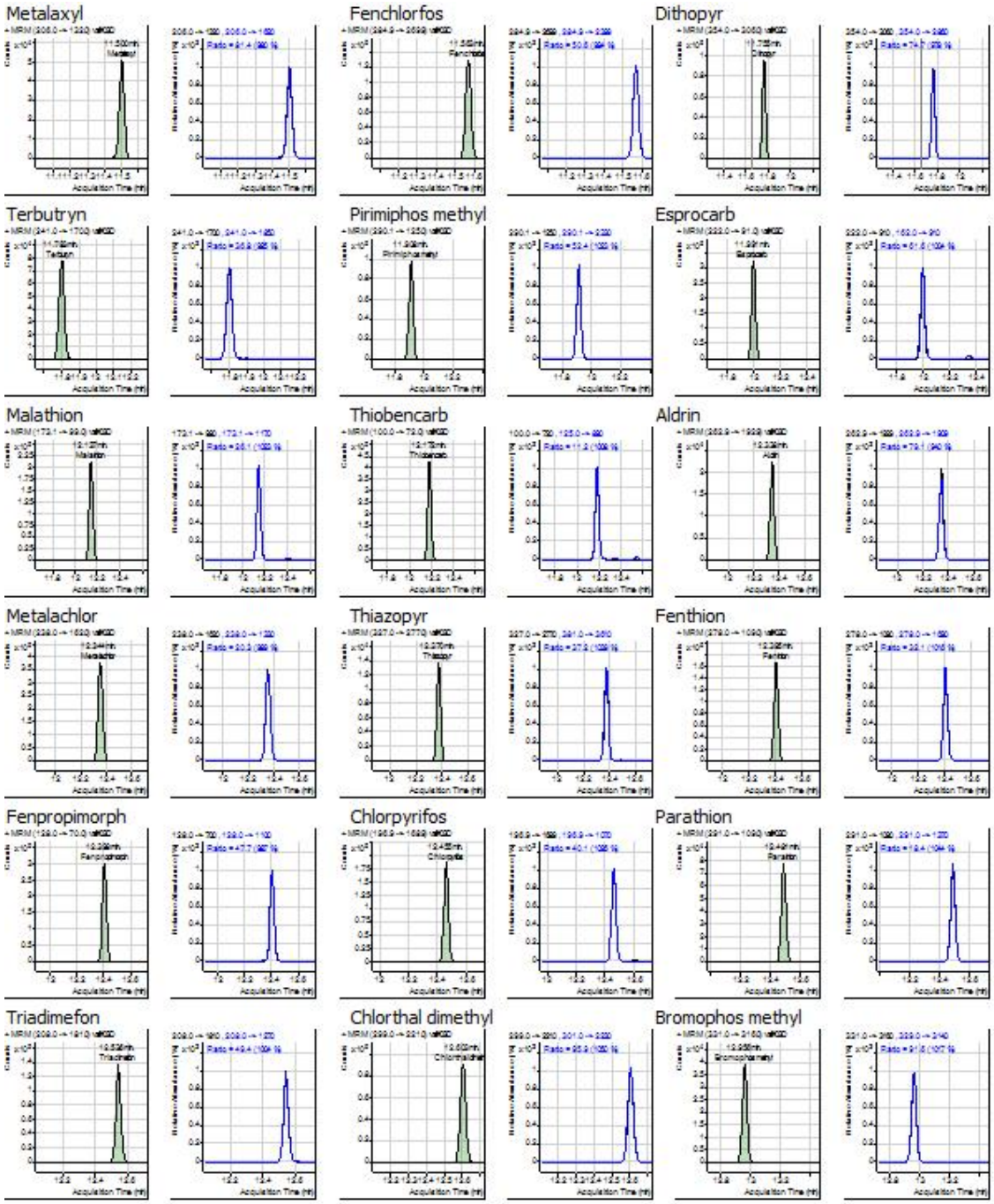
Triticonazole		$C_{17}H_{20}ClN_3O$	317.8
Uniconazole		$C_{15}H_{18}ClN_3O$	291.8
Vinclozolin		$C_{12}H_9Cl_2NO_3$	286.10

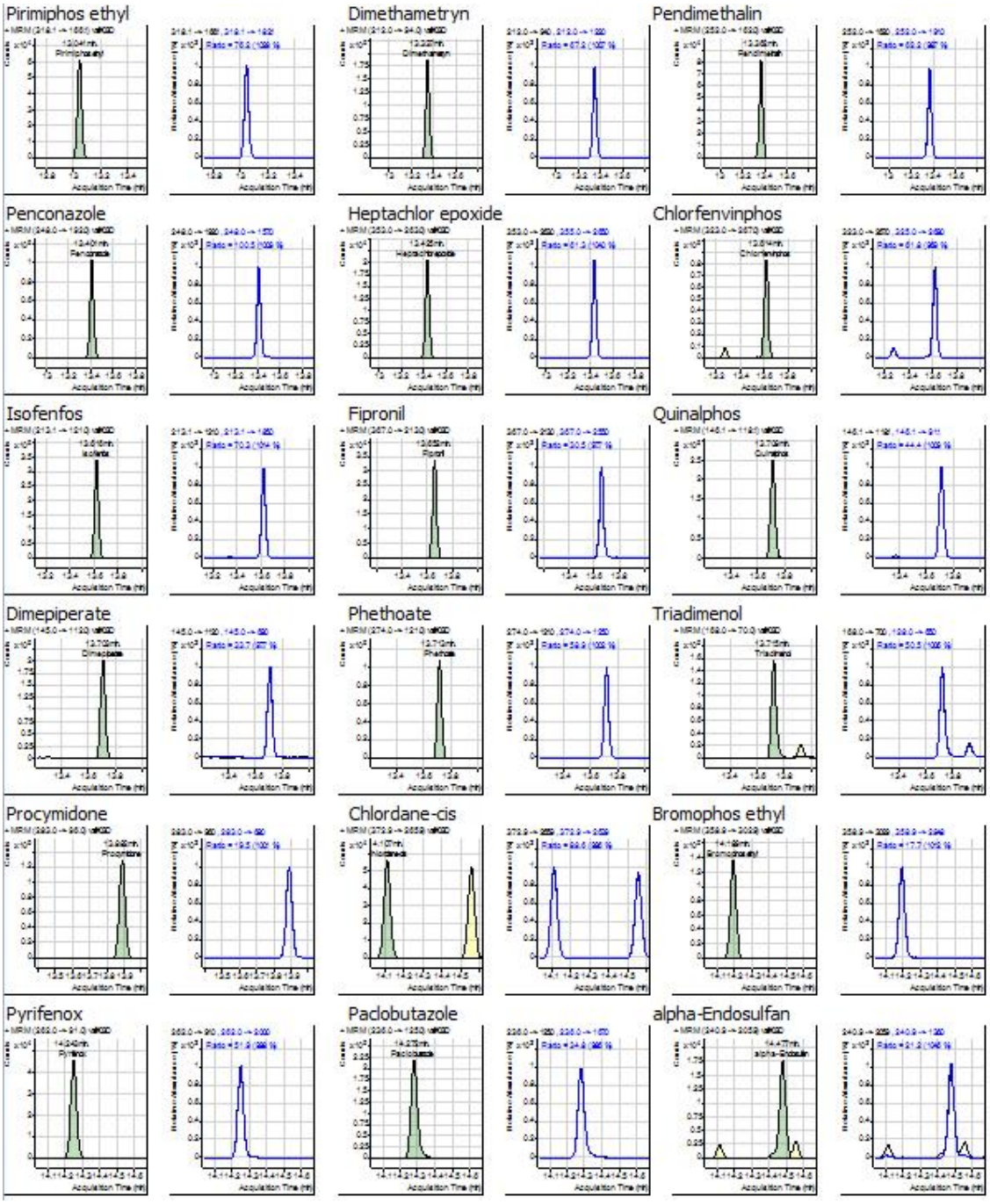
APPENDIX B

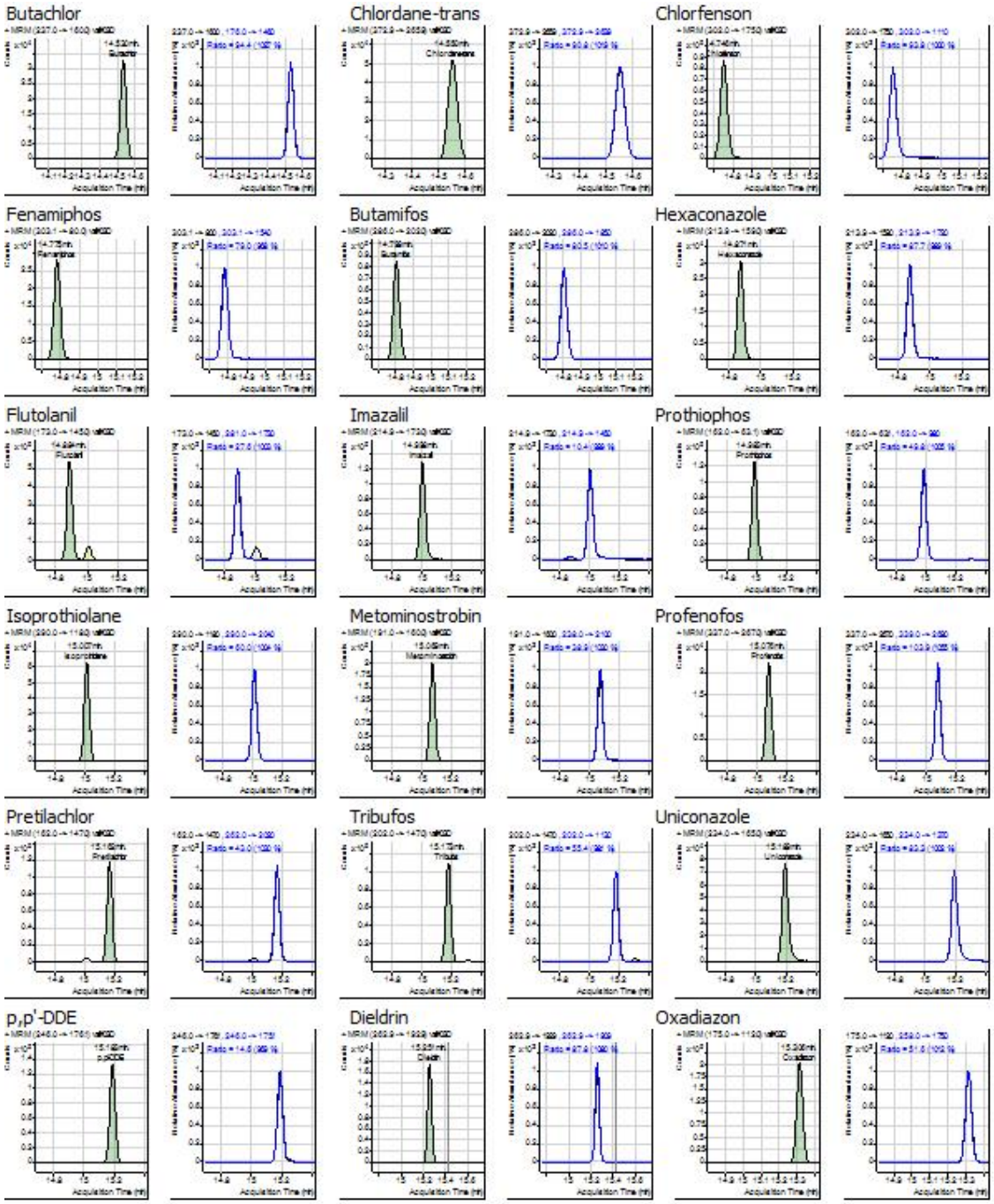


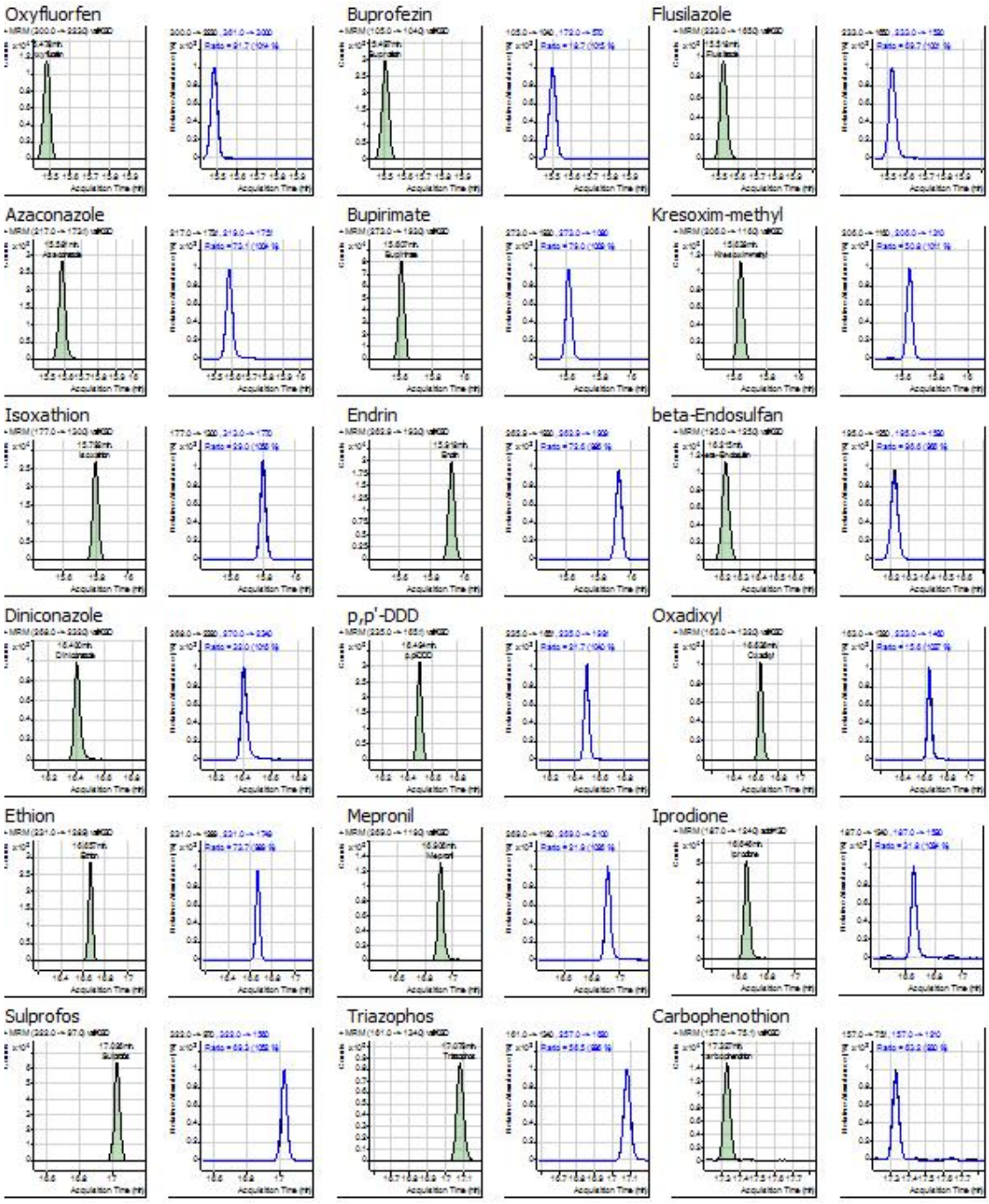


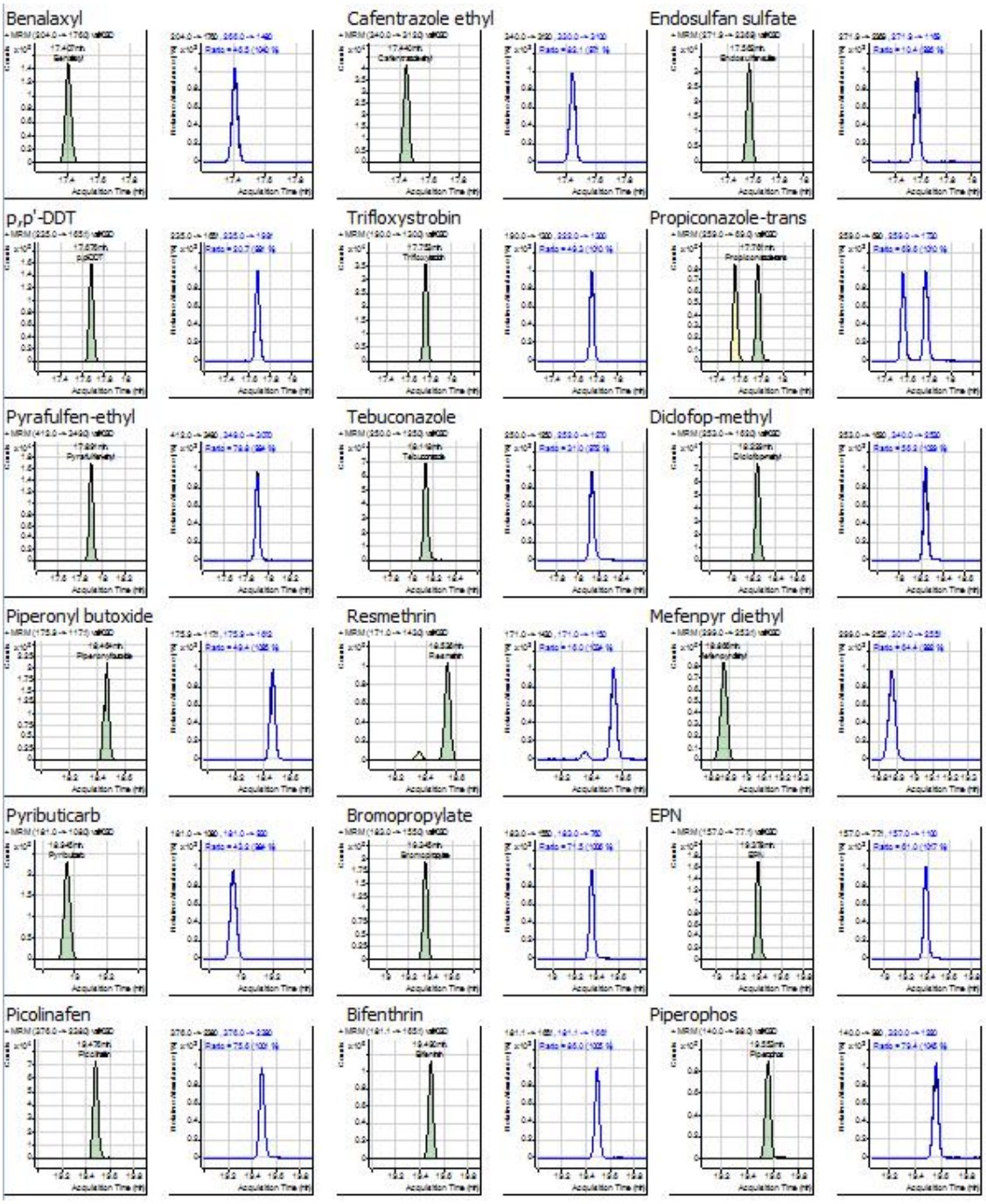


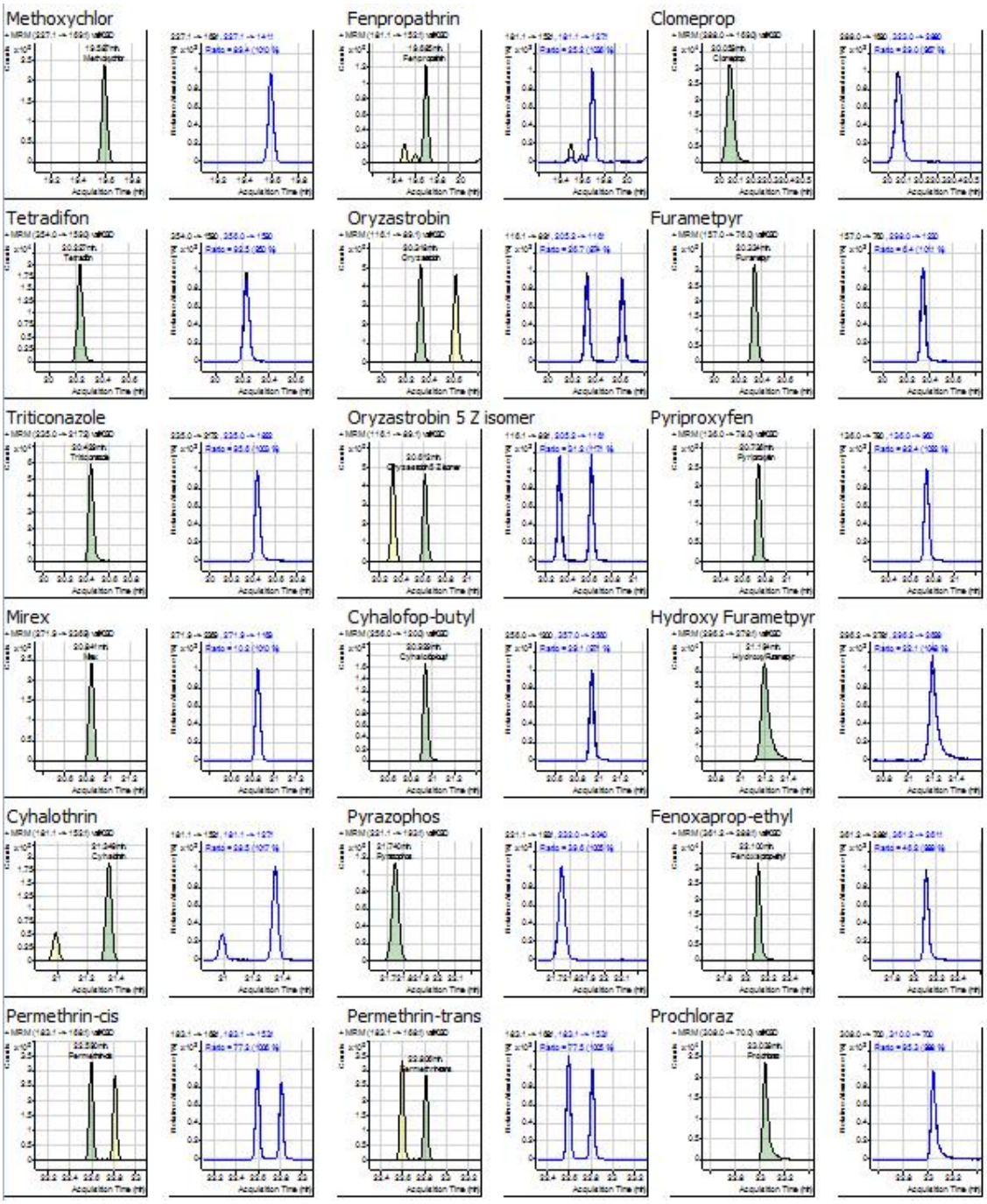












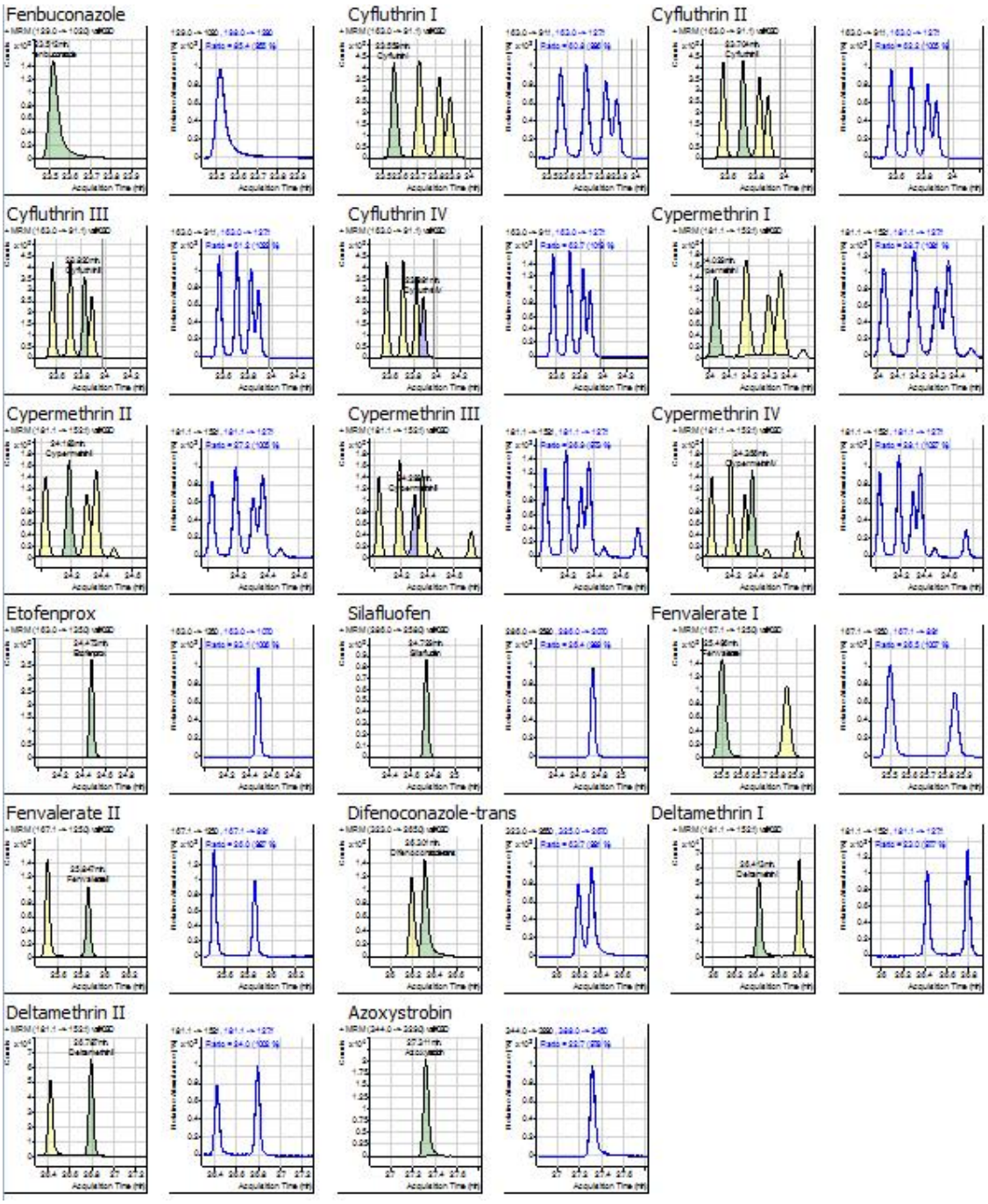


Figure B-1 MRM chromatograms of standard pesticides at 0.1 mg L^{-1} in MeCN under the optimum traditional GC-MS/MS conditions.

APPENDIX C

Table C-1 Average %recoveries (Re) and %RSDs (n=5) of 170 pesticides obtained by traditional GC-MS/MS analyses of spiked onion at 0.1 mg kg^{-1} based on **different %acetic acid in MeCN**.

Analyte	Acetic acid in MeCN									
	0.10%		0.30%		0.50%		0.70%		1%	
	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD
Alachlor	75	7	80	2	89	2	84	7	76	5
Aldrin	116	16	92	1	83	10	80	4	71	4
alpha-Endosulfan	94	11	86	8	87	3	82	5	77	7
alpha-Lindane	111	19	82	1	81	7	73	5	69	1
Ametryn	83	2	82	1	88	1	84	2	85	4
Atazine	80	3	79	3	82	3	81	7	76	7
Azaconazole	83	2	83	1	87	3	83	5	80	3
Azoxystrobin	80	5	86	2	96	2	90	4	84	9
Benalaxyl	85	2	84	1	88	1	86	6	75	6
Benfluralin	92	10	82	2	82	4	81	5	76	2
Benflurasate	85	3	83	1	85	1	83	4	79	4
Benoxacor	74	6	78	2	84	1	80	7	75	7
beta-Endosulfan	76	12	81	2	90	3	90	7	81	6
beta-Lindane	95	8	84	1	85	3	82	4	80	2
Bifenthrin	87	2	84	1	86	1	89	3	88	2
Bromobutide	84	10	80	2	86	2	83	3	78	5
Bromobutide met.	88	4	81	2	87	2	86	4	86	2
Bromophos ethyl	81	4	82	1	87	1	86	2	84	2
Bromophos methyl	66	14	79	2	90	2	85	3	87	5
Bromopropylate	84	2	81	4	87	1	88	3	85	3
Bupirimate	82	1	80	2	85	1	85	6	77	6
Buprofezin	85	1	84	1	87	1	87	2	85	3
Butachlor	66	14	81	3	93	1	90	4	92	4
Butamifos	83	3	83	2	88	1	85	5	79	3
Cadusafos	85	6	84	2	86	3	83	5	80	4
Cafentrazole ethyl	71	6	82	1	93	1	88	2	87	6
Carbophenothion	80	3	83	3	87	2	87	2	88	4
Chlordane-*cis*	94	9	83	2	84	3	85	4	80	2
Chlordane-*trans*	95	8	83	3	85	3	85	6	78	2
Chlorfenson	81	3	84	2	92	1	86	2	89	4
Chlorfenvinphos	72	7	79	2	89	2	86	4	84	8
Chloroneb	85	8	77	3	79	2	75	6	82	3
Chlorpropham	82	3	81	1	84	1	82	3	84	4
Chlorpyrifos	80	3	80	1	86	2	85	4	82	3
Chlorpyrifos methyl	75	13	80	3	87	2	84	5	81	5
Chlorthal dimethyl	81	4	82	2	87	1	85	4	79	5
Cinmethylin	87	3	82	1	85	2	85	4	86	1
Clomazole	85	3	82	1	83	1	80	5	76	5
Clomeprop	87	2	86	1	90	1	86	3	89	4

Cyanophos	68	11	77	4	85	3	79	8	74	9
Cyfluthrin	79	7	85	3	96	1	93	4	106	4
Cyhalofop-butyl	89	2	87	1	89	1	89	1	90	4
Cyhalothrin	81	9	87	1	97	3	93	5	102	1
Cypermethrin	82	8	86	2	96	3	97	6	106	4
delta-Lindane	101	18	87	3	85	6	77	6	67	3
Deltamethrin	69	9	84	2	103	4	95	17	129	2
Demeton-S-methyl	59	15	67	8	73	8	65	12	60	14
Diazinone	83	3	82	2	87	2	85	5	80	3
Dichlorfenthion	85	5	81	1	85	2	84	3	82	3
Dichlorvos	67	7	68	8	71	7	66	12	66	12
Diclobenil	84	12	78	4	77	7	71	18	81	3
Diclofop-methyl	85	3	83	1	89	2	87	2	89	3
Dieldrin	93	8	82	1	89	6	82	3	80	4
Difenoconazole	82	5	83	1	91	4	90	7	95	2
Dimepiperate	86	1	83	1	86	0.3	85	4	81	3
Dimethametryn	86	1	84	2	88	0.3	86	2	88	2
Diniconazole	83	2	83	1	87	4	88	4	84	3
Disulfoton	85	4	79	4	84	2	78	3	77	4
Dithopyr	87	5	84	1	86	1	86	3	83	3
Endosulfan sulfate	54	33	76	5	103	5	91	7	90	8
Endrin	95	9	85	2	86	3	85	7	75	2
EPN	72	3	81	7	93	0.3	89	7	91	5
EPTC	72	11	63	8	70	2	54	14	61	3
Esprocarb	86	3	83	1	86	1	85	2	85	1
Ethafluralin	99	13	84	2	82	5	79	4	71	3
Ethion	79	5	82	1	89	1	88	3	88	4
Ethoprophos	76	2	80	3	82	2	79	6	76	8
Etofenprox	92	2	89	2	90	1	92	1	97	1
Fenamiphos	81	4	80	4	89	2	87	4	80	10
Fenbuconazole	81	4	84	2	92	4	92	10	92	3
Fenchlorfos	70	7	80	4	88	1	85	4	83	5
Fenclorim	78	2	79	2	85	1	81	3	82	2
Fenpropimorph	85	3	84	1	89	1	87	2	84	1
Fenoxaprop-ethyl	86	4	85	2	91	1	87	3	94	3
Fenpropathrin	84	2	81	4	89	1	89	2	87	3
Fenthion	73	7	81	2	88	1	84	5	83	5
Fenvalerate	80	9	86	1	97	3	95	6	108	2
Fipronil	80	7	82	2	92	3	88	4	80	4
Flusilazole	83	3	85	2	88	2	87	4	82	3
Flutolanil	85	2	84	1	89	1	87	2	85	3
Fonophos	88	6	82	1	84	1	81	3	77	2
Furametpyr	83	2	83	1	89	0.4	85	2	76	5
gamma-Lindane	76	7	81	1	89	1	85	6	81	5
HCB	98	10	79	2	79	6	73	5	74	2
Heptachlor	110	27	88	4	80	11	73	8	62	5
Heptachlor epoxide	102	13	84	1	86	6	82	7	74	1
Hexaconazole	84	2	83	2	91	4	84	4	83	2
Hydroxy Furametpyr	82	5	81	2	80	2	77	4	66	9

Imazalil	79	1	79	1	83	4	79	3	75	5
Iprobenfos	86	3	82	2	87	1	85	6	77	6
Iprodione	34	93	76	10	70	6	84	5	93	9
Isazophos	82	4	79	2	86	2	84	6	77	5
Isofenfos	86	3	84	1	87	1	86	3	80	3
Isoprothiolane	83	2	83	1	85	1	84	5	78	5
Isoxathion	70	6	74	1	84	1	82	4	86	6
Kresoxim-methyl	85	2	85	1	88	1	86	4	79	5
Malathion	67	13	81	3	91	2	86	6	82	6
Mefenpyr diethyl	83	2	84	2	89	1	88	4	83	5
Mepronil	85	2	86	2	90	1	89	2	91	2
Metalachlor	77	7	81	2	88	2	85	7	74	6
Metalaxyl	81	3	79	4	81	3	76	9	57	8
Methacrifos	81	6	77	3	81	2	76	6	75	6
Methoxychlor	79	2	81	1	86	1	87	2	86	5
Metominostrobin	85	2	82	2	86	3	84	5	75	5
Mirex	84	3	80	1	83	2	87	4	82	3
Molinate	79	8	77	2	77	2	74	5	81	1
Oryzastrobin	87	2	85	2	90	2	88	4	80	5
Oryzastrobin 5 Z isomer	87	2	85	2	89	1	88	4	79	5
Oxadiazon	86	2	85	1	88	1	87	3	87	3
Oxadixyl	64	5	70	4	80	5	71	7	58	11
Oxyfluorfen	79	5	83	4	86	4	81	5	82	3
p,p'-DDD	83	1	83	1	87	1	87	3	86	2
p,p'-DDE	86	2	82	1	84	1	83	2	84	1
p,p'-DDT	75	2	80	1	86	1	84	2	86	4
Paclobutazole	83	3	84	2	89	3	86	4	82	1
Parathion methyl	62	15	77	4	87	4	83	3	79	8
Parathion-ethyl	78	3	79	1	85	1	83	4	79	5
Penconazole	83	2	85	1	90	2	88	3	88	1
Pendimethalin	84	2	83	1	86	2	84	3	79	2
Permethrin-cis	87	3	85	2	87	3	88	2	91	3
Permethrin-trans	88	2	84	3	87	4	90	2	91	3
Phethoate	73	11	81	2	91	1	88	5	85	5
Phorate	84	6	78	4	81	3	79	6	73	3
Picolinafen	86	2	86	1	89	1	89	1	91	2
Piperonyl butoxide	90	1	85	2	88	1	89	2	93	3
Piperophos	79	4	86	2	95	2	92	3	94	4
Pirimicarb	84	3	81	1	84	3	78	7	70	7
Pirimiphos ethyl	84	4	82	1	86	2	86	3	82	3
Pirimiphos methyl	77	5	81	2	88	1	85	4	81	4
Pretilachlor	64	15	81	3	97	1	90	2	96	5
Prochloraz	79	3	74	2	79	7	83	5	75	15
Procymidone	86	1	84	1	88	1	86	2	86	1
Profenofos	60	13	78	4	95	6	87	5	105	6
Prometryn	84	1	84	0.4	87	2	87	2	86	2
Propachlor	73	8	78	4	85	2	79	8	70	6
Propetamphos	83	4	82	1	85	2	85	5	79	4
Propham	82	4	80	0	81	1	78	3	82	4

Propiconazole-*trans*	85	4	80	5	91	2	87	5	91	3
Prothiophos	81	3	83	0.5	87	1	86	2	84	2
Pyrafulfen-ethyl	78	25	82	1	87	2	88	2	83	4
Pyributicarb	87	1	84	1	88	1	88	3	87	3
Pyrifenox	84	2	82	1	86	2	84	2	81	5
Pyriproxyfen	87	2	86	2	87	3	87	1	91	3
Pyroquilon	82	1	84	1	87	2	82	3	85	2
Quinalphos	78	3	82	1	87	1	85	4	81	4
Resmethrin	84	2	79	1	79	2	79	2	80	4
Silafluofen	90	3	87	2	88	2	93	1	95	1
Simazine	77	3	76	3	81	2	76	7	74	11
Simetryn	83	1	84	1	85	2	84	2	86	2
Simiconazole	86	1	83	1	85	2	84	5	73	5
Sulprofos	84	3	83	4	88	0.5	86	2	86	2
Tebuconazole	84	3	84	1	89	2	88	4	86	3
Tecnazene	97	12	78	3	81	5	74	5	73	1
Terbufos	88	7	81	2	84	2	83	3	80	3
Terbutryn	84	3	81	1	84	3	84	3	83	3
Tetradifon	61	7	81	2	95	1	89	3	94	6
Thiazopyr	84	5	84	1	88	3	83	4	80	5
Thiobencarb	84	2	84	0.4	87	1	85	2	87	2
Thiometon	80	5	78	2	82	1	80	5	78	5
Tolclofos methyl	79	3	80	3	87	2	81	7	79	5
Triadimefon	85	1	83	1	87	1	83	4	79	4
Triadimenol	83	2	82	1	86	2	85	3	79	4
Triallate	88	6	80	1	84	2	83	4	81	2
Triazophos	70	7	78	4	92	3	85	6	93	9
Tribufos	81	3	84	1	88	2	88	2	86	4
Trifloxystrobin	85	2	83	2	89	2	90	5	85	4
Trifluralin	98	12	84	1	83	5	81	5	73	2
Triticonazole	81	4	81	3	87	3	84	5	79	5
Uniconazole	84	2	83	1	88	1	87	4	80	3
Vinclozolin	84	3	82	1	87	2	86	4	81	4

Table C-2 Average %recoveries (Re) and %RSDs (n=5) of 170 pesticides obtained by traditional GC-MS/MS analyses of spiked onion at 0.1 mg kg^{-1} based on **different types of d-SPE sorbent**

Analyte	d-SPE sorbent															
	PSA		PSA + AL-N		PSA +C_{18}		PSA + GCB		PSA + NH_2		PSA+Al-N + GCB		PSA + C_{18} + GCB		PSA + NH_2 + GCB	
	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD	% Re	% RSD
Alachlor	76	10	77	2	70	10	73	7	76	3	84	1	70	11	75	2
Aldrin	81	3	94	4	71	14	91	5	79	16	89	4	75	7	96	13
alpha-Endosulfan	78	6	85	3	73	25	76	7	82	7	80	2	70	10	81	7
alpha-Lindane	78	4	91	3	78	3	88	8	74	13	91	2	80	10	97	13
Ametryn	77	4	80	2	77	9	77	5	83	2	84	1	73	2	80	2
Atazine	74	14	78	4	76	11	74	6	80	3	81	1	69	10	77	4
Azaconazole	76	6	77	2	79	6	78	9	82	3	85	3	74	3	80	1
Azoxystrobin	83	9	80	2	83	15	78	5	92	9	98	6	78	8	85	5
Benalaxyl	79	8	80	2	77	11	76	6	83	1	86	2	72	8	80	2
Benfluralin	76	4	82	1	75	6	83	4	77	5	86	1	73	6	86	7
Benflurasate	79	6	81	2	79	3	77	4	82	2	83	1	74	4	81	2
Benoxacor	75	10	76	2	70	10	73	8	74	4	82	2	68	11	74	2
beta-Endosulfan	79	10	72	3	71	10	74	8	79	3	90	3	70	8	79	2
beta-Lindane	78	3	91	2	77	3	78	7	80	2	84	1	75	4	85	5
Bifenthrin	78	4	79	1	68	6	76	3	84	3	88	2	66	5	80	2

Bromobutide	74	6	81	2	74	7	76	6	81	1	82	2	72	6	81	4
Bromobutide met.	80	3	87	2	79	2	79	6	84	2	81	2	73	3	82	2
Bromophos ethyl	76	8	77	2	68	5	73	5	80	2	82	1	64	6	75	1
Bromophos methyl	72	10	71	3	68	6	70	7	74	12	82	2	67	9	69	7
Bromopropylate	79	6	78	2	74	6	76	4	85	2	88	3	72	6	82	2
Bupirimate	80	9	79	2	77	23	75	6	83	3	87	2	73	7	79	2
Buprofezin	79	5	80	1	73	5	78	5	84	2	85	2	71	4	79	1
Butachlor	81	7	73	1	68	12	73	5	80	8	92	2	70	8	76	7
Butamifos	77	6	77	2	73	24	74	5	80	2	84	3	71	7	79	3
Cadusafos	75	7	79	2	73	8	79	5	79	1	86	3	73	6	84	5
Cafentrazole ethyl	84	8	75	2	73	5	76	4	86	4	104	2	78	7	87	5
Carbophenothion	76	5	76	2	71	6	76	4	82	3	86	3	72	6	77	3
Chlordane-*cis*	74	5	82	1	69	8	77	5	80	4	82	1	68	6	84	5
Chlordane-*trans*	75	5	85	3	69	9	76	5	78	4	83	3	67	7	81	4
Chlorfenson	80	5	78	3	77	3	77	3	84	4	87	1	77	3	82	3
Chlorfenvinphos	74	12	72	3	74	11	73	7	78	9	89	2	71	11	78	5
Chloroneb	79	3	83	3	82	6	85	4	79	4	81	0.4	73	3	87	4
Chlorpropham	77	4	79	4	75	4	76	3	80	3	82	3	73	5	80	2
Chlorpyrifos	76	7	76	1	71	5	74	5	80	3	82	0.5	67	7	77	2
Chlorpyrifos methyl	75	10	74	2	69	8	70	6	75	8	80	2	68	9	73	3
Chlorthal dimethyl	77	8	77	1	74	24	76	5	79	0.5	82	1	71	5	78	2
Cinmethylin	76	3	78	1	73	4	77	6	83	2	82	3	69	3	80	3
Clomazole	77	7	81	2	76	7	76	4	82	2	82	1	72	4	80	2
Clomeprop	80	4	79	1	81	3	69	4	85	4	83	3	65	5	68	3

Cyanophos	67	15	72	5	70	8	68	8	70	8	80	5	69	11	71	6
Cyfluthrin I	87	8	74	2	70	4	74	4	88	7	112	4	78	7	85	5
Cyfluthrin II	86	5	73	1	70	6	76	1	89	3	110	4	77	1	86	1
Cyhalofop-butyl	79	6	82	4	80	4	79	2	89	9	96	3	78	3	83	9
Cyhalothrin	88	7	74	2	71	5	78	2	95	9	116	4	75	6	90	5
Cypermethrin I	85	7	74	2	68	18	76	6	91	16	106	4	76	13	86	13
Cypermethrin II	83	15	75	7	70	9	76	10	91	11	105	5	77	21	85	9
delta-Lindane	78	20	89	9	79	15	88	12	79	10	88	6	80	15	94	8
Deltamethrin I	85	7	73	3	63	10	75	4	89	1	92	2	74	7	83	3
Deltamethrin II	88	5	65	1	64	25	75	4	91	1	106	1	75	5	84	2
Demeton-S-methyl	52	16	70	9	59	10	60	11	54	8	73	7	65	17	63	9
Diazinone	77	8	78	8	74	15	77	10	80	9	81	3	72	13	75	8
Dichlorfenthion	77	5	79	2	73	1	77	2	80	3	82	2	69	1	80	2
Dichlorvos	61	6	72	2	66	13	62	7	65	6	74	3	67	9	70	6
Diclobenil	88	5	90	3	90	15	95	13	86	9	94	7	83	1	99	5
Diclofop-methyl	78	7	79	2	77	7	77	4	85	1	89	1	75	6	81	2
Dieldrin	76	4	84	1	72	3	78	5	79	2	82	2	68	2	77	1
Difenoconazole	81	7	79	3	78	22	71	10	91	1	100	3	76	4	84	2
Dimepiperate	77	5	78	2	74	3	76	3	82	2	82	1	71	5	78	2
Dimethametryn	79	4	79	1	81	8	77	4	84	2	86	1	75	6	81	2
Diniconazole	77	11	78	4	79	25	75	9	85	26	85	7	69	13	79	19
Disulfoton	76	6	79	2	73	13	79	7	76	6	81	3	71	9	81	6
Dithopyr	78	12	81	1	77	6	78	5	82	7	82	4	72	5	83	4
Endosulfan sulfate	86	6	63	2	67	7	76	9	74	9	88	4	76	7	77	5

Endrin	75	3	87	1	69	9	76	5	78	1	83	1	70	1	81	2
EPN	75	3	71	2	72	21	73	6	74	8	92	1	75	8	76	9
EPTC	64	6	79	2	69	7	75	5	64	3	79	2	66	7	75	2
Esprocarb	78	12	80	2	75	10	77	6	80	1	83	4	72	7	80	4
Ethafluralin	76	2	82	1	73	7	83	3	77	5	93	4	75	1	89	1
Ethion	77	8	76	3	71	8	74	6	82	3	88	4	72	9	78	2
Ethoprophos	76	6	78	4	71	18	74	14	79	9	82	4	72	4	79	3
Etofenprox	82	9	82	2	71	7	78	6	90	7	96	3	72	9	81	3
Fenamiphos	75	5	77	1	78	14	74	2	85	1	97	2	74	2	78	2
Fenbuconazole	80	5	80	2	81	4	77	6	87	1	87	1	77	3	82	1
Fenchlorfos	72	5	72	3	68	8	71	2	74	6	80	3	67	1	72	3
Fenclorim	76	6	78	1	72	6	73	4	78	4	78	3	63	5	74	2
Fenoxaprop-ethyl	81	10	78	3	75	6	73	5	90	6	100	2	72	7	79	3
Fenpropathrin	79	8	78	2	73	10	75	5	85	6	90	4	74	10	80	3
Fenpropimorph	79	8	81	2	64	9	77	6	81	4	82	3	63	7	79	1
Fenthion	73	5	74	3	72	5	72	7	76	2	84	4	73	4	75	2
Fenvalerate I	89	5	75	1	67	3	77	7	95	3	103	2	76	2	87	1
Fenvalerate II	83	4	75	1	68	2	74	3	90	3	103	1	76	4	82	4
Fipronil	81	7	79	2	76	4	76	4	86	2	95	4	75	4	80	2
Flusilazole	79	8	78	2	78	10	76	7	85	4	87	3	74	10	82	3
Flutolanil	80	5	80	4	81	6	78	4	86	7	88	2	77	4	82	6
Fonophos	77	5	84	3	76	22	80	9	81	21	83	4	73	15	83	4
Furametpyl	79	3	79	2	76	10	75	5	86	8	87	2	73	8	80	7
gamma-Lindane	73	6	76	3	68	3	70	12	72	3	84	3	70	5	72	1

HCB	78	10	84	5	69	11	67	6	80	7	70	6	54	11	63	9
Heptachlor	79	8	95	3	69	8	91	6	67	3	92	2	75	2	100	2
Heptachlor epoxide	76	10	89	3	74	9	80	6	79	2	83	2	72	10	86	2
Hexaconazole	79	20	79	3	77	18	76	30	83	13	92	13	73	19	78	6
Hydroxy Furametpyr	78	8	74	2	76	5	67	5	89	3	78	2	62	6	71	2
Imazalil	72	6	77	1	75	6	74	5	77	2	86	1	70	6	78	2
Iprobenfos	77	7	79	2	76	4	75	6	81	1	83	3	72	6	79	2
Iprodione	72	12	79	3	77	8	87	5	77	13	77	3	69	5	102	5
Isazophos	76	7	77	1	74	6	75	5	80	2	83	2	72	6	79	2
Isofenfos	77	12	80	4	76	11	77	8	82	12	84	3	72	12	81	7
Isoprothiolane	79	7	79	1	78	16	76	4	83	2	85	3	73	5	81	1
Isoxathion	72	4	72	1	68	3	70	5	77	3	88	3	67	1	72	1
Kresoxim-methyl	78	9	79	2	77	10	77	7	81	1	87	1	75	11	80	2
Malathion	70	15	70	6	70	11	69	10	72	6	87	3	72	13	72	5
Mefenpyr diethyl	79	9	78	3	77	6	78	5	87	3	89	3	73	8	81	5
Mepronil	80	9	81	3	81	5	78	4	87	5	90	3	78	4	82	2
Metalachlor	77	7	78	3	71	6	73	8	79	1	84	2	70	5	77	2
Metalaxyl	75	6	76	2	74	26	71	5	80	1	79	2	67	10	77	2
Methacrifos	71	2	75	1	73	5	71	2	75	3	80	1	71	3	77	4
Methoxychlor	76	8	76	2	73	7	74	6	81	2	84	4	72	6	77	2
Metominostrobin	78	8	80	2	79	7	76	7	83	3	86	4	75	6	80	2
Mirex	74	5	77	1	53	4	74	4	79	2	81	1	52	4	77	2
Molinate	75	13	81	5	77	17	78	8	79	6	80	4	71	17	80	4
Oryzastrobin	82	11	80	3	81	8	77	5	89	3	95	2	80	4	83	3

Oryzastrobin 5 Z	81	6	80	2	79	4	76	4	89	2	91	1	74	5	81	1
Oxadiazon	79	1	79	1	75	2	77	4	82	2	87	1	74	1	82	2
Oxadixyl	77	9	74	2	73	4	71	5	81	6	89	2	67	4	81	2
Oxyfluorfen	76	6	75	3	75	4	74	10	81	3	84	2	72	4	76	3
p,p'-DDD	78	14	78	5	72	8	76	8	81	14	86	6	72	10	79	8
p,p'-DDE	78	9	79	3	68	7	78	6	82	3	82	2	67	8	81	2
p,p'-DDT	75	4	74	4	66	3	74	8	77	2	83	1	65	2	74	2
Paclobutazole	78	6	77	2	79	7	76	4	83	2	85	1	74	5	79	3
Parathion methyl	66	4	68	1	68	3	67	1	69	4	82	3	71	3	69	1
Parathion-ethyl	73	4	74	1	73	3	73	2	77	4	83	3	72	3	76	2
Penconazole	79	10	80	3	77	10	77	4	83	9	84	2	73	10	81	5
Pendimethalin	76	5	76	3	72	18	73	2	81	4	82	2	67	7	77	5
Permethrin-*cis*	79	3	75	1	71	2	76	5	87	4	90	4	71	3	78	1
Permethrin-*trans*	80	4	78	1	72	4	78	3	86	4	89	2	71	3	79	2
Phethoate	76	8	74	3	71	7	72	5	77	6	87	3	73	9	76	3
Phorate	74	9	79	3	73	6	79	6	79	1	84	2	71	7	81	2
Picolinafen	80	7	80	3	78	7	71	5	87	1	85	1	68	6	73	2
Piperonyl butoxide	79	8	85	1	77	8	78	6	86	2	89	2	76	8	82	2
Piperophos	82	9	78	1	76	10	76	6	86	11	97	3	76	6	83	12
Pirimicarb	78	15	79	6	77	18	75	8	81	6	80	7	72	13	79	7
Pirimiphos ethyl	77	3	78	2	72	9	76	6	82	1	82	1	70	2	79	1
Pirimiphos methyl	75	11	77	2	71	7	74	7	80	21	82	5	70	9	76	17
Pretilachlor	85	4	73	2	68	9	73	6	80	1	85	2	73	3	79	1
Prochloraz	75	11	74	3	72	9	70	8	85	6	84	4	69	14	79	4

Procymidone	79	9	80	1	78	5	78	5	83	1	84	1	76	5	79	3
Profenofos	72	3	68	2	71	5	72	2	72	2	90	0.4	71	1	74	2
Prometryn	78	6	79	1	77	6	76	5	83	1	82	1	74	6	80	2
Propachlor	67	6	73	1	66	16	67	4	71	4	79	3	67	4	68	2
Propetamphos	77	4	78	1	76	3	76	3	82	3	83	2	74	3	80	1
Propham	79	7	80	2	79	4	78	3	81	1	81	1	74	4	83	2
Propiconazole-*trans*	77	2	82	1	80	2	79	1	84	4	86	3	76	1	82	1
Prothiophos	76	4	77	3	68	5	74	5	81	3	86	3	64	2	77	2
Pyrafulfen-ethyl	78	9	79	2	78	9	77	6	88	4	93	2	77	8	83	3
Pyrazophos	78	4	75	1	75	8	67	2	84	4	97	3	69	3	75	2
Pyributicarb	79	2	79	1	75	6	77	3	85	5	88	5	73	3	81	2
Pyrifenox	77	18	78	5	76	8	75	10	82	3	87	1	72	8	79	3
Pyriproxyfen	79	1	81	3	76	3	77	4	87	4	93	2	74	2	81	3
Pyroquilon	80	7	81	3	81	7	78	8	82	2	82	2	74	8	80	3
Quinalphos	75	6	75	2	73	5	74	4	80	2	84	2	71	5	78	2
Resmethrin	75	5	73	3	68	2	73	10	80	4	88	4	72	2	80	2
Silafluofen	81	5	80	4	62	5	75	4	91	8	93	2	63	4	78	8
Simazine	72	5	69	1	76	4	74	3	80	2	80	1	68	5	75	4
Simetryn	78	5	79	2	79	2	79	6	84	2	85	3	74	3	79	1
Simiconazole	79	6	81	1	76	5	76	4	83	5	83	3	73	2	81	6
Sulprofos	78	8	78	1	71	7	75	4	81	3	88	3	69	6	78	3
Tebuconazole	79	3	78	1	79	1	76	3	87	1	88	2	74	1	80	1
Tecnazene	79	7	87	2	80	11	82	4	78	2	87	2	74	6	88	4
Terbufos	76	8	80	2	73	17	78	5	79	2	82	2	70	8	81	2

Terbutryn	77	5	77	5	77	8	74	11	81	4	82	5	73	3	79	4
Tetradifon	84	6	72	2	69	5	78	7	82	2	101	1	73	5	83	2
Thiazopyr	78	6	79	2	76	5	77	8	79	1	85	3	70	4	81	1
Thiobencarb	79	3	80	1	76	3	78	1	83	3	83	2	73	2	80	4
Thiometon	73	12	75	2	72	9	74	5	76	11	81	2	70	7	79	9
Tolclofos methyl	75	8	76	1	72	6	75	3	78	2	82	2	70	5	78	2
Triadimefon	79	6	81	1	78	12	77	4	83	3	84	3	75	6	79	2
Triadimenol	80	3	78	2	79	6	77	4	84	7	87	1	75	8	80	8
Triallate	78	8	82	2	72	21	79	7	79	3	83	5	69	5	82	1
Triazophos	75	6	72	3	75	7	74	9	77	2	95	3	75	5	78	1
Tribufos	80	4	77	2	69	5	76	4	83	1	87	1	69	4	79	3
Trifloxystrobin	79	10	80	2	76	10	76	7	85	3	90	1	76	11	80	2
Trifluralin	78	3	86	4	75	14	84	5	77	16	87	4	76	7	90	13
Triticonazole	79	6	78	3	79	25	76	7	87	7	89	2	73	10	81	7
Uniconazole	78	4	80	3	80	3	76	8	85	13	87	2	73	10	79	13
Vinclozolin	76	4	80	2	78	9	76	5	83	2	81	1	73	2	82	2

Table C-3 Average %recoveries (Re) and %RSDs (n=5) of 170 pesticides obtained by **traditional GC-MS/MS** analyses of spiked onion at different concentration levels (low = 0.01, middle = 0.05, and high = 0.10 mg kg^{-1}) for intra-day precision (n=5 each level) and intermediate precision (n=5 each level × 3 days)

Analyte	Intra-day precision (Repeatability), n=5																		Intermediate precision, n=15 (3 days)					
	Low						Middle						High						Low		Middle		High	
	Day 1		Day 2		Day 3		Day 1		Day 2		Day 3		Day 1		Day 2		Day 3							
	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_R$	%Re	$\%RSD_R$	%Re	$\%RSD_R$
Alachlor	84	4	84	3	82	3	93	2	81	3	82	2	96	3	82	3	80	4	83	3	86	7	86	9
Aldrin	98	4	85	9	80	5	97	3	81	9	86	2	81	3	84	5	96	7	88	11	88	9	87	9
alpha-Endosulfan	91	4	86	4	92	11	74	2	86	4	86	2	112	2	84	2	84	2	89	8	82	8	93	15
alpha-Lindane	109	7	85	7	83	15	75	5	89	12	89	3	74	6	89	5	91	7	93	16	85	11	85	11
Ametryn	92	1	91	1	89	1	76	1	92	4	91	3	106	1	85	2	97	4	90	2	86	9	96	9
Atazine	86	4	89	2	90	3	80	2	89	3	87	2	116	3	82	3	90	5	88	4	85	5	96	16
Azaconazole	95	5	93	4	87	4	74	1	96	6	95	4	105	3	86	3	97	5	92	6	88	12	96	9
Azoxystrobin	73	15	71	15	71	9	106	7	89	13	81	3	76	4	86	8	85	9	72	12	92	14	82	9
Benalaxyl	91	3	87	3	85	2	76	0.4	94	5	93	3	97	1	86	2	94	4	88	4	88	11	92	6
Benfluralin	94	1	87	1	86	4	89	1	86	5	87	2	91	2	86	4	97	4	89	5	87	3	91	6
Benflurasate	93	3	90	2	88	2	80	1	91	5	89	3	106	1	87	1	94	3	90	3	87	7	96	9
Benoxacor	83	2	79	4	77	5	99	3	79	5	81	2	111	3	81	4	88	3	80	5	86	11	93	15
beta-Endosulfan	92	7	83	11	86	14	84	2	96	2	88	3	87	2	88	2	85	5	87	11	89	6	87	3

beta-Lindane	96	1	87	1	86	1	71	1	88	3	89	1	110	2	88	1	97	3	90	5	83	10	99	10
Bifenthrin	92	2	91	2	89	2	80	1	95	3	96	4	84	2	88	2	82	3	91	2	90	9	85	4
Bromobutide	95	5	89	5	86	3	73	2	88	4	88	3	110	3	85	4	93	2	90	6	83	10	96	11
Bromobutide met.	97	5	92	5	90	3	79	2	89	4	90	2	96	1	84	1	97	2	93	5	86	6	92	7
Bromophos ethyl	82	2	80	2	78	2	92	3	86	3	85	1	94	2	82	3	84	4	80	3	88	5	87	7
Bromophos methyl	77	11	76	6	71	8	106	8	75	8	72	4	101	7	74	5	88	9	75	9	85	20	88	15
Bromopropylate	94	3	94	2	91	3	71	3	96	5	94	4	102	1	88	3	89	4	93	3	87	14	93	8
Bupirimate	86	4	86	2	82	5	82	1	94	7	93	3	103	1	83	2	85	5	85	4	90	7	90	11
Buprofezin	97	2	95	1	92	3	81	1	93	5	92	3	96	2	88	2	96	3	95	3	89	7	93	5
Butachlor	80	3	74	11	70	15	73	3	84	4	75	6	115	5	82	5	90	11	75	11	77	7	96	16
Butamifos	76	5	80	4	77	4	79	2	87	4	86	4	113	7	87	2	85	3	78	5	84	6	95	15
Cadusafos	94	3	89	2	87	2	77	1	88	3	88	1	96	1	83	3	83	2	90	4	84	7	87	8
Cafentrazole ethyl	79	9	79	11	74	13	96	15	90	3	81	4	105	3	100	12	96	7	77	11	89	11	100	9
Carbophenothion	81	5	85	4	83	4	80	8	87	4	82	3	98	3	81	6	89	7	83	4	83	6	89	10
Chlordane-*cis*	85	4	82	1	80	4	96	1	86	4	87	2	118	1	85	1	97	1	82	4	90	6	100	14
Chlordane-*trans*	85	4	86	1	85	4	96	1	85	3	85	2	118	1	86	2	98	2	86	3	89	6	101	13
Chlorfenson	86	4	82	3	77	5	85	3	92	5	87	3	108	2	85	2	99	4	81	6	88	5	97	11
Chlorfenvinphos	77	10	73	15	75	8	99	7	86	3	75	3	89	5	79	7	74	12	75	11	86	13	81	11
Chloroneb	110	4	86	4	85	10	77	1	95	4	94	1	98	3	90	3	92	2	94	14	89	10	93	5
Chlorpropham	92	3	88	2	87	3	73	2	92	5	90	1	88	1	86	2	96	2	89	4	85	11	90	5
Chlorpyrifos	94	5	89	5	88	4	78	1	87	3	86	2	95	2	84	2	82	3	90	5	84	6	87	7
Chlorpyrifos methyl	74	6	77	4	72	4	99	5	80	7	81	2	98	5	78	5	77	5	74	5	87	11	84	13
Chlorthal dimethyl	88	3	89	2	85	1	89	2	88	4	87	1	82	13	84	2	95	2	87	3	88	3	87	10
Cinmethylin	92	2	90	4	94	2	72	2	86	4	86	3	115	0.3	85	2	94	1	92	3	82	9	98	14

Clomazole	95	2	89	1	87	1	78	1	89	3	89	2	99	2	86	1	92	2	90	4	85	7	93	6
Clomeprop	86	4	89	4	83	5	85	2	94	5	92	6	110	7	89	4	91	7	86	5	90	6	97	12
Cyanophos	76	8	70	4	70	10	88	7	74	7	72	3	89	5	74	6	74	7	72	8	78	11	79	11
Cyfluthrin I	104	5	96	6	92	13	87	9	90	3	92	5	78	2	98	5	78	3	97	9	90	6	85	12
Cyfluthrin II	91	4	91	3	86	4	82	2	93	6	92	6	104	11	89	3	103	6	89	4	89	8	98	10
Cyhalofop-butyl	89	2	79	6	73	3	107	9	93	5	89	5	105	5	88	8	76	2	80	9	96	10	90	15
Cyhalothrin	80	13	71	15	72	18	92	15	89	5	82	3	97	2	97	6	76	4	74	15	87	10	90	12
Cypermethrin I	88	3	83	2	79	4	84	2	83	3	81	2	102	2	86	4	90	3	83	5	83	3	93	8
Cypermethrin II	70	5	71	12	71	12	101	8	87	10	73	9	93	6	101	11	78	12	70	10	87	16	91	14
delta-Lindane	92	3	84	3	80	5	86	3	84	6	84	2	109	6	81	3	79	3	86	7	85	4	90	17
Deltamethrin I	89	5	87	4	83	2	74	2	86	7	85	2	114	2	84	1	84	2	86	5	81	8	94	15
Deltamethrin II	90	3	85	3	83	3	82	1	87	4	86	1	110	5	85	2	81	2	86	5	85	4	92	15
Demeton-S-methyl	80	9	74	10	74	13	73	1	80	14	74	5	95	8	74	6	75	5	76	11	75	9	81	14
Diazinone	111	13	104	6	103	12	98	3	110	5	109	1	107	6	106	7	90	4	106	11	106	6	101	10
Dichlorfenthion	88	3	87	2	83	4	83	2	93	4	91	3	115	6	87	2	97	5	86	4	89	6	100	13
Dichlorvos	92	2	84	4	82	2	88	2	86	3	88	3	97	13	86	1	100	2	86	6	87	3	94	10
Diclobenil	94	8	92	9	81	8	78	3	97	6	96	5	110	3	85	5	99	8	89	10	90	11	98	12
Diclofop-methyl	93	3	90	3	87	2	78	1	90	5	89	3	97	2	88	1	97	3	90	4	86	7	94	5
Dieldrin	93	4	93	3	90	2	81	1	94	4	93	3	102	2	87	2	97	3	92	3	90	7	95	7
Difenoconazole	91	3	94	2	90	2	83	2	94	6	94	4	112	5	88	3	97	5	92	3	90	7	99	11
Dimepiperate	95	1	89	1	88	2	82	1	89	4	88	1	106	1	85	1	82	2	91	4	86	4	91	12
Dimethametryn	90	5	88	5	87	3	88	1	89	5	89	3	93	2	86	2	93	1	88	4	89	3	91	4
Diniconazole	71	10	73	4	71	7	98	8	88	5	75	5	100	10	81	8	75	5	72	7	87	12	85	15
Disulfoton	87	2	83	1	84	4	80	2	88	5	88	2	108	7	85	2	99	2	85	3	85	6	97	11

Dithopyr	84	5	79	4	73	7	79	5	90	6	83	2	91	3	84	9	81	10	79	8	84	7	85	9
Endosulfan sulfate	89	3	86	3	83	3	81	2	83	5	84	2	104	2	85	5	92	2	86	4	83	3	94	9
Endrin	92	1	88	1	87	1	81	1	91	5	90	2	97	1	86	2	97	2	89	3	87	6	93	6
EPN	97	5	83	5	85	4	99	2	86	7	89	3	79	7	85	4	97	7	88	8	91	8	87	11
EPTC	83	3	83	2	80	5	80	5	89	2	88	2	91	3	86	3	82	5	82	4	86	6	86	6
Esprocarb	93	0	88	0	87	2	73	1	88	4	87	1	95	2	83	2	83	2	90	3	83	9	87	7
Ethafluralin	103	4	102	4	98	7	81	1	95	4	97	5	107	5	91	3	103	6	101	5	91	9	100	8
Ethion	77	12	79	11	70	14	84	5	87	6	80	3	100	2	76	7	79	8	75	12	84	6	85	14
Ethoprophos	105	15	103	14	88	8	80	3	98	4	95	4	103	3	88	5	98	9	99	15	91	10	96	9
Etofenprox	74	7	73	3	70	10	89	6	76	9	76	3	87	4	75	5	77	5	72	7	80	10	80	8
Fenamiphos	89	2	83	2	81	2	80	3	84	5	83	2	117	1	82	3	92	3	85	4	82	4	97	16
Fenbuconazole	95	3	92	3	89	1	94	5	90	7	90	3	96	1	86	1	98	2	92	4	91	5	93	6
Fenchlorfos	83	5	84	6	79	10	77	3	91	3	85	5	87	2	87	3	98	7	82	7	84	8	91	7
Fenclorim	88	3	87	3	86	3	84	1	89	3	90	4	78	2	86	3	77	6	87	3	88	4	80	6
Fenpropimorph	81	3	78	2	74	6	93	6	81	5	78	3	97	4	77	5	80	6	78	5	84	9	85	12
Fenoxaprop-ethyl	75	5	77	9	71	14	101	12	83	3	75	3	97	1	94	7	77	9	74	10	86	15	89	12
Fenpropathrin	88	5	95	7	91	7	89	2	89	3	88	3	111	6	100	5	88	7	91	7	89	3	100	11
Fenthion	93	3	93	2	89	3	79	1	95	5	93	4	109	2	87	3	95	5	92	3	89	9	97	10
Fenvalerate I	97	3	95	3	91	3	80	1	98	6	96	4	110	7	90	3	100	5	94	4	91	10	100	10
Fenvalerate II	95	1	88	1	87	2	79	1	86	4	86	1	87	1	84	2	83	2	90	4	84	5	84	3
Fipronil	94	2	90	2	87	4	78	1	95	6	95	5	100	2	89	3	97	6	90	4	89	10	95	6
Flusilazole	105	7	84	5	86	10	73	3	86	11	89	2	77	9	88	6	94	9	92	13	82	11	86	11
Flutolanil	102	4	85	4	83	9	97	1	89	5	90	2	78	8	92	6	81	5	90	11	92	5	84	9
Fonophos	86	6	71	4	70	7	83	6	85	17	87	4	99	8	79	7	85	15	76	12	86	10	88	14

Furametpyr	89	2	81	3	80	4	79	1	86	2	87	2	110	2	87	3	99	6	83	6	84	5	99	10
gamma-Lindane	96	7	95	5	87	5	84	2	96	5	93	4	102	2	86	2	98	5	92	7	91	7	95	8
HCB	90	9	86	7	77	6	74	4	89	9	86	5	84	6	85	6	88	12	85	10	83	10	86	8
Heptachlor	88	5	89	5	84	4	71	2	88	5	85	2	94	2	85	3	86	5	87	5	81	10	88	6
Heptachlor epoxide	90	4	91	3	86	3	70	1	89	3	88	1	84	1	86	2	84	4	89	4	83	11	85	3
Hexaconazole	96	13	91	10	85	6	75	4	99	7	98	4	76	5	92	6	79	8	91	11	91	14	82	10
Hydroxy Furametpyr	94	3	84	3	83	3	77	1	88	4	87	1	83	2	85	2	80	2	87	7	84	6	83	3
Imazalil	90	7	89	7	86	6	75	1	92	4	91	3	86	1	87	2	85	2	88	7	86	10	86	2
Iprobenfos	91	2	90	2	88	3	82	2	93	5	91	3	99	2	86	2	93	3	89	3	89	6	93	6
Iprodione	74	10	73	10	70	12	72	5	88	9	77	3	114	5	99	5	79	7	72	10	79	11	98	16
Isazophos	89	2	88	1	86	3	76	2	93	4	90	7	82	1	87	2	95	4	88	3	86	10	88	7
Isofenfos	79	7	78	6	74	7	102	6	80	5	79	2	84	7	81	4	74	10	77	7	87	13	80	8
Isoprothiolane	89	5	86	5	83	3	84	2	96	5	93	4	103	1	86	3	87	5	86	5	91	7	92	9
Isoxathion	93	3	93	2	90	3	88	1	98	5	96	5	103	2	88	3	100	6	92	3	94	7	97	8
Kresoxim-methyl	89	4	83	4	81	4	99	1	87	3	86	1	104	1	85	3	92	4	84	6	91	7	94	9
Malathion	100	13	96	6	92	15	74	5	91	4	91	2	79	2	85	2	88	3	96	12	85	10	84	5
Mefenpyr diethyl	90	4	74	7	70	7	73	2	84	8	84	2	88	4	79	4	73	4	78	13	80	8	80	9
Mepronil	77	6	80	6	73	11	72	2	93	9	88	3	88	2	82	5	89	11	77	8	84	12	86	7
Metalachlor	92	2	91	1	88	2	73	1	95	6	94	4	104	3	88	3	95	3	90	2	87	13	96	8
Metalaxyl	82	2	81	1	79	2	76	1	87	4	86	2	99	5	83	2	95	3	81	2	83	6	92	8
Methacrifos	104	6	83	10	78	13	82	6	89	8	87	2	92	5	85	3	83	2	89	16	86	7	87	5
Methoxychlor	85	7	91	2	85	6	72	1	92	7	93	7	113	4	93	4	103	5	87	6	86	13	103	9
Metominostrobin	87	3	90	5	83	6	74	1	92	8	92	7	113	4	92	4	103	6	87	6	86	12	103	10
Mirex	92	2	91	2	89	2	73	1	92	4	92	3	100	1	88	1	95	3	91	2	86	11	94	6

Molinate	71	7	74	6	72	8	74	6	75	6	78	10	83	5	102	10	77	3	72	6	76	7	87	14
Oryzastrobin	80	5	83	4	80	8	78	3	87	6	85	3	77	7	88	4	96	6	81	6	83	6	87	11
Oryzastrobin 5 Z iso.	87	3	84	2	82	3	84	1	92	5	90	3	94	1	87	2	88	4	84	3	89	5	89	4
Oxadiazon	86	2	86	1	84	2	86	1	90	5	89	3	105	2	85	1	87	2	85	2	88	4	92	11
Oxadixyl	73	3	78	4	74	9	75	4	93	7	88	2	81	3	80	5	77	11	75	6	85	10	79	7
Oxyfluorfen	96	7	96	6	88	4	79	1	96	6	94	4	95	3	89	2	98	5	93	7	89	10	94	5
p,p'-DDD	77	6	79	3	74	4	82	3	82	3	80	2	90	3	88	3	79	5	77	5	81	3	86	6
p,p'-DDE	75	6	72	6	71	6	100	9	74	6	74	8	101	8	73	8	76	5	73	6	83	17	83	17
p,p'-DDT	97	7	97	7	92	1	82	2	95	6	93	3	110	2	87	2	96	4	95	6	90	8	98	10
Paclobutazole	78	5	83	2	80	4	80	1	85	5	84	2	98	2	86	1	95	3	80	4	83	4	93	6
Parathion methyl	93	1	88	1	87	2	74	4	95	4	95	4	93	2	90	3	82	4	89	3	88	12	88	6
Parathion-ethyl	97	3	87	3	84	5	74	5	92	4	93	5	95	2	90	3	82	4	90	7	87	11	89	7
Penconazole	77	6	81	4	75	7	98	6	81	4	79	2	94	4	84	4	81	9	78	6	86	11	86	9
Pendimethalin	94	6	90	6	90	5	80	2	86	6	87	1	91	3	86	5	78	3	91	5	84	5	85	7
Permethrin-cis	88	4	87	3	85	4	97	2	95	5	94	4	113	6	87	3	100	6	87	4	95	4	100	12
Permethrin-trans	93	2	96	1	94	2	78	1	94	3	96	4	117	2	88	2	99	3	94	2	89	10	101	12
Phethoate	72	10	79	10	72	10	90	8	87	3	79	3	91	3	86	7	83	9	75	11	86	8	87	7
Phorate	91	2	88	3	86	2	76	2	91	4	90	3	108	2	85	1	90	2	88	3	86	9	94	11
Picolinafen	86	2	87	2	85	2	84	2	87	4	87	3	97	1	86	2	84	2	86	2	86	3	89	7
Piperonyl butoxide	85	3	82	2	80	3	94	3	85	3	84	1	104	4	81	6	84	3	83	4	87	6	90	12
Piperophos	82	7	79	15	71	20	87	8	90	1	79	7	109	4	86	5	87	13	77	15	85	8	94	13
Pirimicarb	74	16	73	4	70	11	78	8	85	14	76	2	86	8	76	7	70	12	72	11	80	10	77	13
Pirimiphos ethyl	94	3	92	2	88	3	87	1	94	5	91	3	105	2	87	2	95	4	91	4	91	4	96	9
Pirimiphos methyl	76	7	74	5	73	10	93	15	76	4	74	11	90	10	82	8	77	7	74	7	81	15	83	10

Pretilachlor	93	5	95	3	89	4	76	2	93	5	91	3	114	1	87	2	95	2	92	5	87	10	99	12
Prochloraz	81	7	77	11	77	13	97	4	75	8	78	3	95	6	73	8	81	5	78	10	83	13	83	13
Procymidone	94	3	89	1	86	3	75	1	89	4	88	2	107	1	86	2	84	2	90	4	84	8	92	12
Profenofos	93	3	84	5	82	4	77	1	91	3	89	1	92	1	86	2	92	1	87	7	86	7	90	4
Prometryn	99	11	99	7	97	5	80	0.4	95	5	93	4	98	3	86	3	97	5	99	7	89	9	94	7
Propachlor	81	8	82	3	79	7	80	3	88	4	87	2	92	2	83	2	84	4	81	6	85	5	87	6
Propetamphos	90	6	98	5	91	7	95	3	94	3	96	4	89	3	89	3	96	5	93	7	95	3	91	5
Propham	88	1	88	1	86	3	75	1	94	5	94	4	93	2	88	2	97	4	87	2	87	11	93	5
Propiconazole-*trans*	91	4	86	3	81	6	83	1	92	5	90	3	107	3	86	2	99	4	86	6	88	6	97	9
Prothiophos	90	1	91	2	88	5	86	2	93	5	91	5	101	3	95	14	103	5	89	3	90	5	99	9
Pyrafulfen-ethyl	97	6	94	5	88	4	82	1	91	4	91	2	92	2	83	1	95	4	93	7	88	6	90	6
Pyrazophos	88	3	85	1	80	5	83	5	87	3	85	2	102	4	82	4	79	5	84	5	85	4	88	13
Pyributicarb	82	4	82	3	79	1	82	1	93	4	94	5	115	3	97	3	95	5	81	3	90	7	102	10
Pyrifenox	88	3	88	2	83	4	86	1	94	4	95	5	102	2	88	3	99	5	86	4	92	5	97	7
Pyriproxyfen	81	8	78	3	72	9	76	3	88	4	82	2	86	4	79	4	87	7	77	9	82	7	84	7
Pyroquilon	92	3	91	3	87	2	78	1	94	5	92	3	104	1	85	2	96	5	90	3	88	9	95	9
Quinalphos	92	4	90	2	87	3	74	2	93	5	91	3	96	2	87	1	95	2	90	3	86	11	92	5
Resmethrin	81	2	79	2	75	4	88	4	90	3	86	2	98	3	83	3	82	4	79	4	88	3	87	9
Silafluofen	93	6	91	6	85	2	83	1	95	6	95	4	102	9	87	3	99	6	90	6	91	8	96	9
Simazine	104	7	85	6	88	9	77	4	94	6	91	2	104	4	92	5	89	4	92	12	87	10	95	8
Simetryn	92	2	85	2	83	2	82	1	85	4	86	1	92	1	84	2	81	2	87	5	84	3	86	6
Simiconazole	90	3	90	2	88	3	86	1	93	5	91	3	91	1	86	1	98	4	89	3	90	5	92	6
Sulprofos	80	8	72	10	70	12	103	10	79	4	70	4	113	5	102	10	95	8	74	11	84	18	103	10
Tebuconazole	88	4	91	3	86	5	84	2	88	2	87	2	105	1	85	2	101	3	88	5	86	3	97	9

Tecnazene	96	3	91	3	88	2	83	1	92	4	91	3	84	2	87	1	96	1	92	5	89	6	89	6
Terbufos	101	4	76	5	75	7	73	2	87	7	86	2	86	3	78	4	75	4	84	16	82	9	80	7
Terbutryn	87	2	82	1	80	3	87	3	83	5	83	2	99	3	80	3	78	3	83	4	84	4	86	12
Tetradifon	94	2	91	2	89	3	76	1	92	5	90	3	101	2	87	1	93	2	91	3	86	9	94	7
Thiazopyr	95	3	93	3	89	3	80	2	94	5	93	4	99	2	89	3	97	4	93	4	89	8	95	5
Thiobencarb	90	2	85	2	84	3	86	1	89	5	87	2	90	1	85	1	84	1	86	4	87	3	86	3
Thiometon	70	11	72	8	71	10	97	15	79	9	73	1	88	8	73	12	70	15	71	9	83	16	77	15
Tolclofos methyl	87	2	85	2	83	4	71	1	93	5	91	3	110	2	87	2	86	4	85	3	85	12	94	12
Triadimefon	89	3	91	3	87	6	71	2	94	6	92	3	111	2	88	2	95	3	89	4	86	13	98	11
Triadimenol	99	3	89	2	89	5	94	1	87	5	88	1	108	1	88	5	86	5	92	6	90	5	94	12
Triallate	87	9	89	6	80	8	72	2	91	6	88	5	117	2	85	5	97	6	85	8	84	11	100	14
Triazophos	94	5	94	3	88	6	77	1	98	6	95	5	114	5	90	3	99	6	92	6	90	12	101	11
Tribufos	90	3	85	5	84	2	72	2	89	5	89	2	111	2	84	2	98	2	86	5	84	10	98	12
Trifloxystrobin	84	4	84	3	82	3	93	2	81	3	82	2	96	3	82	3	80	4	83	3	86	7	86	9
Trifluralin	98	4	85	9	80	5	97	3	81	9	86	2	81	3	84	5	96	7	88	11	88	9	87	9
Triticonazole	91	4	86	4	92	11	74	2	86	4	86	2	112	2	84	2	84	2	89	8	82	8	93	15
Uniconazole	109	7	85	7	83	15	75	5	89	12	89	3	74	6	89	5	91	7	93	16	85	11	85	11
Vinclozolin	92	1	91	1	89	1	76	1	92	4	91	3	106	1	85	2	97	4	90	2	86	9	96	9

APPENDIX D

Table D-1 Average %recoveries (Re) and %RSDs (n=5) of 170 pesticides obtained by **LP-GC-MS/MS** analyses of spiked onion at different concentration levels (low = 0.01, middle = 0.05, and high = 0.10 mg kg^{-1}) for intra-day precision (n=5 each level) and intermediate precision (n=5 each level × 3 days)

Analyte	Intra-day precision (Repeatability), n=5																		Intermediate precision, n=15 (3 days)					
	Low						Middle						High						Low		Middle		High	
	Day 1		Day 2		Day 3		Day 1		Day 2		Day 3		Day 1		Day 2		Day 3							
	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_r$	%Re	$\%RSD_R$	%Re	$\%RSD_R$	%Re	$\%RSD_R$
Alachlor	103	6	105	3	91	7	102	2	102	3	103	1	112	1	97	3	104	1	100	8	102	2	104	6
Aldrin	97	13	95	12	87	5	96	8	100	9	91	5	109	9	111	4	113	5	93	11	95	8	111	6
alpha-Endosulfan	101	10	91	14	93	8	94	6	101	5	93	4	112	4	100	3	108	3	95	11	96	6	106	6
alpha-Lindane	95	12	98	12	90	8	96	10	106	8	92	4	106	9	108	3	115	5	94	11	98	9	109	7
Ametryn	96	7	97	6	86	7	102	3	104	5	94	2	108	3	100	4	99	4	93	9	100	6	102	5
Atazine	103	6	104	7	90	10	99	4	102	2	100	2	107	1	97	2	97	2	99	10	100	3	100	5
Azaconazole	99	7	99	6	100	10	106	3	104	8	90	2	108	3	97	6	93	4	99	7	100	9	100	8
Azoxystrobin	95	5	94	5	103	12	106	5	101	7	96	3	110	5	96	7	92	4	97	9	101	6	99	9
Benalaxyl	98	4	98	4	99	8	102	1	103	3	100	1	112	2	95	2	97	4	99	5	102	2	101	8
Benfluralin	93	9	93	7	86	4	97	4	102	5	91	3	111	6	102	3	106	2	91	8	97	6	106	5
Benflurasate	98	7	96	5	93	4	103	2	107	4	97	2	110	3	110	4	104	3	96	6	102	5	108	4
Benoxacor	91	6	95	4	90	7	99	2	100	2	99	4	109	1	101	2	101	2	92	6	99	3	104	4
beta-Endosulfan	97	15	104	10	96	12	98	2	98	3	93	4	107	3	94	6	97	6	99	12	96	4	99	7

beta-Lindane	94	6	94	5	94	5	100	2	105	3	96	2	111	4	102	4	102	3	94	5	100	4	105	5
Bifenthrin	96	7	95	4	86	7	102	2	102	6	93	1	112	3	98	5	96	5	93	8	99	5	102	8
Bromobutide	99	9	101	10	92	10	100	3	105	4	95	5	110	3	99	3	104	2	98	10	100	6	105	5
Bromobutide met.	102	10	102	6	96	7	103	5	107	7	95	3	110	4	106	7	105	5	100	8	102	7	107	5
Bromophos ethyl	89	5	90	6	81	5	94	2	95	5	89	1	107	2	95	3	96	2	86	7	93	4	99	6
Bromophos methyl	86	7	89	7	87	9	96	2	96	4	96	6	102	1	100	1	94	5	87	7	96	4	99	5
Bromopropylate	94	8	96	3	92	9	102	2	103	5	95	2	110	3	97	4	95	5	94	6	100	5	101	8
Bupirimate	84	3	79	9	76	8	99	1	100	3	95	3	110	3	99	4	94	3	80	8	98	3	101	8
Buprofezin	98	10	103	7	95	9	104	1	105	6	94	1	111	3	100	4	100	3	99	8	101	6	104	6
Butachlor	100	11	98	5	95	11	103	4	101	3	95	3	106	1	96	1	102	4	98	9	100	5	101	5
Butamifos	93	5	95	2	87	6	99	2	100	5	94	2	110	4	97	3	99	4	91	6	98	4	102	7
Cadusafos	97	5	95	3	92	4	101	1	103	3	98	2	110	4	101	2	105	1	94	5	101	3	105	4
Cafentrazole ethyl	100	6	99	7	93	11	106	4	102	5	96	3	114	3	96	4	104	4	97	8	101	6	104	8
Carbophenothion	84	9	90	15	95	14	100	4	99	6	86	2	107	2	97	5	96	4	90	13	95	8	100	6
Chlordane-*cis*	90	5	93	6	90	11	96	3	99	4	92	2	111	3	98	4	101	2	91	7	96	5	103	6
Chlordane-*trans*	94	13	99	6	85	8	96	2	100	5	91	2	111	5	96	4	102	1	93	11	95	5	103	7
Chlorfenson	96	7	94	4	93	11	99	2	104	4	95	2	108	3	105	3	99	3	94	8	99	4	104	4
Chlorfenvinphos	98	2	96	3	102	6	103	2	99	3	100	2	108	1	101	1	96	4	99	5	100	3	102	6
Chloroneb	95	15	92	10	90	6	95	5	109	7	95	3	105	8	107	7	108	4	92	11	100	9	106	6
Chlorpropham	94	8	96	3	89	6	103	2	105	4	99	1	109	3	104	3	103	5	93	6	102	4	105	4
Chlorpyrifos	94	6	94	3	86	4	99	1	98	3	93	2	108	2	99	2	101	2	91	6	97	4	102	4
Chlorpyrifos methyl	91	4	91	6	93	6	95	2	96	4	96	2	107	1	100	1	99	1	91	5	95	3	102	3
Chlorthal dimethyl	92	5	95	3	91	5	99	1	102	3	96	1	109	2	98	2	102	2	93	4	99	3	103	5
Cinmethylin	98	10	91	10	90	5	101	4	104	6	95	4	110	6	105	8	106	4	93	9	100	6	107	6

Clomazole	100	7	98	5	90	4	103	1	105	3	99	2	109	2	102	2	104	2	96	7	102	3	105	3
Clomeprop	76	4	79	7	75	4	91	4	92	11	80	3	107	3	88	5	86	6	77	5	88	9	93	11
Cyanophos	96	2	95	2	99	3	101	3	100	3	105	4	107	2	102	3	99	1	97	3	102	4	103	4
Cyfluthrin I	101	6	102	5	93	10	108	6	101	7	89	4	112	3	97	7	103	6	99	8	99	10	104	8
Cyfluthrin II	100	6	100	7	91	7	106	3	104	7	94	2	115	3	101	7	98	5	97	8	101	7	105	9
Cyhalofop-butyl	105	11	109	7	90	14	108	6	102	8	89	5	113	4	95	7	114	4	101	13	100	10	107	9
Cyhalothrin	105	6	102	4	91	9	105	4	99	8	88	2	112	4	97	7	100	6	99	9	97	9	103	8
Cypermethrin I	96	5	95	3	99	5	99	1	100	3	100	2	109	2	97	2	99	2	97	4	100	2	102	5
Cypermethrin II	97	13	101	8	91	16	105	14	94	12	84	6	105	3	93	9	114	4	96	12	94	14	104	10
delta-Lindane	88	6	82	9	94	8	100	5	99	11	108	5	103	5	110	7	93	2	88	9	102	8	102	9
Deltamethrin I	92	6	91	4	90	8	102	1	104	4	92	3	108	3	100	2	104	2	91	6	99	6	104	4
Deltamethrin II	97	6	95	4	90	4	99	2	101	3	95	2	109	3	108	3	103	1	94	6	98	4	107	4
Demeton-S-methyl	100	10	91	15	94	11	93	3	102	8	113	4	97	2	110	6	96	5	95	12	103	10	101	8
Diazinone	94	16	96	15	90	6	93	10	109	12	90	2	101	11	95	13	108	6	93	13	97	12	101	11
Dichlorfenthion	98	7	95	4	84	9	103	3	103	4	95	1	111	4	103	5	98	5	93	9	100	5	104	7
Dichlorvos	96	6	98	4	87	6	97	2	100	5	89	3	111	4	99	3	102	2	94	7	95	6	104	6
Diclobenil	98	8	90	15	99	12	105	5	103	11	87	5	112	4	93	10	92	5	95	12	98	11	99	11
Diclofop-methyl	96	10	96	15	90	13	103	2	98	4	94	3	109	2	101	3	101	2	94	12	98	4	104	5
Dieldrin	99	7	96	5	92	6	103	2	107	7	95	1	110	3	102	6	100	3	96	7	102	6	104	6
Difenoconazole	94	6	94	4	95	7	102	3	101	7	89	1	108	3	95	3	92	5	94	5	97	8	99	8
Dimepiperate	96	6	98	3	86	11	97	5	102	5	94	4	110	4	100	3	104	2	93	9	98	6	105	5
Dimethametryn	96	6	96	5	90	7	99	3	103	5	94	1	112	4	99	4	104	3	94	6	98	5	105	6
Diniconazole	90	9	92	7	108	14	97	7	96	4	101	9	94	3	99	3	104	7	97	13	98	7	99	6
Disulfoton	94	10	92	5	89	4	98	2	98	3	91	2	110	2	96	2	101	3	92	7	96	4	102	6

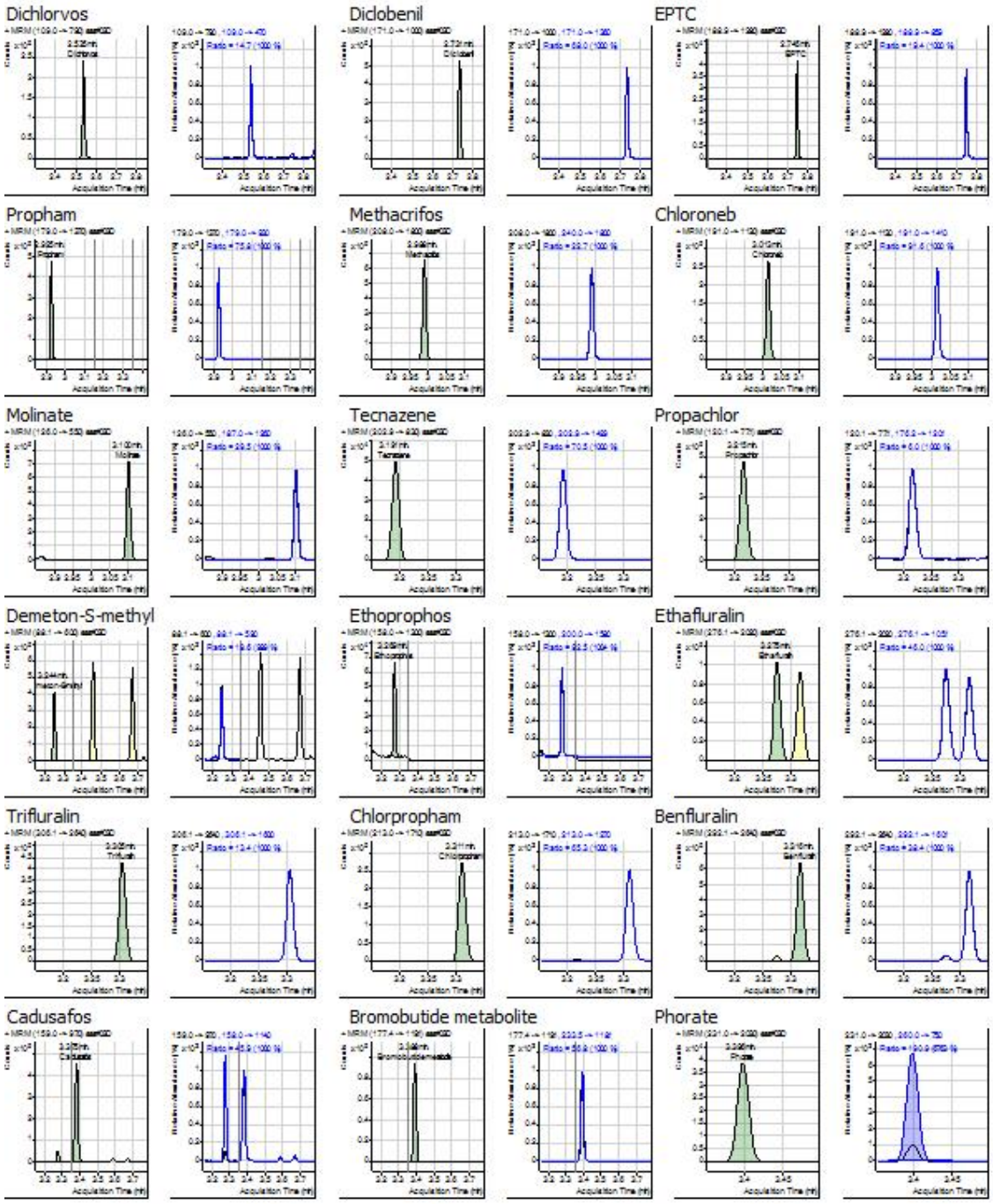
Dithopyr	93	5	95	6	96	12	99	3	97	6	92	4	108	3	97	3	94	4	95	7	96	5	100	7
Endosulfan sulfate	87	19	84	11	86	6	85	6	108	11	94	4	90	8	113	4	103	9	86	12	96	12	102	12
Endrin	97	7	97	5	88	4	102	2	105	5	93	2	109	3	102	5	105	4	94	7	100	6	105	5
EPN	93	13	93	9	84	5	99	7	103	4	95	3	111	7	105	4	111	3	90	10	99	6	109	5
EPTC	94	6	94	1	91	9	101	1	100	4	95	2	110	2	98	2	97	3	93	6	99	4	101	6
Esprocarb	94	12	106	11	103	10	96	3	109	7	102	4	109	4	103	6	102	1	101	11	102	7	105	5
Ethafluralin	96	7	97	4	86	9	104	4	102	9	89	2	115	4	97	8	95	7	93	8	98	9	103	11
Ethion	93	5	87	5	100	7	103	3	100	5	93	1	111	2	102	3	97	4	93	8	99	5	103	6
Ethoprophos	98	7	96	6	99	10	106	6	104	13	87	4	111	4	93	10	92	6	98	8	99	12	99	11
Etofenprox	91	5	87	3	88	7	94	2	98	3	95	2	106	1	101	1	99	2	88	5	96	3	102	3
Fenamiphos	86	4	87	6	81	3	91	2	96	4	88	1	106	3	97	2	98	4	85	5	92	5	100	5
Fenbuconazole	96	8	95	5	90	5	101	4	98	8	87	3	108	3	94	5	95	7	94	6	95	8	99	8
Fenchlorfos	89	6	92	6	82	10	102	3	101	4	92	1	113	3	96	5	95	6	88	8	98	5	101	9
Fenclorim	92	7	96	6	88	6	104	2	106	5	95	2	111	3	102	6	105	3	92	7	102	6	106	5
Fenpropimorph	93	5	91	2	88	5	99	1	100	3	97	2	109	1	100	1	98	2	91	5	99	2	102	5
Fenoxaprop-ethyl	99	3	97	5	93	9	103	2	99	6	94	2	115	3	97	6	89	9	97	6	99	6	100	13
Fenpropathrin	99	5	99	5	98	8	104	2	100	4	96	1	113	4	93	3	98	4	98	6	100	4	102	10
Fenthion	100	10	99	9	94	10	105	3	103	6	94	1	112	3	95	6	95	4	98	10	101	6	101	9
Fenvalerate I	100	8	100	7	92	7	107	2	107	7	95	1	111	3	101	6	99	4	97	8	103	7	103	7
Fenvalerate II	94	8	94	4	92	5	99	1	104	5	96	4	107	5	103	3	105	4	93	6	99	5	105	4
Fipronil	97	6	96	4	95	9	105	3	101	6	92	1	111	3	93	4	94	6	96	6	99	6	99	9
Flusilazole	95	15	95	12	91	9	97	8	104	6	94	5	109	7	88	3	113	6	94	12	98	7	103	12
Flutolanil	88	16	74	5	86	2	73	3	78	7	85	3	100	9	81	5	82	7	83	12	78	8	88	12
Fonophos	93	13	88	9	89	8	95	11	102	8	89	6	108	10	111	5	115	5	90	10	95	10	111	7

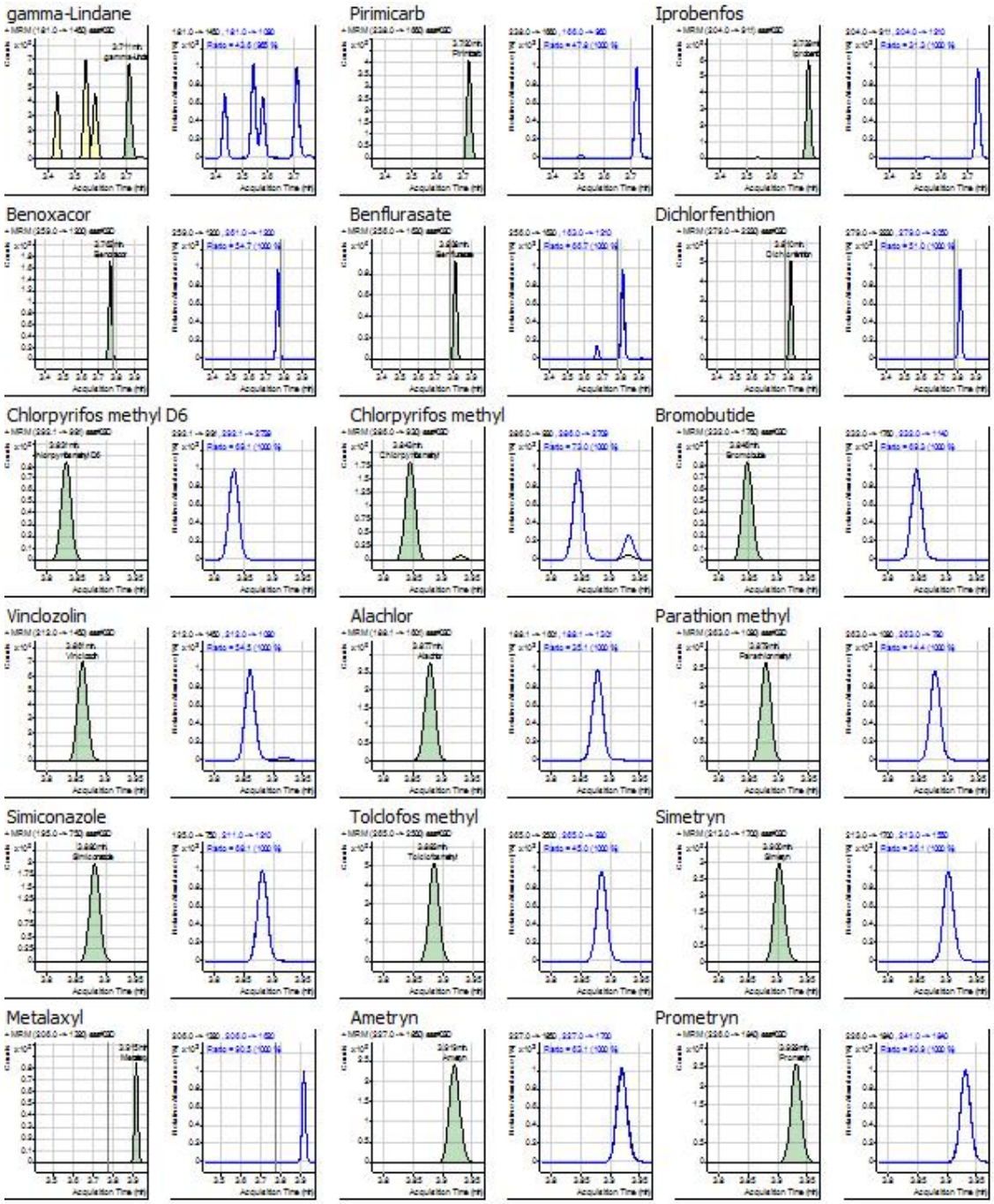
Furametpyr	88	8	91	9	86	7	98	6	100	4	92	4	115	4	103	6	105	4	88	8	97	5	108	7
gamma-Lindane	94	10	100	6	98	9	102	4	104	8	91	3	110	3	96	6	93	5	97	8	99	8	100	9
HCB	79	3	83	9	84	14	83	4	80	10	85	9	96	5	80	6	78	7	82	10	83	8	85	11
Heptachlor	88	8	86	4	85	9	101	3	99	7	89	2	111	2	100	7	92	2	87	7	96	7	101	9
Heptachlor epoxide	100	4	97	4	91	3	105	1	102	2	98	1	112	2	99	1	101	2	96	5	102	3	104	6
Hexaconazole	95	10	98	7	96	13	92	5	109	8	91	7	114	4	92	7	91	5	96	10	97	11	99	12
Hydroxy Furametpyr	105	6	102	3	94	7	102	2	104	1	98	3	110	2	98	1	105	1	100	7	101	3	104	5
Imazalil	96	8	97	3	91	6	102	1	103	4	96	1	111	2	98	3	102	2	95	6	101	4	104	6
Iprobenfos	99	10	101	5	96	7	103	3	102	4	94	2	110	2	97	3	98	4	99	7	100	5	101	7
Iprodione	90	10	85	7	91	10	95	4	93	9	88	2	103	2	91	4	92	5	89	9	92	6	95	7
Isazophos	98	6	98	5	93	9	104	2	103	3	99	1	110	3	95	3	97	4	96	6	102	3	101	8
Isofenfos	96	4	99	3	92	3	104	1	102	3	103	3	107	1	99	2	99	3	96	4	103	2	101	4
Isoprothiolane	97	6	97	3	92	8	104	2	102	4	96	2	112	2	95	4	96	4	95	6	101	4	101	8
Isoxathion	98	8	98	7	93	11	107	2	107	7	93	1	113	4	104	8	97	5	96	8	102	8	105	8
Kresoxim-methyl	98	4	96	3	95	5	102	1	102	3	102	1	110	1	95	0	103	1	96	4	102	1	103	7
Malathion	73	4	76	6	83	11	104	7	101	2	100	2	105	1	91	2	95	3	77	9	101	4	97	7
Mefenpyr diethyl	97	3	93	4	98	6	97	2	104	4	103	1	107	3	110	2	103	1	96	5	101	4	107	3
Mepronil	91	5	91	4	91	10	96	2	96	8	92	2	107	2	94	4	91	3	91	7	94	5	97	8
Metalachlor	100	6	100	4	98	6	103	3	105	4	94	1	111	3	97	4	97	3	99	5	100	6	101	7
Metalaxyl	88	4	88	3	83	6	93	1	93	3	89	3	105	3	93	2	94	2	86	5	92	3	97	6
Methacrifos	90	11	88	10	96	6	96	3	110	8	96	1	102	5	111	4	107	4	91	9	101	8	106	5
Methoxychlor	101	4	101	4	98	7	106	2	101	4	93	2	115	3	92	5	96	6	100	5	100	6	101	11
Metominostrobin	103	4	102	5	100	7	107	3	103	5	93	2	115	3	93	7	95	6	102	5	101	7	101	11
Mirex	101	9	101	8	89	7	102	3	104	5	95	2	111	3	101	5	101	2	97	10	101	5	104	6

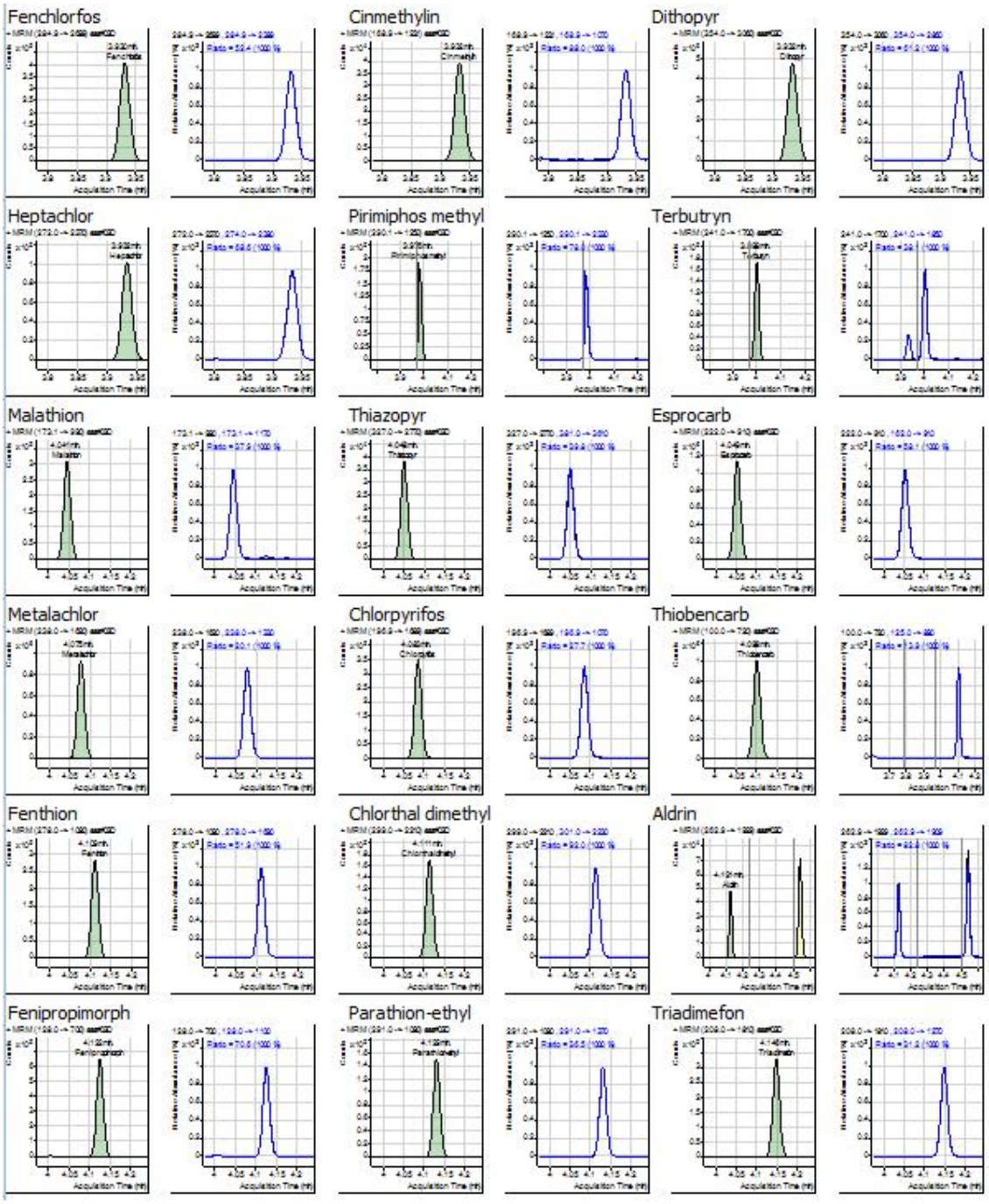
Molinate	93	5	92	3	113	6	98	5	93	2	99	2	99	2	88	4	88	2	100	11	97	4	92	6
Oryzastrobin	93	9	92	9	83	12	97	3	96	8	92	5	109	3	95	3	96	4	89	10	95	6	100	7
Oryzastrobin 5 Z iso.	97	7	95	4	87	6	104	9	106	5	95	3	107	2	99	4	97	3	93	7	102	7	101	5
Oxadiazon	93	8	92	4	85	5	98	4	102	6	90	1	107	3	101	6	101	3	90	7	97	6	103	5
Oxadixyl	91	6	91	4	90	8	94	2	94	7	92	2	104	1	96	3	91	3	91	6	93	4	97	6
Oxyfluorfen	101	8	102	6	97	9	108	3	106	9	92	1	110	3	96	5	96	4	100	7	102	9	101	8
p,p'-DDD	95	4	94	3	100	5	101	2	98	3	102	5	105	4	106	3	97	4	96	4	100	4	103	5
p,p'-DDE	97	4	96	4	90	7	99	1	97	3	94	1	109	3	99	1	101	2	95	6	97	3	103	5
p,p'-DDT	99	8	97	4	92	9	105	4	106	8	93	1	112	3	99	6	97	3	96	8	101	8	103	8
Paclobutazole	92	7	93	6	86	5	97	2	97	4	90	2	109	3	89	1	101	3	90	7	95	5	100	9
Parathion methyl	97	7	97	4	92	7	103	2	102	7	90	1	111	3	99	6	96	6	95	6	98	7	102	8
Parathion-ethyl	101	7	100	4	91	8	105	3	102	7	92	2	115	3	100	7	97	7	97	8	100	8	104	9
Penconazole	102	7	98	1	95	5	101	2	102	1	98	2	110	2	98	1	101	3	98	6	100	2	103	5
Pendimethalin	90	8	85	10	74	3	97	7	104	7	96	3	107	6	104	5	103	4	83	11	99	7	105	5
Permethrin-cis	78	5	82	5	73	3	93	4	92	10	82	2	108	3	90	7	90	6	78	7	89	8	96	11
Permethrin-trans	93	6	93	6	90	7	106	3	104	6	93	2	114	3	100	6	98	6	92	6	101	7	104	8
Phethoate	100	5	100	6	96	9	106	3	101	4	94	3	111	2	97	3	98	4	98	7	100	6	102	7
Phorate	94	6	93	6	88	7	102	1	101	2	95	2	107	1	97	2	99	2	92	7	99	3	101	5
Picolinafen	95	10	96	5	86	5	100	2	99	4	93	2	109	3	96	2	102	3	92	8	97	4	103	6
Piperonyl butoxide	92	6	91	4	86	8	100	1	100	2	98	4	111	2	98	2	100	3	90	7	99	3	103	6
Piperophos	102	7	103	4	98	13	106	5	102	4	102	6	106	2	99	1	104	9	101	9	103	5	103	6
Pirimicarb	88	13	84	6	102	12	95	4	93	4	92	5	97	7	95	5	89	5	91	14	93	5	94	7
Pirimiphos ethyl	97	9	97	6	92	5	102	2	107	5	95	1	110	3	101	5	100	3	95	7	101	6	104	6
Pirimiphos methyl	96	12	93	5	100	9	99	4	95	4	95	6	97	4	106	4	94	5	96	9	96	5	99	7

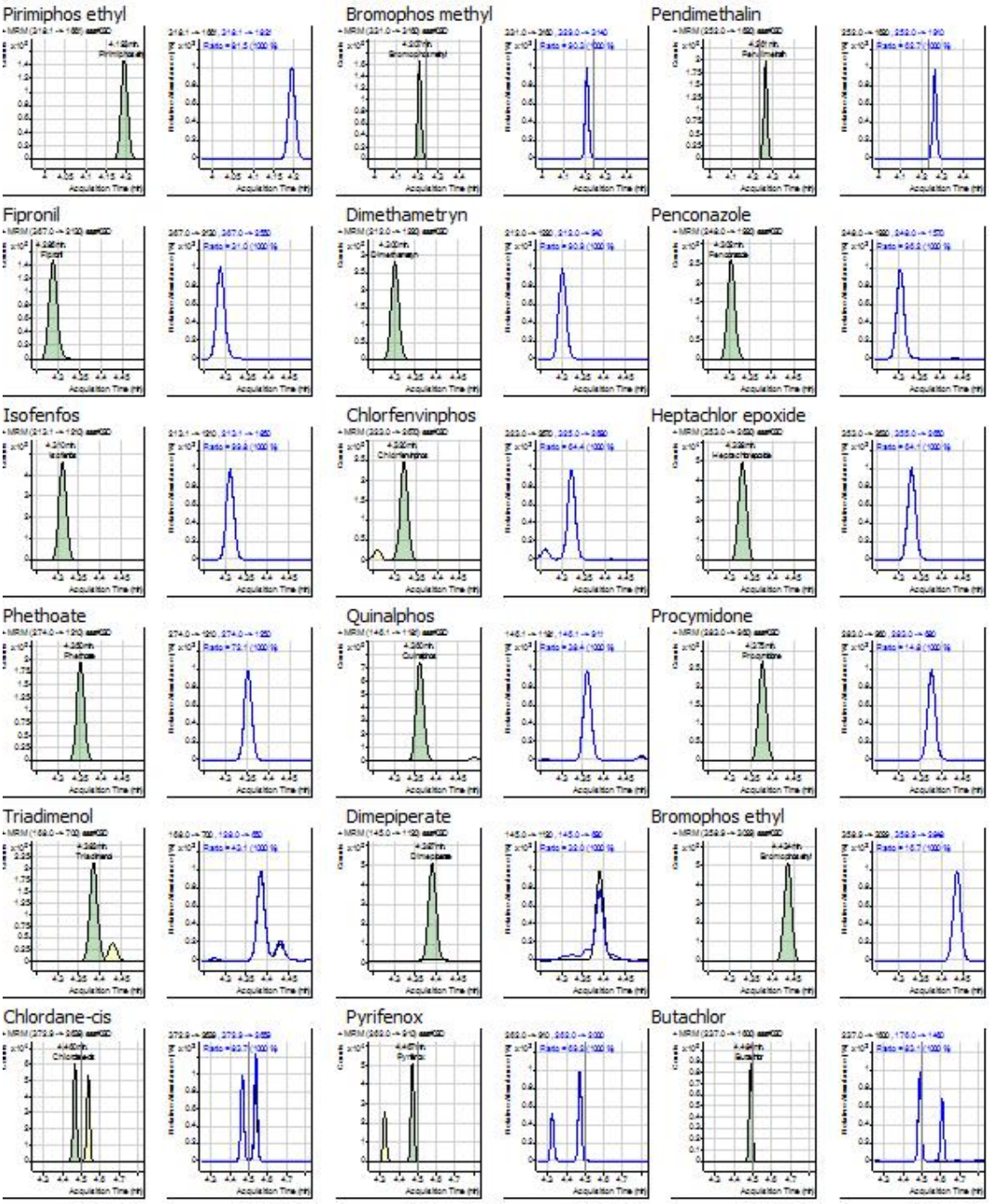
Pretilachlor	98	9	100	8	93	7	103	2	105	6	95	1	110	4	102	5	99	3	97	8	101	6	104	6
Prochloraz	90	6	88	7	98	5	98	2	103	6	109	2	109	2	107	3	101	2	92	7	103	6	106	4
Procymidone	100	7	98	4	92	4	103	2	103	3	99	1	110	3	100	2	104	2	97	6	102	3	105	4
Profenofos	103	9	100	6	101	4	101	2	109	5	99	2	107	4	109	3	107	3	101	7	103	5	108	3
Prometryn	97	9	96	10	88	8	107	3	105	6	93	5	113	4	98	7	94	5	94	10	102	8	102	10
Propachlor	92	7	89	5	80	6	96	1	99	5	92	2	107	4	99	2	98	2	87	8	96	4	101	5
Propetamphos	99	8	98	4	88	9	106	1	104	5	95	2	112	3	98	4	96	7	95	8	101	6	102	8
Propham	97	6	97	4	90	8	103	3	102	6	93	1	112	3	99	6	97	4	95	7	100	6	103	8
Propiconazole-*trans*	88	12	94	6	97	15	107	3	104	5	95	3	111	4	103	4	99	4	93	12	102	6	105	6
Prothiophos	98	8	99	3	89	8	104	2	105	7	92	2	113	4	103	6	98	5	95	8	100	7	105	8
Pyrafulfen-ethyl	98	9	97	11	101	9	105	3	107	10	91	2	107	3	106	7	98	5	99	9	101	10	104	6
Pyrazophos	95	5	94	2	90	3	100	2	100	2	96	1	107	1	99	1	98	3	93	4	98	3	101	5
Pyributicarb	83	9	99	7	98	9	97	4	99	6	88	2	114	3	99	5	97	3	93	11	94	6	103	9
Pyrifenox	92	8	93	5	81	7	99	3	98	9	85	2	114	4	95	9	93	8	89	9	94	9	101	12
Pyriproxyfen	104	6	104	8	103	12	98	2	100	3	97	2	104	1	99	3	94	2	104	8	98	3	99	4
Pyroquilon	93	6	94	6	89	5	101	2	105	6	92	2	108	3	103	7	98	4	92	6	100	7	103	6
Quinalphos	96	4	97	5	99	5	102	2	103	4	96	2	110	2	97	3	99	3	97	5	101	4	102	6
Resmethrin	91	7	89	6	82	12	100	2	99	6	94	1	109	2	98	4	96	3	87	9	98	5	101	7
Silafluofen	100	5	95	5	93	10	103	3	102	7	92	1	111	3	100	6	94	5	96	7	99	7	101	8
Simazine	93	14	94	7	87	8	92	7	104	6	91	3	106	9	102	5	111	5	91	10	96	8	106	7
Simetryn	96	7	96	6	86	5	97	3	103	4	94	2	109	4	100	3	104	3	93	7	98	5	105	5
Simiconazole	105	11	111	10	106	8	106	4	109	6	98	1	109	3	101	6	102	2	107	9	104	6	104	5
Sulprofos	85	12	90	5	97	17	98	7	98	9	89	6	107	3	97	3	100	3	91	13	95	8	101	5
Tebuconazole	95	7	99	6	93	5	96	4	102	4	97	3	107	2	97	3	102	3	96	6	99	4	102	5

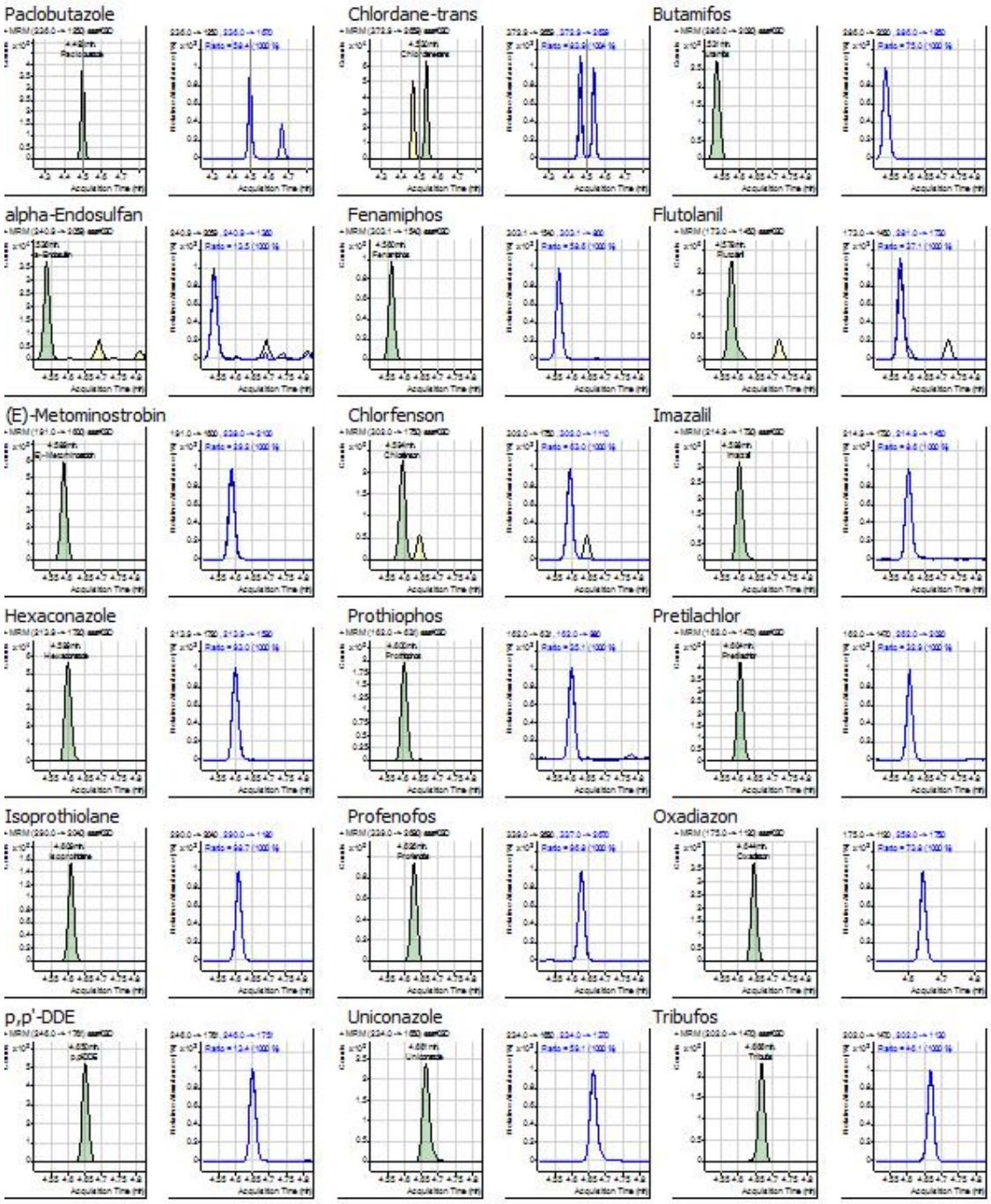
Tecnazene	98	9	97	5	91	5	102	2	105	5	95	1	109	3	103	5	104	4	95	7	101	5	105	5
Terbufos	90	6	86	4	86	5	97	1	103	3	98	0.5	108	3	104	1	104	1	87	5	99	3	105	3
Terbutryn	93	4	91	5	90	6	98	1	100	2	96	1	109	2	99	1	103	2	91	5	98	2	103	5
Tetradifon	95	7	96	3	90	7	104	1	106	3	96	1	111	2	98	4	99	2	94	6	102	5	103	6
Thiazopyr	98	7	97	6	98	8	103	3	106	5	94	1	110	4	99	5	96	3	98	6	101	6	101	7
Thiobencarb	94	9	94	3	90	6	99	1	101	6	91	4	108	5	100	4	106	3	93	6	97	6	105	5
Thiometon	88	7	89	5	104	12	102	4	100	4	97	3	102	3	103	3	95	4	94	12	100	4	100	5
Tolclofos methyl	97	8	96	5	87	8	102	2	98	5	92	1	111	3	93	9	99	3	94	8	97	5	101	9
Triadimefon	97	9	98	6	82	12	104	1	103	5	96	2	111	3	98	3	95	4	92	11	101	5	101	8
Triadimenol	94	10	95	7	85	4	97	6	103	6	94	3	113	7	107	4	111	3	91	9	98	6	110	5
Triallate	97	6	96	9	99	10	105	4	103	8	88	5	111	4	101	7	94	6	97	8	99	9	102	9
Triazophos	96	8	95	4	97	9	106	3	104	7	91	2	108	3	98	5	96	3	96	7	100	8	101	7
Tribufos	101	5	97	2	89	5	99	2	102	5	96	2	109	2	103	4	105	3	96	7	99	4	106	4
Trifloxystrobin	103	6	105	3	91	7	102	2	102	3	103	1	112	1	97	3	104	1	100	8	102	2	104	6
Trifluralin	97	13	95	12	87	5	96	8	100	9	91	5	109	9	111	4	113	5	93	11	95	8	111	6
Triticonazole	101	10	91	14	93	8	94	6	101	5	93	4	112	4	100	3	108	3	95	11	96	6	106	6
Uniconazole	95	12	98	12	90	8	96	10	106	8	92	4	106	9	108	3	115	5	94	11	98	9	109	7
Vinclozolin	96	7	97	6	86	7	102	3	104	5	94	2	108	3	100	4	99	4	93	9	100	6	102	5

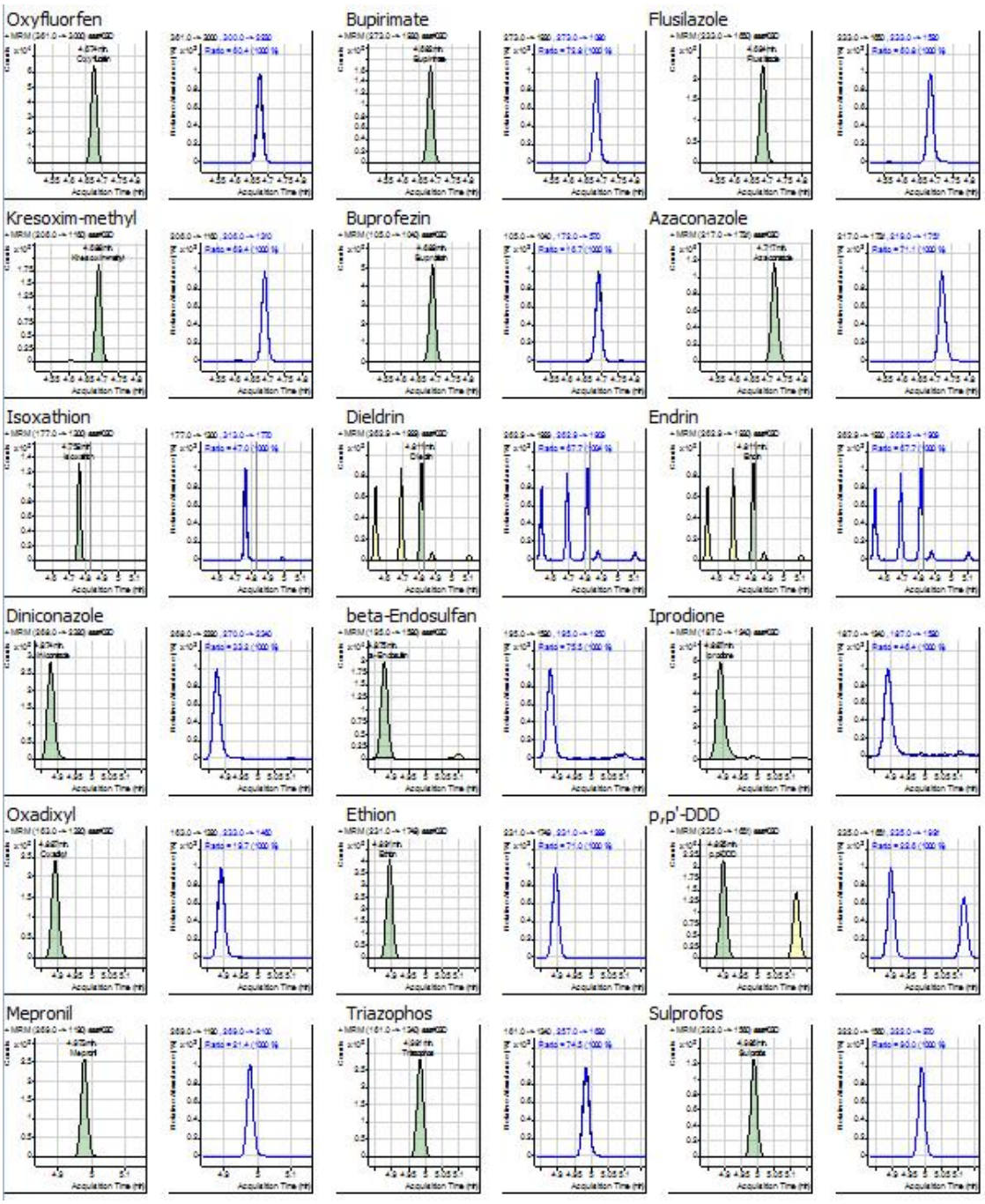


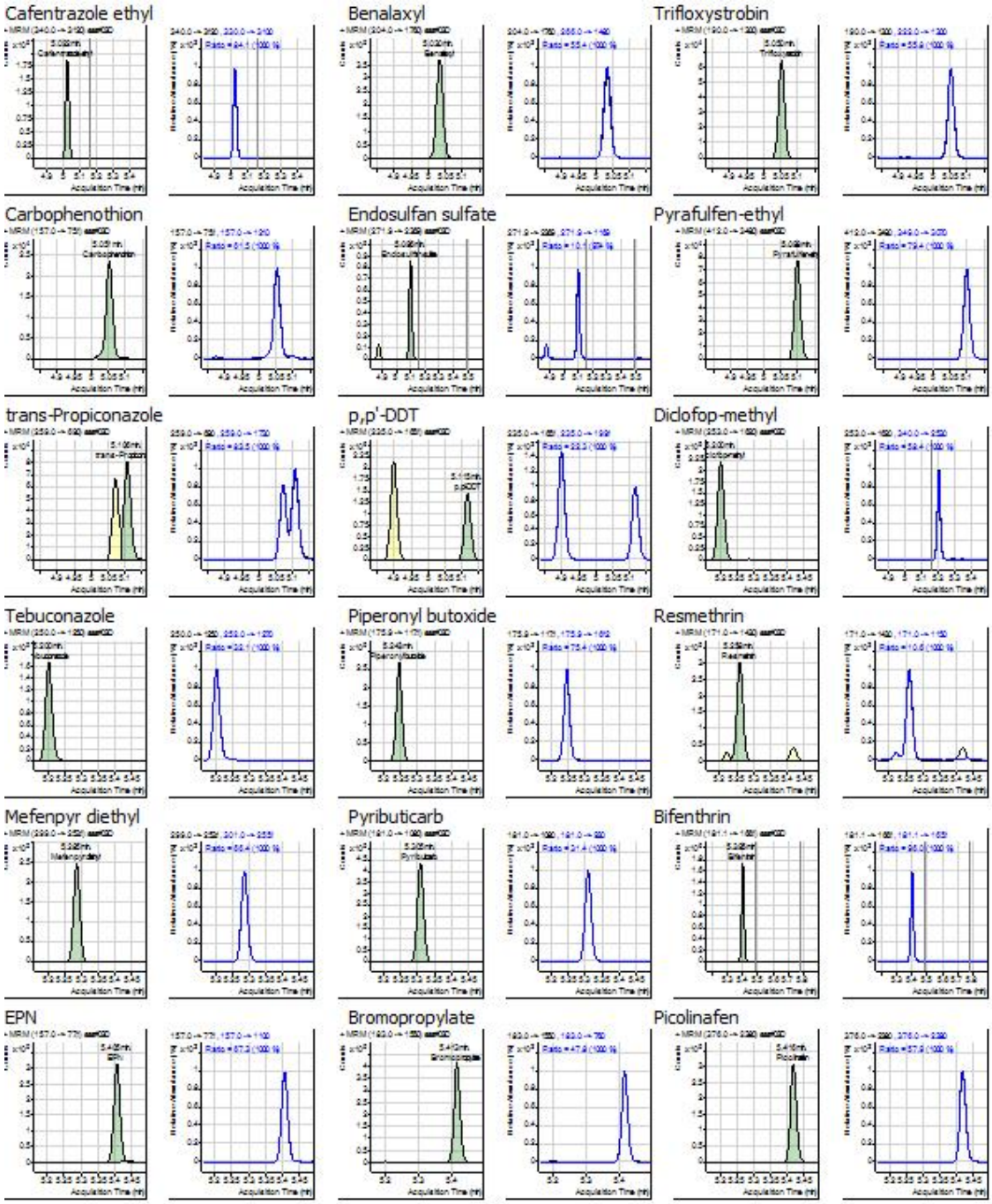


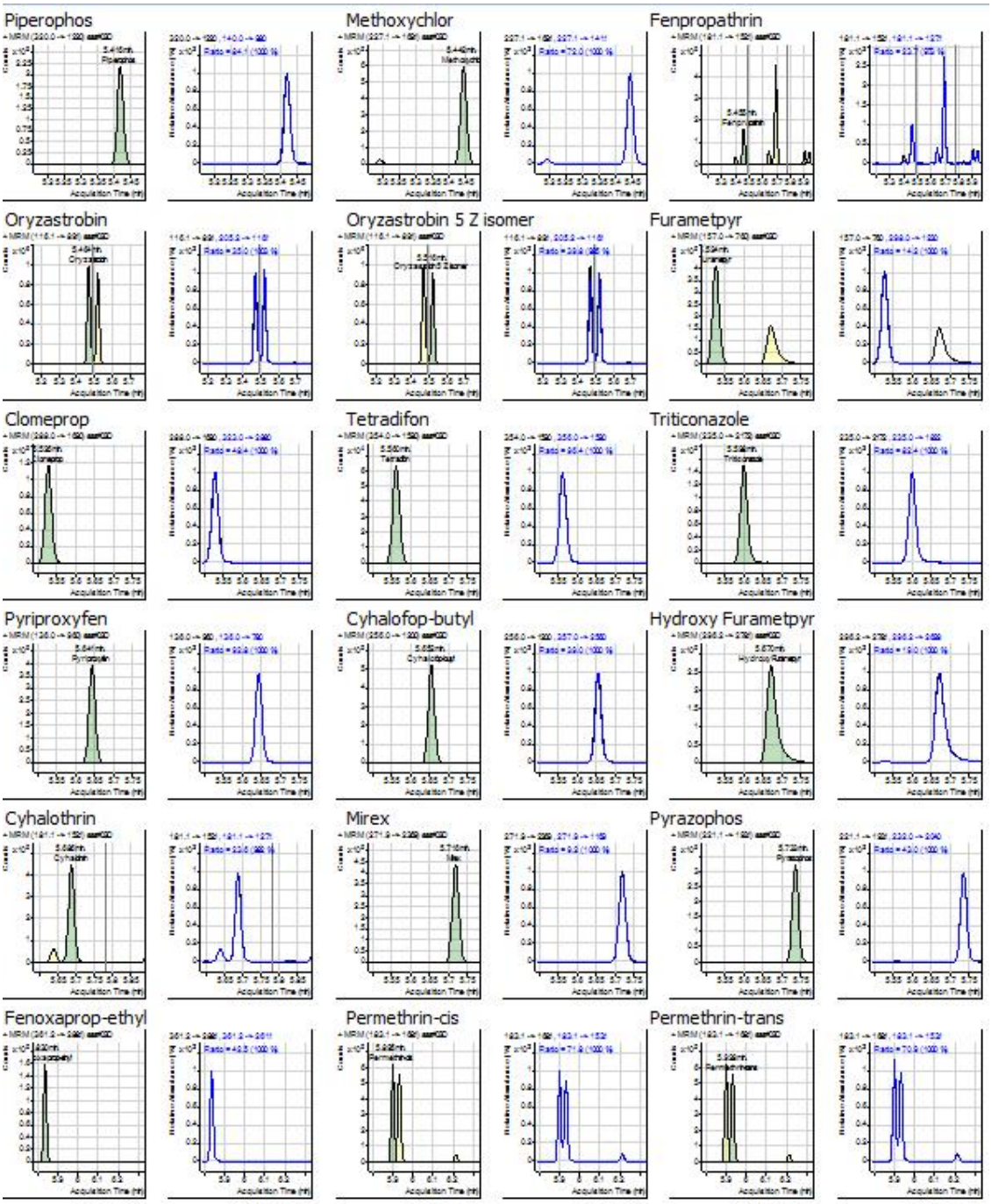












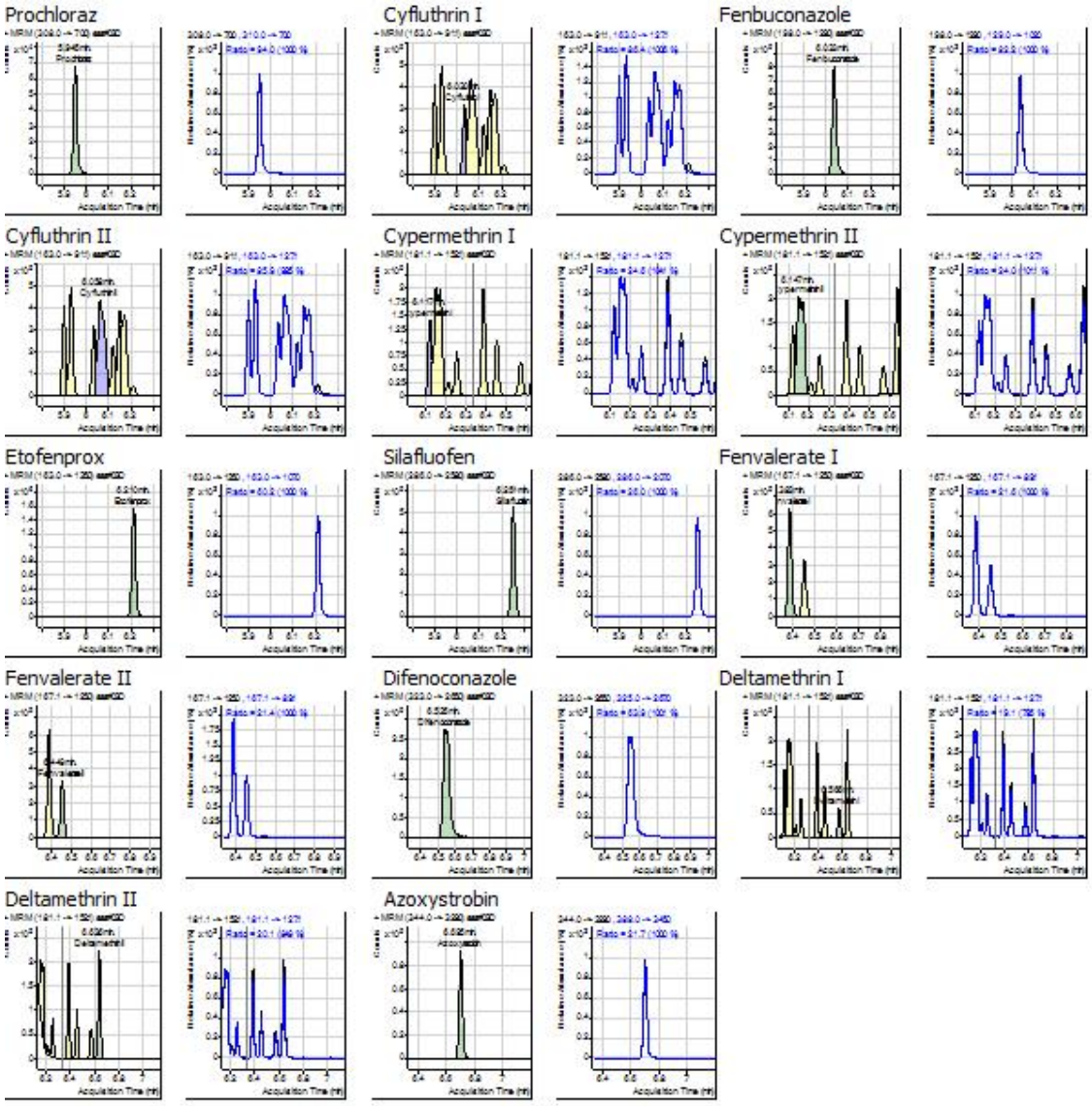


Figure D-1 MRM chromatograms of standard pesticides at 0.1 mg L^{-1} in MeCN under the optimum LP-GC–MS/MS conditions.

VITA

Miss. Thanutchaporn Semathong was born on June 30, 1975 in Sakaew, Thailand. She graduated with a bachelor's degree of Science in Chemistry from Mahasarakham University in 1998. Since 2009, she has been studying for a master's degree of Science in Analytical of Chemistry, at the Faculty of Science, Chulalongkorn University, and will complete in 2012. Whilst, studying in Chulalongkorn University, she was granted a scholarship from the Thailand Research Fund and the Commission on Higher Education, Research Grant for Mid-Career University Faculty (TRF-CHE-RES-MR) (RDC5350010) (TRF-MAG-WI535S001). In the meantime, she is working in the laboratory as a team leader GCMS in the chromatography section with Overseas Merchandise Inspection Co., Ltd. (OMIC) of Bangkok branch.