Exploration of the suitability of coated blade spray for rapid analysis of pesticides in agricultural commodities and byproducts

by

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Author's declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

I hereby declare that I am the sole author of **Chapter 1, 3, 4, and 5**, written under the supervision of Prof. Janusz Pawliszyn.

Chapter 2 contains a study outlining the development of an autosampler along with the applicability of coated blade spray for the analysis of a multi-residue panel of pesticides extracted from apple juice. Preliminary construction of the autosampler was completed at Professional Analytical System (PAS) Technology in Magdala, Germany, with final modifications, manufacture and usage of SPME tools, as well as instrumental analysis completed at the University of Waterloo. The chapter has been published as an article entitled *Breaching the 10 Second Barrier of Total Analysis Time for Complex Matrices via Automated Coated Blade Spray* (*Analytical Chemistry*, **2019**, 91(20), 13039–13046), co-authored by Germán Augusto Gómez-Ríos, Dietmar Hein, and Janusz Pawliszyn. The autosampler design was proposed and finalized by G.A. Gómez-Ríos, D. Hein, and J. Pawliszyn. Modifications of the autosampler to ensure instrument compatibility were performed by G.A. Gómez-Ríos and A. Kasperkiewicz. Experiment design and manuscript outline were completed by G.A. Gómez-Ríos and A. Kasperkiewicz. A. Kasperkiewicz carried out the experiments, completed data processing, and manuscript writing.

Abstract

The multiresidue analysis of pesticides in domestic and imported agricultural products is completed on hundreds of thousands of samples yearly by regulatory agencies in the United States, Canada, and Europe. Currently, regulatory agencies rely on derivatives of the Quick, Easy, Cheap, Effective, Rugged, Safe analytical workflow, which suffers from high sample and organic solvent usage, as well as automation difficulties. In order to improve scalability, in terms of time of analysis, amenability to automation, and sample size requirements, alternative techniques based on solid-phase microextraction (SPME) directly coupled to mass spectrometry (MS) are worth exploring. This thesis presents the exploration of one of such techniques, known as coated blade spray (CBS), to improve upon existing sample preparation shortfalls through the development of autosampling hardware, and applications for the analysis of pesticides in fruit juice, fruit, and cannabis product matrices.

Firstly, automation reduces analysis time, human intervention, and cost per sample. In this thesis, a suitable automated CBS workflow is proposed for the screening and quantitation of multiple substances (*i.e.* drugs of abuse and pesticides) in complex matrices. In an attempt to reduce the total sample analysis time, several parameters were investigated, including tandem mass spectrometry (MS/MS) dwell time, CBS spray time, and extraction time. Model compounds with a moderately wide range of molecular weights, polarities, and structural diversity were selected in order to monitor analytical figures of merit during method optimization and autosampler development. As a proof-of-concept as well as to set the stage for the subsequent chapters of this thesis, an automated method for the screening and quantitation of more than 150 pesticides from apple juice was demonstrated on both triple quadrupole and orbitrap instruments in under 15 seconds total sample analysis time.

Building on the aforementioned fruit juice proof-of-concept, the method development of a similar panel of pesticides in apple, blueberry, grape, and strawberry matrices was explored, however with the goal of further CBS-MS/MS method validation with liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). For all four matrices, over 125 compounds were found to meet EU SANTE guidelines with regards to linearity, precision, and accuracy while reaching limits of quantitation for both CBS-MS/MS

and SPME-LC-MS/MS methods below their minimum regulatory limit. Additionally, real-world samples of all matrices were processed with detected residues (n = 57) yielding good agreement between instrumental methods (percent differences < 20 % for 73 % residues), supporting CBS as a stand-alone analysis technique or a suitable complement to LC confirmation of pesticides in fruit matrices.

Nearing the upper limit of matrix difficulty (*i.e.* author-defined as inversely proportional to water content and proportional to the concentration of matrix-sourced interferences in a matrix) explored in this thesis, the method development steps for the extraction of 74 target pesticides from cannabis oil via SPME for analysis with both LC-MS/MS and CBS are communicated. The exploration of a washing step to remove adhered oil whilst minimally desorbing extracted analytes along with the implementation of central composited design investigation to examine compound extraction kinetics in the non-polar matrix yielded a workflow that was validated via both instrumental techniques. Of the initial target list, 48 pesticides were found to be suitable for screening or quantitation via CBS with performance validated via LC-MS/MS. The majority of compounds were found to meet the EU SANTE guidelines for analysis (*i.e.* linearity, precision, accuracy) whilst reaching limits of quantitation below or at Health Canada minimum regulatory limits (majority at 10 ng/mL). Examination of factors contributing to poor quantitation of pesticides via CBS are shared and explored, such as contributing isobaric interference sourced from plant byproducts and carrier oil. Following this, experiences regarding dried cannabis flower analysis are shared, with significant analyte-matrix binding along with plant-sourced co-extractives determined as sources of difficulty to method development efforts.

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Many individuals made an impact on the work presented in this thesis and without them the contents would be dramatically different. Firstly, I would like to thank Prof. Janusz Pawliszyn for supporting my work and providing the environment to foster self-critic, self-improvement, and exposure to a diverse selection of character traits—with the admirable hopefully co-opted into my humanity.

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Abbreviations

ACE acetone 50, 67

ACN acetonitrile 15, 32, 50, 67

AMS ambient mass spectrometry 6, 7, 9, 12, 31, 71, 73

APCI atmospheric pressure chemical ionization 3, 49

CBD cannabidiol 51

CBS coated blade spray 7, 8, 10, 13, 27, 32, 49, 71, 73

CCD central composite design 53

DART direct analysis in real-time 12, 45

DESI desorption ionization mass spectrometry 12, 31

DI-SPME direct-immersion solid-phase microextraction 5, 7, 73

EFSA European Food Safety Authority 1

ESI electrospray ionization 3, 6, 7, 29, 49, 72

EU MRL European Union Minimum Regulatory Limit, set by ESFA 40

EXCREMENT onlinE matriX-sourced aCcuRatE-Mass intErfereNce filTering 70

FDA Food and Drug Administration 1

GC-MS gas chromatography coupled to mass spectrometry 2, 3, 49

HEX hexane 50

HLB hydrophilic-lipophilic balance 15, 33, 50

HRMS high-resolution mass spectrometry 17, 27

HS-SPME headspace solid-phase microextraction 5

IS internal standards 38

ISO iso-octane 50

LC-MS liquid chromatography coupled to mass spectrometry 2, 49

LC-MS/MS coupling of liquid chromatography to tandem mass spectrometry 3, 4, 10

LDTD laser-diode thermal-desorption 12

LOD limit of detection 19

LOQ limit of quantification 4, 18, 32, 36, 50, 54

MCT medium-chain triglyceride 51, 54

MeOH methanol 15, 18, 32, 50

MRL maximum residue limit 4, 48, 67

MRPL minimum regulatory performance limit (semantically identical to MRL) 20

MS mass spectrometry 3, 6–9, 13, 32

MS/MS tandem mass spectrometry 9, 10, 13

MS^n multiple-stage trapping mass spectrometry 8, 9

OEM original equipment manufacturer 15, 33

PAN-C_{18} polyacrylonitrile-C_{18} 7

PAN-HLB polyacrylonitrile-hydrophilic-lipophilic balance 7

PS paper spray 6, 7, 12, 31

Q_2 collision cell 10

QuEChERS Quick, Easy, Cheap, Effective, Rugged, Safe 1, 2, 4, 31, 49, 71, 72

REIMS rapid evaporative ionization mass spectrometry 12

RSD relative standard deviation 18, 19

S/N signal-to-noise ratio 13, 19, 40, 54, 57

SDL screening detection limit 54, 118

SE solvent extraction 31, 71, 72

SPE solid-phase extraction 12, 49

SPME solid-phase microextraction 5, 7, 10, 13, 38, 49, 71

SRM selected reaction monitoring 10, 13, 15, 35, 51

THC Δ^9-tetrahydrocannabinol 51, 67

THCa Δ^9-tetrahydrocannabinolic acid 67

USDA United States Department of Agriculture 1

WADA World Anti-Doping Agency 20

Chapter 1

Introduction

1.1 Multiresidue analysis: state of affairs

Analytical methods for the monitoring and quantification of tens to hundreds of compounds simultaneously are routinely used by regulatory agencies and in clinical settings for a wide variety of target analytes such as drugs of abuse in biofluids, pharmaceutical contaminants in wastewater, and veterinary drugs and pesticides in consumables.[1–7] The substantial cost and time savings offered by monitoring hundreds of compounds in a sample comes at the price of methodological fine tuning, where finalized methods often seek conditions for the best compromise. In the case of pesticide residues, simultaneous monitoring of hundreds of compounds of vastly different chemical properties (*e.g.* molecular weight, polarity, presence of ionizable moieties) can prove difficult or impossible to complete with the same analytical workflow. Regardless of developmental hardships, novel multiresidue pesticide monitoring methods are in high demand due to their extensive regulatory usage. Hundreds of thousands of food samples are analyzed yearly in the United States and Europe by the Food and Drug Administration (FDA), the United States Department of Agriculture (USDA), and the European Food Safety Authority (EFSA).[8,9] Focusing on high water content produce, current methods used by the regulatory agencies mentioned are derivatives of the Quick, Easy, Cheap, Effective, Rugged, Safe (QuEChERS) sample preparation technique.[10] The workflow, shown in Figure 1.1, can be summarized into the cryogrinding

of the sample, addition of acetonitrile, buffers, drying salts followed by sample centrifugation, with a final addition of a powdered sorbent of choice to remove pigments, lipids, sugars, or other undesirable contaminants. The final extract can be solvent exchanged to suit the requirements of the instrumental analysis to be performed, usually liquid chromatography coupled to mass spectrometry (LC-MS) or gas chromatography coupled to mass spectrometry (GC-MS).

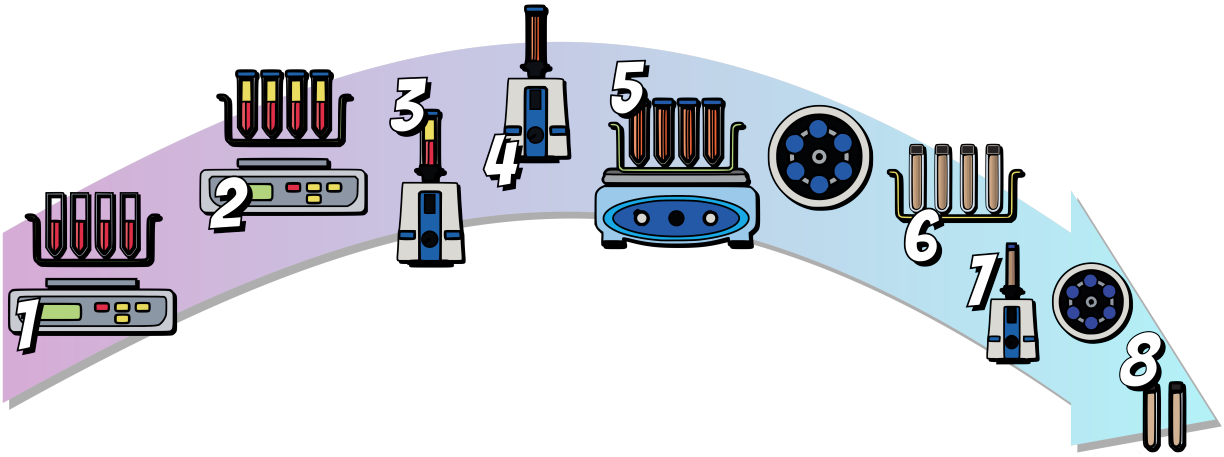

Figure 1.1: A general QuEChERS workflow for the analysis of high water-content matrices with labelled steps including weighing of 15 g of homogenized sample into an extraction tube (1), the addition of 15 mL of 1 % glacial acetic acid/acetonitrile (2), votexing (3), addition of salts and buffers (4), commencement of the liquid-liquid extraction with 15 minutes of shaking followed by a 5 minute centrifuge (5), supernatant treatment with dispersive solid-phase extraction sorbents (6), a final vortex and centrifugation (7) prior to supernatant analysis (8).

The extraction technique has demonstrated robustness and suitability for multiresidue pesticide applications, producing high recoveries (> 85 %) even for analytically difficult pesticides such as the highly polar (*e.g.* acephate, omethoate, mesotrione) and the base sensitive (*e.g.* imazilil, thiabendazole) in a wide variety of fruit and vegetable matrices.[5] All major limitations of the industry-standard QuEChERS-based methods are due to the method's poor scalability. Due to the variety of individual sample preparation steps required to complete the method, and automation has proven difficult. Existing automated systems have large laboratory footprints due to the robotic movement of the 10-50 mL sample tubes between solid powder dispensers, liquid dispensers, and centrifuges—yielding a

final extract which requires instrument coupling by the analyst. Improvements have been made yielding less convolved automation, such as pipette tip cartridges containing the sorbents required for clean-up, however still requiring the fruit-particulate-free extract from earlier steps.[11] Additionally, reliance on organic solvent, and fairly large sample requirements (*e.g.* 10-15 g) when compared to other more sample-limited analysis (*e.g.* neonatal, forensic) have opened the technique to *green* chemistry criticisms. We are left with the question, do techniques exist which limit solvent usage, energy requirements, and sample size while improving amenability to automation, speed of analysis, and integration of sample preparation steps?

Upon extraction of hundreds of compounds of interest, analysts are tasked with determining the ideal analytical approach for their detection and quantification. The analysis of pesticides in food and feed is completed via a separation technique of choice coupled to mass spectrometry (MS). Separation techniques are chosen depending on the chemical nature of the compounds under study, with the thermally stable and volatile completed in the gas phase, while the large, polar, thermally liable, or non-volatile in the liquid phase.[12] With regards to pesticide analysis, LC-MS based methods are regarded as having broader scope, which has only widened with the development of next-generation pesticides possessing LC-amenable characteristics.[13–16] As well, the coupling of liquid chromatography to tandem mass spectrometry (LC-MS/MS) instruments has resulted in substantial improvements in detection limits of select compounds when compared to GC-MS analyses.[13] In multiresidue pesticide analysis completed via LC-MS/MS, most methods utilize either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) ionization techniques. The former is more prone to matrix effects, which manifest as the suppression or enhancement of ion signal caused by co-extractives or interferences from the sample, while the latter suffers from generally lower sensitivities, and more limited compound compatibility.[17] As a result, ESI is the most common ionization method used in multiresidue pesticide analysis.[1,13,18] The use of a separation technique provides the analyst with the additional compound identification power of retention time, as well as proven precision, robustness, and automation capability. It is imperative to note however, that the figures of merit provided by LC-MS/MS are influenced by the sample preparation techniques applied, as extracts lacking adequate clean-up can result in higher limit of quantification

(LOQ) due to matrix effects and chemical noise, or more frequent instrument maintenance due to fouling of separation columns or detector components (*e.g.* MS source ion optics). Impressively, modern LC methods for multiresidue pesticide monitoring are capable of separation of 200+ compounds in single 15 minute analyses.[5] Compound confirmation with current instrumental methods is centered around the tandem mass spectrometry instrument used in the analysis (and not by retention time), specifically the acquisition of 2 product ions for both unit mass resolution and accurate mass measurement instruments.[19] One of which is used for quantitation of signal, and the other added compound confirmation. Again, a question concerning workflow optimization is proposed, could LC separation be side-stepped by a faster direct-to-MS technique if figures of merit of existing modern LC workflows are conserved?

The incumbent QuEChERS-LC-MS/MS suite of methodologies are more than adequate in the context of analytical figures of merit and cost of analysis—but again we reach shortcomings on the topic of scalability. Interestingly, pesticides, as possibly the most regulated and analyzed group of compounds in the regulatory environment, are present on goods frequently traded between regions—regions where maximum residue limit (MRL) differ by orders of magnitude.[8] Goods deemed for export from countries with relaxed pesticide MRLs are expected to comply with the legislation of the importing country, however it has been shown that violations of MRLs on fruit and vegetable imports in the US occur substantially more frequently then violations on domestic products.[8,20] With the growing trend of produce-rich diets being recommended to citizens in regions lacking the climate or agricultural capacity to quench the demand of year-round produce, there are fears of unexpected concentrations of pesticides slipping through regulatory cracks. With these threats recognized by regulatory bodies, one avenue (of the many) to reduce the economic and bureaucratic load of the analysis of an increasing number of imported produce samples is to investigate more efficient analytical methods.

1.2 Proven capability of solid phase microextraction techniques

The pursuit of integration of sample preparation techniques resulted in the development of solid-phase microextraction (SPME) in the early 1990s.[21,22] The technique was intended as a one-step tool for sample extraction, analyte pre-concentration, and instrument introduction. Pre-concentration is achieved via a polymer-coated solid support, where upon exposure to the sample in the liquid or gas phase, extraction of analytes of interest occur due to their high affinity for the coating[23] Initially envisioned as a gas-phase, equilibrium extraction, fibre-geometry technique, SPME has developed into a behemoth of versatility with a plethora of geometries, coating chemistries, instrument couplings, and multiresidue applications described in the literature.[23]

The technique today can be defined through two examples. For the analysis of volatile and semi-volatile compounds from complex matrices, headspace solid-phase microextraction (HS-SPME) is preferred due to the elimination of extraction of non-GC-amenable compounds, reducing instrument fouling. Alternatively, and with more relevance to the work to be proposed, direct-immersion solid-phase microextraction (DI-SPME) is completed by introducing the extracting media (*i.e.* fibre, blade, mesh) directly into the liquid sample. A huge leap for the growth of DI-SPME was the development of biocompatible polyacrylonitrile-based coating chemistries.[24] These novel coatings provided means for immobilizing extractive particles, while minimizing adherence of matrix particulate in the form of proteins and other biomolecules. The general DI-SPME fibre geometry workflow follows as such: the fibre sorbent coating is cleaned and preconditioned prior to sample exposure, the fibre is exposed to the liquid sample for some set extraction time then washed in water briefly to eliminate adhered matrix components, before finally desorbed in a solution formulated to best recover extracted analytes of interest prior to instrumental analysis. Due to space limitations, extensive background on past DI-SPME fiber pesticide multiresidue applications developed by Emanuela Gionfriddo, Érica A. Souza-Silva, and others will not be discussed, however the extraction-side method development steps undertaken (*i.e.* method development steps unrelated to instrument usage such as extraction time, and temperature), along with investigations of analyte-matrix binding behaviour

provide tremendous value and direction for the work to be proposed.[25–28] Encouragingly, the technique is no stranger to automation, with 96-blade automated systems used for the extraction, washing, desorption, and cleaning of SPME devices for whole blood analysis.[29] More fittingly, recent work completed using SPME provides the springboard to achieve the goals of automated, reduced sample size, and simplified multiresidue analysis—the direct coupling of SPME to MS.

Similarly motivated by analytical method simplification, the advent of ambient mass spectrometry (AMS) techniques in the mid-2000s allowed for the introduction and analysis of a sample of interest to an MS without sample preparation or separation, and at ambient pressure.[30–32] Substrate-spray techniques, such as paper spray (PS), use a consumable substrate to introduce the sample of interest upon the application of solvent and a potential difference of the appropriate magnitude to induce ESI.[32,33] PS uses a paper sheet cut into a triangle to either hold a drop of the sample of interest (*e.g.* blood or urine spot, fruit homogenate, crude oil spot) or as a tool to collect sample via wiping (*e.g.* fruit skin).[34–36] Upon sample deposition and drying, an ESI-compatible solvent is added to wet the paper substrate, and while applying voltage, ESI is observed through the formation of a Taylor cone at the point of the paper substrate. The technique has been demonstrated for a variety of multiresidue applications, and most importantly, amenable to automation, with a commercial autosampler available and novel devices allowing for high-speed sample introduction (*e.g.* 2.6 s per sample).[37,38] Even as a mature substrate-spray technique, PS does have a flaw with regards to compound ionization selectivity. Generally, the matrix under study undergoes no sample preparation before deposition onto the paper, thus resulting in the introduction of unwanted matrix components into the MS ion source, which can result in matrix effects via ESI and potentially more frequent instrument maintenance.[39,40] Attempts have been made in the coating of paper substrates with materials possessing extraction/pre-concentration capability, however paper substrates lack the structural robustness required for immersion and agitation in complex matrices to truly take advantage of the coatings pre-concentrative capabilities from larger sample volumes ($>$ 1 mL).[41,42]

The exclusion of any sample preparation steps, although provides simplicity, limits analytical figures of merit through increased matrix effects, limited compatibility with larger liquid samples, and decreased instrumental uptime due to introduction of complex

samples. Thus, the inclusion of a discreet sample preparation step within AMS techniques would address these limitations, and upon reviewing the growing portfolio of SPME to MS techniques, one can see that it has.[43]

1.3 Coated blade spray

Coated blade spray (CBS) is a substrate-spray technique developed and invented by Gómez-Ríos and Pawliszyn as an answer to the matrix-compatibility shortcomings of substrate-spray techniques such as PS.[44] The device, as shown in Figure 1.2, consists of a sharpened stainless steel support with the tip coated with a polymer sorbent of choice. The device is used as a DI-SPME geometry, with extraction facilitated by the polymer coating. Upon extraction, samples are directly introduced into a MS of choice through the application of a desorption solvent and voltage to generate ESI. Examples of polymer coatings used in CBS applications include polyacrylonitrile-C_{18} (PAN-C_{18}) and polyacrylonitrile-hydrophilic-lipophilic balance (PAN-HLB).[45] When compared to traditional fibre geometries, the blade possesses substantially larger surface area allowing for increased mass transfer rates enabling the use of fast extraction times.[46] Similarly, the high sensitivity of the technique is bolstered by the reduction of dilution during desorption due to the techniques small desorption volume (5-20 μL).[44] Not surprisingly, CBS has shown huge versatility, with modifications to the extraction phase, extraction time, sample temperature, sample composition, and desorption solution present as pursuable avenues to method development for a compound or group of compounds of interest. CBS as rapid technique for multiresidue analysis has been demonstrated for the determination of pharmaceuticals in wastewater, immunosuppressants in whole blood, as well as the quantitation of drugs of abuse in biofluids.[45,47–49] Initially completed manually in 2 mL LC vials, the technique has shown tremendous promise in scalability with the development of 96-blade cartridges (with a general workflow displayed in Figure 1.2) and automation systems enabling analyst-free blade cleaning, conditioning, extractions, and rinses.[29,49]

Limitations of CBS are primarily sourced from the ionization and introduction of all compounds of interest and co-extractives from the matrix simultaneously. Isobaric inter-

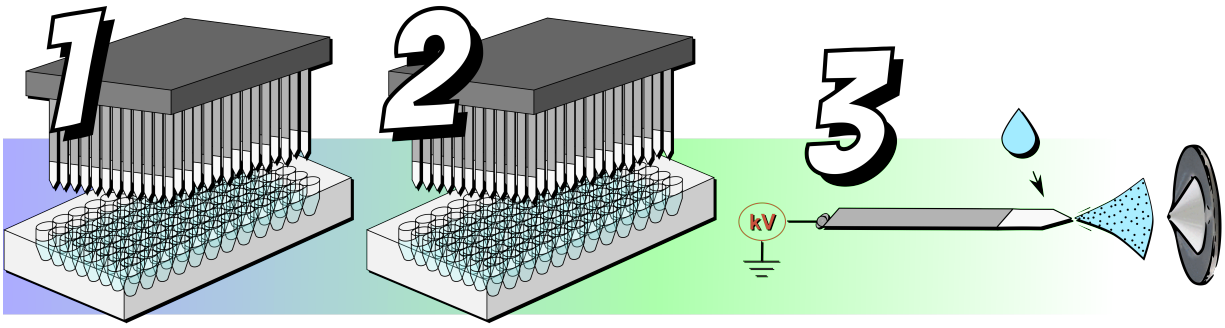

Figure 1.2: A general CBS workflow for the analysis of liquid matrices with labelled steps including the extraction of the sample of interest (shown in the 96-well plate format) (1), the rinsing step employed to remove non-specifically bound matrix components and salts (2, shown with the usage of water), and finally the coupling of the blade to the MS instrument of choice via desorption solvent and voltage application (3).

ferences, even on tandem unit-mass resolution instruments, are a limitation for all direct-to-MS techniques, with attempts to overcome them made with multiple-stage trapping mass spectrometry (MS^n) instrumentation.[50] With a substantial increase in number of compounds of interest comes an increase in the observations of these limitations, as is expanded in later chapters of this thesis.

Further limitations relate to equilibrium extraction techniques (*i.e.* SPME), as analyte extraction occurs in competition with matrix components. Analytes with specific characteristics (such as the hydrophobic in aqueous matrices) may be significantly bound to matrix particulate, significantly reducing the free concentration of the analyte (*i.e.* the proportion of analyte amenable to extraction) as simplified in Figure 1.3 below.

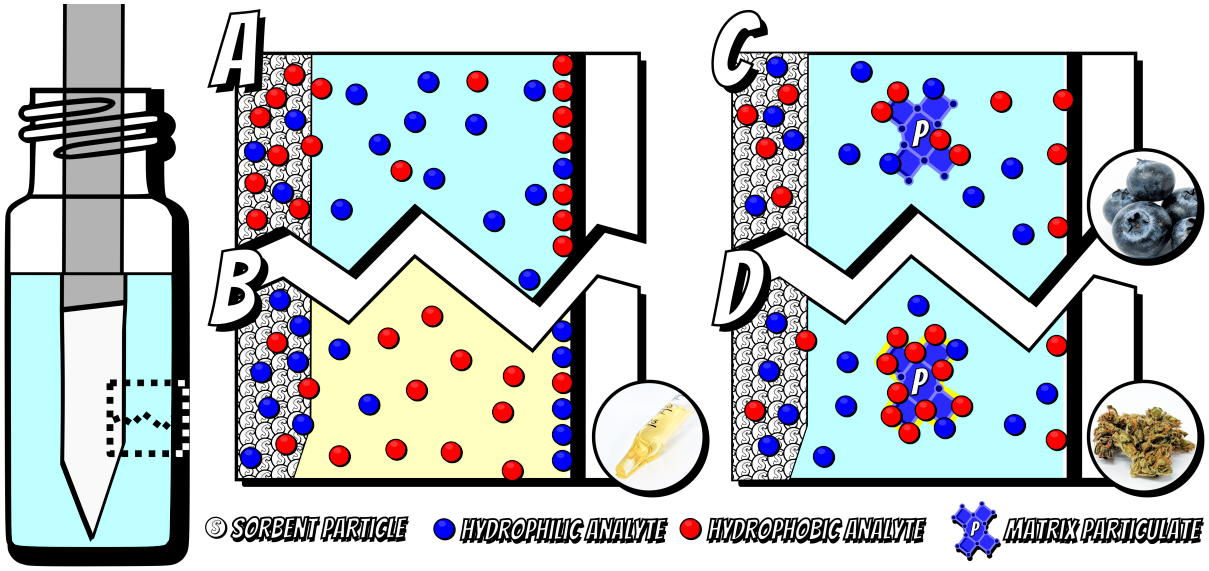

Figure 1.3: A simplified diagram of analyte behaviour in relevant matrices in this thesis. In A, a particulate-free aqueous sample displays high hydrophilic analyte partitioning in the matrix compared to binding/adsorbant sites found on the sorbent particles introduced with the SPME device (important to specify the validity of this simplification only holds for adsorbent extraction phases) and the surface of the vessel, while a reverse is shown for hydrophobic analytes, with greater partitioning coefficents for binding/adsorbant sites. In B, the reverse behaviour for both types of analytes is hypothesized, due to the hydrophobic nature of the matrix (*i.e.* agriculturally-derived oils). In C and D, the results of the introduction of a particle into an aqueous environment is demonstrated, with differing adsorbant characteristics (reduced and increased binding affinity in C and D, respectively), which is hypothesized in as behaviour occurring in high-water content, pectin and cellulose rich matrices such as fruits (C), and in high lipid content, low water content matrices such as cannabis flower (D).

1.4 Leveraging instrumental advancements

At the backbone of AMS techniques mentioned is the instrument they are coupled with. Advances in instrument speed, mass resolution, and sensitivity open doors for novel sample introduction methods. As an example, tandem mass spectrometry (MS/MS) and MS^n instruments substantially increased the signal-to-noise of LC coupled to MS, with their ability to filter solvent adducts, and confirmation power of multiple fragmentation exper-

iments.[13,51] Similarly, instrumental hardware improvements can have tremendous impacts on the work of researchers but are often hidden in the bullet points of an instrument's promotional brochure. As an example, with direct impact on multiresidue analysis via LC-MS/MS: the improvement in collision cell electronics in triple-quadrupole instruments. Due to the sensitivity and compound confirmatory benefits of selected reaction monitoring (SRM), the acquisition mode is used extensively in multiresidue pesticide methods. The speed limitation of SRM is found in the flight time of the ion through the ion path of the instrument, reduced by the ion momentum loss in the collision cell (Q_2).[52] This limits the scan rate through a list of SRM transitions of interest due to two reasons. If the ion path is inadequately purged of the prior introduced transitions, lingering ions could result in false positives of subsequent measured transitions. Additionally, if the duration of the transition signal collection time, known as dwell time, is shorter than the time required to traverse the ion path to the detector, substantial ion signal loss is observed. These manifest as limitations to the number of transitions that can be cycled through in a method before observing a reduction in quantitation abilities.[53,54] The response to the ion path slow-down has been the development of a so-called *active* collision cell, which compensates for momentum loss by acceleration of ions through the Q_2 via dynamic electrical potentials.[6,55] The improvement enables the monitoring of upwards of 500 SRM transitions per second with no sensitivity loss, enabling future MS/MS multiresidue work via CBS, as the wide compound extraction coverage offered by SPME can be experimentally demonstrated with the simultaneous extraction, ionization, and targeted monitoring of multiresidue experiments with tens to hundreds of compounds.

Chapter 2

Amenable to automation and proof-of-concept

2.1 Preamble

The following chapter contains sections that have already been published as an article in *Analytical Chemistry*. The contents of the article *Breaching the 10 Second Barrier of Total Analysis Time for Complex Matrices via Automated Coated Blade Spray* (*Analytical Chemistry*, **2019**, 91(20), 13039–13046), co-authored by A. Kasperkiewicz, G. A. Gómez-Ríos, D. Hein, and J. Pawliszyn have been modified to abide by University of Waterloo thesis format requirements and policies. The article has been adapted with permission from © American Chemical Society 2019. We are grateful to the Natural Science and Engineering Research Council of Canada for their financial support through an Industrial Research Chair program, and to the financial support of Restek Corporation. We would also like to thank our collaborators at Thermo Fisher Scientific, particularly Bradley Hart and Mari Prieto-Conaway, for their technical expertise as well as for lending us the triple quadrupole mass spectrometer that was used in this work. Thank you to Varoon Singh for synthesis of the particles used in this work and to Milaan Thirukumaran for assistance in preliminary data processing. Finally, we would like to extend our utmost gratitude to members of the University of Waterloo's Technical Services Department. Specifically,

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2.2 Introduction

Broadly speaking, the ability to integrate sampling, sample preparation, and analysis into a single analytical step allows for significant reductions in analysis time, analysis costs, and sources of error. This pursuit of total analytical method integration has motivated the development of many modern analytical techniques, such as AMS.[23,43,56–58] Specifically, the proliferation of AMS techniques has been fueled by the economic savings afforded by removing the sample-preparation and separation steps. Techniques such as desorption ionization mass spectrometry (DESI), direct analysis in real-time (DART), rapid evaporative ionization mass spectrometry (REIMS), and PS have leveraged lower costs, more comprehensive sample information, and faster analysis speeds to justify full analyst attention required for operation when compared to more robust, automated, separation-based technologies.[30,31,33,59] Analytical workflow automation and the integration of a sample handling system to a mass spectrometer have been leaps in the development of novel analytical techniques. Furthermore, reductions in analysis times and improvements in mass-spectrometer hardware have led to the development of additional direct-to-MS technologies——for example, online solid-phase extraction (SPE) systems, like RapidFire, and laser-diode thermal-desorption (LDTD), such as the Luxon—which have further increased throughput via automation.[60–64] Autosampler integration has also received considerable attention in the development of new AMS techniques. For instance, sample-slide handlers have been incorporated into DESI imaging sources to enable fully automated tissue imaging,[65] multi-sample holders have been fed through the DART ionizing gas stream to enable the analysis of 12-samples in under 2 minutes,[32] sample handlers fitted with a REIMS probe for high-throughput microbial colony analysis,[66] and a variety of PS autosampler concepts have been developed, with the more recent enabling instrument analysis times of 2.6 seconds per sample.[38,67] On the separation front, advances in ultrafast chromatography have allowed analysts to perform separations in a matter of seconds, although at the expense

of peak capacity, prompting the acceleration of direct-to-MS techniques.[68–70] AMS techniques can result in significant ion suppression when a complex matrix is collected on the substrate, thus limiting its quantitative performance, especially in ESI.[40,71] Enhanced technologies such as CBS may be able to provide faster, quantitatively superior results due to their ability to take advantage of SPME amalgamation of the sampling and sample preparation steps and the ease and speed of analysis offered by direct-to-MS techniques. Initially, CBS extraction and analyses were performed sequentially, on a sample by sample basis; however, high-throughput adaptations have allowed automated, parallel sample extraction using 96-sample batches, which have drastically decreased total analysis time.[49] In the high-throughput configuration, instrument-related requirements were the major bottle neck in analysis time. This was largely due to the time required to position the CBS device, apply desorption solution, and manually operate the instrument. Given the time savings offered by concurrent extraction, augmenting CBS with parallel blade preparation and positioning via an autosampler would appear to be a natural developmental leap forward (with a workflow for the automated coupling shown in Figure 2.1). As a precursor to automated coupling, several MS parameter changes were investigated in this study in order to try to further reduce CBS-MS/MS analysis times. Decreasing the dwell time provides the benefit of either shortening the spray times required for equivalent analysis (*i.e.* the same number of compounds) or increasing the number of compounds that can be analyzed during the same spray time. However, it has yet to be explored how such changes affect CBS' analytical figures of merit. Additionally, we evaluated a CBS method development step in which extraction time is optimized using signal-to-noise ratio (S/N). Optimum performance (*i.e.* higher S/N) in direct-SPME-to-MS technologies is not necessarily attained with longer extraction times. A longer extraction time and a lack of separation during MS analysis can lead to the co-extraction of undesired molecules, which can result in higher noise (*i.e.* same SRM transitions) or ionization suppression. Shortened dwell times, spray times, and extraction times culminated in a 12-blade autosampler enabling analysis speed not possible manually. Leveraging reduced spray times and automated blade positioning, cocaine, fentanyl, and methamphetamine were analyzed in urine from 12 samples in 1.7 seconds. Similarly, reduced dwell times allowed for a substantial increase in the number of compounds which can be monitored concomitantly. As an application, automated CBS was

demonstrated to perform multiresidue pesticide screening and quantitation for 150 compounds from apple juice using both a targeted and untargeted screening approach on triple quadrupole and orbitrap instrumentation, respectively. Succinctly, the work presents the capabilities of automated CBS sample handling, novel pathways for method optimization of microextraction technologies for direct-to-MS coupling via signal to noise ratios, and the usage of one sample to perform both automated quantitative and automated qualitative analysis for multi-residue pesticide analysis.

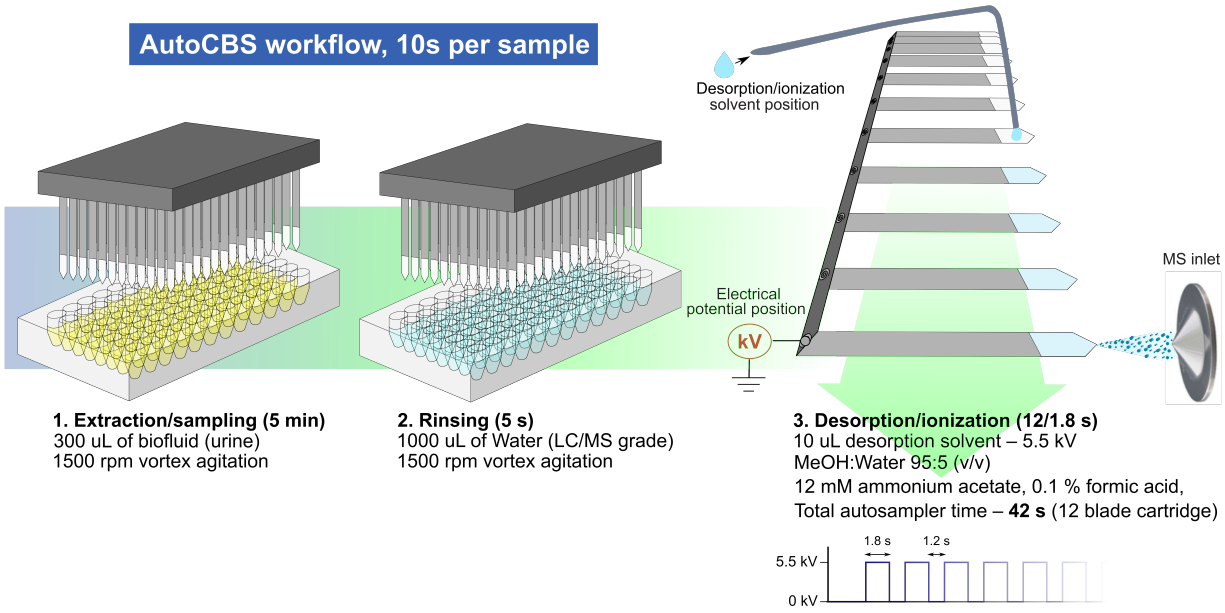

Figure 2.1: Proposed experimental setup for the extraction, desorption, and ionization of analytes from complex matrices via automated CBS.

2.3 Experimental

2.3.1 Materials and supplies

LC/MS-grade methanol (MeOH) and water were acquired from Fischer Scientific (Hampton, NJ, USA), while LC/MS-grade formic acid was acquired from Sigma Aldrich (St. Louis, MO, USA). A full list of model compounds and internal standards used can be found in Table A.2 in the Appendix. All model compounds and internal standards were acquired from Cerilliant Corporation (Round Rock, TX, USA). Deuterated analogues were used to correct for inter-experiment and intra-experiment variability. Pesticide application development was completed using the iDQuant standards kit from SCIEX (Concord, ON, Canada), with compounds of interest dissolved in acetonitrile (ACN). The deuterated analogues used for pesticide analysis were acquired from Toronto Research Chemicals (Toronto, ON, Canada) and included: atrazine-d_5, azoxystrobin-d_4, metalaxyl-d_6, cyprodinil-d_5, imazalil-d_5, and pyrimethanil-d_5. Organic apple juice (pH 4.6, 20 °C) was acquired from a local organic grocery store. Further details regarding the SRM transitions for the pesticides can be found Table A.1 in the Appendix. All standards were stored at original equipment manufacturer (OEM) concentrations (1000 or 100 μg·mL^{-1} in MeOH or ACN) at –80 °C. Human urine was collected from 5 healthy male donors and pooled. The stainless-steel blades that were used to manufacture the CBS devices were purchased from Shimifrez Inc. (Concord, ON, CAN). The blades were coated with hydrophilic-lipophilic balance (HLB) particles using a procedure that had been developed in-house, including particle synthesis as described and characterized elsewhere.[4,48,72] The coating length used were 10 mm with one-layer thickness (hypothesized thickness of $> 10\mu$m).

2.3.2 Analytical protocols

The CBS protocol can be simplified to four steps: 1.) analyte preconcentration/extraction onto the blade; 2.) blade-coating rinsing; 3.) analyte desorption; and 4.) analyte ionization. All steps were examined for parameter changes that could potentially reduce analysis times, with close attention being paid to ensuring that quantitation was minimally im-

pacted. In all model compound experiments, analyte extraction was completed using the 96-well-plate CBS holder assembly, which has been described in detail elsewhere.[49] Extractions were performed from 300 μL sample volumes (human urine) and vortexed at 1500 rpm for 15 minutes. The same 96-well-plate CBS holder assembly was also used for the dwell-time and shortened-spray experiments, as well as for the extraction time optimization experiments, which were performed with variable extraction times (5 min, 7.5 min, 10 min, 15 min, 20 min) at a concentration of 1, 2.5, 5, and 10 ng·mL^{-1}. Similarly, the automated CBS experiments were completed using extraction times of 5 minutes, with identical equipment. Pesticide analysis of apple juice was performed using the 96-well-plate CBS holder assembly with 2 mL plates. For these tests, extractions were performed from 1.5 mL samples, which were agitated at 1500 rpm for 15 minutes. The blade-coating rinsing step remained constant for all experiments: 5s of rinsing and vortex agitation at 1500 rpm in water. This step was completed in duplicate for all experiments.

2.3.3 Autosampler interface

The autosampler hardware system was co-designed and manufactured by Professional Analytical System Technology (Magdala, GER) and the University of Waterloo. Changes to the electric potential application assembly were completed by Science Technical Services at the University of Waterloo (Waterloo, ON, CAN). The autosampler is composed of a stepper motor that moves the 12-CBS cartridge (a plastic component made of polytetrafluoroethylene with one internal electrical connection per blade slot, and insulates each blade from adjacent blades), a solvent pump, a solvent reservoir, and an electric potential application brass spring (see details in Figure 2.2). The stepper motor delivers blades sequentially to the electric potential application position (*i.e.* spray position) following the application of desorption solution, which occurs at the solvent application position. The movement intervals between positions and the actuator speed can be set to control the desorption time and, consequently, the maximum spray time. The solvent application pump, which deposits 5 μL per drop, can also be programmed to deposit varying numbers of drops. The autosampler was coupled to the mass spectrometer by modifying the CBS source that has been described elsewhere.[44] Synchronization between the autosampler

and the instrument was completed via connection to the peripheral port and by adjusting contact closure settings.

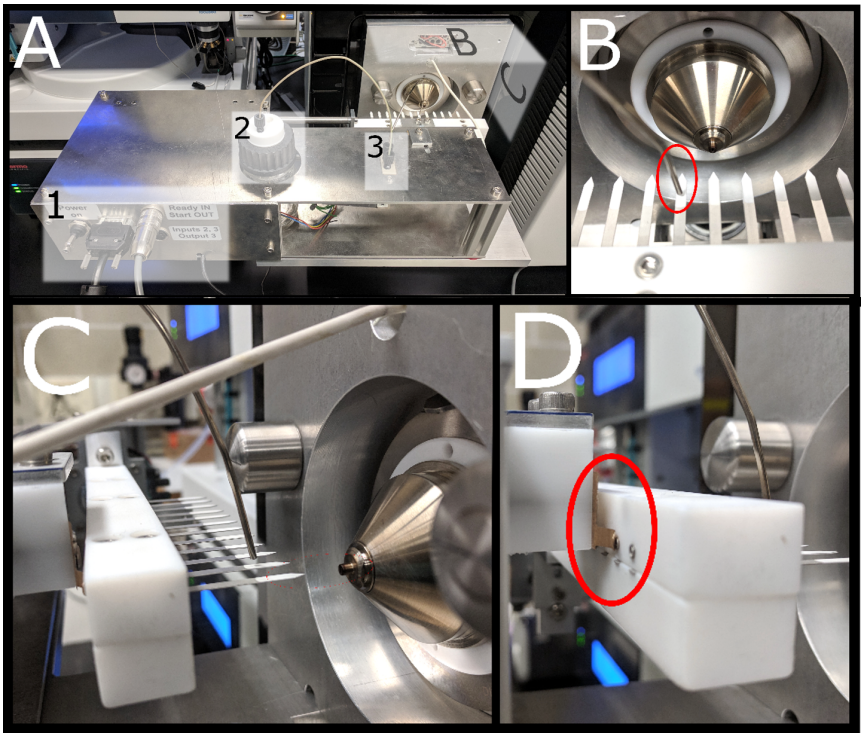

Figure 2.2: The 12-blade autosampler developed for CBS. Enclosed in the metal housing (A) is the stepper motor, stepper motor controller, solvent bottle (2), uL solvent pump (3), and the high-voltage passthrough cable from the instrument. The I/O panel (1) contains a DC power port, USB connection to the computer used for autosampler programming, and a connection to the peripheral input of the MS (enabling sample sequence coordination with the autosampler). Solvent is deposited onto the blade surface through a stainless-steel tube (circled in B, side-profile in C). Voltage is applied to the blade via a metal passthrough the 12-blade cartridge (circled in D).

2.3.4 Mass-spectrometer parameters

All model compound experiments were performed using a TSQ Quantiva from Thermo Scientific (San Jose, CA, USA), with data analysis complete using TraceFinder 4.1, also from Thermo Scientific. high-resolution mass spectrometry (HRMS) pesticide analysis ex-

periments were completed using an Exactive Orbitrap from Thermo Scientific. All manual CBS desorption and ionization experiments were performed using a custom CBS source that was built at the University of Waterloo, mentioned prior. The desorption solution was composed of MeOH/water (95:5 v/v), 0.1 % formic acid, and 12 mM ammonium acetate. Experimental CBS conditions for each experiment are displayed in Table 2.1. Following analyte desorption, 5.5 kV voltage was applied to initiate electrospray at the tip of the blades, which enabled ionization and the introduction of the analytes to the entrance of the mass spectrometer. Transfer line temperature was set to 350 °C. Orbitrap analysis was completed at a resolution of 100,000 at 1 Hz, transfer line temperature at 275 °C. Positive ESI was used for all analyses, and MS/MS compound transitions and conditions were optimized via direct infusion from methanolic and acetonitrile standards (see Table A.2 and A.1 in the Appendix).

Table 2.1: Instrumental and experimental conditions.

Experiment	**Desorption time (s)**	**Spray time (s)**	**Dwell time (ms)**
Dwell time	20	22	50, 25, 10, 5
Extraction time vs S/N	20	22	5
Automated CBS drugs of abuse	12	1.8	5
Automated CBS rapid spray	12	< 0.1	1
Automated CBS pesticides	12	5	1

2.3.5 Compound classification

The CBS workflow was only altered once comparable results had been achieved with respect to linearity, accuracy, precision or relative standard deviation (RSD), and LOQ. Calibration curves for all experiments were made in the range of 0.05 to 100 ng·mL^{-1}, and three validation points at 3, 30, and 90 ng·mL^{-1} were used to quantify precision and accuracy. LOQs were determined as the lowest calibration point with precision values below 20% across replicates (n = 4). The classification of pesticides into screening, semi-quantitative, and quantitative brackets was completed using figures of merit for linearity, precision, and accuracy. Compounds were classified as quantitative if they were able to

yield excellent precision (RSD < 15%), and accuracy (80 - 120%) for all calibration and validation points. In contrast, compounds were defined as semi-quantitative if they yielded reduced precision (RSD < 30%) and accuracy (70 - 130%). Compounds not meeting the requirements for quantitative or semi-quantitative classification were deemed amenable for screening applications and the limit of detection (LOD) was stated as the concentration yielding a S/N of greater than 3. The fitting method used for all compounds was weighted least squares regression, weight by 1/x.

2.4 Results and discussion

2.4.1 Decreasing dwell time with constant spray time

If one wishes to reduce total analysis time, one must find a way to decrease the time required for each step of the workflow. MS analysis time can be decreased by shortening the spray event, which can be achieved by using faster transition scanning (*i.e.* shorter dwell time per SRM). Dwell times were systematically decreased with spray time held constant in order to verify comparable figures of merit. The dwell times investigation during these experiments were 50 ms, 25 ms, 10 ms, and 5 ms. Comprehensive analytical figures of merit are shown in Tables A.3, A.4, A.5, and A.6 in the Appendix, respectively. Median LOQs remained statistically unchanged across dwell times at $ng \cdot mL^{-1}$, which suggests no relationship between S/N and dwell time, for the range tested. SRM dwell times down to 1 ms have been validated for the instrumentation used in the study, largely due to ion transmission enhancement.[6,55] Thus, unchanged LOQ, slope, accuracy, and precision qualifiers with dwell time reduction were expected, and they encouraged further CBS refinement through spray time reduction.

2.4.2 CBS-MS provides continuous, constant signal during the spray event

Prior to the experiments examining shortened spray and dwell times, a preliminary experiment was conducted using a dwell time of 5 ms and a spray time ion chronogram of 22 s. The 22 s spray events were selectively integrated at different time points for the length of the shortened spray experiments, simulating shortened spray events. A visualization of the ion chronogram integration windows and their effects on the analyte signals is shown in Figure 2.3. Figures of merit for all compounds at all integration windows ($n = 3$) were comparable with minimal corrected slope differences (< 1 %) and marginal LOQ differences (Tables A.7, A.8, and A.9 found in the Appendix). Good linearity ($R^2 > 0.99$) was observed for most compounds, which, when coupled with unchanging slopes, suggests signal continuity throughout the spray event. Due to the bottle-necking in CBS analysis that occurs as a result of the time taken to operate the instrument, it is necessary to validate the shortened spray parameters. Shortened spray experiments were conducted with a 5 ms dwell time and a spray time of 1.8 s. The shortened-spray experiment used standard CBS methodology and the adapted time-saving parameters; the data produced from this experiment was then compared to results produced by the standard 50 ms dwell time, 22 s spray time method. As shown in Table A.10, comparable results were observed regardless spray length. Comparable slopes were obtained (< 1 % difference) for all experimental groups, along with median LOQs of 2.5 ng·mL^{-1}, which were comparable to those obtained using the standard 50 ms dwell time, 22 s spray time methodology. With the LOQs of all but one compound, clenbuterol, remaining under the World Anti-Doping Agency (WADA) 2019 minimum regulatory performance limit (semantically identical to MRL) (MRPL) (Table A.2), the MS parameter changes were deemed suitable for implementation in the automated CBS workflow. As previously reported, it has proven difficult to reach the MRPL for clenbuterol without adding a chromatographic step due to the co-extraction of isobars that share the same MS/MS transition set (m/z 277 $\longrightarrow$ 203). However, some possible solutions have been reported, including MS-through-time analysis, which would allow more comprehensive and compound-specific transition set to be monitored thus yielding LOQs below the MRPL.[50,73]

2.4.3 Reduced extraction time signal-to-noise optimization

As a final investigation prior to implementing the automated CBS workflow, a series of experiments were conducted with human urine to better understand the relationship between S/N and extraction times (5 min, 7.5 min, 10 min, 15 min, and 20 min). For all compounds, S/N remained constant or decreased as extraction times increased. This relationship is shown for select compounds in Figure 2.4. Although further time profile experiments are required to fully characterize the equilibrium times of the compounds tested, the resultant data provides a new perspective on CBS method design. Since all compounds are introduced simultaneously in CBS, extracted interferences are expected to impact detection limits to a greater extent than in methods that include a separation step. Decreased S/N with greater extraction times may be due to several reasons. Increased extraction of interferences with the same SRM transition with longer extraction time (*i.e.* more lipophilic substances which take longer to reach equilibrium), or the increased extraction of interferences that suffer in-source fragmentation yielding fragments with the same SRM transition, or the increased extraction of interferences that cause ionization suppression at an equal or greater rate than the target compounds, or a combination of all possibilities. Further experimentation is required in order to draw definitive conclusions about the cause of the reduced S/N; such experiments should incorporate LC-MS/MS in order to monitor both the target compounds and the interference concentrations over time, without convoluting these concentrations with potential ionization suppression effects. Regardless, lower extraction times were validated as yielding the same or greater S/N for the target compounds, which further reduced total analysis times, as well as suggesting that the equilibrium time may not be the optimum extraction time for CBS method development.

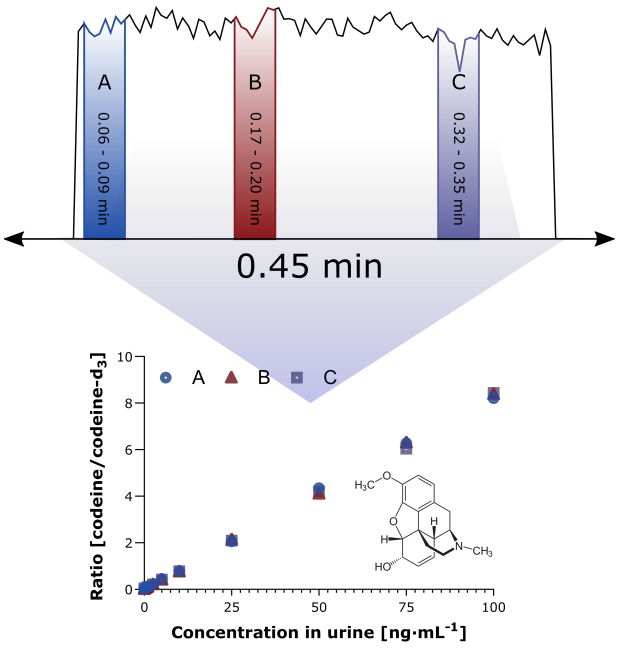

Figure 2.3: Consistency between the signal and figures of merit was observed for all three analyzed segments of the CBS signal, which suggests CBS-signal continuity. Quantitative analysis of urine spiked with codeine (0.5 to 100 ng·mL^{-1}) and its isotopologue, codeine-d_3 (10 ng·mL^{-1}). The signals for segments A, B, and, C are superimposed.

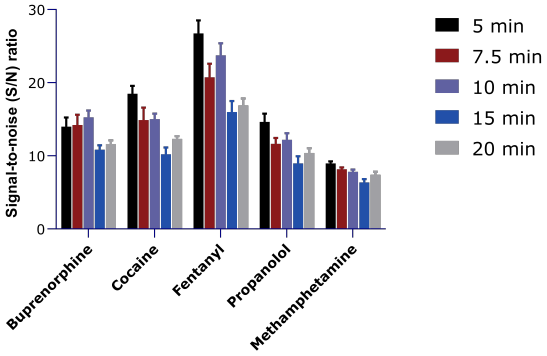

Figure 2.4: Relationship between S/N and extraction time (extraction completed for designated time at 1500 rpm vortex agitation).

2.4.4 Autosampler utilization for rapid spray events

Once the method parameters had been validated for the compounds of interest using manual CBS, they were applied to the autosampler. Using an extraction time of 5 minutes, a desorption time of 12 seconds, and a spray time of 1.8 seconds with the dwell time set at 5 ms, we were able to achieve figures of merit for the suite of model compounds that were comparable to those obtained in short-spray experiments (Table 2.2). Moreover, we were able to achieve a total sample analysis time of less than 10 seconds (3.2 s [sample preparation time] + 1.8 s [instrument time]); as such, automated CBS' analysis speed for detecting drugs of abuse in urine is comparable to online-SPE-MS and LDTD methods,

both of which are recognized for their speed.[74,75] However, the signal generated via CBS is not Gaussian; it is an adjustable continuous square wave. Thus, the number of compounds that can be monitored is not limited by mass-spectrometer performance (*i.e.* scan rate) but by signal generation time. Employing lower dwell times and decreasing the number of compounds to be monitored allows for the spray event to be shortened even further. As shown in Figure 2.5, it is possible to achieve quantitative spray events on the order of 100 ms at dwell times of 1 ms for 6 monitored compounds (3 compounds + 3 IS), with 12 samples run in less than 1.7 seconds. Analytical figures of merit for the rapid automated CBS analyses can be found in Table 2.3.

Table 2.2: Figures of merit for the quantitation of multiple analytes in human urine via automated CBS-MS/MS.

Compound	LogP	Slope	Intercept	R^2	LOQ ($ng \cdot mL^{-1}$)	A (n = 3), % 30 $ng \cdot mL^{-1}$	P (n = 3), % 30 $ng \cdot mL^{-1}$
Salbutamol	0.4	6.60E-02	6.40E-02	0.999	10	113	5
Oxycodone	1	2.40E-01	-5.00E-01	0.998	10	112	9
Codeine	1.2	1.40E-01	-6.20E-02	0.996	2.5	95	3
Cocaine	2	2.10E-01	-2.50E-02	0.999	0.5	96	6
Methamphetamine	2.2	2.30E-01	-9.90E-02	0.999	2.5	102	2
Bisoprolol	2.3	1.10E-03	3.30E-03	0.999	5	105	5
Trenbolone	2.5	2.30E-03	1.90E-02	0.998	10	120	12
Diazepam	2.6	2.50E-01	-1.90E-01	0.999	2.5	103	9
Carbamazepine	2.8	8.90E-02	5.10E-01	0.989	10	116	5
Clenbuterol	2.9	2.60E-01	-8.20E-02	0.999	2.5	110	8
Propanolol	3	4.90E-01	-1.40E-01	0.999	1	99	4
Citalopram	3.6	9.60E-02	3.70E-01	0.995	10	105	6
Fentanyl	4.1	1.30E-01	-3.50E-02	0.999	0.5	100	1
Methadone	4.1	2.00E-01	-4.00E-02	0.999	1	98	2
Buprenorphine	4.5	2.40E-01	-1.70E-01	0.999	1	94	4
Sertraline	5.1	1.00E-01	3.60E-03	0.999	1	95	8

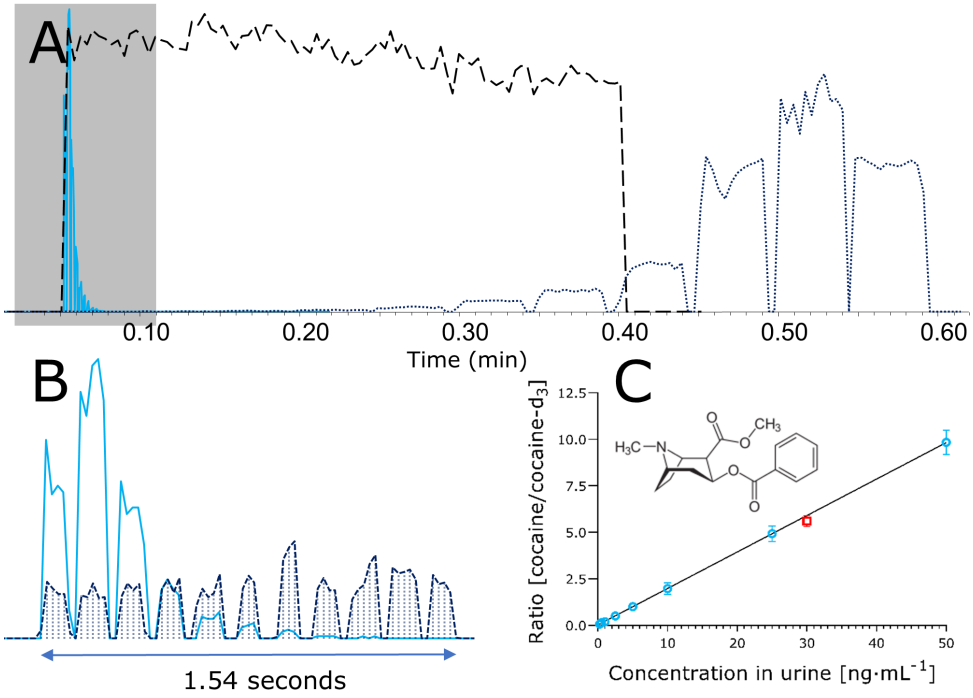

Figure 2.5: Autosampler integration into CBS urine analysis for drugs of abuse. (A) 22 s, 50 ms dwell time spray event (dashed line); 12-sample, 36 s, 5 ms dwell time spray event (dotted line); and 11 sample (blank sample not shown), 1.54 s, 1 ms dwell time for 6 compounds (grey). (B) Grey area in (A) enlarged with internal standard chronogram (dark blue) overlaid on analyte calibration curve (left to right 30 ng·mL^{-1} validation point followed by calibration curve 50 to 0.1 ng·mL-1) (blue) with scans. (C) Quantitative analysis of urine spiked with cocaine (0.1 to 50 ng·mL^{-1}) and its isotopologue [cocaine-d^3] (10 ng·mL^{-1}) using the rapid CBS method.

Table 2.3: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 1 ms with a 12-blade calibration curve.

Compound	Slope	Intercept	R^2	LOQ (ng·mL^{-1})	Accuracy, % 30 ng·mL^{-1}	Precision, % 30 ng·mL^{-1}
Methamphetamine	2.96E-01	5.73E-02	0.9956	1	101.9	4.7
Cocaine	1.96E-01	2.27E-02	0.993	0.25	95	5.3
Fentanyl	1.61E-01	-5.34E-03	0.9932	0.5	97.5	3.6

2.4.5 Culmination of MS-side refinement to yield a 400 transition CBS method

To demonstrate the capabilities of MS and CBS optimizations explored in this study, a multiresidue pesticide analysis was conducted. Operating at dwell times of 1 ms, 400+ transitions were monitored via automated CBS (206 compounds and 6 internal standards) (Table A.1). Of these compounds, 165 were found suitable for screening or quantitation. The poor analytical figures of merit (non-linearity, no-signal, irreproducibility) for the remaining compounds were found to be caused by sub-optimal coating chemistry, extraction conditions, or poor amenability to positive mode ESI. This was expected, as the method was designed with little focus on SPME optimization; rather, it was designed to showcase the ability of automated CBS to perform multiresidue analysis. Thus, future research might explore optimization possibilities for the SPME component of this method. Abridged figures of merit are displayed in Table 2.4, with comprehensive results available in Table A.11 in the Appendix. MRLs based off European Regulation (EC) No. 396/2005 of the European Parliament listed with whole apple used as the best match for the tested matrix of apple juice. While a host of compounds were analyzed, pesticides most frequently quantified and those most frequently found to violate the MRL in apples were of interest. In 2016, boscalid and chlorantraniliprole were detected in levels that exceeded EU LOQs in 21.0% and 9% of apple samples (n = 1680), respectively.[9] These compounds are quantified under the MRL via the automated CBS method applied. The method's total sample analysis time was less than 15 s (9.5 s [sample preparation time] + 5 s [instrument time]). In contrast, traditional LC-MS/MS methodologies for multiresidue quantification require 15 minutes per sample for instrument time alone.[5] However, the benefit for this time-cost is the separation of potential interferences and the additional compound confirmation power of retention time.

Isobar and isomeric challenges

In this application, compounds within a larger set of compound targets can be isomeric, and unable to be individually quantitated via MS. Examples of such compounds include prometon, secbumeton, and terbumeton. Additionally, the larger the set of target

Table 2.4: Figures of merit for the quantitation of multiple pesticide residues in apple juice via automated CBS-MS/MS

				MRL	LOQ	A ($ng \cdot mL^{-1}$), %			P ($ng \cdot mL^{-1}$), %		
Compound	**LogP**	**IS**	**R^2**	**($ng \cdot mL^{-1}$)**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Oxamyl	-0.5	Metalaxyl-d_6	0.9858	10	5		109	97		5	11
Acetamiprid	0.6	Metalaxyl-d_6	0.9315	800	5		98	100		8	7
Pirimicarb	1.5	Metalaxyl-d_6	0.9907	500	1	91	102	103	11	6	6
Carbofuran	1.8	Metalaxyl-d_6	0.9779	1	5		107	96		12	11
Carbaryl	2.4	Atrazine-d_5	0.9939	10	5		103	95		8	8
Myclobutanil	2.6	Atrazine-d_5	0.9845	600	5		103	103		4	9
Cyproconazole	2.7	Atrazine-d_5	0.9934	100	1	111	101	101	6	6	7
Fenobucarb	3	Atrazine-d_5	0.9901	-	5		102	97		2	3
Imazalil	3.6	Imazalil-d_5	0.9946	-	1	90	101	98	10	9	5
Siduron	3.7	Atrazine-d_5	0.9939	-	1	114	104	99	7	5	10
Benalaxyl	3.9	Azoxystrobin-d_4	0.9960	50	1	99	99	101	16	3	8
Boscalid	4.3	Atrazine-d_5	0.9726	2000	5		111	107		23	13
Azoxystrobin	5.1	Azoxystrobin-d_4	0.9991	10	0.5	101	100	100	5	3	3
Trifloxystrobin	5.1	Azoxystrobin-d_4	0.9909	700	1	127	93	102	28	20	17
Chlorantraniliprole	5.6	Azoxystrobin-d_4	0.9824	500	5		97	106		28	12

compounds, the higher probability of encountering chemical interference either from the target compounds, or from co-extractives in the matrix. As a potential solution, pesticide multiresidue analysis was completed in untargeted mode on a high-resolution mass spectrometer in order to eliminate interference from selected compounds in the screening bracket, which would in turn reduce the LODs achieved via SRM analysis to levels that fall below EU MRLs. As shown in Figure 2.6, several kresoxim-methyl and methomyl nominal-mass isobars are separated via Orbitrap MS, allowing for an order of magnitude reduction in LODs. The geometry of the CBS device, supported by the results of the intra-blade analysis of drugs of abuse, makes automated CBS's suitability for pesticide analysis intuitive; one side of the blade can be used for targeted analysis, while the other can be used for accurate-mass untargeted studies at different times. This double-sampling ability is predicated on leveraging the coated device's excess surface for repeat sample analysis, as has been shown with TM-SPME for more comprehensive pesticide analysis via DART.[48]

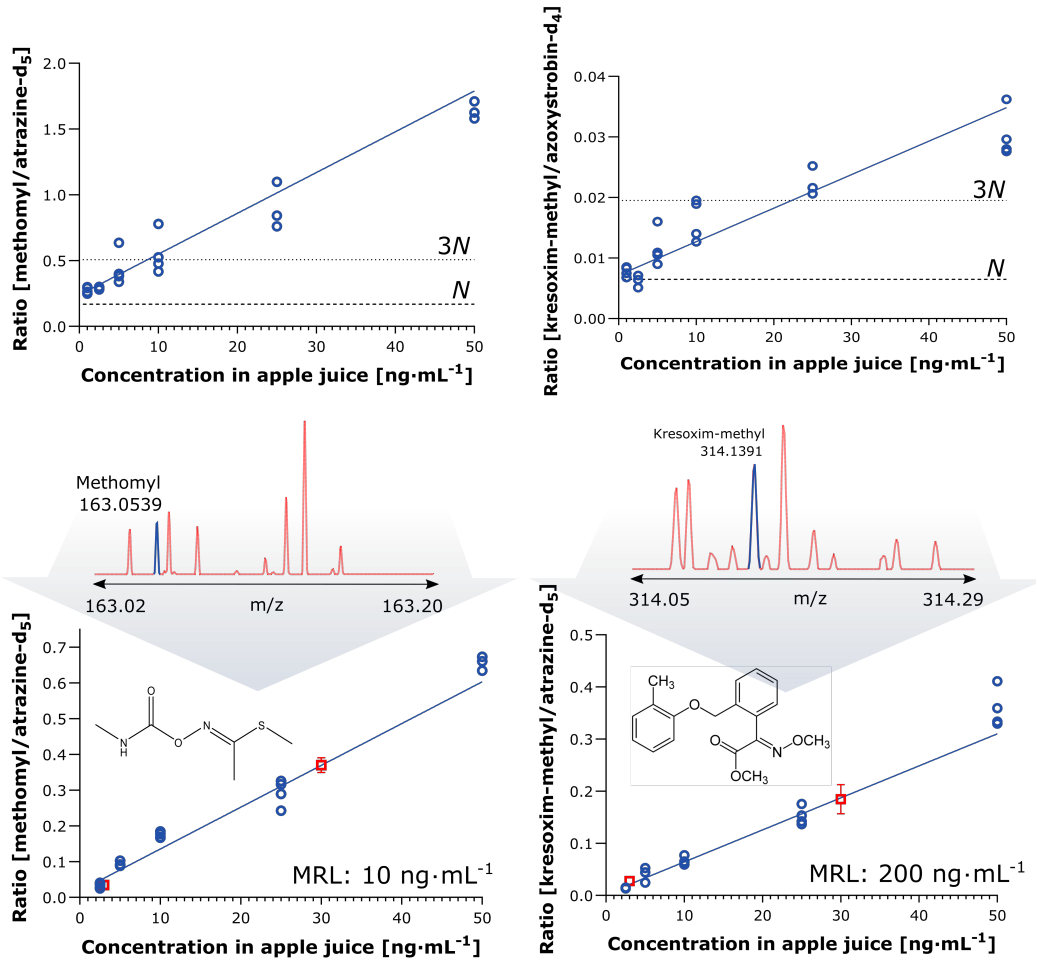

Figure 2.6: Improvement in limits of detection for methomyl and kresoxim-methyl via CBS-to-HRMS coupling. (top row) Calibration plots generated using the triple quadrupole instrument with all replicates. The dashed and dotted horizontal lines represent the noise (N) and three times noise (3N) qualifiers used for LOD determination, respectively. In both cases, LODs were determined to be 25 ng·mL^{-1}. (bottom row) Upon untargeted full scan acquisition via coupling to an orbitrap instrument, a narrow mass range was selected bracketing the mass peak corresponding to the compound of interest highlighting potential interferences in dashed red line within 1-unit mass resolution. Although no improvement in quantitation capability was made (due to conserved poor correction via internal standards), LODs were substantially improved due to the complete removal of noise for both target compounds, allowing for detection at 2.5 ng·mL^{-1}.

Pathways to improved figures of merit

Internal standard pairing is critical to yielding suitable quantitative results in an electrospray technique such as CBS.[76,77] Practically speaking, deuterated analogues of compounds of interest are ideal for correction. Since obtaining deuterated analogues for every compound of interest is unreasonable in multiresidue analysis, compromises must be made in CBS quantitation, such as using fewer internal standards. In this study, several compounds with strict MRLs (1 $ng \cdot mL^{-1}$), such as carbofuran derivatives, were unable to be quantitated (RSD $>$ 30 %) at acceptable levels; however, these compounds produced signal-to-noise values of more than 3 below the MRL. In future work, internal standard optimization with a more chemically representative internal standard panel may yield substantially improved figures of merit for poorly corrected compounds. Similarly, limitations in both ESI and instrument detector saturation impact the figures of merit of such a large set of compounds. All compounds of interest were extracted and analyzed simultaneously, which is not representative of the expected findings in samples where single-digit numbers of different residues are often the worst case. It is hypothesized that the signal response of certain or all analytes was in the nonlinear ESI regime due to the number and concentrations of analytes ionized simultaneously.[77] Thus, in a worst-case scenario, analyte sensitivity was measured with hundreds of pesticides competing for ESI capacity. In real samples with substantially fewer residues, perhaps higher sensitivity can be observed if the extraction of the matrix co-extractives does not, in an absence of pesticide residues, initially place the signal in the nonlinear regime.

2.5 Conclusions, self-critic, and future perspectives

This study has documented the coupling of CBS with autosampling, which vastly broadens the technique's applicability for high-throughput screening or quantitation. The impact of dwell time on quantitation was investigated and deemed insignificant with instrumentation used; this enabled the investigation of shortened spray experiments, which ultimately resulted in electrospray events of less than 1s. Novel S/N extraction optimization strategies were demonstrated to further reduce sample preparation times for drugs of abuse in human

urine, while instrument and sample preparation optimizations culminated in substantial reductions in analysis time when analysis was performed via automated CBS. The findings presented herein indicate automated CBS's parity with existing high-throughput solutions, as was demonstrated by the 1.7 s 12-sample quantitation of select drugs of abuse. Finally, advancements in mass-spectrometer technology were leveraged to produce a method capable of monitoring over 150 pesticides. This method, which also employed automated CBS, provided total per sample analysis times below 15 seconds and the ability to perform multiple analyses of the same sample on both HRMS and MS/MS instruments. Further improvements in the optimization of SPME coating chemistry, sample dilution, and organic solvent addition[25] will be pursued for improved figures of merit for multiresidue pesticide analyses. Design of experiments could have been beneficial to study parameters that are known to be confounding during the transfer of ions to the mass spectrometer such spray voltage, distance to the MS-inlet, temperature of the MS-inlet, declustering potential and auxiliary gas. Similarly during the analyte enrichment process, such as temperature of extraction, agitation speed, sample volume, and sample modifiers (*e.g.* ACN). In retrospect, auto-sampler validation and development would ideally have been performed using a representative panel of the future pesticides of interest. However, during the development of the autosampler it was not yet clear the feasibility of performing such a large number of compounds screening study considering the limitations of ESI as well as the capability of the triple-quadrupole used in the work. The proof of concept work did encourage further exploration of multi-residue pesticide screening in matrices with higher practical impact (*i.e.* analysis of whole apples is substantially more common than analysis of the derivative product of apple juice), along with evaluation of the performance of the technique with particulate-containing liquid matrices.

Chapter 3

Advancing to fruit pesticide analysis with validation via liquid chromatography

3.1 Preamble

The following chapter contains sections which have been accepted for publication as an article in *Food Chemistry*. The contents of the article *Multi-residue pesticide quantitation in multiple fruit matrices via automated coated blade spray and liquid chromatography coupled to triple quadrupole mass spectrometry*, *Food Chemistry*, **2021**, 331, *Just Accepted*, co-authored by A. Kasperkiewicz and J. Pawliszyn have been modified to abide by University of Waterloo thesis format requirements and policies. The article has been adapted with permission from © Elsevier 2020. We are grateful to the Natural Science and Engineering Research Council of Canada for their financial support through the Industrial Research Chair program. We would also like to thank our collaborators, German Gomez and David Bell at Restek Corporation, for providing the standards and column used in this work as well as financial support through the Industrial Research Chair program. We would also like to thank Thermo Scientific for lending the mass spectrometer and Mohammad Huq and Varoon Singh for the synthesis of the particles used in this work.

3.2 Introduction

Varying global pesticide regulatory limits and legislation coupled with the increasingly globalized produce trade can result in the concomitant import of significant pesticide residues.[8,20] Seasonality, produce-focused dietary trends, and climate restrictions result in the reliance of many countries on fruit import to meet demand. As a side effect, pesticide residue regulation can involve extensive product screening programs numbering in the hundreds of thousands of samples tested per year over tens of matrices for hundreds of pesticide products and additives.[9,78] The gold-standard sample preparation workflow for such analysis involves a form of sample homogenization followed often by a workflow based on the QuEChERS extraction technique[10] which has been demonstrated to be broadly applicable to many food matrices with minor modification, low cost, environmental impact, and cleaner final extracts when compared with solvent extraction (SE) protocols.[5,79] However, the technique suffers from significant sample, standard, and solvent usage, which results in non-trivial automation — a compromise for suitable sample preparation prior to chromatographic analysis. As a contrast, the advent of the field of AMS and the pledges of sample preparation-less and separation-free analysis methods have resulted in promising applications of pesticide screening in produce matrices—be it on-site or in-lab.[80] DESI and PS are two of such AMS techniques for which an assortment of applications has been described, with some spilling into food and pesticide residue analysis. For example, PS has been demonstrated as a pesticide screening tool for homogenized samples prepared with organic solvent dilution and with direct produce peel wiping as a sampling method, however with noted lack of elegance (*i.e.* spotting produce homogenate on cartridge impacting spray reproducibility, and the quantitation limitations of wiping protocols) in coupling of the sample preparation steps to the screening approach of PS and the confirmation approach of LC.[35,81] Similarly, untreated peel and homogenate sample analyses have been demonstrated with DESI with the encounter of ionization suppression from peel analysis with non-trivial internal standard application limiting quantitation efforts.[82,83] These difficulties warrant the investigation of hybrid methodologies that provide integrated sample preparation, the speed and simplicity of AMS, and ease of coupling to separation techniques for more robust analysis. Typical food control workflows involve screening of samples for contaminants of

interest followed by confirmation/quantitation of any suspected samples from the screening workflow. Given the substantial sample-load that regulatory agencies typically encounter, the incorporation of an AMS screening or quantitation tool to reduce analysis time, cost, and improve scalability while also remaining compatible with follow-up sample confirmation via LC-MS can prove beneficial.[84] Due to the cross-compatibility of CBS with both direct-to-MS coupling along with vial desorption for additional sample characterization or validation via chromatographic analysis, as demonstrated in previous SPME food analysis applications.[4,25,48,85] we were eager to explore the suitability of such an approach. Concisely, this work presents a workflow for the multiresidue (*e.g.* organophosphates, organonitrogen, carbamates, neonicotinoids, strobilurins, triazines, spinosyns) quantitative analysis of 126 pesticides in apples, 139 pesticides in blueberries, 136 pesticides in grapes, and 135 pesticides in strawberries via CBS-MS/MS and CBS-LC-MS/MS with a comparison of analytical figures of merit (*e.g.* linearity, accuracy, precision, LOQ), analysis properties (*e.g.* solvent usage, analysis time), and real sample quantification and comparison between techniques. The comparable results between methodologies (*i.e.* real sample percent difference > 30 % and comparable) support CBS-MS/MS as a rapid quantification tool for pesticides in the fruit matrices investigated, implementable as either a stand-alone workflow or as an *a priori* complement to LC-MS/MS validation required by regulatory bodies.

3.3 Experimental

3.3.1 Chemicals and sample preparation devices

LC/MS grade MeOH, ACN, and water were acquired from Fischer Scientific (Hampton, NJ, USA). LC/MS grade formic acid was acquired from Sigma Aldrich (St. Louis, MO, USA). LC/MS grade ammonium formate and ammonium acetate were acquired from Sigma Aldrich. Sodium acetate and acetic acid were acquired from Sigma Aldrich. Pesticide standards, acquired and used as part of a series of mixtures, totaling 204 compounds (LC Multiresidue Pesticide Kit), were provided in-kind by Restek Corporation (Bellefonte, PA, USA). Deuterated analogues used as internal standards (atrazine-d_5, carbofuran-d_3, cyprodinil-d_5, dimethoate-d_6, imazalil-d_5, kresoxim-methyl-d_7, malathion-d_6, metalaxyl-

d_5, methiocarb-d_3, oxamyl-d_6, spirotetramat-d_5, trifloxystrobin-d_6, fludioxonil-$^{13}C_2$) were acquired from Toronto Research Chemicals (Toronto, ON, CA). All standards were stored at OEM concentrations (1000 or 100 $\mu g \cdot mL^{-1}$ in MeOH or ACN) at –80 °C. The stainless-steel blades used for the manufacture of the CBS devices were purchased from Shimifrez Inc. (Concord, ON, CAN). The 5 μm HLB particles were synthesized in-house and have been characterized and described in detail elsewhere.[4] Blades consisted of a coating length of 10 mm were prepared and dip-coated with HLB particles via a procedure developed in-house, described elsewhere.[72]

3.3.2 Sample preparation

Fruit sample processing

Blank matrices (apples, blueberries, strawberries, and grapes) used for matrix-match calibration and validation were sourced from local grocery markets of the organic variety. Real samples were purchased during July – August 2019 from local grocery markets with species, country of origin, and purchase data recorded in Table 3.1. Matrices were cryoground in batches of 20 grams each, using a liquid nitrogen bath cryogrinder (6875 Freezer/Mill from SPEX SamplePrep, Metuchen, NJ, USA) until a fine powder consistency was observed (approximately 3 minutes). Ground matrices were stored in glass at -80 °C until use. The same protocol was used for the preparation of real samples. Grinding vessels were cleaned thoroughly with detergent, water, and methanol between samples.

Analytical procedures for optimization experiments, validation, and real samples

Standard spiking was completed by mass, with initial method optimization experiments utilizing batches of 10 ± 0.05 g of each matrix. A dilution level investigation was carried out by spiking 1.0 g, 1.5 g, 3 g, and 5 g of fruit homogenate with 50 ng/g of the pesticide mixture and subsequently diluting these mixtures with 9 mL, 6 mL, and 3 mL of water to yield 0.1, 0.2, 0.5, and 1 dilution levels, respectively. Final method validation was performed

Table 3.1: Real fruit sample information and labels.

Matrix	Internal Label	Sample Number	Country of Origin	State/Province
Apple	T3	Sample 1	NEW ZEALAND	-
	W1	Sample 2	CHILE	-
	Z3	Sample 3	NEW ZEALAND	-
Blueberry	T1	Sample 1	USA	CA
	S2	Sample 2	USA	CA
	Z1	Sample 3	USA	NJ
Grape	F10W	Sample 1	USA	CA
	S10W	Sample 2	USA	CA
	S3	Sample 3	MEXICO	-
	T2	Sample 4	MEXICO	-
	Z4	Sample 5	MEXICO	-
Strawberry	Z2	Sample 1	CANADA	ON
	F1	Sample 2	USA	CA
	S1	Sample 3	CANADA	ON
	T4	Sample 4	USA	CA

using spiked 1 ± 0.01 g aliquots of matrix per concentration level (i.e. calibration point, validation point, real sample) diluted in 9 mL water. Internal standards were spiked at the 20 ng·g^{-1} level for calibration and validation experiments. Calibration and validation working standards were spiked into the sample at the required concentration levels, with the undiluted fruit homogenate spiked to not exceed addition of more than 2 % organic solvent content (pre-dilution). Prior to extraction, spiked samples were incubated at 4 °C for 12 hours to allow for equilibration of pesticides in the biological compartments of the sample. Extractions were performed from 1 mL sample volume (corresponding to 0.1 g of fruit homogenate per sample) from all matrices at room temperature, with agitation (approximately 1200 rpm) for 15 minutes. A coating washing step in water of 10 seconds was implemented to remove matrix particulate from extracted blades prior to desorption for CBS-MS/MS or LC-MS/MS analysis.

3.3.3 Instrumental parameters

All experiments described were completed using a TSQ Quantiva from Thermo Scientific (San Jose, CA, USA), with data analysis completed using Trace-Finder 4.1 from Thermo Scientific. Positive ESI coupled with SRM mode was used for all analyses, and MS/MS compound transitions and conditions (found in Table A.1) were optimized via

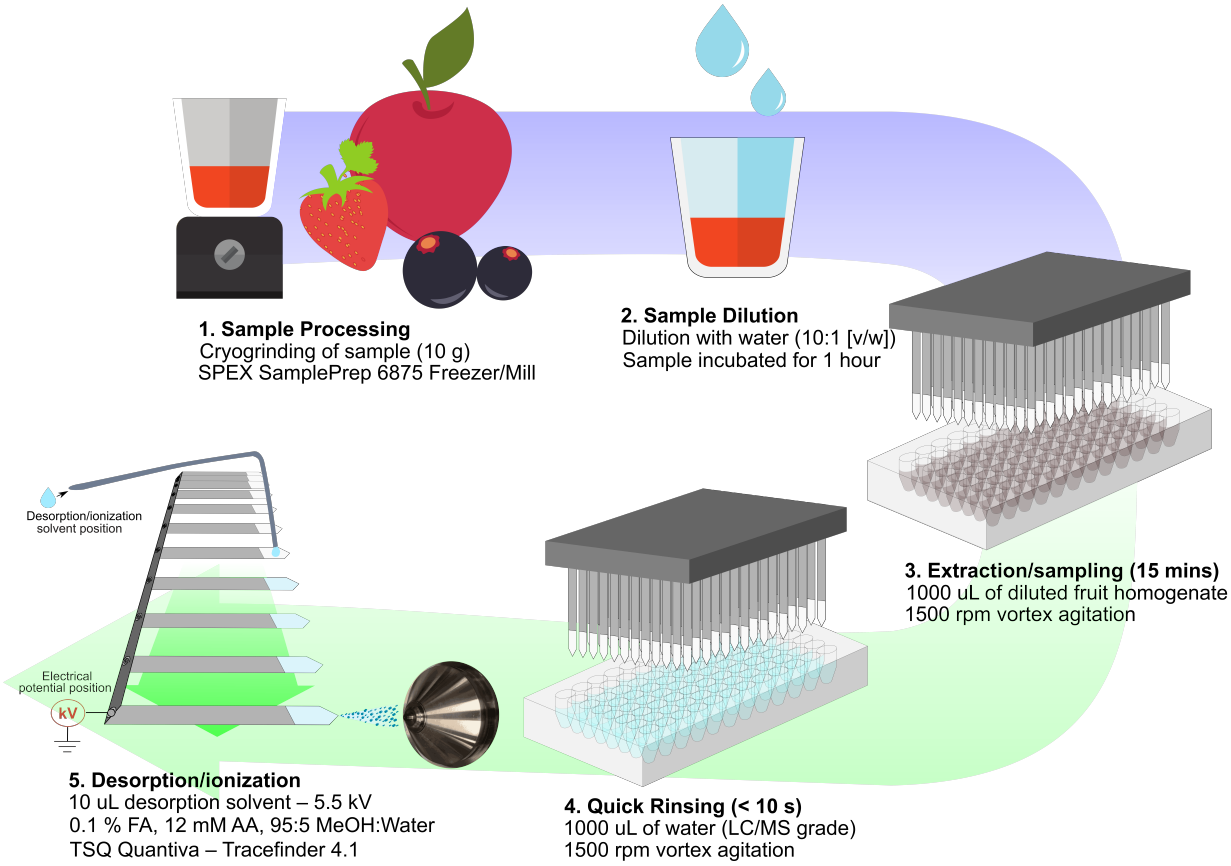

Figure 3.1: Demonstrated workflow for the analysis of pesticides in fruit matrices for CBS-MS/MS and LC-MS/MS analysis.

direct infusion from methanolic standards.

CBS-MS/MS analysis

All manual CBS desorption and ionization experiments were performed using a custom CBS source built at the University of Waterloo, which is described elsewhere.[49] Automated CBS analysis was performed using an autosampler built by Professional Analytical Systems Technology and modified in-house; its development and validation are described elsewhere.[86] The desorption solution used was 95:5 MeOH/water v/v, 0.1 % formic acid, and 12 mM ammonium acetate. All experiments utilized 10 µL of the desorption solution.

A desorption time of 12 s was used for both manual experiments and AutoCBS experiments. Upon analyte desorption, 5.5 kV voltage was applied for 10 s, resulting in the ionization and introduction of analytes to the MS entrance via the electrospray generated at the tip of the blade. A spray time of 10 s was chosen to provide 10 scans of each compound transition (both quantitation and confirmation) at a dwell time of 1 ms.

LC-MS/MS analysis

All separation experiments were performed with an Ultimate 3000RS UHPLC system from Thermo Scientific (San Jose, CA, USA) outfitted with an ARC-18 LC column (2.7 μm, 100 mm, 2.1 mm) provided in-kind by Restek Corporation. Separation conditions, gradient details, and mass spectrometry ESI parameters are available in Table 3.2 and Table 3.3.

Table 3.2: Liquid chromatography instrumental conditions and gradient program

LC Instrument	Thermo Fisher Scientific Ultimate 3000RS UHPLC
Guard column	Restek EXP guard cartridge ARC-18 (2.7 μm, 5 mm, 2.1 mm)
Column	Restek ARC-18 LC column (2.7 μm, 100 mm, 2.1 mm)
Mobile phase	A: Water with 2mM ammonium formate, 0.2 % formic acid B: Methanol with 2mM ammonium formate, 0.2 % formic acid
Column temperature	50 °C
Flow rate	400 μL/min
Total run time	9.5 minutes
Gradient program	initial conditions (5 % B), ramp to 60 % B by 2 min, ramp to 75 % B by 4 min, ramp to 100 % B by 6 min hold until 7.5 min, 5 % B at 7.51 min until 8.5 min.
Injection volume	10 μL

Analytical figures of merit

Calibration curves for all experiments were obtained in the range 0.01 to 100 ng·mL^{-1}. Four validation points at 0.8, 4, 40, and 80 ng·mL^{-1} were used to quantify precision and accuracy. LOQs were designated as the lowest calibration point with precision values

Table 3.3: MS ESI instrumental conditions

Instrument	Thermo Fischer Scientific TSQ Quantiva
Spray voltage	3500 V (+)/2500 V (-)
Sheath gas	45 Arb
Aux gas	13 Arb
Sweep gas	1 Arb
Ion transfer tube temp	342 °C
Vaporizer temp	358 °C

across replicates (n = 4) lower than 20 %. Analytical validation and performance criteria were followed based on EU SANTE/12682/2019 guidelines; namely linearity (deviation of back-calculated concentration from true concentration +/- 20 %), precision ($\leqslant$ 20 %), and accuracy (70 – 120 %). The CBS methodology identified several isobars amongst the compounds of interest; thus, combined analytical figures of merit are reported for those compounds.

3.4 Results and discussion

3.4.1 Importance of standard-internal standard pairing

The deuterated isotopologue is a hallmark of quantitative ambient mass spectrometric analysis, often used at a ratio to target compounds of approaching 1. Upon expansion of a set of targeted compounds to triple digits——as is often the case in the analysis of pesticides, veterinary drugs, and the pharmacopoeia——this implementation is quickly rendered economically, instrumentally, and practically unfeasible. One of the goals of the current work was to explore the usage of a small, although chemically diverse, number of internal standards (IS) for multiresidue ambient MS quantitation. For the analysis of fruit matrices for a multiresidue panel of pesticides via CBS-MS/MS, internal standard-analyte matching is of the utmost importance. In this study, target compounds were matched with IS *a posteriori* with a panel of internal standards (n = 13) added to the homogenized sample before dilution and extraction. Pairing of internal standards was completed by comparing

squared correlation coefficients (*i.e.* R) across the linear range tested, with the highest observed value selected for correction and further quantitation. The process was repeated for both LC-MS/MS and CBS-MS/MS analysis. Potential sources of inadequate correction can stem from misrepresentative IS behaviour during the extraction, desorption, or ionization processes, or from potential matrix-sourced interferences sharing the same SRM transition as the IS. There is room for additional IS optimization, specifically concerning the concentration of IS per sample. Ideally, the signal observed from the IS should be comparable to the signal observed from the analyte of interest; however, in such a diverse panel of analytes with differing ionization efficiencies, such fine-tuning was not explored, and all IS were spiked at one concentration for all matrices. Perhaps the most important goal of the report was to demonstrate that this internal-standard pairing approach (*i.e.* correction of $>$ 100 compounds with a comparatively small number $<$ 10 internal standards) can correct for matrix effects originating from both the extraction and ionization steps, allowing for the attainment of comparable quantitative results (+/- 20 %) between direct-to-MS and LC-MS methodologies as shown in Figure 3.3.[77]

3.4.2 Advantages of sample dilution

Dilution of complex, particulate-containing samples for SPME provides several benefits. From an extraction perspective, dilution of the sample can reduce the proportion of particulate surface area to water, reducing the proportion of analyte bound to matrix components and subsequently increasing the amount of analyte extracted.[25,87] This is particularly important when rapid analysis is desired and where the desorption kinetics from the matrix are slow. Simultaneously, the increased dilution of a sample (*e.g.* fruit homogenate) can result in the use of substantially less sample material per analysis, as well as less standard and internal standard usage, while also enabling practicality improvements in sample handling (*e.g.* volumetric sample distribution when compared to mass-based sample distribution). Similarly, as a SPME-to-MS technique, CBS is expected to be more susceptible to ionization suppression from matrix-sourced co-extractives or extracted compounds of interest than a SPME-LC-MS methodology. Due to the polarity range of the compounds under study (*e.g.* logP -1.2 [thiamethoxam] to 5.9 [etoxazole]) an analyte-matrix binding

component negatively impacting extraction was expected. Pesticide sorption to organic matter is well described in the literature for pesticide-soil systems and correlated with the octanol-water partition coefficient, and thus similar behaviour was expected in our fruit-water pesticide systems.[88] Thus, an investigation of the impact of dilution on the extraction of the pesticide panel from all fruit matrices was paramount. Signal-to-noise ratios (S/N) and absolute intensity at various fruit homogenate dilution levels were compared, and three relationships were observed (as shown for select compounds in Figure 3.2): a reduction of S/N with sample dilution, constant S/N with sample dilution, and increasing S/N with sample dilution.

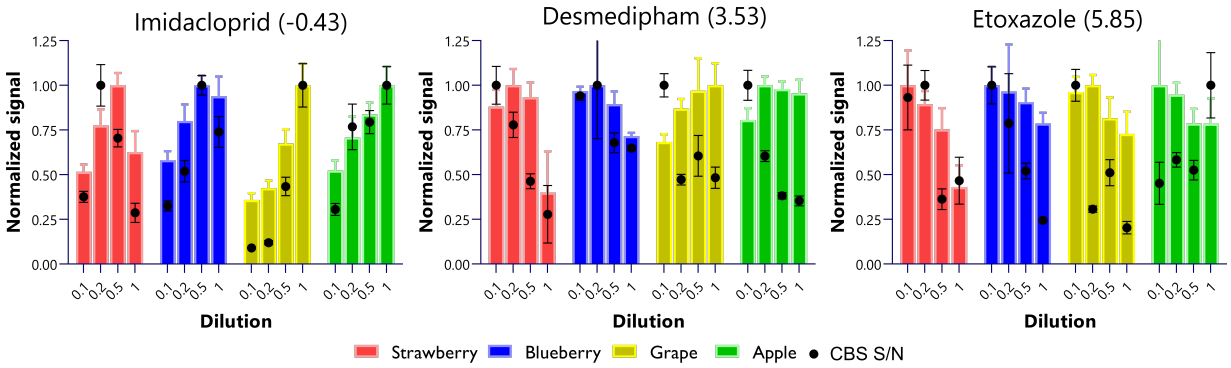

Figure 3.2: Investigation of fruit homogenate dilution on signal intensity and S/N ratio given in normalized terms to maximum value (assigned 1.00) and summary of analyte behaviour observed in the compound data set. Dilution levels correspond to 1 g of homogenate spiked at 50 ng/g diluted with 9 mL of water (0.1), 4 mL of water (0.2), 1 mL of water (0.5), and no water added (1). Plots are arranged in increasing logP value, with imidacloprid displaying trends of reduction of S/N and absolute signal intensity with dilution, desmedipham displaying constant/increasing S/N with dilution, and etoxazole displaying increasing S/N and intensity with dilution.

The division of S/N with dilution behavior can be attributed to hydrophobicity differences, with more hydrophilic compounds (logP < 2) expected to have reduced matrix binding and thus be more negatively impacted by dilution, as shown in select neonicotinoids and polar organophosphorus compounds. Mid-polarity compounds ($2 <$ logP < 4) displayed a mixture of behaviour with dilution; however, in cases of reduced S/N with dilution, the observed reduction was lesser than the dilution factor. Finally, more hydrophobic compounds ($4 <$ logP) displayed increased S/N values with dilution, likely because of

their high particulate binding and slow desorption kinetics, resulting in an increase in the amounts of such compounds available in their free form after dilution. It is worth mentioning ionization suppression as a confounder. In less dilute samples, the potential increased extraction of matrix endogenous compounds can contribute to absolute ESI signal suppression (and thus S/N suppression), and thus contribute to the apparent effects of matrix-analyte binding. Separation of the confounding variables could be made via a replicate dilution experiment with the incorporation of a chromatographic separation step to reduce/remove the impact of matrix co-extractive ion suppression. Although not the optimal course of action for detection of all compounds of interest—significant sacrifice was made in S/N values for neonicotinoids and select polar organophosphorus compounds as an example—the methodology improvements were deemed to outweigh the reduced S/N performance observed. Giving lower priority to compounds in cases where S/N observed were high (> 100) at the concentration tested which was below the European Union Minimum Regulatory Limit, set by ESFA (EU MRL) for the matrix. The improvements or lack of change in S/N with dilution observed for the majority of compounds as well as the 10-fold reduction of fruit homogenate, standards for matrix-match calibration curve construction, internal standards for correction, and volumetric sample handling enabled with such a high dilution level. Thus, the compromise to pursue the 0.1 dilution level for further method development was made.

3.4.3 Coated blade spray as a rapid sample screening and quantitation tool

Upon selection of dilution level, a method comparison of both instrumental approaches was carried out with respect to analytical figures of merit. As shown in Table 3.4, differences in figures of merit differ marginally for strawberry, with deviations in LOQs within 1 calibration level. Additionally, this comparison of method performance using both direct coupling and a separation technique allowed for a more robust determination of quantifiable candidates within the concentration range tested. As an example, propiconazole ($C_{15}H_{17}Cl_2N_3O_2$, 341.068794 Da) can generate signal in an SRM channel of prothioconazole ($C_{14}H_{15}Cl_2N_3OS$, 343.031281 Da) for the commonly monitored transition of 344 $\longrightarrow$

189. Propiconazole has a low contributing 187 Da fragment, which when coupled with the isotopic distribution of the compound, results in cross-talk in the same channel as prothioconazole. With the differing separation characteristics of the compounds in question their differentiation is made trivial; however, this occurrence could result in a false positive if only one transition is monitored using a direct-to-MS technique, highlighting the importance of dual transition monitoring in the workflow presented. Another distinction between instrumental methods is the economy of time and consumables. The removal of the separation step reduced the analysis time 9-fold, while also reducing solvent usage 460-fold. Full quantitative results can be found in the Appendix for apple analyzed by CBS-MS/MS (A.12), LC-MS/MS (A.13), blueberry analyzed by CBS-MS/MS (A.14), LC-MS/MS (A.15), grape analyzed by CBS-MS/MS (A.16), LC-MS/MS (A.17), and strawberry analyzed by CBS-MS/MS (A.18), LC-MS/MS (A.19)

Table 3.4: Abridged figures of merit for compounds found in real strawberry samples via CBS-MS/MS and LC-MS/MS.

				LOQ	Accuracy (%, n = 4, ng/g)				Precision (%, n = 4, ng/g)			
Compound	**Method**	**Internal Standard**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
acetamiprid	CBS	dimethoate-d6	0.9904	2.5		104.8	93.3	92.4		4.3	15.5	10.1
	LC	dimethoate-d6	0.9923	1		101	97.6	102.3		8.2	8.2	12
azoxystrobin	CBS	malathion-d6	0.9969	0.5	110.8	102	102	95.2	8.1	6.4	7.9	3.2
	LC	atrazine-d5	0.9960	0.5	96.7	94.3	88.3	88.6	15.7	4.6	4.3	6.8
boscalid	CBS	atrazine-d5	0.9857	2.5		106.2	105	86.5		4.8	12.9	3.2
	LC	atrazine-d5	0.9947	2.5		93.9	92.8	93.2		9.3	9.5	6.2
chlorantraniliprole	CBS	malathion-d6	0.9940	2.5		106.6	84.1	90		15.1	7.3	6.4
	LC	dimethoate-d6	0.9939	1		94.8	92.6	91.8		20.6	8.3	9.9
cyprodinil	CBS	malathion-d6	0.9887	5			96.3	99.8			6.6	2.7
	LC	cyprodinil-d5	0.9935	2.5		109.6	115	104.1		12.9	10.3	10.3
difenoconazole	CBS	malathion-d6	0.9866	2.5		103.8	94.4	93.5		25	21.1	13.8
	LC	trifloxystrobin-d6	0.9913	1		104.8	107.3	112.4		16.9	12.1	13.8
imidacloprid	CBS	carbofuran-d3	0.9934	1		97.6	86.3	92.6		12.8	16.3	8.7
	LC	dimethoate-d6	0.9911	5			93.5	97.6			5	8.9
metalaxyl	CBS	metalaxyl-d6	0.9902	0.5	97.1	121.4	113.1	88.9	6	13.9	12.3	6.1
	LC	metalaxyl-d6	0.9979	0.5	104.7	99.3	98.8	99.5	16	4.8	3.2	4.2
mevinphos	CBS	dimethoate-d6	0.9906	2.5		118	100.2	93.9		5.8	11.2	8.9
	LC	carbofuran-d3	0.9948	2.5		97.3	95.6	95.4		12.2	4.5	8.2
myclobutanil	CBS	atrazine-d5	0.9921	2.5		98.3	106.2	91		10.4	8	8.3
	LC	atrazine-d5	0.9937	1		96.6	106.7	101.2		7.5	4.1	6
propiconazole	CBS	atrazine-d5	0.9856	1		97.7	97.4	89.8		20.1	10.6	11.5
	LC	atrazine-d5	0.9935	2.5		100.6	93.7	94.7		14	4.5	3.2
pyraclostrobin	CBS	malathion-d6	0.9822	2.5		105.2	85.8	95		10	13.5	10.5
	LC	trifloxystrobin-d6	0.9877	5			102.6	99.3			10.1	7.5
pyrimethanil	CBS	malathion-d6	0.9853	2.5		105.5	87.9	98		15	12	4.9
	LC	atrazine-d5	0.9932	1		96.6	95.4	95.7		3.1	4.3	4.6
quinoxyfen	CBS	malathion-d6	0.9759	10			90.8	93.3			13.1	12.3
	LC	trifloxystrobin-d6	0.9821	10			116	95.4			12.9	19.3

3.4.4 Analysis of a panel of real samples with LC-MS/MS confirmation

Across the 4 matrices under investigation, 15 real samples were analyzed. Within the 3 apple, 3 blueberry, 5 grape, and 4 strawberry samples, a total of 45 pesticide residues were quantified and confirmed within the linear range tested, with an additional 12 residues detected outside of the linear range (> 100 ng/g). Notably, a locally sourced strawberry

sample contained the largest number of individual pesticide residues at 13, although all residues complied with MRLs designated by Health Canada. However, one of the detected compounds, propiconazole, was quantified at a concentration above the EU MRL of 50 ng/g at 51.7 ± 7.2 and 51.1 ± 3.6 ng/g via CBS-MS/MS and LC-MS/MS, respectively. In general, good agreement was found between samples analyzed by CBS-MS/MS and LC-MS/MS with Bland-Altman plot analysis for pesticides quantified above 10 ng/g (level chosen as a low concentration cut-off to not bias 95 % CI due to inversely proportional percent differences with concentration) resulting in a bias of 2.307 with 95 % CI -30.86 to 35.47 %, as shown in Figure 3.3 with real sample quantification for strawberry samples shown in Table 3.5 (expanded real sample data set found in Table A.20).

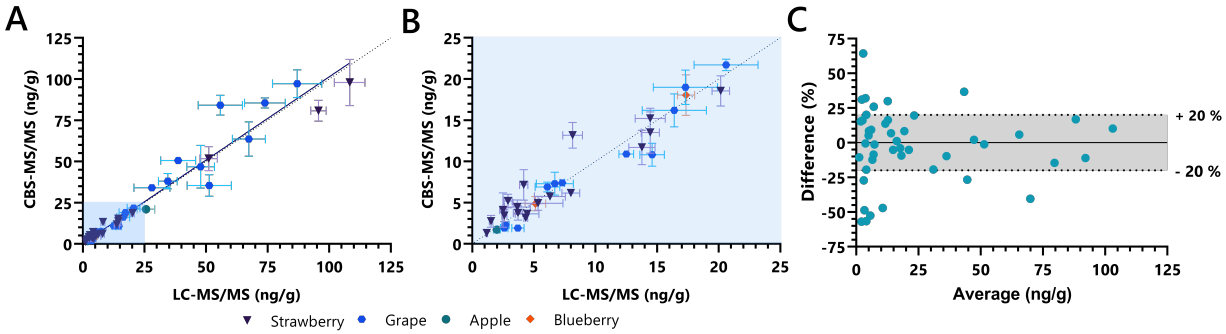

Figure 3.3: Summary of all real sample quantitation of pesticides (n = 44) with both CBS-MS/MS and LC-MS/MS marked by matrix and by concentration range with the full 0 – 100 ng/g in panel A, with an enlarged 0 – 25 ng/g in panel B (1:1 line displayed as a dotted line). Acceptable agreement was observed between instrumental approaches, with a slope of 1.011 (95 % CI: 0.9692 to 1.052), intercept of 0.2855 (95 % CI: -0.1949 to 0.7659), R2 of 0.9291. Percent differences (from the average of two results) are displayed in panel C between the concentrations of 0 – 100 ng/g with full numerical data presented in Table A.20.

k

The results on comparability of methodologies with this small sample set broadly distributed over the compounds under study suggests that the internal standards selected correct for hypothesized ionization suppression differences between LC-MS/MS and CBS-MS/MS, with the former yielding reduced co-elution of matrix extractives and compounds of interest. Further expansion of the sample size using the methodology presented would be desired to form more robust conclusions on method comparability. Pesticide prod-

uct formulations contain surfactants and stabilizers to improve product application and lifespan in-field[89,90] that have been shown to contribute to ESI suppression of ambient mass spectrometric analysis when compared to a pesticide standard.[83] The good agreement demonstrated between instrumental real sample results inspires confidence in the method's correction for these effects via internal standard selection or integrated sample preparation via SPME, or both. Additional support for the validity of real sample quantitation can be found upon comparison of ratios of pesticides found in commercially available pesticidal products such as boscalid and pyraclostrobin (found at a 1.96875 ratio) or cyprodinil and fludioxonil (found at a 1.5 ratio) with those found in real samples. For example, one grape sample was found to contain pyraclostrobin and boscalid at a ratio of 1.86 ± 0.208, while one strawberry sample was found to contain cyprodinil and fludioxonil at a ratio of 1.67 ± 0.251, closely matching the ratios found in commercial product examples (shown in Figure 3.4).[91,92]

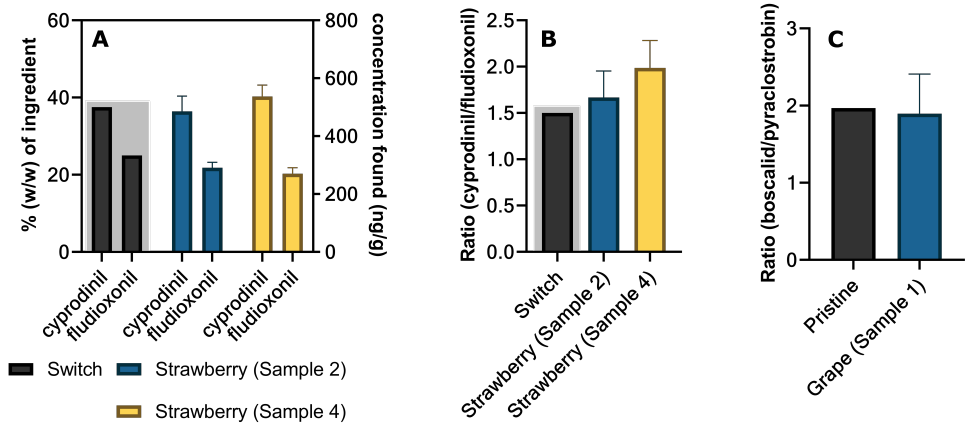

Figure 3.4: Ratios of pesticides matching ratios found in commercial pesticide formulations in real samples. In panel A, cyprodinil and fludioxonil sample concentrations are shown and compared to the w/w % found in the commercial formulation, with panels B and C showing the comparison of ratios in real samples to products Switch and Pristine.

Table 3.5: Comparison of residues found in real strawberry samples by LC-MS/MS and CBS-MS/MS

Compound	Sample 1 (ng/g)		Sample 2 (ng/g)		Sample 3 (ng/g)		Sample 4 (ng/g)	
	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD
acetamiprid			573.5 ± 41.7	606.9 ± 44				
azoxystrobin			80.8 ± 6.4	95.7 ± 3.2				
boscalid	13.2 ± 1.6	8.2 ± 0.8	5.2 ± 0.8	2.9 ± 0.3	7.1 ± 1.9	4.2 ± 0.3	3.4 ± 0.7	2.6 ± 0.2
chlorantraniliprole	3.6 ± 0.2	4.4 ± 1			3.7 ± 0.9	3.7 ± 0.4	3.1 ± 0.4	4.3 ± 0.1
cyprodinil			346.7 ± 24.7	485.9 ± 52.1			391.8 ± 29.8	537 ± 39.3
difenoconazole			97.9 ± 14	108.3 ± 6.2				
fludioxonil			N/A	291.3 ± 18.4			N/A	270.3 ± 20.4
imidacloprid			5.7 ± 0.5	6.3 ± 1.3				
metalaxyl	1.3 ± 0.2	1.2 ± 0.1					13.5 ± 2.5	14.4 ± 0.7
mevinphos			6.2 ± 0.1	8 ± 0.7				
myclobutanil			18.6 ± 1.8	20.2 ± 0.7			2.7 ± 0.7	1.5 ± 0.1
propiconazole			51.7 ± 7.2	51.1 ± 3.6				
pyraclostrobin	4.4 ± 0.9	3.7 ± 1	770 ± 63	849.8 ± 45.9	4.1 ± 2.1	2.5 ± 0.3	4.9 ± 0.8	5.3 ± 2
pyrimethanil	140.5 ± 4.1	162 ± 9			11.7 ± 2.1	13.8 ± 1.1		
quinoxyfen			186.4 ± 18.8	161 ± 7.6				
spinetoram			15.2 ± 1.3	14.4 ± 1.2				

3.4.5 Problematic compound classes and future directions

The extraction methodology presented is not a panacea for all compound classes. Of the 204 pesticides investigated in the preliminary method developmental steps, several pesticide classes remained difficult to quantify at the MRLs required by regulatory bodies. In general, difficulties are expected with highly polar (logP > -1) and non-polar (logP > 5) analyte classes. Low extraction of polar compounds is expected since the aqueous matrix effectively competes for polar analytes. On the other hand, poor solubility of very hydrophobic compounds and their strong association with the matrix leads to slow desorption kinetics, which results in slow mass transfer conditions. In this work, polar organophosphates such as acephate and methampidphos were unable to be quantified below EU MRLs; however, implementation of lower sample dilution levels, zirconia-based extraction phases to increase selectivity, and/or DART as a ionization technique remain avenues to be explored.[48,93] On the opposite side of the hydrophobicity spectrum, the increasing popularity of biopesticides of the avermectin and spinosyn classes and their synthetic analogues present a challenge for the method described due to their suspected substantial matrix-binding.[94,95] Addition of organic solvents to reduce the proportion of bound analyte has been demonstrated for non-polar analytes in biological matrices,[45] and was thus pursued herein to investigate its impact on such a broad range of compounds in blueberry matrix, with 10-fold increases

in S/N observed for these non-polar molecules. However, such increases came at the expense of the S/N of more polar analytes of interest due to the simultaneous reduction of affinity to the extraction phase with the addition of acetonitrile (elaborated on in Figure 3.5 and Table 3.6). Similar analyte-matrix binding difficulties have been reported for the SPME of pyrethroids from grape homogenate.[25] These under-performing compound classes remain the compromise of the method presented, and the largest area of improvement to be further explored in future work through investigations of different sorbents, organic matrix modifiers, and analyte-matrix partitioning with temperature. Since the presented CBS method yields a very fast overall time of analysis, repeated extraction of the same sample after addition of small amounts of an appropriate solvent to facilitate mobilization of the hydrophobic compounds can be further explored as a possible solution.

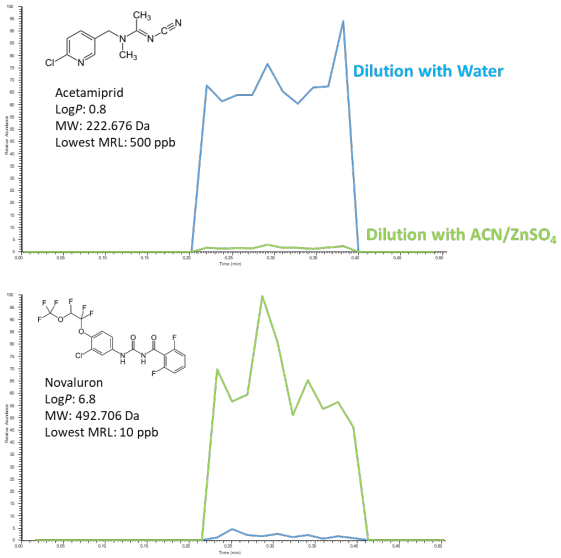

Figure 3.5: Comparison of spiked (100 ng/g) blueberry homogenate dilution with water and dilution with 60:30:10 (0.1 M $ZnSO_4$:ACN:Water) on the absolute signal observed following the extraction for acetamiprid and novaluron. Substantial increases in absolute signal were observed for high logP compounds in the organic case, while a reduction was observed for low logP compounds.

		S/N	
Compound	**LogP**	**H_2O**	**ACN**
novaluron	6.78	4	1306
pyridaben	4.73	2	49
etoxazole	5.85	94	880
trifloxystrobin	5.11	431	3908
carbofuran	1.76	135	166
imidacloprid	-0.43	89	15
dimethoate	0.48	238	38

Table 3.6: Selected compound signal-to-noise values upon extraction of a 1 g 100 ng/g sample of blueberry diluted in 9 mL of H2O compared to a 1 g 100 ng/g sample of blueberry diluted with 9 mL of 60:30:10 (0.1 M $ZnSO_4$:Acetonitrile:Water).

3.5 Conclusions and future perspectives

CBS-MS/MS was demonstrated as a complementary technique to LC-MS/MS analysis for the quantitation of a multiresidue panel of pesticides in apple, blueberry, grape, and strawberry matrices. The presented workflow significantly reduces analysis time, amount of sample required, and laboratory footprint compared to regulatory gold standards, while providing the analyst with freedom to further increase throughput with direct-to-MS coupling or increase analytical confidence via LC-MS/MS coupling for confirmation with the same sample preparation methodology. For the majority of the studied compounds (126 pesticides in apples, 139 pesticides in blueberries, 136 pesticides in grapes, and 135 pesticides in strawberries), analytical figures of merit were found to meet EU SANTE/12682/2019 regulatory standards in terms of linearity, accuracy, and precision. Encouragingly, real sample analysis yielded comparable results (percent differences ¡ 20 % for 73 % residues) between direct-to-MS and LC-MS/MS approaches, with pesticide ratios found to closely resemble commercially available formulations. Compromises for multiresidue method development in certain pesticide classes, notably the highly polar and non-polar (*e.g.* avermectins, polar organophosphates), were discussed, with sample preparation strategies regarding organic solvent dilution, ionization method, and extraction phase exploration presented as future avenues of research. Additionally, future LC-MS/MS side optimization could be explored, such as desorption time and solvent optimization, to yield a faster LC confirmation complement.

Chapter 4

Cannabis oil pesticide analysis—conserved performance in complex non-polar matrices?

4.1 Introduction

Tandem with the introduction of cannabis and cannabis value-added products into the medical and recreational market is the implementation of consumer protection legislation to govern the use of pesticides for cannabis cultivation.[96] Countries and regions have nimbly reacted with pesticide and plant growth regulator legislation varying in levels of austerity (in stark contrast to similar method-of-consumption agricultural products sought for their psychoactive natural products),[97–99] with the MRLs enacted by Health Canada regarded as particularly strict.[97,100] Concern by regulatory agencies has been extended to downstream cannabis-derived products, with separate regulatory levels for dried flower products and concentrates (such as oils, extracts, and capsules) due to differing toxicological impact and potential for concomitant concentration of pesticides with desirable compounds such as cannabinoids, terpenes, and flavonoids during extraction of raw flower by common extraction techniques (seemingly side-stepping the thought-experiment that significant pesticide concentration in oil products could only result if the products contained significantly greater

concentrations of psychoactive ingredients than in source plants).[96,101]

Few demonstrated and validated workflows are available in literature, however the standard set by Health Canada includes a diverse set of compounds ($n = 96$) analyzable by a wide range of mass spectrometric techniques as demonstrated by GC-MS via electron impact ionization, LC-MS via ESI or APCI.[102,103]

The novelty of regulation presents an opportunity for the exploration of sample preparation workflows to meet the MRLs required by regulatory bodies whilst prioritizing techniques which accelerate analysis time, reduce sample usage,[104] and will scale with increased demand via automation. Currently, sample preparation steps for the analysis of pesticides in oils involve either dilution with solvent, liquid extraction followed by SPE, or modification of the QuEChERS extraction technique.[5,105,106] Methods coupling these sample preparation approaches to multi-instrument methods with LC-ESI-MS/MS and GC-MS/MS,[107] as well as multi-ionization implementations of LC-APCI-MS/MS and LC-ESI-MS/MS[108] have been demonstrated in cannabis flower matrices.

Recent applications of SPME have shown the techniques ability to satiate the aforementioned desired qualities, with high-throughput automation capability[86,109] and multi-residue pesticide analysis in liquid matrices.[25,85,110,111] The coupling of an SPME device direct-to-MS (through a variety of ambient ionization configurations), bypassing the separation step, has been demonstrated to further leverage reduction in analysis time and solvent usage for pesticide analysis,[48,86,112] with the technique under investigation in this work known as CBS. A CBS device acts as both a sampling device and ion source upon the addition of desorption solution (to liberate the extracted analytes from the coating) and application of voltage sufficient to establish ESI (to persuade the extracted analytes to the gas phase).[44]

As a preliminary foray into the suitability of SPME and CBS for cannabis oil analysis, the method development for the analysis of 74 ESI-amenable pesticides which have substantial overlap between the regulatory cannabis legislation of several regions and nations (*e.g.* regulations published by Health Canada, California Department of Food & Agriculture, Oregon Department of Agriculture) is documented via LC-MS/MS and CBS-MS/MS. The exploration of a washing solvent step for the removal of matrix-sourced oil

residue while limiting desorption of compounds of interest, the kinetic behaviour of pesticides in a non-polar matrix via central-composite design for investigation of temperature and time impacts during extraction. In the CBS methodology, ionization suppression and isobaric interference caused by matrix co-extractives was explored, and quantitation or screening capabilities were shown to be conserved when paired with a suitable internal standard with the majority of 49 compounds meeting EU SANTE guidelines for accuracy, precision, linearity with LOQs below or equal to Health Canada legislative requirements using both LC-MS/MS and CBS-MS/MS techniques.

4.2 Experimental

4.2.1 Chemicals and sample preparation devices

LC/MS-grade MeOH, ACN, and water were acquired from Fischer Scientific (Hampton, NJ, USA). LC/MS-grade formic acid was acquired from Sigma Aldrich (St. Louis, MO, USA). LC/MS grade ammonium formate and ammonium acetate were acquired from Sigma Aldrich (St. Louis, MO, USA). HPLC-grade acetone (ACE), hexane (HEX), and iso-octane (ISO) were acquired from Sigma Aldrich. Target pesticides consisted of 74 compounds and were acquired from Chem Service Incorporated (West Chester, PA, USA) a list of the compounds of interest along with relevant properties can be found in Table A.21 in the Appendix. Deuterated analogues used as internal standards (acephate-d_3, atrazine-d_5, carbofuran-d_3, cyprodinil-d_5, chlorpyrifos-d_{10}, dimethoate-d_6, imazalil-d_5, kresoxim-methyl-d_7, malathion-d_6, metalaxyl-d_5, oxamyl-d_6, spirotetramat-d_5, trifloxystrobin-d_6, fludioxonil-$^{13}C_2$) were acquired form Toronto Research Chemicals (Toronto, ON, CA), with compound details located in Table A.22. The stainless-steel blades used as the substrate for the CBS devices were provided by Restek Corporation (Bellefonte, PA, USA). The 20 μm HLB particles were provided by Waters Corporation (Milford, MA, USA). The blades were prepared and dip coated (coating length; 10 mm) with HLB particles via a procedure developed in-house, described elsewhere.[48] The cannabis concentrate product used for method development was Balance Harmonizer from Aphria Inc. (Leamington, ON, Canada) with 4.90 – 5.31 mg/mL of Δ^9-

tetrahydrocannabinol (THC) and 4.95 – 5.17 mg/mL of cannabidiol (CBD) as stated by the manufacturer, acquired from the Ontario Cannabis Retail Corporation (Toronto, ON, Canada). The product is cannabis flower distillate (extracted via supercritical CO_2) diluted in a medium-chain triglyceride (MCT) carrier oil.

4.2.2 Instrument parameters

All experiments described were completed using a TSQ Quantiva from Thermo Scientific (San Jose, CA, USA), with data analysis completed using Trace-Finder 4.1 from Thermo Scientific. Positive and negative ESI coupled with SRM mode was used for all analyses, and MS/MS compound transitions and conditions (found in Tables A.21 and A.22) were optimized via direct infusion from acidified methanolic standards. Chromatographic separation experiments were completed with an Ultimate 3000RS UHPLC system from Thermo Scientific outfitted with an ARC-18 LC column (2.7 μm, 100 mm, 2.1 mm) provided kindly by Restek Corporation. Separation conditions, gradient details, and mass spectrometry parameters are available in Table 4.1 below. Manual CBS-MS/MS experiments were completed via a Nanospray Flex NG interface from Thermo Fischer (modified by Science Technical Services). Desorption solution used, voltages, spray times, and other CBS method parameters are available in Table 4.2 below.

Table 4.1: LC-MS/MS conditions.

Instrument (LC)	Thermo Fisher Scientific Ultimate 3000RS HPLC
Guard column	Restek EXP guard cartridge ARC-18 (2.7 μm, 5 mm, 2.1 mm)
Column	Restek ARC-18 LC column (2.7 μm, 100 mm, 2.1 mm)
Mobile phase	A: Water with 2mM ammonium formate, 0.2 % formic acid B: Methanol with 2mM ammonium formate, 0.2 % formic acid
Column temperature (°C)	50
Flow rate (μL/min)	400
Total run time (min)	9.5
Gradient program (min)	initial conditions (5 % B), ramp to 60 % B by 2 min, ramp to 75 % B by 4 min, ramp to 100 % B by 6 min hold until 7.5 min, 5 % B at 7.51 min until 8.5 min.
Injection volume	10 µL
Instrument (MS)	Thermo Fischer Scientific TSQ Quantiva
Spray voltage (V)	3500 (+)/2500 (-)
Dwell time (ms)	1
Sheath gas (Arb)	45
Aux gas (Arb)	13
Sweep gas (Arb)	1
Ion transfer tube temperature (°C)	342
Vaporizer temperature (°C)	358

Table 4.2: CBS-MS/MS conditions.

Instrument (MS)	Thermo Fischer Scientific TSQ Quantiva
Spray voltage (V)	3500 V (+)/2500 V (-)
Dwell time (ms)	1 (+)/10 (-)
Desorption solvent	95:5 MeOH:H_2O + 0.1 % formic acid + 12 mM ammonium acetate
Volume of desorption solvent (μL)	8
Desorption time (s)	12
Distance from inlet (mm)	6
Spray voltage program	0 V until 0.05 min, start spray at + 3000 V until 0.35 min, 0 V from 0.36 to 0.45 min, start spray - 2500 V until 0.55 min
Ion transfer tube temperature (°C)	300

4.2.3 Sample preparation and extraction methodologies

Cannabis oil (ordered, stored, and handled in accordance with the *Cannabis Act* and *Cannabis Regulations* as part of a cannabis research licence) used for matrix-match calibration and validation was prepared and spiked volumetrically. Oil was spiked at the required concentration level with caution taken to not introduce more than 2 % organic solvent into the oil matrix (to avoid influencing matrix behaviour with organic solvent addition), with internal standards. Spiked oil was equilibrated for 12 hours at 4 C. For extraction, sample volumes used were 300 μL, with optimization of the washing solvent resulting in the usage of a 5 second, 1000 μL isooctane rinse at 1000 rpm, completed in duplicate. Sample extraction times and temperatures were varied as part of the extraction method optimization as mentioned below. CBS-MS/MS desorption conditions were kept constant,

and can be found in Table 4.2. LC-MS/MS desorption conditions were completed with the same desorption solvent as CBS-MS/MS, but with a volume of 150 μL, with a desorption time of 60 minutes without agitation, unless otherwise specified. All CBS-MS/MS samples were completed in quadruplicate, and all LC-MS/MS samples were completed in triplicate.

Solvent washing investigation

Washing solvent combinations under investigation included HEX, ISO, and ACE-water and ACN-water combinations at the following compositions (10-90, 25-75, 40-60, 55-45, and 70-30 [%]). Extractions were completed for 30 minutes from 300 μL cannabis oil spiked at 100 ng·mL^{-1} with 1500 rpm agitation. Following extraction, blades were rinsed with 1000 μL of the solvent mixtures under investigation for 5 seconds at 1500 rpm agitation. Oil washing effectiveness/suitability was determined by qualitative (*i.e.* oil residue left on surface of coating) and quantitative factors (*i.e.* signal-to-noise S/N of each transition under study via CBS-MS/MS and nanograms desorbed via LC-MS/MS). For CBS analysis, 10 μL of 95-5 methanol-water with 0.1 % formic acid and 12 mM ammonium acetate was applied to the blade for 12 seconds prior to application of 4500 V for a spray time of 15 seconds. For LC-MS/MS analysis, blades were desorbed in 75-25 methanol-water with 0.1 % formic acid for 60 minutes with 1500 rpm agitation.

Extraction time and temperature optimization

A central composite design (CCD) experiment was devised to investigate the impact of extraction time and temperature on the amount of pesticide extracted onto the blade, as this was anticipated to substantially differ with analyte behaviour observed in aqueous matrices.[25] Generally speaking, temperatures between 18.8 and 61.2 °C along with extraction times between 6.7 and 63.3 minutes were investigated. A 2-factor ($\alpha = \sqrt{2}$), 2 centre point, 2 replicate (for a total of 3 data points per factor combination) design was generated using JMP Student Edition 14.1.0 (SAS Institute, Cary, NC, USA). Variable assignment, coded, and non-coded unit tables can be found in Table A.23 in the Appendix. Extractions were performed according to the factor specifications from 300 μL 100 ng·mL^{-1} spiked

samples at 1000 rpm agitation. LC-MS/MS analysis was completed according to the aforementioned instrumental parameters and sample preparation and extraction methodologies. Response was compared in terms of nanograms (ng) desorbed, with CCD data analyzed using Minitab 19 (Minitab, LLC, State College, PA, USA)..

Matrix co-extractives and ionization suppression

As further investigation into the impact of co-extractives on signal intensity of our compounds of interest when analyzed via CBS, an extraction study was completed. A comparison of the S/N (via CBS-MS/MS) ratios and amount extracted (via LC-MS/MS) of target analytes from the cannabis oil product and cannabis-free MCT oil were examined. The organic MCT oil used as the cannabis-free matrix was obtained from Nutiva (Richmond, CA, USA). Extractions were performed for 15 minutes from 300 μL at room temperature with agitation at approximately 1000 rpm, followed by rinsing with 1 mL of isooctane for 5 seconds in duplicate.

Method validation

Calibration curves for all analytes were made in the range 0.1 to 200 ng·mL^{-1} (0.1, 0.5, 1, 2.5, 5, 10, 25, 50, 75, 100, 200 ng·mL^{-1}). Three validation points at 15, 80, 150 ng·mL^{-1} were used to quantify precision and accuracy. Validation parameters were based on the SANTE/11813/2017 guidelines.[113] LOQs were designated as the lowest calibration point meeting the method performance criteria for accuracy (70 – 120 %) and precision (RSD $\leqslant$ 20 %). Linearity was evaluated as a deviation of back-calculated concentration from true concentration $\leqslant \pm$20 %. Calibration curves were all weighted $1/x$, with analyte-internal standard pairing completed based on largest R^2 value. Screening detection limit (SDL) for compounds not meeting quantitative criteria were set as calibration points resulting in a S/N of greater than 5.

4.3 Results and discussion

4.3.1 Device washing solvent investigation

Upon extraction of compounds of interest from the matrix of choice, an important step is the removal of matrix residue non-specifically bound to the coating (*i.e.* particulate matter, liquid, matrix sourced protein or lipid assemblies) as they act as an irreproducible vessel for analytes on the coating. In the case of direct-immersion extraction from oils, this step is complicated by the potential pre-mature desorption of extracted analytes within the particles embedded on the surface in pursuit of removal of adhered oil (primarily composed of medium chain triglycerides, with potential solubility overlap with compounds of interest, with majority constituents such as capric 10:0 and lauric acid 12:0 in this work)[114] from the coating. In Figure 4.2, the exploration of various rinsing solvent combinations are displayed in both S/N terms as determined via CBS-MS/MS and amount extracted as determined via LC-MS/MS. With polar organic solvent-water combinations (*i.e.* ACE and ACN) total oil residue removal was only observed at 70 % concentration of the organic additive (as shown in Figure 4.1), which also results in substantial reduction in amount extracted across the polarity range under study, but more notably with more hydrophilic pesticides. Non-polar solvents such as HEX and ISO were found to effectively wick the oil from the surface of the sampling device while minimally desorbing analytes. ISO was chosen for further method development as a rinsing agent over HEX due to environmental and safety considerations.[115]

4.3.2 Impact of temperature and time on extraction

Due to substantial differences in the composition of the cannabis oil matrix under study with aqueous matrices, differences in kinetic behaviour of compounds was expected.[25] Most notably an inversion of recovery behaviour between hydrophilic and hydrophobic (in terms of ACD/LogP) analytes, with those in the former extracted more efficiently by the device due to reduced analyte affinity for the hydrophobic matrix, and thus conserving concepts of balanced coverage.[87] As an example, polar organophosphates (*i.e.* acephate) displayed

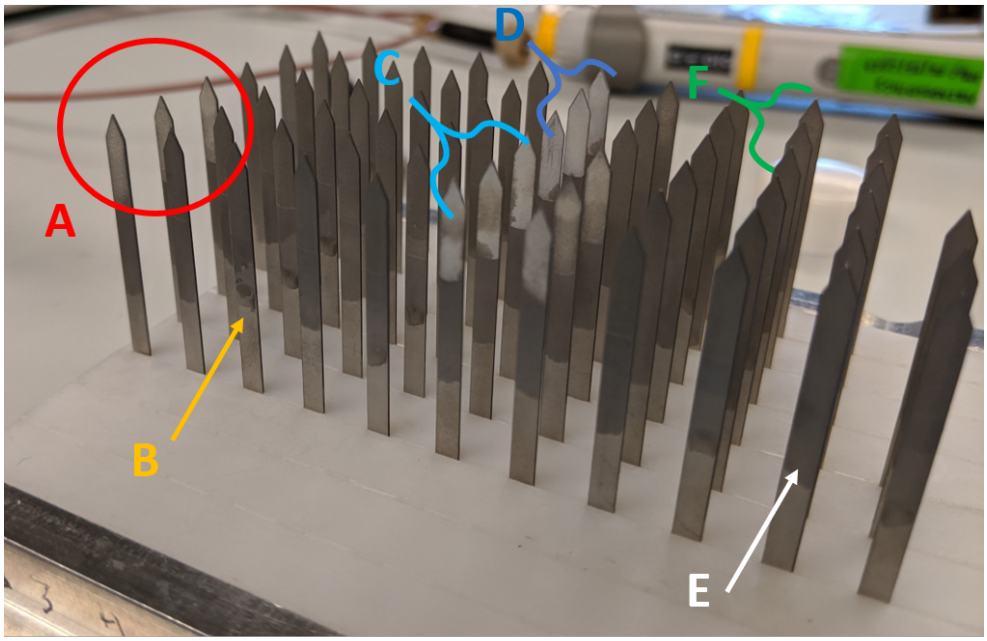

Figure 4.1: Image of the blades after washing steps tested before analysis. Blades circled in A have undergone washing with 70 % ACN with minimal oil wetting present on the coating. Blades rinsed with 10 % ACN (B), still have a large amount of oil adhered to the blade, shown pooling down the surface of the blade. Sets of blades washed in hexane (D) and isooctane (C) show similar removal of oil residue from the surface of the blade as in A. No blades rinsed with acetone (over the water mixtures tested) were cleaned as well as 70 % ACN, ISO, or HEX washed blades, with the 55 % ACE washed blades and 70 % ACE washed blades still wet with oil in E and F (55 % and 70 % ACE, respectively).

high relative recoveries, leveraging analyte-matrix relationships much how one would leverage the relationships of salt and aromatics with oils in *confit* cooking. Response surface plots for select analytes are shown in Figure 4.3, with trends in greater recovery in more hydrophilic compounds for compounds opposite on the hydrophobicity range under study, thiamethoxam and cyantraniliprole. Consequently, the extraction of certain classes of compounds was expected to be limited by matrix affinity, such as high logP pesticide families such as strobilurins, spinosyns, and non-polar organophosphates. Notably, strobulins displayed negligible changes in amount desorbed over the parameters tested, as shown in trifloxystrobin in Figure 4.4, however for the spinosyn class improved recovery was observed

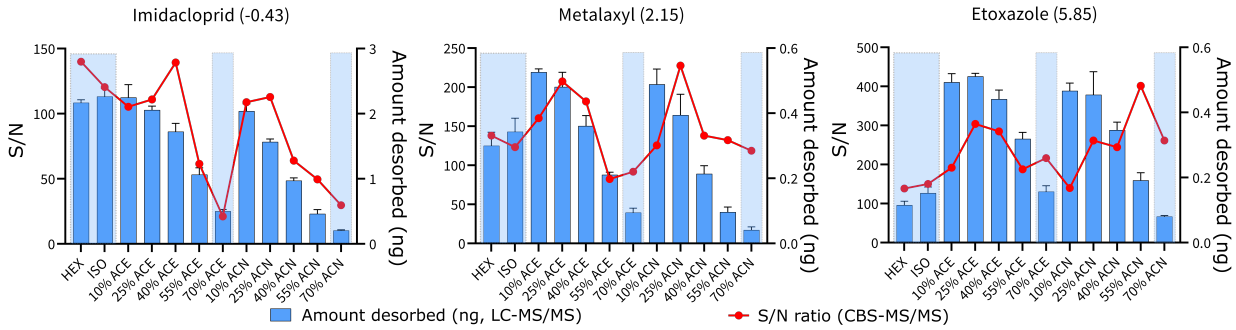

Figure 4.2: Results of oil washing experiments presented as both amount desorbed (analyzed by LC-MS/MS) and S/N (analyzed by CBS-MS/MS), in both cases higher values proportional to desirability. Values highlighted (shaded blue) represent feasible washing conditions with total removal of oil from the surface of the sampling device, whereas non-highlighted results acquired from blades where the washing step was inadequate resulting in significant oil residue remaining. Increases in S/N and amount desorbed in non-highlighted regions (when compared to HEX and ISO conditions) are due to oil matrix remaining on the device, facilitating the transfer of analytes in addition to those extracted by the coating. The effect is more pronounced in more hydrophobic analytes (such as etoxazole above) due to greater affinity for the matrix. Graphs are labelled by compound and logP in parentheses.

when compared to other compound at similar ACD/LogP, likely due to the presence of a charged moiety. Similarly, oxamyl recovery was shown to be independent of temperature (also included in Figure 4.4). Contributions to increased amount extracted include improved extraction kinetics from temperature increase, a likely more significant contributor than in an aqueous sample due to steeper viscosity-temperature slope present in oil as compared to water.[116] Regardless of family and compound specific behaviour observed, no order-of-magnitude level improvements were harvested during the CCD optimization steps, with selection of extraction conditions to fall to practical considerations and not pursuit of maximum recovery. In order to leverage the recovery improvements for specific low-MRL compound classes of interest (*i.e.* polar organophosphates, neonicotinoids), while considering the diminishing returns observed for hydrophobic analyte classes and compounds at long extraction times (*i.e.* ryanoids, strobulins, etoxazole) a middle ground selection of 40 minute extraction time performed at a temperature of 40 °C was chosen for future steps. Additionally, the extraction time selected (be it 5 minutes or 60 minutes) has reduced impact on the total time of analysis on a per sample basis, due to the completion of the

analysis in a 96-blade, automated workflow.[49,109]

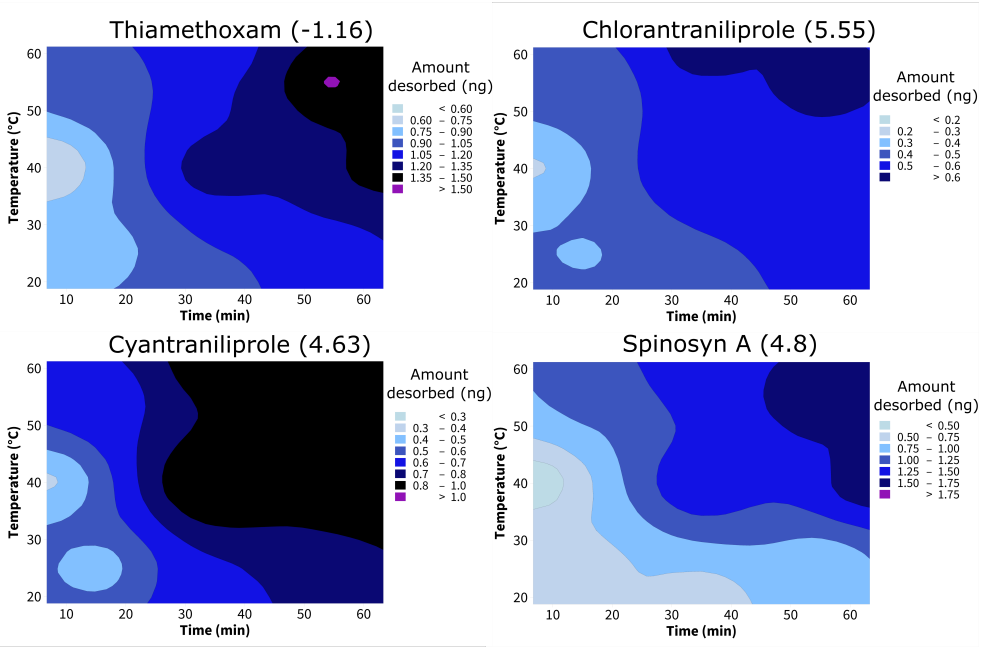

Figure 4.3: Selected surface response diagrams for compounds (ACD/LogP) thiamethoxam (-1.16), cyantraniliprole (4.63), chlorantraniliprole (5.55), and spinosyn A (4.8). Owing to the hydrophobicity of the cannabis oil, more hydrophilic compound classes (*i.e.* neonicotinoids, such as thiamethoxam) resulted in higher recovery than more hydrophobic analyte classes (*i.e.* ryanoids, such as cyantraniliprole and chlorantraniliprole), with intra-class recovery differences associated with ACD/LogP value differences (*i.e.* the lower recovery observed for chlorantraniliprole compared with cyantraniliprole). Notable exceptions to ACD/LogP and recovery relationships observed include the spinosyn class of compounds, likely due to presence of a positive charge on the tertiary amine moiety.

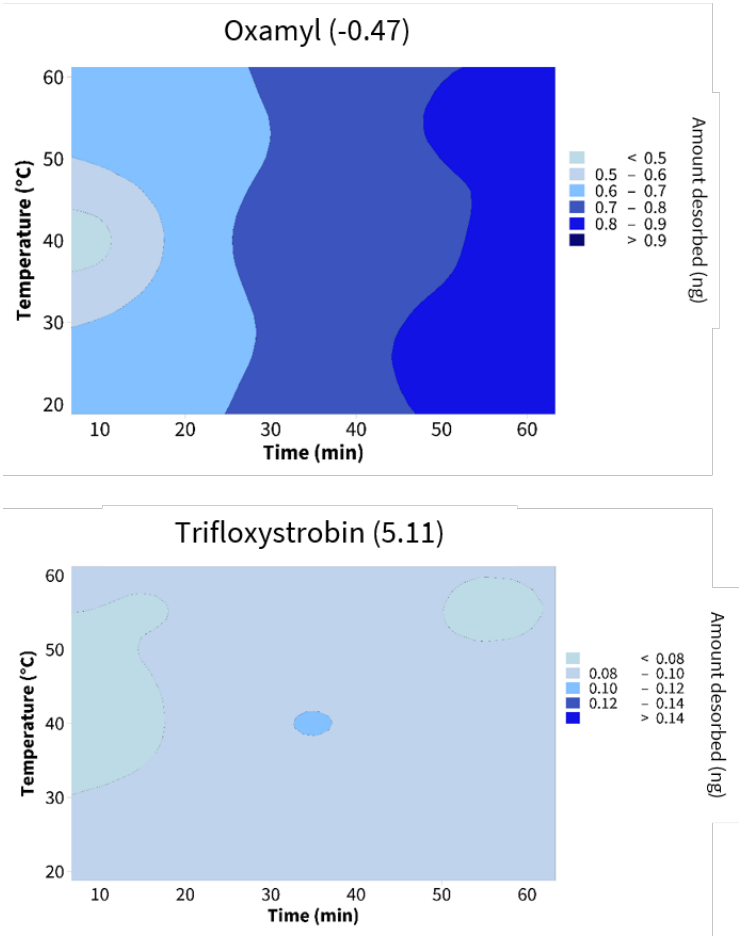

Figure 4.4: Additional analyte surface response behaviour observed with varying time and temperature of cannabis oil extraction. Amount desorbed independence from temperature was observed in oxamyl (A), a relatively small (219 Da), hydrophilic (ACD/LogP: -0.47), member of the carbamate class. Additionally, low recovery for members of the hydrophobic strobilurin class with no significant change in amount desorbed over the conditions tested were observed, as shown with trifloxystobin (ACD/LogP: 5.11) (B).

4.3.3 Method implementation and validation

Following determination of washing and extraction conditions, the performance of the method was evaluated via both CBS-MS/MS and LC-MS/MS according to the properties described in the prior section. As a summary, the CBS-MS/MS coupling resulted in 37

analytes meeting the quantitative criteria outlined, with 11 compounds resulting in figures of merit shy of the criteria, however displaying S/N values above 5 within the linear dynamic range tested. Upon comparison to the LC-MS/MS data a slight, expected, increase in compounds meeting quantitative criteria was observed at 55, with select compounds compared in the abridged figures of merit found in Table 4.3, with full figures of merit available in Table A.24, A.25, and A.26 in the Appendix. The causes of the deviation between methods are elaborated on in the following section. Satisfactory analytical performance (in terms of meeting quantitative requirements and MRLs) were achieved most frequently with compounds paired with their isotopologue as an internal standard. In this work, the internal standard-analyte matching was performed via 1 variable—the magnitude of the coefficient of determination. This basic algorithm likely has substantial room for improvement, however was not examined in depth due to the large suite of compounds under study. Inclusion of additional parameters (such as validation point precision contribution), could strengthen the quantitative capability of the technique, along with the monitoring of multiple internal-standard transitions to avoid matrix-sourced interference impacting correction. Similarly, due to the breadth of cannabis concentrate products available, the validation of the methodology with products containing differing psychoactive ingredient concentrations and composed of differing carrier oils, is desired.

Table 4.3: Abridged CBS-MS/MS and LC-MS/MS figures of merit for pesticides extracted from cannabis oil.

				LOQ	MRL	Accuracy, $ng \cdot g^{-1}$ (%)			Precision, $ng \cdot g^{-1}$ (%)		
Compound	**Method**	**IS**	$\mathbf{R^2}$	$(ng \cdot g^{-1})$	$(ng \cdot g^{-1})$	**15**	**80**	**150**	**15**	**80**	**150**
acephate	LC	atrazine-d_5	0.9864	10	50	91	103	101	11	4	5
	CBS	dimethoate-d_6	0.9821	10		114	102	85	8	6	6
acetamiprid	LC	dimethoate-d_6	0.9920	5	50	86	103	96	21	5	13
	CBS	imazalil-d_5	0.9899	5		97	110	111	27	12	10
azoxystrobin	LC	acephate-d_3	0.9954	2.5	10	87	98	95	9	17	2
	CBS	spirotetramat-d_6	0.9904	5		75	98	108	10	16	10
chlorantraniliprole	LC	dimethoate-d_6	0.9938	5	-	86	97	92	4	7	9
	CBS	spirotetramat-d_6	0.9889	10		89	99	109	17	7	16
fludioxonil	LC	dimethoate-d_6	0.9736	10	10	91	97	94	16	17	2
	CBS	fludioxonil-$^{13}C_2$	0.9785	10		127	105	94	36	6	9
imazalil	LC	imazalil-d_5	0.9950	2.5	10	81	103	98	4	7	3
	CBS	imazalil-d_5	0.9987	2.5		88	97	96	3	2	4
imidacloprid	LC	atrazine-d_5	0.9941	2.5	10	91	102	98	9	10	6
	CBS	dimethoate-d_6	0.9597	25			106	89		25	22
metalaxyl	LC	metalaxyl-d_6	0.9913	5	10	88	101	90	18	15	10
	CBS	metalaxyl-d_6	0.9938	2.5		79	92	92	9	9	5
spinosyn A	LC	imazalil-d_5	0.9945	2.5	10	82	89	99	9	14	12
	CBS	carbofuran-d_3	0.9897	2.5		84	105	90	12	23	27
thiacloprid	LC	dimethoate-d_6	0.9917	2.5	10	83	96	102	9	11	6
	CBS	imazalil-d_5	0.9746	10		75	110	115	24	14	16
trifloxystrobin	LC	carbofuran-d_3	0.9932	10	10	84	83	84	10	13	13
	CBS	atrazine-d_5	0.9631	25			128	99		18	19

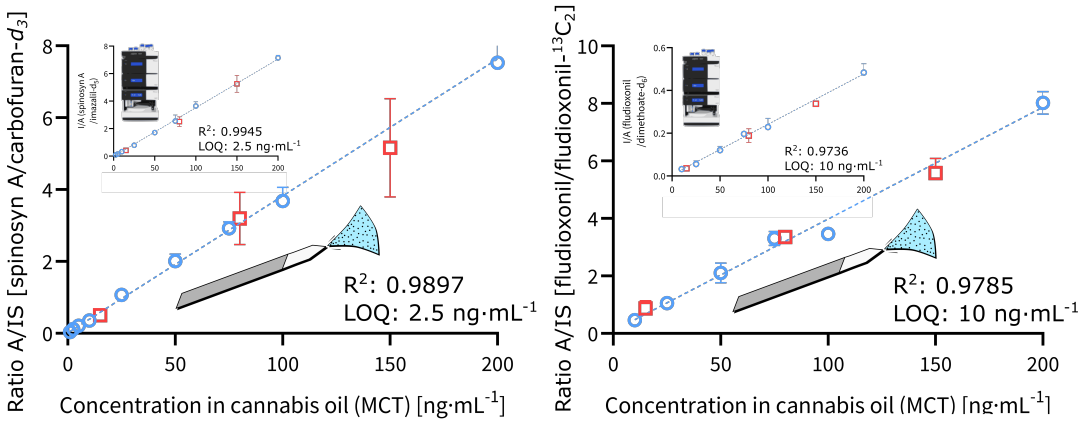

Figure 4.5: The quantitative performance of select compounds spinosyn A and fludioxonil are shown with calibration (blue circular points) and validation (orange square points) points plotted. CBS-MS/MS generated data is enlarged whilst comparable LC-MS/MS calibration plots were achieved and are shown in the top left-hand corner of each plot. For both compounds, MRLs are at the 10 ng·g^{-1} level, met via both instrumental approaches.

4.3.4 Method application for CBS-MS/MS analysis

Due to the non-selective nature of cannabis extraction via commonplace methods,[117,118] the complexity of the chemical profile present in oil is only rivaled by the source plant material — translating into several expected difficulties for any direct-to-MS approach. Although direct-to-MS techniques with integrated SPME sample preparation allow for significant instrumental and practical flexibility, the pre-concentration step is governed by compound affinity to the extraction phase, and thus carries the advantage (or disadvantage) of non-specificity. In the context of multi-residue screening, broad analyte variety can be extracted from the matrix, along with an array of constituents of the aforementioned chemical profile. In this case, isobaric interference (relevant due to the triple quadrupole instrument used in this work) were found to be sourced from plant endogenous compounds[96] (as shown for benzovindiflupyr, carbofuran, dichlorvos in Figures 4.6) or compounds found sourced from the MCT carrier oil (as shown for carbaryl in Figure 4.6). Similarly, differences in S/N values between compounds extracted from cannabis-free MCT oil and the cannabis oil product suggest contributions to noise, ionization suppression, or desorption

competition due to the co-extraction of high concentration metabolites as shown for select compounds in Table A.27 in the Appendix (*i.e.* such as the cannabinoid class compounds, reported at several mg/mL for THC and CBD, with precursors and others at unreported concentrations) as the primary bad actors impacting quantitative performance—however this represents an area where additional research is desired. The importance of method development with representative matrices to the target matrix cannot be understated. In fact, simply the inter-matrix variability with a class like cannabis oils is immense (*i.e.* differing carrier oils, order of magnitude differences in concentration ranges of psychoactive ingredients [and thus co-extractives], differences in plant chemical profile due to variability in raw flower extraction methods) and thus method development on cannabis-free carrier oils is not advisable. In some cases, it was found that isobaric interference can be bypassed to achieve quantitative or screening performance (shown as an example in phosmet in Figure 4.7) through the implemention of less common parent-product transitions, such as in-source fragments of compounds of interest[119] (taking care to ensure internal standards used do not produce in-source fragments shedding their prized isotopically-labelled moieties as was unfortunately realized for methiocarb-d_3). Finally, exploration of different mass-analyzers allowing for high-resolution or multi-stage fragmentation analysis could alleviate interference based quantitative difficulties, as has been demonstrated.[49,86]

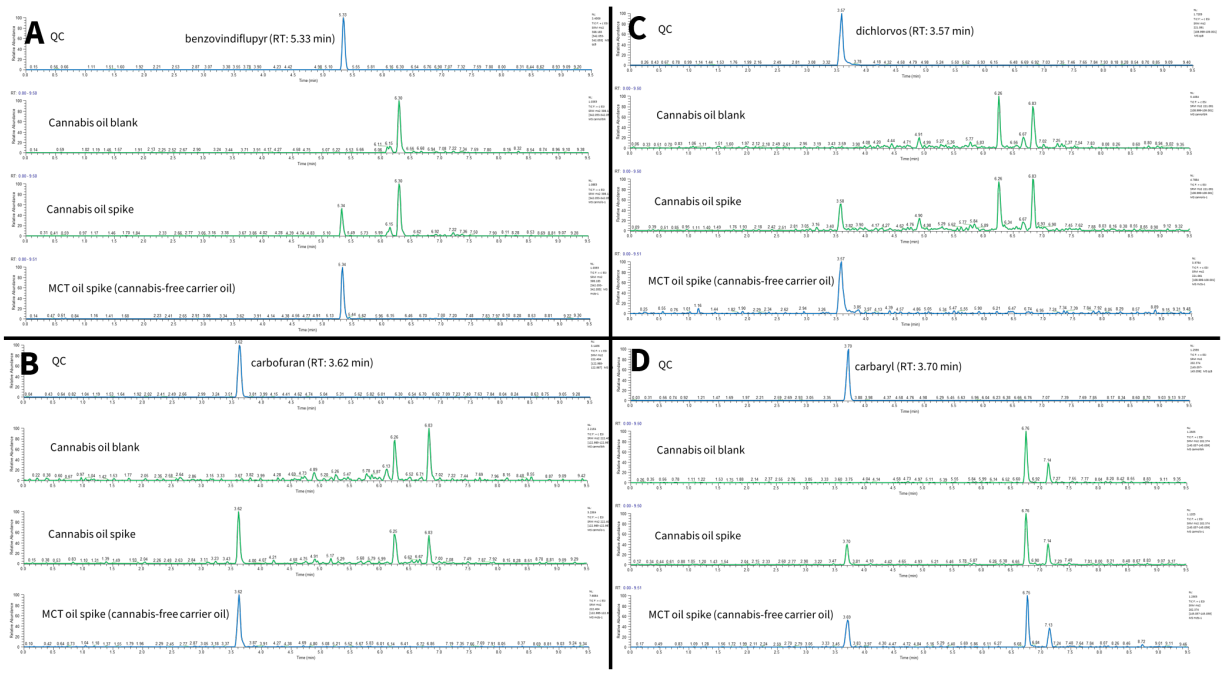

Figure 4.6: Various sample chromatograms monitoring benzovindiflupyr (Q_1 398 m/z $\longrightarrow$ Q_3 342 m/z), with interference found sourced from the cannabis oil matrix (green), with an interference-free chromatogram in the MCT oil spike sample.

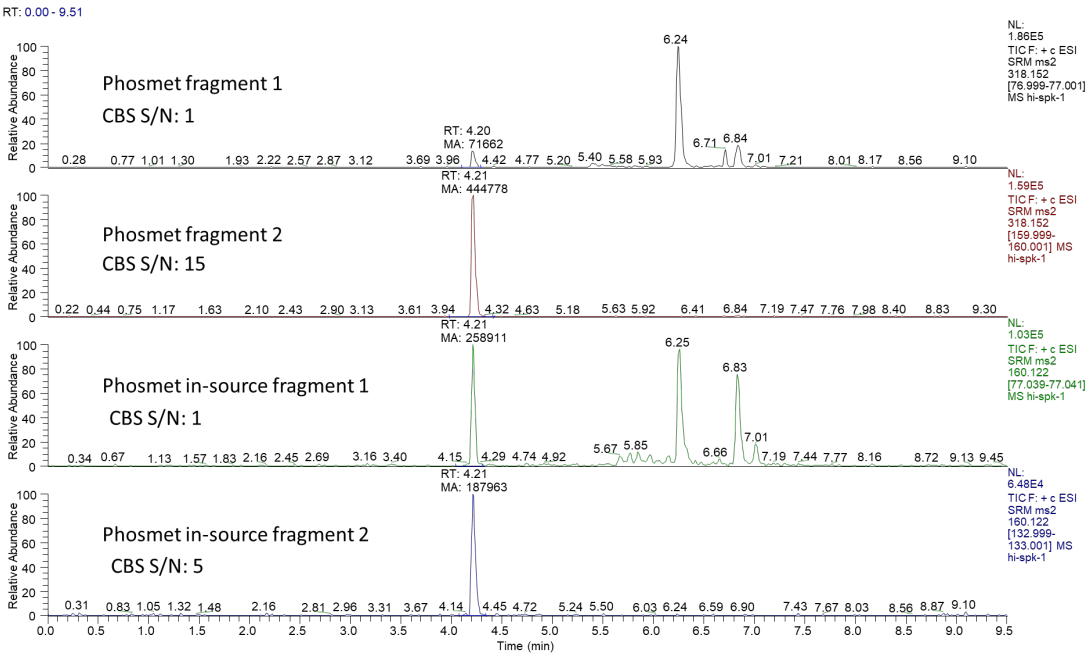

Figure 4.7: LC chromatograms for the 4 SRM transitions investigated for the quantitation of phosmet, matrix sourced (compared with blank) interferences found at 6.24 and 6.83 min in two of the transitions. CBS-MS/MS S/N data correlates with interferences found, with the optimal S/N shown for phosmet fragment 2.

4.4 Conclusions

In this work, avenues of application of CBS to pesticide screening, quantification, and confirmation via LC-MS/MS are demonstrated for the non-polar matrix of cannabis oil (*i.e* cannabis distillate diluted in a edible carrier oil). Methodological optimizations including determination of ISO as the optimal washing solvent in order to minimize extracted compound loss while maximizing removal of oil residue from the surface of the device and optimum time and temperature of extraction determination via central composite design experiments were demonstrated. The presented method optimization steps enable a better understanding of pesticide kinetic behaviour, as well as the hindrances that can be encountered upon developing a direct-to-MS methodology for a matrix with the complexity

of cannabis oil. Regardless of the quantitative challenges encountered for some compounds, the strengths of CBS are conserved for compounds meeting or exceeding quantitative requirements (*i.e.* MRLs, linearity, accuracy, precision). Namely the low sample usage used in this work (sub-1 mL sample volumes), throughput enabled with 96-blade simultaneous extraction and washing, rapid analysis times achieved with sub-minute spray times, and versatility provided with the usage of the same workflow in both instrumental couplings. We believe the work presented highlights areas lacking in exploration—hydrophobic analyte extraction from hydrophobic matrices remains an area of great interest (comparable to the similar antithesis of equilibrium extraction techniques of hyrdophilic compound extraction from aqueous matrices). Additionally, owing to the immense concentration of plant-sourced compounds compared to pesticides ($> 10^6$ and 10^{-1} ppm, respectively), cannabis-related matrices provide a surprisingly practical excuse for the study of displacement and analyte competition[120] in adsorptive coatings used in the direct immersion extraction format, an area woefully unexplored. As a final thought, the Canadian cannabis industry is generally vertically integrated (*i.e.* cannabis distillate is produced from Canadian plants, extracted in Canadian facilities, and integrated into Canadian-made value-added products), and one may wonder what is the value (from a regulatory perspective) of the introduced analytical complexity of an MRL for *each* compound for *each* product (*i.e.* oil permutations, dry flower, fresh flower). Revisions are being introduced[121] (hopefully considering this) to reduce potential redundant analysis, and it is likely that pesticide analysis in cannabis oil products will fade into irrelevance—leaving behind lessons in plant byproduct oil analysis.

4.5 What about cannabis flower?

As mentioned above, cannabis oil pesticide method development may not be the most effective use of time to regulate pesticide use on cannabis plants, and perhaps an investigation of the analysis of the raw flower itself is in order? As previously discussed and visually simplified, the matrices attempted thus far represent the ground floor of pesticide agricultural analysis (in terms of difficulty). There has yet to be an exploration into the suitability of SPME—and further, SPME coupled to MS—techniques for the extraction of pesticides from fat-containing, wax-containing, low-water content matrices (*i.e.* legumes,

nuts, herbs, hops, and—of specific interest—raw cannabis flower). The purpose of the following subsection is to share and communicate failure, outlining the causes of hardship for such matrices—hoping to save the time of future readers.

All mentioned experiments below were completed with dried cannabis flower procured from the Ontario Cannabis Store; The Green Organic Dutchman, with the product name 'Unite Organic' (with a THC content (w/w) of 8.33 % and a total THC and Δ^9-tetrahydrocannabinolic acid (THCa) content (w/w) of 19.96 %). Methods of analysis are mentioned in-text alongside the presentation of results.

4.5.1 What if the *matrix* is an excellent sorbent?

The significant binding of pesticides to the oil-rich matrix components of agricultural products originating from on unfertilized flowers (*i.e.* cannabis, hops) is well documented.[103,122,123] As an equilibrium extraction technique, release of compounds from the dried cannabis particle binding sites is paramount to reaching the low MRLs stipulated for this matrix by Health Canada. Matrix modification via addition of ACN displays the difficulty best in Figure 4.8, with multiple optima observed depending on analyte hydrophobicity (correlating to hypothesized proportion bound).[88] A potentially fruitful pursuit would be the modification of the matrix (*i.e.* addition of an organic dilutant) at several levels, optimized for maximum recovery of analytes spanning the hydrophobicity spectrum. The exploration of other matrix modification techniques has also been attempted, to no avail (read: no statistically significant recovery increase from control): the digestion of cellulose/lignocellulose/pectin particulate core with cellusase (sourced from *Trichoderma reesei*) and Viscozyme L (sourced from *Aspergillus* sp. and *Aspergillus* sp.), investigation of dilution with water and surfactant mixtures (*i.e.* 2 % Tween 20, 10 mM sodium dodecyl sulfate). Most promisingly, investigation of dilution with solvents such as iso-octane and ethyl acetate, yielded broader coverage compounds above LOD in one extraction step when compared to water or water/ACN or water/ACE mixtures, however still not meeting regulatory requirements. In the ideal case, say a matrix modification is found enabling the liberation of 100-fold more bound residues, this liberation would have to be selective for the analytes of interest as the liberation of endogenous compounds (*i.e.* cannabinoids)

at the concentrations found in our matrix (20 % by mass, or 200,000 ppm) impacts our goals downstream when we pursue simultaneous ionization of what is extracted onto the coating.

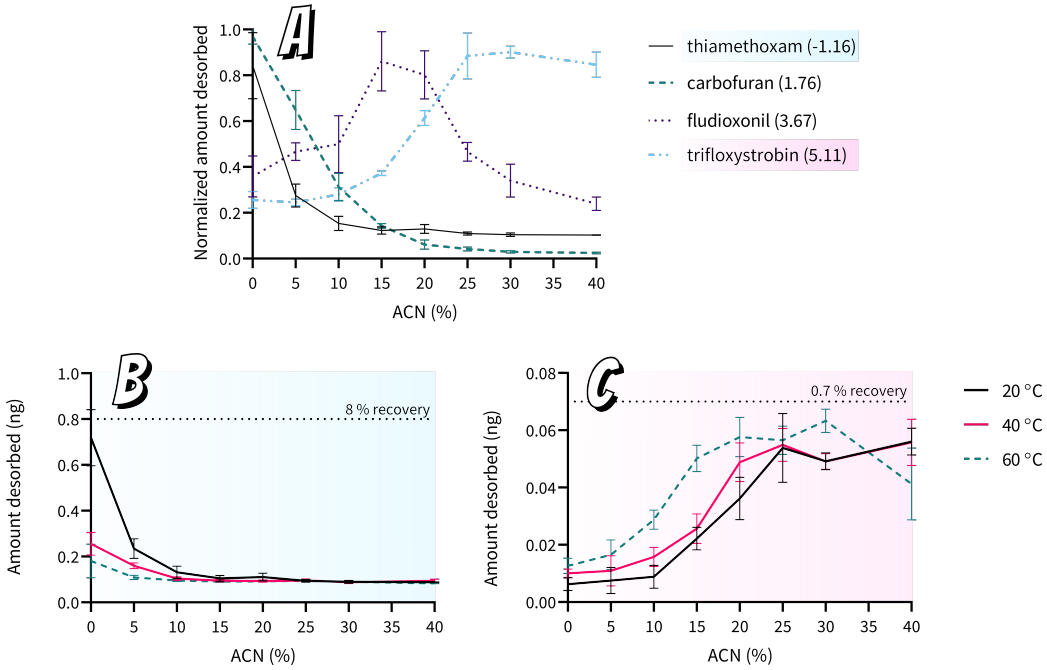

Figure 4.8: Select pesticide absolute and relative recovery (LC-MS/MS) at differing % ACN compositions and extraction temperatures. Samples were composed of 1 mL of 10 times diluted spiked cannabis flower at 100 ng/g (corresponding to 0.1 g of cannabis flower per sample, with 10 ng of pesticide in each sample). In A, relative recoveries of pesticides representing the breadth of the logP range under study show the multiple optima observed depending on pesticide chemical properties and % ACN in the dilution solution (acting as a aid to increase the free concentration of suspected bound pesticides, allowing for their extraction via SPME). In B, the relationship with absolute recovery (in ng) and % ACN as well as temperature of extraction is displayed for a fairly polar, hydrophilic compound in the panel under study—thiamethoxam. In C, the relationship with absolute recovery (in ng) and % ACN as well as temperature of extraction is displayed for a fairly non-polar, hydrophobic compound in the panel under study—trifloxystrobin. Percent recovery for both compounds is noted at maxima.

4.5.2 You want to ionize all of that at once?

Along with ionization of potential matrix-sourced interference resulting in S/N ratios of 1 observed (due to nominal-mass isobars as discussed in the prior figure), one must consider the amounts of cannabinoids co-extracted along with our pesticides of interest. To compare amount recoveries of cannabinoids extracted at similar conditions to those in Figure 4.8, the mass of THC co-extracted was determined using similar methodology. The determination of the mass of THC extracted from the dried cannabis flower was 0.139 ± 0.023 μg and 8.06 ± 0.99 μg for the aqueous (99:1, water:acetone) and organic (75:25, water:acetonitrile) dilutions, respectively. It is important to note that these values could vary substantially between cannabis strains and products due to the variability of cannabinoid concentration (approximately 0 – 30 % [w/w] for THC and 0 – 20 % [w/w] for CBD in dried flower products). As a comparison with a highly bound residue in trifloxystrobin at the 25 % ACN condition, 1.3E5 more THC was extracted. The impact this amount disparity has on extraction, desorption, and ionization competition has not been explored. Additionally, although THC and CBD concentrations are labelled on each product, other cannabinoids and precursors in the biosynthetic pathway are likely also present at percent-mass concentrations.

4.5.3 Doped if you do, doped if you don't

Experiments presented thus far demonstrate the difficulties with dried cannabis flower extraction and analysis via CBS (specific to the analytes of interest) with low S/N values being commonplace for the panel of pesticides under study. Matrix modification seems to result in a 'catch-22',[124] where the release of pesticides not extracted due to suspected high analyte-matrix binding also causes the release of ionization or desorption suppressing compounds (cannabinoids and biosynthetic precursors) in large quantities. The prevention of co-extraction of these compounds without significantly impacting the extraction of the analytes of interest (compounds of a broad range of classes, with similar size and moieties to cannabinoid class compounds in many cases [aromatic rings, lipophilic carbon chains]) is hypothesized to be extremely challenging.

Perhaps future instrument vendors will provide instrumentation with enough mass-filtering, ion mobility, and trapping elements[125] to allow for onlinE matriX-sourced aCcuRatE-Mass intErfereNce filTering (EXCREMENT), however ESI capacity will remain a concern.[77] Barring instrumentation, ionization, and sorbent advancements, SPME coupled to MS is simply not the correct approach.

Chapter 5

Conclusions

5.1 Summary

The increasing reliance on imported agricultural products, regulation of previously unregulated agricultural matrices (*i.e.* as demonstrated by the legitimization of cannabis cultivation), shifting consumer demand, and the ever increasing global population all result in increasing pressure on pesticide regulation bodies—culminating in an ever increasing lust for increasing type and number of samples analyzed. Existing sample preparation methods, such as those based on SE or QuEChERS, lack the scalability both in terms of environmental impact and resources (*e.g.* time, sample size, volume of solvent) when compared to SPME-based protocols. These strengths, along with the further resource-reduction enabled by AMS techniques, such as CBS, encourage their exploration for the ever-demanding analysis of multi-residue pesticides in agricultural matrices.

Although routine in the privileged world of chromatography coupled to tandem mass spectrometry, >100 target compound analysis was demonstrated as feasible in an initial proof of concept study as part of the development of another requirement for real-world application—autosampler operation. Following encouraging results, pesticide analysis *via* CBS was expanded to fruit matrices (*e.g.* apple, blueberry, grape, and strawberry) with validation of the methodology completed with LC-MS/MS and further applied to 15 real-world samples resulting in the quantitation and confirmation (*via* LC-MS/MS) of over 50

pesticide residues in locally-procured products. Finally, the technique was tested with the substantially more problematic cannabis suite of matrices, with full method development demonstrated in cannabis oil, and several preliminary studies completed in dried cannabis flower.

The studies presented lay the foundation of, what the author believes, the ideal AMS coupling for pesticide analysis in a variety of agricultural matrices. With automation and same-device LC-MS/MS validation compatibility allowing the analyst to leverage both rapid screening and chromatographic confidence.

5.2 Shortcomings, self-reflection, and future challenges

Notably, many references to *routine* (*i.e.* QuEChERS, SE) workflows are made in this thesis—however a comprehensive comparison between the routine and CBS-MS/MS or SPME-LC-MS/MS has not been undertaken. The claims of cost savings, time savings, and analytical figures of merit conservation may have been demonstrated for *select* compounds in *select* matrices, however the exploration of if this will hold true at the scale of thousands of samples has (understandably) yet to be demonstrated. Similarly, to compete with a methodology as far-reaching as QuEChERS, comprehensive inter-laboratory studies of the proposed workflows would have to be undertaken.

Shifting gears to the small scale, there are classes of pesticides and types of matrices which— as attempted in this thesis—proved difficult. Ignoring the plethora of pesticides with poor amenability to proton deposition or removal *via* ESI, these include analytes on the extremes of hydrophilicity and hydrophobicity. Compounds in which the Δ of LogP (if such a term was known) is low between the matrix of interest and the target (*e.g.* such as acephate in water, or the pyrethroid class in cannabis oil) are difficult intrinsically due to competition for partitioning with the matrix. Additionally, hydrophobic compounds in aqueous, particulate-containing matrices can prove problematic due to particulate binding. Particulate binding can be exacerbated (analyte affinity to the particle increased) if the bad-acting particle is coated in a hydrophobic oil itself—as was observed with dried cannabis flower. These long-standing weaknesses of SPME will continue to be explored by

researchers through sorbent development and matrix modification.

Finally, many of the experiments in this thesis were validated *via* LC-MS/MS. Although daunting (as the experiment is doubled in scope), I believe it to be necessary to garner maximum confidence in the data collected whilst working with a technique family prone to generating as many false-leads as the AMS cohort. Additionally, with CBS, this validation step is made trivial in comparison to other AMS workflows, as it is compatible with instrumental couplings as any DI-SPME device before it.

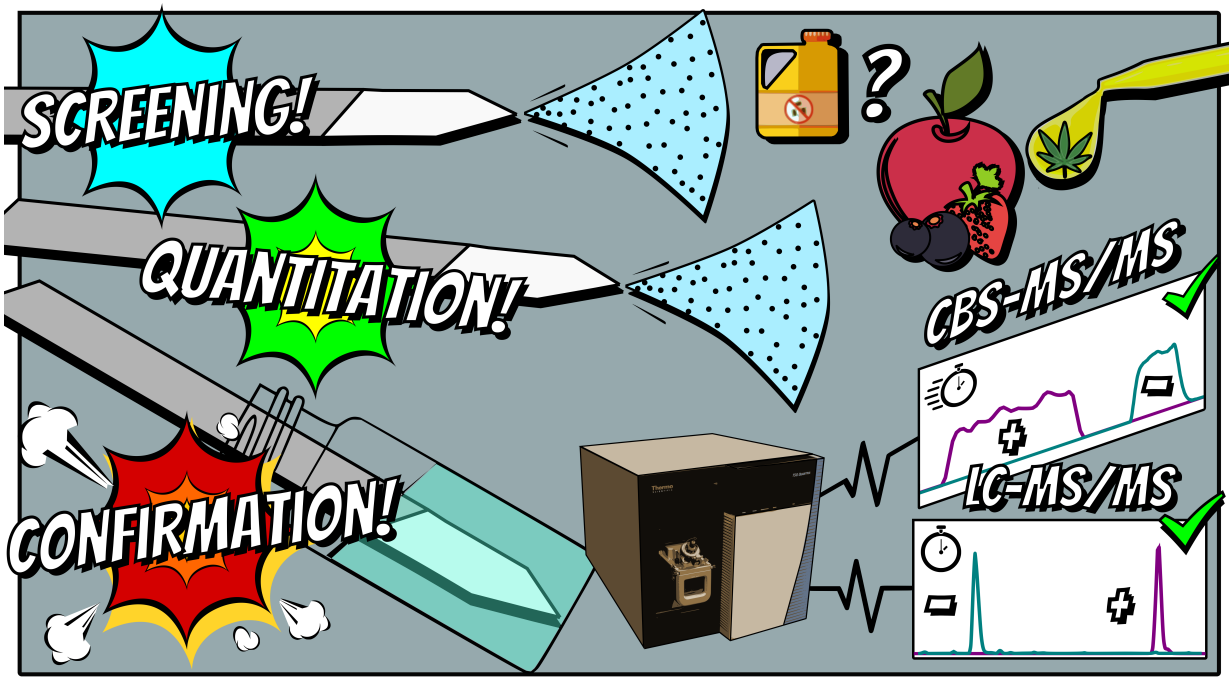

Figure 5.1: You need to love to measure twice if you want to measure once.

References

(1) M. Gros, M. Petrović and D. Barceló, *Analytical and Bioanalytical Chemistry*, 2006, **386**, 941–952 [Take me back!]

(2) D. R. Baker and B. Kasprzyk-Hordern, *Journal of Chromatography A*, 2011, **1218**, 1620–1631 [Take me back!]

(3) L. Zhao, D. Lucas, D. Long, B. Richter and J. Stevens, *Journal of Chromatography A*, 2018, **1549**, 14–24 [Take me back!]

(4) A. Khaled, E. Gionfriddo, V. Acquaro, V. Singh and J. Pawliszyn, *Analytica Chimica Acta*, 2019, **1056**, 34–46 [Take me back!]

(5) K. Zhang, J. W. Wong, P. Yang, K. Tech, A. L. Dibenedetto, N. S. Lee, D. G. Hayward, C. M. Makovi, A. J. Krynitsky, K. Banerjee, L. Jao, S. Dasgupta, M. S. Smoker, R. Simonds and A. Schreiber, *Journal of Agricultural and Food Chemistry*, 2011, **59**, 7636–7646 [Take me back!]

(6) E. Stover, M. Blackburn, O. Silivra, J. Wang, J. Beck, C. Yang, D. Ghosh, T. Fisher Scientifi and S. Jose, 61st ASMS Conference on Mass Spectrometry and Allied Topics, Minneapolis, 2013 [Take me back!]

(7) J. Al-Alam, Z. Fajloun, A. Chbani and M. Millet, *Analytical and Bioanalytical Chemistry*, 2017, **409**, 5157–5169 [Take me back!]

(8) R. A. Neff, J. C. Hartle, L. I. Laestadius, K. Dolan, A. C. Rosenthal and K. E. Nachman, *Globalization and Health*, 2012, **8**, DOI: 10.1186/1744-8603-8-2 [Take me back!]

(9) EFSA (European Food Safety Authority), *EFSA Journal*, 2018, **16**, 139 [Take me back!]

(10) M. Anastassiades, S. J. Lehotay, D. Štajnbaher and F. J. Schenck, *Journal of AOAC International*, 2003, **86**, 412–431 [Take me back!]

(11) P. Kaewsuya, W. E. Brewer, J. Wong and S. L. Morgan, *Journal of Agricultural and Food Chemistry*, 2013, **61**, 2299–2314 [Take me back!]

(12) R. Raina, in *Pesticides - Strategies for Pesticides Analysis*, InTechOpen, 2011, ch. 5 [Take me back!]

(13) L. Alder, K. Greulich, G. Kempe and B. Vieth, *Mass Spectrometry Reviews*, 2006, **25**, 838–865 [Take me back!]

(14) L. G. Freitas, C. W. Götz, M. Ruff, H. P. Singer and S. R. Müller, *Journal of Chromatography A*, 2004, **1028**, 277–286 [Take me back!]

(15) M. Pastor-Belda, I. Garrido, N. Campillo, P. Viñas, P. Hellín, P. Flores and J. Fenoll, *Journal of Chromatography A*, 2015, **1394**, 1–8 [Take me back!]

(16) I. Ishaaya, S. Kontsedalov and A. R. Horowitz, *Pest Management Science*, 2002, **58**, 1091–1095 [Take me back!]

(17) B. K. Matuszewski, M. L. Constanzer and C. M. Chavez-Eng, *Analytical Chemistry*, 2003, **75**, 3019–3030 [Take me back!]

(18) E. M. Thurman, I. Ferrer and D. Barceló, *Analytical Chemistry*, 2001, **73**, 5441–5449 [Take me back!]

(19) S. Reynolds, R. Fussell, A. de Kok and M. Anastassiades, *European Commission, Health & Consumer Protection Directorate-General*, 2013, 2–44 [Take me back!]

(20) R. E. Galt, *Global Environmental Change*, 2008, **18**, 786–799 [Take me back!]

(21) R. P. Belardi and J. B. Pawliszyn, *Water Pollut. Res. J. Can.*, 1989, **24**, 179–191 [Take me back!]

(22) C. L. Arthur and J. Pawliszyn, *Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers*, 1990 [Take me back!]

(23) N. Reyes-Garcés, E. Gionfriddo, G. A. Gómez-Ríos, M. N. Alam, E. Boyacl, B. Bojko, V. Singh, J. Grandy and J. Pawliszyn, *Analytical Chemistry*, 2018, **90**, 302–360 [Take me back!]

(24) M. L. Musteata, F. M. Musteata and J. Pawliszyn, *Analytical Chemistry*, 2007, **79**, 6903–6911 [Take me back!]

(25) É. A. Souza-Silva and J. Pawliszyn, *Journal of Agricultural and Food Chemistry*, 2015, **63**, 4464–4477 [Take me back!]

(26) E. Gionfriddo, É. A. Souza-Silva and J. Pawliszyn, *Analytical Chemistry*, 2015, **87**, 8448–8456 [Take me back!]

(27) É. A. Silva, V. Lopez-Avila and J. Pawliszyn, *Journal of Chromatography A*, 2013, **1313**, 139–146 [Take me back!]

(28) É. A. Souza-Silva, E. Gionfriddo and J. Pawliszyn, *TrAC - Trends in Analytical Chemistry*, 2015, **71**, 236–248 [Take me back!]

(29) D. Vuckovic, E. Cudjoe, F. M. Musteata and J. Pawliszyn, *Nature Protocols*, 2010, **5**, 140–161 [Take me back!]

(30) Z. Takáts, J. M. Wiseman, B. Gologan and R. G. Cooks, *Science*, 2004, **306**, 471–473 [Take me back!]

(31) R. B. Cody, J. A. Laramée and H. D. Durst, *Analytical Chemistry*, 2005, **77**, 2297–2302 [Take me back!]

(32) M. Domin and R. Cody, in *Ambient Ionization Mass Spectrometry (New Developments in Mass Spectrometry)*, The Royal Society of Chemistry, Cambridge, UK, 2nd edn., 2015, ch. 18, pp. 445–461 [Take me back!]

(33) J. Liu, H. Wang, N. E. Manicke, J. M. Lin, R. G. Cooks and Z. Ouyang, *Analytical Chemistry*, 2010, **82**, 2463–2471 [Take me back!]

(34) Y. Su, H. Wang, J. Liu, P. Wei, R. G. Cooks and Z. Ouyang, *Analyst*, 2013, **138**, 4443–4447 [Take me back!]

(35) H. Evard, A. Kruve, R. Lõhmus and I. Leito, *Journal of Food Composition and Analysis*, 2015, **41**, 221–225 [Take me back!]

(36) D. Kim, U. H. Yim, B. Kim, S. Cha and S. Kim, *Analytical Chemistry*, 2017, **89**, 9056–9061 [Take me back!]

(37) L. Shen, J. Zhang, Q. Yang, N. E. Manicke and Z. Ouyang, *Clinica Chimica Acta*, 2013, **420**, 28–33 [Take me back!]

(38) H. Zhu and G. Huang, *Rapid Communications in Mass Spectrometry*, 2019, **33**, 392–398 [Take me back!]

(39) C. Vega, C. Spence, C. Zhang, B. J. Bills and N. E. Manicke, *Journal of the American Society for Mass Spectrometry*, 2016, **27**, 726–734 [Take me back!]

(40) B. J. Bills, J. Kinkade, G. Ren and N. E. Manicke, *Forensic Chemistry*, 2018, **11**, 15–22 [Take me back!]

(41) Z. Zhang, W. Xu, N. E. Manicke, R. G. Cooks and Z. Ouyang, *Analytical Chemistry*, 2012, **84**, 931–938 [Take me back!]

(42) T. Wang, Y. Zheng, X. Wang, D. E. Austin and Z. Zhang, *Analytical Chemistry*, 2017, **89**, 7988–7995 [Take me back!]

(43) G. A. Gómez-Ríos and M. F. Mirabelli, *TrAC - Trends in Analytical Chemistry*, 2019, **112**, 201–211 [Take me back!]

(44) G. A. Gómez-Ríos and J. Pawliszyn, *Angewandte Chemie - International Edition*, 2014, **53**, 14503–14507 [Take me back!]

(45) G. A. Gómez-Ríos, M. Tascon, N. Reyes-Garcés, E. Boyaci, J. J. Poole, J. Pawliszyn, E. Boyacı, J. J. Poole and J. Pawliszyn, *Analytica Chimica Acta*, 2018, **999**, 69–75 [Take me back!]

(46) J. Pawliszyn, in *Handbook of Solid Phase Microextraction*, Elsevier, London, England, 2012, ch. 3, pp. 61–97 [Take me back!]

(47) J. J. Poole, G. A. Gómez-Ríos, E. Boyaci, N. Reyes-Garcés and J. Pawliszyn, *Environmental Science and Technology*, 2017, **51**, 12566–12572 [Take me back!]

(48) G. A. Gómez-Ríos, E. Gionfriddo, J. Poole and J. Pawliszyn, *Analytical Chemistry*, 2017, **89**, 7240–7248 [Take me back!]

(49) M. Tascon, G. A. Gómez-Ríos, N. Reyes-Garcés, J. Poole, E. Boyacl and J. Pawliszyn, *Analytical Chemistry*, 2017, **89**, 8421–8428 [Take me back!]

(50) G. A. Gómez-Ríos, C. Liu, M. Tascon, N. Reyes-Garcés, D. W. Arnold, T. R. Covey and J. Pawliszyn, *Analytical Chemistry*, 2017, **89**, 3805–3809 [Take me back!]

(51) S. Perez, P. Eichhorn and D. Barceló, *Applications of Time-of-Flight and Orbitrap Mass Spectrometry in Environmental, Food, Doping, and Forensic Analysis*, 2016 [Take me back!]

(52) D. J. Douglas, *Journal of the American Society for Mass Spectrometry*, 1998, **9**, 101–113 [Take me back!]

(53) A. Kaufmann, P. Butcher, K. Maden, S. Walker and M. Widmer, *Rapid Communications in Mass Spectrometry*, 2011, **25**, 979–992 [Take me back!]

(54) M. Kellmann, H. Muenster, P. Zomer and H. Mol, *Journal of the American Society for Mass Spectrometry*, 2009, **20**, 1464–1476 [Take me back!]

(55) O. Silivra, H. Oser, J. T. Maze, T. Olney and A. Schoen E., *Optimizing Drag Field Voltages in a Collision Cell for Multiple Reaction Monitoring (MRM) Tandem Mass Spectrometry*, 2015 [Take me back!]

(56) R. Javanshad and A. R. Venter, *Analytical Methods*, 2017, **9**, 4896–4907 [Take me back!]

(57) M. E. Monge, G. A. Harris, P. Dwivedi and F. M. Fernández, *Mass spectrometry: Recent advances in direct open air surface sampling/ionization*, 2013 [Take me back!]

(58) C. L. Feider, A. Krieger, R. J. DeHoog and L. S. Eberlin, *Analytical Chemistry*, 2019, **91**, 4266–4290 [Take me back!]

(59) K. C. Schäfer, J. Dénes, K. Albrecht, T. Szaniszló, J. Balogh, R. Skoumal, M. Katona, M. Tóth, L. Balogh and Z. Takáts, *Angewandte Chemie - International Edition*, 2009, **48**, 8240–8242 [Take me back!]

(60) W. Jian, M. V. Romm, R. W. Edom, V. P. Miller, W. A. Lamarr and N. Weng, *Analytical Chemistry*, 2011, **83**, 8259–8266 [Take me back!]

(61) B. T. Veach, T. K. Mudalige and P. Rye, *Analytical Chemistry*, 2017, **89**, 3256–3260 [Take me back!]

(62) J. Wu, C. S. Hughes, P. Picard, S. Letarte, M. Gaudreault, J. F. Lévesque, D. A. Nicoll-Griffith and K. P. Bateman, *Analytical Chemistry*, 2007, **79**, 4657–4665 [Take me back!]

(63) P. B. Fayad, M. Prévost and S. Sauvé, *Analytical Chemistry*, 2010, **82**, 639–645 [Take me back!]

(64) Z. Haarhoff, A. Wagner, P. Picard, D. M. Drexler, T. Zvyaga and W. Shou, *Journal of Biomolecular Screening*, 2016, **21**, 165–175 [Take me back!]

(65) E. Jones, B. Shrestha, L. Doria, D. Gurung, R. F. Soares, F. Henderson, S. Pringle, K. J. Williams, A. McMahon and Z. Takáts, AACR Annual Meeting, American Association for Cancer Research, Chicago, IL, 2018, Poster 5654 [Take me back!]

(66) F. Bolt, S. J. S. Cameron, T. Karancsi, D. Simon, R. Schaffer, T. Rickards, K. Hardiman, A. Burke, Z. Bodai, A. Perdones-Montero, M. Rebec, J. Balog and Z. Takats, *Analytical Chemistry*, 2016, **88**, 9419–9426 [Take me back!]

(67) X. Chen, Z. Bian, H. Hou, F. Yang, S. Liu, G. Tang and Q. Hu, *Journal of Agricultural and Food Chemistry*, 2013, **61**, 5746–5757 [Take me back!]

(68) A. Wang, S. Hynynen, A. R. Hawkins, S. E. Tolley, H. D. Tolley and M. L. Lee, *Journal of Chromatography A*, 2014, **1374**, 216–223 [Take me back!]

(69) D. C. Patel, M. F. Wahab, T. C. O'Haver and D. W. Armstrong, *Analytical Chemistry*, 2018, **90**, 3349–3356 [Take me back!]

(70) M. F. Wahab, R. M. Wimalasinghe, Y. Wang, C. L. Barhate, D. C. Patel and D. W. Armstrong, *Analytical Chemistry*, 2016, **88**, 8821–8826 [Take me back!]

(71) I. Lanekoff, S. L. Stevens, M. P. Stenzel-Poore and J. Laskin, *Analyst*, 2014, **139**, 3528–3532 [Take me back!]

(72) S. Lendor, G. A. Gómez-Ríos, E. Boyacl, H. Vander Heide and J. Pawliszyn, *Analytical Chemistry*, 2019, **91**, 10141–10148 [Take me back!]

(73) N. Reyes-Garcés, B. Bojko, D. Hein and J. Pawliszyn, *Analytical Chemistry*, 2015, **87**, 9722–9730 [Take me back!]

(74) W. M. Niessen and R. A. Correa C., *Interpretation of MS-MS Mass Spectra of Drugs and Pesticides*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2016, pp. 1–388 [Take me back!]

(75) E. Jagerdeo and A. Wriston, *Rapid Communications in Mass Spectrometry*, 2017, **31**, 782–790 [Take me back!]

(76) L. B. Nilsson and P. Skansen, *Rapid Communications in Mass Spectrometry*, 2012, **26**, 1399–1406 [Take me back!]

(77) D. G. Beach and W. Gabryelski, *Analytical Chemistry*, 2013, **85**, 2127–2134 [Take me back!]

(78) Agricultural Marketing Service, *Pesticide Data Program. Annual Summary, Calendar Year 2018*, tech. rep. 9, 2019, pp. 1689–1699 [Take me back!]

(79) Á. Santana-Mayor, B. Socas-Rodríguez, A. V. Herrera-Herrera and M. Á. Rodríguez-Delgado, *TrAC - Trends in Analytical Chemistry*, 2019, **116**, 214–235 [Take me back!]

(80) H. Lu, H. Zhang, K. Chingin, J. Xiong, X. Fang and H. Chen, *Ambient mass spectrometry for food science and industry*, 2018 [Take me back!]

(81) A. C. M. Moura, I. N. Lago, C. F. Cardoso, A. dos Reis Nascimento, I. Pereira and B. G. Vaz, *Food Chemistry*, 2020, **310**, DOI: 10.1016/j.foodchem.2019.125938 [Take me back!]

(82) S. Gerbig, G. Stern, H. E. Brunn, R. A. Düring, B. Spengler and S. Schulz, *Analytical and Bioanalytical Chemistry*, 2017, **409**, 2107–2117 [Take me back!]

(83) L. Mainero Rocca, J. Cecca, N. L'Episcopo and G. Fabrizi, *Journal of Mass Spectrometry*, 2017, **52**, 709–719 [Take me back!]

(84) M. H. Blokland, A. Gerssen, P. W. Zoontjes, J. Pawliszyn and M. W. Nielen, *Food Analytical Methods*, 2020, **13**, 706–717 [Take me back!]

(85) C.-H. H. Xu, G.-S. S. Chen, Z.-H. H. Xiong, Y.-X. X. Fan, X.-C. C. Wang and Y. Liu, *TrAC - Trends in Analytical Chemistry*, 2016, **80**, 12–29 [Take me back!]

(86) A. Kasperkiewicz, G. A. Gómez-Ríos, D. Hein and J. Pawliszyn, *Analytical Chemistry*, 2019, **91**, 13039–13046 [Take me back!]

(87) M. N. Alam and J. Pawliszyn, *Analytical Chemistry*, 2018, **90**, 2430–2433 [Take me back!]

(88) A. Sabljić, H. Güsten, H. Verhaar and J. Hermens, *Chemosphere*, 1995, **31**, 4489–4514 [Take me back!]

(89) A. Knowles, *Environmentalist*, 2008, **28**, 35–44 [Take me back!]

(90) L. Wang, X. Li, G. Zhang, J. Dong and J. Eastoe, *Journal of Colloid and Interface Science*, 2007, **314**, 230–235 [Take me back!]

(91) BASF Corporation, *Current Label Pristine*, 2020 [Take me back!]

(92) Syngenta, *Current Label Switch 62.5WG*, 2020 [Take me back!]

(93) A. Liu, W. Kou, H. Zhang, J. Xu, L. Zhu, S. Kuang, K. Huang, H. Chen and Q. Jia, *Analytical Chemistry*, 2020, **92**, 4137–4145 [Take me back!]

(94) G. D. Crouse, T. C. Sparks, J. Schoonover, J. Gifford, J. Dripps, T. Bruce, L. L. Larson, J. Garlich, C. Hatton, R. L. Hill, T. V. Worden and J. G. Martynow, Pest Management Science, John Wiley & Sons, Ltd, 2001, vol. 57, pp. 177–185 [Take me back!]

(95) A. C. Dionisio and S. Rath, *Chemosphere*, 2016, **151**, 17–29 [Take me back!]

(96) M. M. Lewis, Y. Yang, E. Wasilewski, H. A. Clarke and L. P. Kotra, *ACS Omega*, 2017, **2**, 6091–6103 [Take me back!]

(97) N. Seltenrich, *Environmental Health Perspectives*, 2019, **127**, 042001 [Take me back!]

(98) D. Stone, *Cannabis, pesticides and conflicting laws: The dilemma for legalized States and implications for public health*, 2014 [Take me back!]

(99) M. C. Vann, L. R. Fisher and A. M. Stewart, *Tobacco Science*, 2008, **50**, 25–30 [Take me back!]

(100) Health Canada, *Mandatory cannabis testing for pesticide active ingredients: List and limits*, Government of Canada, Ottawa, ON, 2019, pp. 4–6 [Take me back!]

(101) A. Taylor and J. W. Birkett, *Drug Testing and Analysis*, 2020, **12**, 180–190 [Take me back!]

(102) J. R. Moulins, M. Blais, K. Montsion, J. Tully, W. Mohan, M. Gagnon, T. Mcritchie, K. Kwong, N. Snider and D. R. Blais, *Journal of AOAC International*, 2018, **101**, 1948–1960 [Take me back!]

(103) S. N. Atapattu and K. R. Johnson, *Journal of Chromatography A*, 2020, **1612**, 460656 [Take me back!]

(104) P. Valdes-Donoso, D. A. Sumner and R. Goldstein, *PLoS ONE*, 2020, **15**, ed. R. Sane, e0232041 [Take me back!]

(105) E. Hakme, A. Lozano, C. Ferrer, F. J. Díaz-Galiano and A. R. Fernández-Alba, *Analysis of pesticide residues in olive oil and other vegetable oils*, 2018 [Take me back!]

(106) A. Narváez, Y. Rodríguez-Carrasco, L. Castaldo, L. Izzo and A. Ritieni, *Toxins*, 2020, **12**, 114 [Take me back!]

(107) W. J. Maguire, C. W. Call, C. Cerbu, K. L. Jambor and V. E. Benavides-Montes, *Journal of Agricultural and Food Chemistry*, 2019, **67**, 12670–12674 [Take me back!]

(108) A. Dalmia, E. Cudjoe, T. Astill, J. Jalali, J. P. Weisenseel, F. Qin, M. Molly and T. Ruthenberg, *Cannabis Science and Technology*, 2018, **1** [Take me back!]

(109) D. Vuckovic, E. Cudjoe, D. Hein and J. Pawliszyn, *Analytical Chemistry*, 2008, **80**, 6870–6880 [Take me back!]

(110) Y. Ilias, S. Rudaz, P. Christen and J. L. Veuthey, *Chimia*, 2006, **60**, 846–851 [Take me back!]

(111) E. Gionfriddo, D. Gruszecka, X. Li and J. Pawliszyn, *Talanta*, 2020, **211**, DOI: 10.1016/j.talanta.2020.120746 [Take me back!]

(112) M. F. Mirabelli, E. Gionfriddo, J. Pawliszyn and R. Zenobi, *Analyst*, 2018, **143**, 891–899 [Take me back!]

(113) T. Pihlström, A. Fernández-Alba, M. Gamón, M. Erecius Poulsen, R. Lippold, M. Anastassiades, A. de Kok, P. Gros, C. Ferrer Amate, A. Valverde, H. Mol, M. Jezussek and O. Malato, *Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed*, 2017 [Take me back!]

(114) S. Sankararaman and T. J. Sferra, *Are We Going Nuts on Coconut Oil?*, 2018 [Take me back!]

(115) F. P. Byrne, S. Jin, G. Paggiola, T. H. M. Petchey, J. H. Clark, T. J. Farmer, A. J. Hunt, C. Robert McElroy and J. Sherwood, *Sustainable Chemical Processes*, 2016, **4**, 7 [Take me back!]

(116) B. Esteban, J. R. Riba, G. Baquero, A. Rius and R. Puig, *Biomass and Bioenergy*, 2012, **42**, 164–171 [Take me back!]

(117) L. J. Rovetto and N. V. Aieta, *Journal of Supercritical Fluids*, 2017, **129**, 16–27 [Take me back!]

(118) A. Wise, *Cannabis Science and Technology*, 2019, **2**, 20–26 [Take me back!]

(119) Z. He, Y. Xu, Y. Zhang, B. Liu and X. Liu, *Journal of Agricultural and Food Chemistry*, 2019, **67**, 10800–10812 [Take me back!]

(120) S. N. Semenov, J. A. Koziel and J. Pawliszyn, *Kinetics of solid-phase extraction and solid-phase microextraction in thin adsorbent layer with saturation sorption isotherm*, tech. rep., 2000, pp. 39–51 [Take me back!]

(121) Health Canada, *Mandantory cannabis testing for pesticide active ingredients: Requirements*, Government of Canada, Ottawa, ON, 2019, ch. 7, pp. 12–13 [Take me back!]

(122) M. Dušek, V. Jandovská and J. Olšovská, *Journal of Agricultural and Food Chemistry*, 2018, **66**, 10113–10121 [Take me back!]

(123) H. Sandermann, *Pest Management Science*, 2004, **60**, 613–623 [Take me back!]

(124) J. Heller, *Catch-22*, Random House, New York, 1961, p. 453 [Take me back!]

(125) Thermofischer.com, *Orbitrap Fusion Lumos Tribrid Mass Spectrometer — Thermo Fisher Scientific - CA* [Take me back!]

Appendix A

Auxiliary tables

A.1 General reference

Table A.1: Chemical, instrumental, and regulatory details of compounds under study. [Take me back!]

Compound	Molecular formula	M_{mi} (Da)	LogP	Adduct	RT (min)	Q1 (m/z)	Q3 (m/z)		EFSA MRL (mg/kg) (ppm) Apple	Blueberry	Strawberry	Grape
3-Hydroxycarbofuran	$C_{12}H_{15}NO_4$	237.1001079	0.21	$[M + H]^+$	2.99	238	181	163	0.001	0.01	0.005	0.002
Abamectin	$C_{48}H_{72}O_{14}$	872.4922066	6.51	$[M+Na]^+$	7.01	896	751	567	0.03	0.01	0.15	0.01
Acephate	$C_4H_{10}NO_3PS$	183.0119003	-0.85	$[M+H]^+$	1.9	184	143	49	0.1	0.1	0.1	0.1
Acetamiprid	$C_{10}H_{11}ClN_4$	222.067224	0.62	$[M+H]^+$	3.04	223	126	99	0.8	2	0.5	0.5
Acibenzolar-S-Methyl	$C_8H_6N_2OS_2$	209.9921542	2.18	$[M+H]^+$	4.5	211	136	91	0.3	0.01	0.15	0.01
Aldicarb	$C_7H_{14}N_2O_2S$	190.0775983	1.13	$[M\text{-}C_2H_5NO_2]^+$	3.35	116	89	61	0.02	0.02	0.02	0.02
Aldicarb Sulfone	$C_7H_{14}N_2O_4S$	222.0674275	-0.57	$[M+NH_4]^+$	2.33	240	89	86	0.02	0.02	0.02	0.02
Aldicarb Sulfoxide	$C_7H_{14}N_2O_3S$	206.0725129	-1.13	$[M+H]^+$	2.28	207	148	132	0.02	0.02	0.02	0.02
Ametryn	$C_9H_{17}N_5S$	227.1204662	3.09	$[M+H]^+$	3.88	228	186	96	-	-	-	-
Aminocarb	$C_{11}H_{16}N_2O_2$	208.1211777	2.01	$[M+H]^+$	2	209	137	152	-	-	-	-
Amitraz	$C_{19}H_{23}N_3$	293.1891977	5.64	$[M+H]^+$	5.54	294	148	91	0.05	0.05	0.05	0.05
Azoxystrobin	$C_{22}H_{17}N_3O_5$	403.1168205	5.13	$[M+H]^+$	4.41	404	372	344	0.01	5	10	3
Benalaxyl	$C_{20}H_{23}NO_3$	325.1677935	3.88	$[M+H]^+$	5.56	326	148	294	0.05	0.05	0.05	0.3
Bendiocarb	$C_{11}H_{13}NO_4$	223.0844578	1.86	$[M+H]^+$	3.58	224	167	109	-	-	-	-
Benfuracarb$^{\alpha}$	$C_{20}H_{30}N_2O_5S$	410.187531	4.54	$[M+H]^+$	-	411	190	252	-	-	-	-
Benzoximate	$C_{18}H_{18}ClNO_5$	363.0873502	3.76	$[M+H]^+$	5.68	364	199	105	-	-	-	-
Bifenazate	$C_{17}H_{20}N_2O_3$	300.1473924	3.12	$[M+H]^+$	4.81	301	170	198	0.7	0.7	3	0.7
Bitertanol	$C_{20}H_{23}N_3O_2$	337.1790269	4.02	$[M+H]^+$	5.63	338	269	70	0.01	0.01	0.01	0.01
Boscalid	$C_{18}H_{12}Cl_2N_2O$	342.0326684	4.31	$[M+H]^+$	4.55	343	307	140	2	15	6	5
Bromuconazole	$C_{13}H_{12}BrCl_2N_3O$	374.95408	2.73	$[M+H]^+$	4.9	378	159	70	0.05	0.05	0.05	0.5
Bupirimate	$C_{13}H_{24}N_4O_3S$	316.1569112	2.7	$[M+H]^+$	4.73	317	108	166	0.2	0.05	2	1.5
Buprofezin	$C_{16}H_{23}N_3OS$	305.156183	4.29	$[M+H]^+$	6.1	306	201	116	3	0.05	3	1
Butafenacil	$C_{20}H_{18}ClF_3N_2O_6$	474.0805484	3.63	$[M+NH_4]^+$	4.93	492	331	349	-	-	-	-
Butocarboxim	$C_7H_{14}N_2O_2S$	190.0775983	1.49	$[M+Na]^+$	3.33	213	75	116	-	-	-	-
Butoxycarboxim	$C_7H_{14}N_2O_4S$	222.0674275	-0.72	$[M+H]^+$	2.75	223	166	106	-	-	-	-
Carbaryl	$C_{12}H_{11}NO_2$	201.0789785	2.4	$[M+H]^+$	3.7	202	145	127	0.01	0.01	0.01	0.01
Carbendazim	$C_9H_9N_3O_2$	191.0694765	1.52	$[M+H]^+$	2.42	192	160	132	0.2	0.1	0.1	0.3
Carbetamide	$C_{12}H_{16}N_2O_3$	236.1160923	1.52	$[M+H]^+$	3.42	237	192	118	0.01	0.01	0.01	0.01
Carbofuran	$C_{12}H_{15}NO_3$	221.1051933	1.76	$[M+H]^+$	3.63	222	123	165	0.001	0.01	0.005	0.002
Carboxin	$C_{12}H_{13}NO_2S$	235.0666993	3	$[M+H]^+$	3.72	236	143	87	0.05	0.05	0.05	0.05
Carfentrazone-Ethyl	$C_{15}H_{14}Cl_2F_3N_3O_3$	411.0364312	3.21	$[M+H]^+$	5.29	412	346	366	0.01	0.01	0.01	0.01
Chlorantraniliprole	$C_{18}H_{14}BrCl_2N_5O_2$	480.9707926	5.55	$[M+H]^+$	4.21	484	453	286	0.5	1.5	1	1
Chlorfluazuron	$C_{20}H_9Cl_3F_5N_3O_3$	538.9629652	5.97	$[M+H]^+$	6.6	540	383	158	-	-	-	-
Chlorotoluron	$C_{10}H_{13}ClN_2O$	212.071641	2.46	$[M+H]^+$	3.86	213	72	46	-	-	-	-
Chloroxuron	$C_{15}H_{15}ClN_2O_2$	290.0822053	3.2	$[M+H]^+$	4.72	291	72	218	0.01	0.01	0.01	0.01
Clethodim	$C_{17}H_{26}ClNO_3S$	359.132192	4.5	$[M+H]^+$	6.04	360	164	268	0.1	0.1	0.5	1
Clofentezine	$C_{14}H_8Cl_2N_4$	302.0126016	3.27	$[M+H]^+$	5.6	303	138	102	0.5	0.02	2	0.02
Clothianidin	$C_6H_8ClN_5O_2S$	249.0087228	0.4	$[M+H]^+$	2.84	250	169	132	0.4	0.01	0.02	0.7
Cyazofamid	$C_{13}H_{13}ClN_4O_2S$	324.044774	1.75	$[M+H]^+$	4.96	325	108	261	0.01	0.01	0.01	2
Cycluron	$C_{11}H_{22}N_2O$	198.1732133	2.98	$[M+H]^+$	4.25	199	89	46	-	-	-	
Cymoxanil	$C_7H_{10}N_4O_3$	198.0752901	0.67	$[M+H]^+$	3.12	199	128	111	0.01	0.01	0.01	0.3
Cyproconazole	$C_{15}H_{18}ClN_3O$	291.1138398	2.7	$[M+H]^+$	4.67	292	70	125	0.1	0.05	0.05	0.2
Cyprodinil	$C_{14}H_{15}N_3$	225.1265975	4	$[M+H]^+$	4.81	226	93	77	2	3	5	3
Cyromazine	$C_6H_{10}N_6$	166.0966943	-0.04	$[M+H]^+$	0.58	167	85	125	0.05	0.05	0.05	0.05
Desmedipham	$C_{16}H_{16}N_2O_4$	300.1110069	3.53	$[M+NH_4]^+$	4.08	318	182	154	0.01	0.01	0.01	0.01
Diclobutrazol	$C_{15}H_{19}Cl_2N_3O$	327.0905176	3.6	$[M+H]^+$	5.29	328	70	59	-	-	-	-
Dicrotophos	$C_8H_{16}NO_5P$	237.076609	-0.36	$[M+H]^+$	2.82	238	112	193	-	-	-	-
Diethofencarb	$C_{14}H_{21}NO_4$	267.147058	2.92	$[M+H]^+$	4.42	268	226	124	0.01	0.01	0.01	0.01
Difenoconazole	$C_{19}H_{17}Cl_2N_3O_3$	405.0646967	4.92	$[M+H]^+$	5.85	406	251	253	0.8	0.1	0.5	3

$^{\alpha}$compound target in Chapter 2 only, $^{\beta}$compound target in Chapter 3 only

Continued on next page

Table A.1: Chemical, instrumental, and regulatory details of compounds under study – continued from previous page

Compound	Molecular formula	M_{mi} (Da)	LogP	Adduct	RT (min)	Q1 (m/z)	Q3 (m/z)		EFSA MRL (mg/kg) (ppm) Apple	Blueberry	Strawberry	Grape
Diflubenzuron	$C_{14}H_9ClF_2N_2O_2$	310.0320616	3.68	$[M+H]^+$	4.97	311	158	141	5	2	2	1
Dimethoate	$C_5H_{12}NO_3PS_2$	228.9996211	0.48	$[M+H]^+$	2.97	230	199	125	0.01	0.01	0.01	0.01
Dimethomorph	$C_{21}H_{22}ClNO_4$	387.1237358	3.71	$[M+H]^+$	4.69	388	301	165	0.01	0.01	0.7	3
Dimoxystrobin	$C_{19}H_{22}N_2O_3$	326.1630425	5.08	$[M+H]^+$	5.25	327	116	205	0.01	0.01	0.01	0.01
Diniconazole$^{\alpha}$	$C_{15}H_{17}Cl_2N_3O$	325.074860	4.23	$[M+H]^+$	-	326	70	159	0.01	-	-	-
Dinotefuran	$C_7H_{14}N_4O_3$	202.1065902	-0.7	$[M+H]^+$	2.22	203	129	157	-	-	-	0.9
Dioxacarb	$C_{11}H_{13}NO_4$	223.0844578	0.57	$[M+H]^+$	3.58	224	167	123	-	-	-	-
Diuron	$C_9H_{10}Cl_2N_2O$	232.0170183	2.78	$[M+H]^+$	4.01	235	72	72	0.01	0.01	0.01	0.01
Doramectin$^{\alpha}$	$C_{50}H_{74}O_{14}$	898.507874	7.16	$[M+H]^+$	-	917	331	593	-	-	-	-
Emamectin$^{\alpha}$	$C_{49}H_{75}NO_{13}$	885.523865	6.84	$[M+H]^+$	-	887	158	82	0.02	-	-	-
Epoxiconazole	$C_{17}H_{13}ClFN_3O$	329.0731179	3.44	$[M+H]^+$	5.05	330	121	101	0.05	0.05	0.05	0.05
Eprinomectin	$C_{50}H_{75}NO_{14}$	913.5187557	6.22	$[M+H]^+$	6.94	915	186	154	-	-	-	-
Etaconazole	$C_{14}H_{15}Cl_2N_3O_2$	327.0541321	3.35	$[M+H]^+$	5.1	328	159	205	-	-	-	-
Ethiofencarb	$C_{11}H_{15}NO_2S$	225.0823494	2.04	$[M+H]^+$	3.81	226	107	164	-	-	-	-
Ethiprole	$C_{13}H_9Cl_2F_3N_4OS$	395.9826216	3.54	$[M+H]^+$	4.42	397	351	255	-	-	-	-
Ethirimol	$C_{11}H_{19}N_3O$	209.1528122	2.53	$[M+H]^+$	3.15	210	140	98	0.1	0.05	0.2	0.5
Ethofumesate	$C_{13}H_{18}O_5S$	286.0874942	2	$[M+H]^+$	4.42	287	121	259	0.03	0.03	0.03	0.03
Etoxazole	$C_{21}H_{23}F_2NO_2$	359.1696853	5.85	$[M+H]^+$	6.54	360	141	304	0.07	0.01	0.2	0.5
Famoxadone	$C_{22}H_{18}N_2O_4$	374.1266569	4.76	$[M+NH_4]^+$	5.44	392	331	238	0.01	0.01	0.01	2
Fenamidone	$C_{17}H_{17}N_3OS$	311.1092328	3.61	$[M+H]^+$	4.48	312	236	92	0.01	0.01	0.04	0.6
Fenarimol	$C_{17}H_{12}Cl_2N_2O$	330.0326684	3.22	$[M+H]^+$	5.03	331	268	81	0.1	0.02	0.3	0.3
Fenazaquin$^{\alpha}$	$C_{20}H_{22}N_2O$	306.173218	5.54	$[M+H]^+$	-	307	162	147	0.1	-	-	-
Fenbuconazole	$C_{19}H_{17}ClN_4$	336.1141742	3.35	$[M+H]^+$	5.04	337	125	70	0.5	1	0.05	1
Fenhexamid	$C_{14}H_{17}Cl_2NO_2$	301.0636341	4.02	$[M+H]^+$	4.9	302	97	55	0.01	20	10	15
Fenobucarb	$C_{12}H_{17}NO_2$	207.1259287	3.04	$[M+H]^+$	4.37	208	95	152	-	-	-	-
Fenoxycarb	$C_{17}H_{19}NO_4$	301.131408	3.83	$[M+H]^+$	5.18	302	116	88	1	0.05	0.05	1
Fenpropimorph	$C_{20}H_{33}NO$	303.2562146	5.2	$[M+H]^+$	4.17	304	147	117	0.01	0.9	0.01	0.01
Fenpyroximate	$C_{24}H_{27}N_3O_4$	421.2001562	6.44	$[M+H]^+$	6.73	422	366	135	0.3	0.4	0.3	0.3
Fenuron	$C_9H_{12}N_2O$	164.094963	0.98	$[M+H]^+$	2.96	165	72	46	-	-	-	-
Fipronil$^{\alpha}$	$C_{12}H_4Cl_2F_6N_4OS$	435.938706	4.76	$[M+H]^+$	5.08	437	368	290	0.005	0.005	0.005	0.005
Fipronil$^{\beta}$	$C_{12}H_4Cl_2F_6N_4OS$	435.938706	4.76	$[M-H]^-$	5.08	435	330	250	0.005	0.005	0.005	0.005
Flonicamid	$C_9H_6F_3N_3O$	229.0462964	0.84	$[M+H]^+$	2.51	230	203	174	0.3	0.03	0.03	0.03
Fluazinam$^{\beta}$	$C_{13}H_4Cl_2F_6N_4O_4$	463.951379	8.19	$[M+H]^+$	6.17	463	416	398	0.3	3	0.01	-
Flubendiamide	$C_{23}H_{22}F_7IN_2O_4S$	682.02332	3.25	$[M+H]^+$	5.27	683	408	274	0.8	0.01	0.2	2
Fludioxonil$^{\beta}$	$C_{12}H_6F_2N_2O_2$	248.0397338	3.67	$[M-H]^-$	4.41	247	126	180	5	2	4	5
Flufenacet	$C_{14}H_{13}F_4N_3O_2S$	363.0664601	3.98	$[M+H]^+$	4.95	364	152	194	0.05	0.05	0.05	0.05
Flufenoxuron	$C_{21}H_{11}ClF_6N_2O_3$	488.036239	5.6	$[M+H]^+$	6.42	489	158	141	0.5	0.05	0.05	1
Fluometuron	$C_{10}H_{11}F_3N_2O$	232.0823475	2.36	$[M+H]^+$	3.78	233	72	46	0.01	0.01	0.01	0.01
Fluoxastrobin	$C_{21}H_{16}ClFN_4O_5$	458.0793254	5.34	$[M+H]^+$	4.9	459	427	188	0.01	0.01	0.01	0.01
Fluquinconazole	$C_{16}H_8Cl_2FN_5O$	375.0089934	2.79	$[M+H]^+$	4.86	376	349	307	0.1	0.05	0.05	0.1
Flusilazole	$C_{16}H_{15}F_2N_3Si$	315.1003303	3.84	$[M+H]^+$	5.16	316	165	247	0.01	0.01	0.01	0.01
Flutolanil	$C_{17}H_{16}F_3NO_2$	323.1133133	3.7	$[M+H]^+$	4.58	324	242	262	0.01	0.01	0.01	0.01
Flutriafol	$C_{16}H_{13}F_2N_3O$	301.1026684	2.31	$[M+H]^+$	3.94	302	70	123	0.4	0.01	1.5	0.8
Forchlorfenuron	$C_{12}H_{10}ClN_3O$	247.0512396	3.45	$[M+H]^+$	3.96	248	129	93	0.01	0.01	0.01	0.01
Formetanate	$C_{11}H_{15}N_3O_2$	221.1164266	0.86	$[M+H]^+$	1.95	222	120	165	0.01	0.01	0.4	0.1
Fuberidazole$^{\beta}$	$C_{11}H_8N_2O$	184.0636628	2.67	$[M+H]^+$	2.72	185	157	65	0.01	0.01	0.01	0.01
Furalaxyl	$C_{17}H_{19}NO_4$	301.131408	2.52	$[M+H]^+$	4.49	302	242	95	-	-	-	-
Furathiocarb	$C_{18}H_{26}N_2O_5S$	382.1562425	4.52	$[M+H]^+$	6.19	383	195	252	0.001	0.01	0.005	0.002
Halofenozide	$C_{18}H_{19}ClN_2O_2$	330.1135055	3.34	$[M+H]^+$	4.47	331	105	275	-	-	-	-
Hexaconazole	$C_{14}H_{17}Cl_2N_3O$	313.0748675	3.66	$[M+H]^+$	5.52	314	70	159	0.01	0.01	0.01	0.01
Hexaflumuron	$C_{16}H_8Cl_2F_6N_2O_3$	459.9816166	5.87	$[M+H]^+$	5.83	461	158	141	-	-	-	-
Hexythiazox	$C_{17}H_{21}ClN_2O_2S$	352.1012262	3.41	$[M+H]^+$	6.38	353	228	168	1	0.5	0.5	1

$^{\alpha}$compound target in Chapter 2 only, $^{\beta}$compound target in Chapter 3 only

Continued on next page

Table A.1: Chemical, instrumental, and regulatory details of compounds under study – continued from previous page

Compound	Molecular formula	M_{mi} (Da)	LogP	Adduct	RT (min)	Q1 (m/z)	Q3 (m/z)		EFSA MRL (mg/kg) (ppm) Apple	Blueberry	Strawberry	Grape
Hydramethylnon	$C_{25}H_{24}F_6N_4$	494.1905159	8.27	$[M+H]^+$	5.66	495	151	323	-	-	-	-
Imazalil	$C_{14}H_{14}Cl_2N_2O$	296.0483184	3.58	$[M+H]^+$	3.71	297	159	201	2	0.05	0.05	0.05
Imidacloprid	$C_9H_{10}ClN_5O_2$	255.0523022	-0.43	$[M+H]^+$	2.82	256	209	175	0.5	5	0.5	1
Indoxacarb	$C_{22}H_{17}ClF_3N_3O_7$	527.070712	2.77	$[M+H]^+$	5.84	528	203	218	0.5	0.8	0.6	2
Ipconazole	$C_{18}H_{24}ClN_3O$	333.16079	3.64	$[M+H]^+$	5.9	334	70	125	0.01	0.01	0.01	0.01
Iprovalicarb	$C_{18}H_{28}N_2O_3$	320.2099926	3.56	$[M+H]^+$	4.94	321	119	203	0.01	0.01	0.01	2
Isocarbophos	$C_{11}H_{16}NO_4PS$	289.0532167	1.66	$[M+NH_4]^+$	4.05	307	231	121	-	-	-	-
Isoprocarb	$C_{11}H_{15}NO_2$	193.1102787	2.51	$[M+H]^+$	3.97	194	95	137	-	-	-	-
Isoproturon	$C_{12}H_{18}N_2O$	206.1419131	2.32	$[M+H]^+$	4.05	207	72	46	0.01	0.01	0.01	0.01
Ivermectin$^{\alpha}$	$C_{48}H_{74}O_{14}$	874.507874	6.61	$[M+NH_4]^+$	-	893	569	307	-	-	-	-
Kresoxim-Methyl	$C_{18}H_{19}NO_4$	313.131408	4.34	$[M+H]^+$	5.33	314	116	131	0.2	0.9	1.5	1
Linuron	$C_9H_{10}Cl_2N_2O_2$	248.0119329	3.2	$[M+H]^+$	4.33	249	160	182	0.05	0.05	0.05	0.05
Lufenuron	$C_{17}H_8Cl_2F_8N_2O_3$	509.978423	6.27	$[M+H]^+$	6.2	511	158	141	0.15	0.01	0.01	0.01
Mandipropamid	$C_{23}H_{22}ClNO_4$	411.1237358	4.16	$[M+H]^+$	4.57	412	328	356	0.01	0.01	0.01	2
Mefenacet	$C_{16}H_{14}N_2O_2S$	298.0775983	3.85	$[M+H]^+$	4.85	299	148	120	-	-	-	-
Mepanipyrim	$C_{14}H_{13}N_3$	223.1109474	3.28	$[M+H]^+$	4.84	224	119	106	0.01	0.01	3	2
Mepronil	$C_{17}H_{19}NO_2$	269.1415788	4.12	$[M+H]^+$	4.67	270	228	228	0.01	0.01	0.01	0.01
Mesotrione	$C_{14}H_{13}NO_7S$	339.0412723	-0.7	$[M+H]^+$	3.24	340	178	104	0.01	0.01	0.01	0.01
Metaflumizone	$C_{24}H_{16}F_6N_4O_2$	506.1177449	6.05	$[M+H]^+$	6.15	507	302	287	0.05	0.05	0.05	0.05
Metalaxyl	$C_{15}H_{21}NO_4$	279.147058	2.15	$[M+H]^+$	4.15	280	220	192	1	0.01	0.6	2
Metconazole	$C_{17}H_{22}ClN_3O$	319.14514	3.3	$[M+H]^+$	5.56	320	125	70	0.02	0.4	0.02	0.02
Methabenzthiazuron	$C_{10}H_{11}N_3OS$	221.0622826	1.63	$[M+H]^+$	4.02	222	150	165	0.01	0.01	0.01	0.01
Methamidophos	$C_2H_8NO_2PS$	141.0013356	-0.82	$[M+H]^+$	1.4	142	94	125	0.01	0.01	0.01	0.01
Methiocarb	$C_{11}H_{15}NO_2S$	225.0823494	2.88	$[M+H]^+$	4.44	226	121	169	0.1	0.2	1	0.3
Methomyl	$C_5H_{10}N_2O_2S$	162.0462982	0.6	$[M+H]^+$	2.54	163	88	106	0.01	0.01	0.01	0.01
Methoprotryne	$C_{11}H_{21}N_5OS$	271.1466809	2.37	$[M+H]^+$	3.97	272	198	240	-	-	-	-
Methoxyfenozide	$C_{22}H_{28}N_2O_3$	368.2099926	3.72	$[M+H]^+$	4.74	369	313	149	2	4	2	1
Metobromuron	$C_9H_{11}BrN_2O_2$	258.0003901	2.32	$[M+H]^+$	3.9	259	170	148	-	-	-	-
Metribuzin	$C_8H_{14}N_4OS$	214.0888317	1.3	$[M+H]^+$	3.59	215	187	84	0.1	0.1	0.1	0.1
Mevinphos	$C_7H_{13}O_6P$	224.0449745	0.28	$[M+H]^+$	3.24	225	127	193	0.01	0.01	0.01	0.01
Mexacarbate	$C_{12}H_{18}N_2O_2$	222.1368277	2.47	$[M+H]^+$	2.75	223	151	166	-	-	-	-
Monocrotophos	$C_7H_{14}NO_5P$	223.0609589	-0.45	$[M+H]^+$	2.67	224	193	127	0.01	0.01	0.01	0.01
Monolinuron	$C_9H_{11}ClN_2O_2$	214.0509052	2.3	$[M+H]^+$	3.77	215	126	99	0.01	0.01	0.01	0.01
Moxidectin$^{\alpha}$	$C_{37}H_{53}NO_8$	639.377136	8.43	$[M+H]^+$	-	640	528	498	-	-	-	-
Myclobutanil	$C_{15}H_{17}ClN_4$	288.1141742	2.82	$[M+H]^+$	4.71	289	70	125	0.6	0.02	1	1
Neburon$^{\beta}$	$C_{12}H_{16}Cl_2N_2O$	274.0634201	4.38	$[M+H]^+$	5.16	275	88	114	-	-	-	-
Nitenpyram	$C_{11}H_{15}ClN_4O_2$	270.0883534	1.9	$[M+H]^+$	2.36	271	225	126	-	-	-	-
Novaluron	$C_{17}H_9ClF_8N_2O_4$	492.01231	6.78	$[M+H]^+$	5.9	493	158	141	2	7	0.5	0.01
Nuarimol	$C_{17}H_{12}ClFN_2O$	314.0622189	2.68	$[M+H]^+$	4.52	315	252	81	-	-	-	-
Omethoate	$C_5H_{12}NO_4PS$	213.022465	-0.74	$[M+H]^+$	2.15	214	125	183	0.01	0.01	0.01	0.01
Oxadixyl	$C_{14}H_{18}N_2O_4$	278.1266569	0.68	$[M+H]^+$	3.43	279	219	132	0.01	0.01	0.01	0.01
Oxamyl	$C_7H_{13}N_3O_3S$	219.0677619	-0.47	$[M+NH_4]^+$	2.42	237	90	72	0.01	0.01	0.01	0.01
Paclobutrazol	$C_{15}H_{20}ClN_3O$	293.1294899	2.99	$[M+H]^+$	4.62	294	70	125	0.5	0.5	0.5	0.05
Penconazole	$C_{13}H_{15}Cl_2N_3$	283.0643028	3.66	$[M+H]^+$	5.38	284	159	70	0.2	0.05	0.5	0.4
Pencycuron	$C_{19}H_{21}ClN_2O$	328.1342409	4.82	$[M+H]^+$	5.72	329	125	218	0.05	0.05	0.05	0.05
Phenmedipham	$C_{16}H_{16}N_2O_4$	300.1110069	3.45	$[M+H]^+$	4.14	301	168	108	0.01	0.01	0.3	0.01
Picoxystrobin	$C_{18}H_{16}F_3NO_4$	367.1031425	4.48	$[M+H]^+$	5.19	368	145	205	0.01	0.01	0.01	0.01
Piperonyl Butoxide	$C_{19}H_{30}O_5$	338.2093239	4.23	$[M+NH_4]^+$	6.32	356	177	119	-	-	-	-
Pirimicarb	$C_{11}H_{18}N_4O_2$	238.1429757	1.7	$[M+H]^+$	3.25	239	182	72	0.5	1	1.5	0.01
Prochloraz	$C_{11}H_{15}BrClO_3PS$	371.9351417	3.8	$[M+H]^+$	5.51	376	308	70	0.05	0.05	0.05	0.05
Promecarb	$C_{12}H_{17}NO_2$	207.1259287	2.96	$[M+H]^+$	4.6	208	109	151	-	-	-	-
Prometon	$C_{10}H_{19}N_5O$	225.1589602	2.91	$[M+H]^+$	3.64	226	142	86	-	-	-	-

$^{\alpha}$compound target in Chapter 2 only, $^{\beta}$compound target in Chapter 3 only

Continued on next page

Table A.1: Chemical, instrumental, and regulatory details of compounds under study – continued from previous page

Compound	Molecular formula	M_{mi} (Da)	LogP	Adduct	RT (min)	Q1 (m/z)	Q3 (m/z)		EFSA MRL (mg/kg) (ppm)			
									Apple	Blueberry	Strawberry	Grape
Prometryne	$C_{10}H_{19}N_5S$	241.1361163	3.44	$[M+H]^+$	4.31	242	158	200	-	-	-	-
Propamocarb	$C_9H_{20}N_2O_2$	188.1524778	1.12	$[M+H]^+$	2.01	189	102	144	0.01	0.01	0.01	0.01
Propargite	$C_{19}H_{26}O_4S$	350.1551799	4.81	$[M+NH_4]^+$	6.53	368	231	175	0.01	0.01	0.01	0.01
Propham	$C_{10}H_{13}NO_2$	179.0940802	2.65	$[M+H]^+$	3.93	180	138	120	0.01	0.01	0.01	0.01
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	341.0697821	3.88	$[M+H]^+$	5.57	342	159	69	0.15	0.01	0.01	0.3
Propoxur	$C_{11}H_{15}NO_3$	209.1051933	1.6	$[M+H]^+$	3.6	210	111	168	0.05	0.05	0.05	0.05
Prothioconazole	$C_{14}H_{15}Cl_2N_3OS$	343.0312882	1.77	$[M+H]^+$	5.57	344	189	125	0.01	0.01	0.01	0.01
Pymetrozine$^{\beta}$	$C_{10}H_{11}N_5O$	217.0963599	-0.51	$[M+H]^+$	1.99	218	105	78	0.02	0.7	0.3	0.02
Pyracarbolid	$C_{13}H_{15}NO_2$	217.1102787	2.52	$[M+H]^+$	3.65	218	125	97	-	-	-	-
Pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	387.0985836	4.25	$[M+H]^+$	5.6	388	194	163	0.5	4	1.5	1
Pyridaben	$C_{19}H_{25}ClN_2OS$	364.1376118	4.73	$[M+H]^+$	6.91	365	147	309	0.5	0.5	1	0.5
Pyrimethanil	$C_{12}H_{13}N_3$	199.1109474	2.84	$[M+H]^+$	4.1	200	107	82	15	8	5	5
Pyriproxyfen	$C_{20}H_{19}NO_3$	321.1364934	4.84	$[M+H]^+$	6.29	322	96	185	0.2	0.2	0.05	0.05
Quinoxyfen	$C_{15}H_8Cl_2FNO$	306.9966974	6.29	$[M+H]^+$	6.39	308	197	162	0.05	2	0.3	1
Rotenone	$C_{23}H_{22}O_6$	394.1416383	4.65	$[M+H]^+$	5.2	395	213	192	0.01	0.01	0.01	0.01
Secbumeton	$C_{10}H_{19}N_5O$	225.1589602	3.09	$[M+H]^+$	3.66	226	170	100	-	-	-	-
Siduron	$C_{14}H_{20}N_2O$	232.1575632	3.66	$[M+H]^+$	4.45	233	94	137	-	-	-	-
Simetryn	$C_8H_{15}N_5S$	213.1048162	2.74	$[M+H]^+$	3.5	214	124	144	-	-	-	-
Spinetoram J	$C_{42}H_{69}NO_{10}$	747.49215	5.51	$[M+H]^+$	6.21	749	142	98	0.2	0.4	0.2	0.5
Spinetoram L	$C_{43}H_{69}NO_{10}$	759.49215	5.92	$[M+H]^+$	6.42	761	142	98	0.2	0.4	0.2	0.5
Spinosyn A	$C_{41}H_{65}NO_{10}$	731.460847	4.8	$[M+H]^+$	5.58	733	142	98	0.3	1.5	0.3	0.5
Spinosyn D	$C_{42}H_{67}NO_{10}$	745.476497	5.39	$[M+H]^+$	5.84	747	142	98	0.3	1.5	0.3	0.5
Spirodiclofen	$C_{21}H_{24}Cl_2O_4$	410.1051645	6.36	$[M+H]^+$	6.72	411	313	71	0.8	4	2	2
Spiromesifen	$C_{23}H_{30}O_4$	370.2144093	6.07	$[M+H]^+$	6.57	371	273	255	0.02	0.02	1	0.02
Spirotetramat	$C_{21}H_{27}NO_5$	373.1889228	4.59	$[M+H]^+$	5	374	302	330	1	0.1	0.4	2
Spiroxamine	$C_{18}H_{35}NO_2$	297.2667793	4.88	$[M+H]^+$	4.34	298	144	100	0.1	0.01	0.01	0.6
Sulfentrazone	$C_{11}H_{10}Cl_2F_2N_4O_3S$	385.9818726	2.21	$[M+H]^+$	3.66	387	307	146	-	-	-	-
Tebuconazole	$C_{16}H_{22}ClN_3O$	307.14514	3.58	$[M+H]^+$	5.35	308	70	125	0.3	1.5	0.5	0.5
Tebufenozide	$C_{22}H_{28}N_2O_2$	352.215078	4.24	$[M+H]^+$	5.24	353	133	105	1	3	0.05	3
Tebufenpyrad	$C_{18}H_{24}ClN_3O$	333.16079	3.9	$[M+H]^+$	6.24	334	117	145	0.3	1.5	1	0.6
Tebuthiuron	$C_9H_{16}N_4OS$	228.1044818	1.79	$[M+H]^+$	3.69	229	172	116	-	-	-	-
Teflubenzuron	$C_{14}H_6Cl_2F_4N_2O_2$	379.9742456	5.49	$[M+H]^+$	6.06	381	158	141	1	0.01	0.01	0.7
Terbumeton	$C_{10}H_{19}N_5O$	225.1589602	2.91	$[M+H]^+$	3.66	226	170	100	-	-	-	-
Terbutryn	$C_{10}H_{19}N_5S$	241.1361163	3.44	$[M+H]^+$	4.35	242	186	68	-	-	-	-
Tetraconazole	$C_{13}H_{11}Cl_2F_4N_3O$	371.0215301	3.19	$[M+H]^+$	4.9	372	159	70	0.3	0.2	0.2	0.5
Thiabendazole$^{\beta}$	$C_{10}H_7N_3S$	201.0360679	2.47	$[M+H]^+$	2.62	202	175	131	4	0.01	0.01	0.01
Thiacloprid	$C_{10}H_9ClN_4S$	252.0236447	0.55	$[M+H]^+$	3.18	253	126	99	0.3	1	1	0.01
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	291.0192875	-1.16	$[M+H]^+$	2.57	292	211	181	0.3	0.01	0.3	0.4
Thidiazuron	$C_9H_8N_4OS$	220.0418815	1.43	$[M+H]^+$	3.5	221	102	128	-	-	-	-
Thiobencarb	$C_{12}H_{16}ClNOS$	257.0641125	3.53	$[M+H]^+$	5.71	258	125	89	0.01	0.01	0.01	0.01
Thiophanate-Methyl	$C_{12}H_{14}N_4O_4S_2$	342.0456462	1.16	$[M+H]^+$	3.51	343	151	311	-	-	-	-
Triadimefon	$C_{14}H_{16}ClN_3O_2$	293.0931044	2.77	$[M+H]^+$	4.8	294	197	225	0.01	0.01	0.01	0.01
Triadimenol	$C_{14}H_{18}ClN_3O_2$	295.1087544	3.04	$[M+H]^+$	4.8	296	227	70	0.2	0.9	0.3	0.4
Trichlorfon	$C_4H_8Cl_3O_4P$	255.9225782	0.48	$[M+H]^+$	2.96	257	109	221	0.01	0.01	0.01	0.01
Tricyclazole	$C_9H_7N_3S$	189.0360679	2.28	$[M+H]^+$	3.41	190	163	136	0.01	0.01	0.01	0.01
Trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	408.1296916	5.11	$[M+H]^+$	5.9	409	186	206	0.7	3	1	3
Triflumizole	$C_{15}H_{15}ClF_3N_3O$	345.0855744	4.66	$[M+H]^+$	5.85	346	278	73	0.5	0.1	0.2	3
Triflumuron	$C_{15}H_{10}ClF_3N_2O_3$	358.0332044	4.55	$[M+H]^+$	5.51	359	156	139	0.5	0.05	0.05	0.2
Triticonazole	$C_{17}H_{20}ClN_3O$	317.1294899	3.07	$[M+H]^+$	4.95	318	70	125	0.01	0.01	0.01	0.01
Vamidothion	$C_8H_{18}NO_4PS_2$	287.0414858	0.15	$[M+H]^+$	3	288	146	118	-	-	-	-
Zoxamide	$C_{14}H_{16}Cl_3NO_2$	335.0246618	4.84	$[M+H]^+$	5.42	336	187	159	0.02	0.02	0.05	5

A.2 Chapter 2

Table A.2: Model compounds chosen for autosampler development, along with parameters of interest.

Compound	LogP	MRPL ($ng \cdot mL^{-1}$)	Q1 (m/z)	Q3 (m/z)
Methamphetamine	2.07	100	150	91
Methamphetamine-d_5 (IS)			155	92
Carbamazepine	2.45	-	237	194
Salbutamol	0.44	100	240	148
Carbamazepine-d_{10} (IS)			247	204
Propanolol	3.48	100	260	116
Propanolol-d_7 (IS)			267	116
Clenbuterol	2.94	0.2	277	203
Diazepam	2.82	5	285	193
Morphine	0.89	50	286	152
Clenbuterol-d_9 (IS)			286	204
Diazepam-d_5 (IS)			290	198
Morphine-d_6 (IS)			292	152
Codeine	1.19	2	300	165
Codeine-d_3 (IS)			303	165
Cocaine	1.97	100	304	182
Sertraline	5.06	300	306	159
Cocaine-d_3 (IS)			307	185
Sertraline-d_3 (IS)			309	159
Methadone	3.93	50	310	265
Methadone-d_3 (IS)			313	268
Oxycodone	1.07	50	316	241
Lorazepam	2.39	240	321	275
Citalopram	3.5	300	325	109
Bisoprolol	1.87	100	326	116
Citalopram-d_6 (IS)			331	109
Fentanyl	4.12	1	337	188
Fentanyl-d_5 (IS)			342	188
Buprenorphine	4.63	5	468	396
Buprenorphine-d_4 (IS)			472	400

Table A.3: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 50 ms.

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.82E-01	1.20E-02	0.9995	1	91.3	102.2	99.4	2	1.4	1.2
Carbamazepine	6.69E-02	1.10E-01	0.9957	5		109.1	100.7		2.2	2.6
Propanolol	2.37E-01	-4.61E-03	0.9996	0.5	90.1	101.9	98.5	1.3	1	0.4
Clenbuterol	1.15E-01	2.37E-02	0.9994	1	90.2	100.5	96.7	4.2	2	0.6
Diazepam	1.15E-01	9.83E-03	0.9995	0.5	91.7	100.3	97.1	1.9	2.2	1.9
Codeine	7.97E-02	-1.56E-03	0.9996	2.5	95	100.2	98.5	2.4	2.4	4.7
Cocaine	9.81E-02	1.16E-03	0.9997	0.1	95	103.2	98.6	2.5	0.7	1.4
Sertraline	5.14E-02	8.55E-03	0.9992	0.5	86.7	101.9	97.1	0.8	4.2	0.8
Citalopram	7.77E-02	5.13E-03	0.9988	0.5	95.7	104.9	98.8	4.4	2.2	2.2
Fentanyl	6.36E-02	1.20E-04	0.9997	0.1	92.8	103.2	98.5	0.9	1.5	1.2
Buprenorphine	1.12E-01	-4.05E-03	0.999	0.5	89.4	99.2	98.8	4.3	4	6.4
Morphine	5.85E-02	1.19E-01	0.9983	5		98.5	100.5		6.6	4.3
Methadone	9.24E-02	1.89E-03	0.9997	0.1	94	102.2	97.2	0.8	1.4	0.5
Salbutamol	2.70E-01	3.89E-02	0.9959	1	93.5	100.7	101.5	7.7	5.8	4.5
Oxycodone	1.41E-01	4.89E-02	0.998	2.5	92.6	104.1	104.9	13.8	4.4	5.5
Lorazepam	1.96E-02	-1.39E-02	0.9823	10		107.7	114.8		26.3	22.1
Bisoprolol	8.62E-04	1.35E-03	0.9993	2.5	91.6	103.3	100.3	5.1	4.3	4.6

Table A.4: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 25 ms.

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.19E-01	1.69E-02	0.9996	0.5	91.9	101.6	98.5	0.9	1.2	0.7
Carbamazepine	6.72E-02	8.06E-02	0.9964	2.5	72.9	111.4	95.6	9.2	1.5	3.8
Propanolol	2.39E-01	4.03E-03	0.9995	1	90.3	102.1	97.3	1.6	1.9	1.9
Clenbuterol	1.14E-01	2.94E-02	0.9995	1	91.1	102.5	98.6	1.2	1.3	1
Diazepam	1.14E-01	2.33E-02	0.9996	1	88.8	103.1	99.3	4.1	1.9	0.2
Codeine	7.97E-02	5.40E-03	0.9992	2.5	93.9	98	97.2	2.5	2.3	3.4
Cocaine	9.80E-02	1.13E-02	0.9993	1	92.5	102.4	98.4	3	0.4	0.9
Sertraline	5.26E-02	1.31E-02	0.9993	0.5	85.6	101.3	99.2	2.8	1.8	2.5
Citalopram	7.73E-02	8.67E-03	0.9986	1	96.6	105.2	102.6	2.7	2.5	4.9
Fentanyl	6.41E-02	1.65E-03	0.9997	0.1	94.1	102.5	98.2	1.9	1	0.7
Buprenorphine	1.10E-01	-1.74E-02	0.9991	2.5	95.1	96.2	95.8	1.1	2.4	0.8
Morphine	5.61E-02	1.11E-01	0.9968	5		105.8	101.3		6.8	7.8
Methadone	9.17E-02	2.06E-02	0.9996	1	90	103.5	98.7	3	0.3	0.9
Salbutamol	2.67E-01	7.00E-02	0.9974	2.5	90.2	99.7	101.1	7.2	9.6	6.4
Oxycodone	1.43E-01	6.40E-02	0.9983	1	95.6	112.3	105.6	3.3	5.9	5
Lorazepam	1.99E-02	4.31E-02	0.9843	25		123.9	110.7		14.2	32.8
Bisoprolol	8.64E-04	1.21E-03	0.9979	2.5	94.2	102.9	102.4	6.9	2.4	4

Table A.5: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 10 ms.

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.21E-01	8.31E-03	0.9998	1	92.7	102.6	98.2	1.7	0.3	1.1
Carbamazepine	6.98E-02	6.66E-02	0.9971	2.5	78.2	108.1	95.8	5	1.9	1.8
Propanolol	2.36E-01	1.72E-03	0.9998	0.25	89	102.7	98.8	1.1	0.8	1
Clenbuterol	1.13E-01	2.17E-02	0.9998	1	91.5	103.3	98.3	1.4	0.5	0.9
Diazepam	1.14E-01	1.55E-02	0.9997	1	92.3	101.7	98.8	3.7	0.8	1.2
Codeine	8.29E-02	1.30E-02	0.9996	1	92	99.4	97.6	0.9	1.5	2.3
Cocaine	9.99E-02	3.21E-03	0.9997	0.25	94.3	101.2	97.6	1.7	0.3	1.2
Sertraline	5.63E-02	9.88E-03	0.9995	1	94	101.5	98.1	5.1	1.3	2.2
Citalopram	7.72E-02	5.05E-03	0.9985	0.25	90	107.8	97.8	8.8	5.3	10.5
Fentanyl	6.74E-02	2.87E-03	0.9998	0.5	93.3	102	98.2	0.8	0.5	0.9
Buprenorphine	1.11E-01	-5.19E-03	0.9996	1	90.7	95.9	96.7	1.9	1.7	2.5
Morphine	5.56E-02	1.24E-01	0.997	5		99.4	100.5		3.8	8.1
Methadone	8.92E-02	1.11E-02	0.9997	1	92.4	102.7	97.8	2.1	0.4	0.4
Salbutamol	2.52E-01	8.44E-02	0.9964	1	84.4	103.2	101.1	16.4	8.3	11.5
Oxycodone	1.38E-01	4.71E-02	0.9986	1	93.2	107.8	100	3.9	1.9	5.2
Lorazepam	2.03E-02	6.19E-02	0.9534	25		94.3	106.2		9.2	18.1
Bisoprolol	8.53E-04	1.11E-03	0.9977	5		103.2	98.3		5.1	10.7

Table A.6: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 5 ms.

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.21E-01	1.13E-02	0.9998	1	93.1	102.1	98.3	1.6	0.6	0.3
Carbamazepine	7.13E-02	5.28E-02	0.9972	2.5	80.4	109.4	94.5	2.7	1.1	0.4
Propanolol	2.37E-01	-6.32E-03	0.9998	0.5	90.1	102.2	98.1	1.5	0.8	0.7
Clenbuterol	1.14E-01	1.91E-02	0.9997	0.5	91.9	102.2	98.5	2.3	1.3	0.4
Diazepam	1.14E-01	1.20E-02	0.9998	0.5	89.9	101.4	98.3	1.2	1.1	1.2
Codeine	8.35E-02	1.33E-02	0.9996	0.5	90.6	99.4	96.7	2.3	1	1.3
Cocaine	9.92E-02	6.84E-04	0.9998	0.5	93.5	102.4	98.5	0.3	0.2	0.4
Sertraline	5.79E-02	1.27E-02	0.9996	0.25	89.4	100.5	98	8.5	1.3	0.7
Citalopram	7.78E-02	1.44E-03	0.9979	0.5	98.1	104.2	102	4.9	5.7	3.3
Fentanyl	6.83E-02	-3.60E-04	0.9998	0.5	93.2	102	98.3	0.8	0.5	0.2
Buprenorphine	1.10E-01	-4.35E-03	0.9996	0.5	86.9	97.6	96.7	2.9	1.8	1.1
Morphine	5.73E-02	8.66E-02	0.9964	5		100.4	102.1		6.8	3
Methadone	8.92E-02	2.41E-03	0.9997	0.5	94.2	102.9	98.1	0.8	0.5	0.2
Salbutamol	2.67E-01	6.82E-02	0.9955	2.5	84.2	104.6	96	5.9	14.6	6.8
Oxycodone	1.40E-01	4.87E-02	0.9987	2.5	100.5	105.5	106.1	9.3	6.5	3.1
Lorazepam	2.12E-02	4.04E-02	0.9804	5		97.8	107.4		13.4	13.4
Bisoprolol	8.42E-04	1.41E-03	0.9969	5		101.3	103.6		6.3	5.4

Table A.7: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 5 ms for segmented spray A (0.06 – 0.09 min).

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.22E-01	1.64E-02	0.9996	1	91.5	101.1	96.6	1.4	2.8	2.6
Carbamazepine	7.00E-02	-1.14E-02	0.9962	5		108.2	93.7		1.1	2.7
Propanolol	2.26E-01	-3.52E-03	0.9992	0.5	90.5	102.8	98.1	1.3	2.3	2.5
Clenbuterol	1.15E-01	1.55E-02	0.9995	0.5	90.9	101.1	95.8	3.8	1.5	2.5
Diazepam	1.14E-01	8.98E-03	0.9983	0.5	91	100.2	98.1	3.7	2.7	0.5
Codeine	8.32E-02	8.93E-03	0.9983	2.5	90.3	98	94.6	2.5	4.1	6.2
Cocaine	1.07E-01	-2.54E-03	0.9955	0.5	94.7	104.4	101.9	7.1	5.9	6.7
Sertraline	6.04E-02	1.05E-02	0.9961	0.5	87.4	102	96.8	8.4	6.3	6.8
Citalopram	6.96E-02	1.15E-02	0.9947	1	100.2	110.4	107.8	14.2	13.9	5.7
Fentanyl	6.88E-02	2.41E-04	0.9998	0.5	92.1	100.6	98.4	1.6	0.6	1
Buprenorphine	1.09E-01	-2.77E-03	0.9984	0.5	87.7	96.3	97.8	7.2	3.3	6.8
Morphine	5.64E-02	1.27E-01	0.9886	2.5	112.9	99.2	107.1	33.5	18.1	9
Methadone	8.91E-02	6.31E-03	0.9995	0.5	93.3	101.3	97.9	2	5.1	0.7
Salbutamol	2.89E-01	-6.09E-03	0.9927	2.5	82.4	96.8	85.7	11.9	25.8	9.7
Oxycodone	1.26E-01	9.31E-02	0.9824	2.5	101.2	106	108.2	26.7	14.2	6.8
Lorazepam	1.92E-02	4.63E-03	0.9808	10		107.4	109.4		6.7	24
Bisoprolol	7.61E-04	1.62E-03	0.9831	5		105.6	106.6		19.6	7.2

Table A.8: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 5 ms for segmented spray B (0.17 – 0.20 min).

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.21E-01	1.15E-02	0.9996	1	93.4	101.9	98.2	2.5	0.9	1.7
Carbamazepine	6.72E-02	1.23E-01	0.9876	5		107.1	96.9		7.1	7.1
Propanolol	2.38E-01	-3.44E-03	0.9995	0.25	88.6	98.4	98.6	3.3	3.7	1.1
Clenbuterol	1.15E-01	1.75E-02	0.9987	0.5	92.7	102.1	98.5	1.7	1.7	2.3
Diazepam	1.15E-01	9.02E-02	0.9989	0.5	89.8	101.9	98.7	3.2	1.6	2.7
Codeine	8.35E-02	-6.33E-03	0.9978	2.5	99.8	98.9	95.9	4.4	2.7	2.2
Cocaine	9.81E-02	2.24E-03	0.999	0.5	94	103.6	98.7	2.2	0.8	1.2
Sertraline	5.76E-02	1.29E-02	0.9985	0.25	91.3	101.3	100.7	12.9	1.6	2.2
Citalopram	8.65E-02	-2.22E-02	0.9926	2.5	102.5	105.9	101.8	2.5	8.9	8
Fentanyl	6.86E-02	-6.71E-04	0.9997	0.25	93.4	102	98.2	1.5	0.7	0.6
Buprenorphine	1.07E-01	-9.89E-03	0.9933	1	85.2	104.6	95.9	15.4	5.8	5.6
Morphine	5.76E-02	1.09E-01	0.9913	2.5	112.8	95.4	99.4	16.7	5.6	5.8
Methadone	8.91E-02	3.90E-03	0.9996	0.5	92.8	101.6	98	1.4	2.1	0.4
Salbutamol	2.69E-01	-5.81E-03	0.989	2.5	89.2	102.7	93.3	7.8	11.7	9.5
Oxycodone	1.40E-01	2.19E-02	0.9926	2.5	105.3	106	103.5	11	6.7	9.4
Lorazepam	2.20E-02	5.05E-03	0.9773	2.5	165.4	94.9	104.8	33.8	4.5	10.6
Bisoprolol	9.32E-04	7.34E-04	0.9847	5		106.6	105.1		7.6	10.6

Table A.9: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 5 ms for segmented spray T3 (0.32 – 0.35 min).

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.21E-01	8.23E-03	0.9998	1	94	101.7	98.4	4.2	1.2	1.2
Carbamazepine	7.04E-02	9.32E-02	0.9975	5		110.2	95		3.3	1.3
Propanolol	2.35E-01	-5.85E-03	0.9995	0.5	91.9	102.3	99.5	6.4	1.5	2.3
Clenbuterol	1.23E-01	7.35E-04	0.9954	2.5	95.5	104.2	100.7	6.2	6.3	6.4
Diazepam	1.22E-01	-1.70E-03	0.9953	1	93.6	103.8	101.1	8.4	5.3	6.1
Codeine	8.33E-02	-7.93E-04	0.9988	2.5	94	103.1	98.3	5.1	0.9	3.7
Cocaine	9.49E-02	-7.61E-04	0.9962	0.5	95.7	107.3	100.3	5.6	11.3	6.6
Sertraline	5.75E-02	4.25E-04	0.9974	2.5	101	100.3	98.7	13.5	1.4	3.6
Citalopram	7.68E-02	6.52E-04	0.9975	0.5	98.3	104.3	102.7	4	6	1.7
Fentanyl	6.82E-02	-3.29E-04	0.9998	0.5	93.1	102.4	98.4	0.6	1.3	2
Buprenorphine	1.10E-01	-1.43E-02	0.9989	1	89.7	99.6	100	8.6	3.8	1.9
Morphine	5.78E-02	9.93E-02	0.9948	2.5	126.4	101	105.1	7	10	9.9
Methadone	8.62E-02	1.52E-02	0.9963	1	86.9	102.8	97.7	7.1	6.3	6.4
Salbutamol	3.06E-01	-1.18E-02	0.9945	2.5	99.8	103.5	98.6	11.3	23.1	8
Oxycodone	1.54E-01	2.76E-02	0.9978	2.5	106.2	106.5	109.2	5.6	12.5	2.4
Lorazepam	2.38E-02	2.36E-02	0.9794	5		97.1	109.8		19.7	4.8
Bisoprolol	8.32E-04	1.34E-03	0.9945	5		99.4	103.5		3.3	5

Table A.10: Figures of merit for the quantitation of multiple analytes in human urine via CBS-MS/MS at a dwell time of 5 ms for a short spray event on side A of all blades (1.8 seconds).

				LOQ	Accuracy, % ($ng \cdot mL^{-1}$)			Precision, % ($ng \cdot mL^{-1}$)		
Compound	**Slope**	**Intercept**	**R^2**	**($ng \cdot mL^{-1}$)**	**3**	**30**	**90**	**3**	**30**	**90**
Methamphetamine	1.17E-01	-1.71E-02	0.9983	1	96.6	100.6	94.5	2.8	0.6	1.6
Carbamazepine	5.25E-02	2.20E-01	0.9898	10		106.3	92.8		3.2	5.8
Propanolol	2.33E-01	3.20E-02	0.9964	2.5	97.8	98.1	93.6	3.6	3.3	2.3
Clenbuterol	1.13E-01	5.50E-03	0.9978	1	94.4	99	94.2	5.5	0.5	1.7
Diazepam	1.13E-01	-1.63E-02	0.9968	2.5	105.5	99.9	95.3	7.6	1	3.8
Codeine	7.34E-02	1.70E-02	0.9965	1	95.8	94.9	99	13.7	3.6	3.6
Cocaine	9.59E-02	-1.78E-03	0.9955	1	97.8	100.1	97.8	5	8.4	10.3
Sertraline	4.99E-02	-7.01E-03	0.991	2.5	109	97.3	98.4	3.8	4.8	5.2
Citalopram	6.73E-02	4.58E-03	0.9966	1	100.5	97.4	95.1	6.4	4.8	6.7
Fentanyl	5.87E-02	1.11E-03	0.9979	1	97	98.4	95.2	5	0.9	1.6
Buprenorphine	1.07E-01	-9.13E-03	0.9964	1	94.8	91.8	96.6	6.2	5.5	2.4
Morphine	1.96E-03	4.70E-03	0.9931	2.5	108.1	98.5	95.6	8.1	4.9	8.3
Methadone	8.87E-02	1.25E-02	0.9974	1	99.2	100.8	95.6	5.1	2.6	2.7
Salbutamol	2.95E-02	1.03E-03	0.9922	2.5	97.2	101.4	96.3	9.4	4.4	7.9
Oxycodone	1.36E-01	4.43E-02	0.9934	2.5	112.4	95.1	95.4	12.2	5.3	6.4
Lorazepam	9.87E-03	5.84E-02	0.9854	5		95.3	96.8		7.5	4
Bisoprolol	5.35E-04	2.92E-03	0.9928	2.5	96.7	101.9	92.4	16.5	12.7	8.2

Table A.11: CBS-MS/MS figures of merit of pesticides extracted from apple juice matrix. [Take me back!]

Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (ng/g)			Precision, % (ng/g)			Class
					(ng/g)	3	30	90	3	30	90	
Azoxystrobin	Azoxystrobin-d_4	1.54E-02	6.41E-04	0.9991	0.5	101.2	100.4	99.8	5.2	2.8	2.9	Q
Benalaxyl	Azoxystrobin-d_4	5.90E-03	1.20E-03	0.996	1	99.2	98.8	101.1	16.1	3	8.2	Q
Bupirimate	Azoxystrobin-d_4	1.33E-02	-1.12E-04	0.9958	0.25	100.4	99.8	93.1	9.9	2.4	2.8	Q
Carbaryl	Atrazine-d_5	1.02E-02	2.65E-02	0.9939	5		103.4	94.6		8.4	7.5	Q
Chlorotoluron	Atrazine-d_5	1.63E-02	4.55E-02	0.9908	5		110.7	100.5		11.9	3.4	Q
Cycluron	Metalaxyl-d_6	6.29E-02	1.11E-03	0.9943	5		101.2	94.3		11.2	3.4	Q
Cyproconazole	Atrazine-d_5	1.44E-02	6.42E-03	0.9934	1	111.3	101.1	100.5	6.3	6.2	6.6	Q
Desmedipham	Azoxystrobin-d_4	1.18E-02	1.80E-04	0.9884	5		102.3	99.6		17.6	3.3	Q
Diclobutrazol	Atrazine-d_5	2.02E-02	-1.75E-02	0.9912	5		99.6	104.6		11.7	11.7	Q
Dimethoate	Metalaxyl-d_6	2.13E-02	2.98E-02	0.9865	5		115.6	105.2		11.1	12.5	Q
Dimoxystrobin	Azoxystrobin-d_4	4.93E-03	1.79E-03	0.9955	1	104.4	101.2	97.4	15.3	3.8	7.8	Q
Diuron	Atrazine-d_5	5.83E-03	2.43E-02	0.9918	5		110.9	98		8.1	3.1	Q
Ethiprole	Atrazine-d_5	1.73E-02	3.26E-02	0.9909	10	109.3	111.5	96.5	19.9	11.6	10.8	Q
Ethirimol	Imazalil-d_5	5.38E-02	1.05E-02	0.9907	1	100.8	106.8	99	9.5	8.3	15.6	Q
Fenamidone	Atrazine-d_5	1.07E-02	-5.88E-04	0.9873	1	108	100.3	104.8	8.4	13.3	6.1	Q
Fenhexamid	Atrazine-d_5	6.58E-03	2.16E-02	0.9822	10		113.9	103.8		11.9	5.4	Q
Fenuron	Metalaxyl-d_6	6.48E-02	-6.99E-04	0.9936	1	95	108.8	96.5	6.9	8.4	12.4	Q
Forchlorfenuron	Atrazine-d_5	2.83E-02	-3.53E-02	0.9864	5		91.1	105.9		10.3	10.8	Q
Furalaxyl	Metalaxyl-d_6	1.94E-01	3.25E-02	0.9917	1	117.1	103.9	98.7	11	7.9	3.6	Q
Imazalil	Imazalil-d_5	7.50E-02	3.09E-02	0.9946	1	89.9	101.2	98.4	9.5	8.8	5.1	Q
Isoproturon	Metalaxyl-d_6	6.10E-02	3.01E-03	0.9931	0.5	94.4	101	94.5	2.2	8.9	2.9	Q
Mefenacet	Azoxystrobin-d_4	6.90E-03	1.78E-03	0.9938	1	104.6	100.7	107	8.4	10	13.1	Q
Metalaxyl	Metalaxyl-d_6	1.49E-01	5.92E-03	0.9979	0.5	102.9	102.8	98	2	2.8	2.9	Q
Methabenzthiazuron	Atrazine-d_5	2.50E-02	-9.12E-03	0.9924	1	115	100.7	101.7	15.2	14.2	9.3	Q
Methoprotryne	Metalaxyl-d_6	2.40E-01	-1.47E-01	0.9871	2.5	111.7	105.9	100.4	7.1	7.1	6.8	Q
Metribuzin	Atrazine-d_5	8.15E-03	2.37E-02	0.9882	5		103.9	103.8		7.7	3.4	Q
Monolinuron	Atrazine-d_5	3.55E-03	5.51E-03	0.9881	5		116.6	113.3		11.7	6.2	Q
Myclobutanil	Atrazine-d_5	7.55E-03	-2.41E-03	0.9845	5		102.8	103.2		4	8.8	Q
Paclobutrazol	Atrazine-d_5	3.30E-02	2.64E-03	0.9971	1	100	104.6	100.4	9.8	7.3	4.8	Q
Pirimicarb	Metalaxyl-d_6	8.80E-02	-2.02E-02	0.9907	1	91.2	102.4	102.6	10.6	5.7	5.8	Q
Promecarb	Atrazine-d_5	2.31E-02	5.38E-02	0.9941	5		108.5	98.4		7.9	6.2	Q
Prometryne	Metalaxyl-d_6	1.81E-01	-6.12E-02	0.9953	1	94.3	92.9	93.4	6.3	12	6.5	Q
Pyracarbolid	Atrazine-d_5	7.51E-02	5.97E-02	0.9942	2.5	104.7	107.9	101.4	15.9	13.6	5.7	Q
Siduron	Atrazine-d_5	3.27E-02	7.97E-02	0.9939	1	113.8	103.6	99.2	6.9	5	10.3	Q
Tebuthiuron	Atrazine-d_5	6.73E-02	-1.85E-02	0.9922	1	98.8	101.5	92.6	16	5.7	7	Q
Terbutryn	Metalaxyl-d_6	4.18E-01	-9.55E-02	0.9944	1	101.4	96.9	97.4	10.8	12.3	2.8	Q
Triadimenol	Atrazine-d_5	1.07E-02	-8.20E-04	0.9909	1	104.3	103.3	99.6	13.3	5.4	6.1	Q
Tricyclazole	Atrazine-d_5	7.66E-02	5.18E-02	0.9884	5	98.2	103.4	98.8	2.3	11.2	4.5	Q
Triticonazole	Atrazine-d_5	1.81E-03	1.07E-03	0.9918	5		102.1	95		7	9.6	Q
Dioxacarb	Metalaxyl-d_6	5.83E-03	1.27E-02	0.991	5		111.6	106.9		4.8	6	Q
Fenobucarb	Atrazine-d_5	3.97E-02	7.38E-02	0.9901	5		102.4	96.7		2	2.8	Q
Oxadixyl	Metalaxyl-d_6	3.64E-02	4.22E-02	0.9913	1	117.6	107.5	94.3	8.4	7.6	11.3	Q
3-Hydroxycarbofuran	Metalaxyl-d_6	7.40E-03	5.32E-03	0.9653	5		103.4	91.3		15.4	15.1	SQ
Acetamiprid	Metalaxyl-d_6	9.73E-03	1.46E-02	0.9315	5		98	99.7		8.4	7.4	SQ
Ametryn	Metalaxyl-d_6	5.62E-02	-7.16E-03	0.9863	5		99.2	96.5		9.2	3.3	SQ
Aminocarb	Metalaxyl-d_6	1.14E-01	8.66E-02	0.9762	5		114.6	97.4		8.6	9.7	SQ
Bendiocarb	Metalaxyl-d_6	5.93E-02	3.14E-02	0.981	5		105.3	99.2		11.5	13	SQ
Bifenazate	Azoxystrobin-d_4	1.78E-03	2.68E-03	0.9848	5		108.1	107.6		16.4	11	SQ
Bitertanol	Azoxystrobin-d_4	2.73E-04	-8.11E-05	0.9668	5		105.4	109.2		14.3	2.8	SQ
Boscalid	Atrazine-d_5	1.18E-02	3.73E-02	0.9726	5		111.1	106.6		22.6	13.3	SQ
Bromucanozole	Azoxystrobin-d_4	2.73E-03	-4.34E-03	0.9708	5		92.7	107.4		25.7	3.9	SQ
Buprofezin	Azoxystrobin-d_4	6.13E-03	-2.89E-03	0.9805	1	104.2	92	101.4	19.8	16.8	11.7	SQ
Butafenacil	Azoxystrobin-d_4	4.50E-03	1.57E-03	0.9877	1	107.9	106.4	104.4	19.8	14.6	2.8	SQ
Carbendazim	Metalaxyl-d_6	1.83E-02	-2.23E-03	0.9797	5		105	102.7		7.8	15.5	SQ
Carbetamide	Metalaxyl-d_6	6.79E-03	5.67E-04	0.9812	5		102.1	94.6		19.1	17.3	SQ
Carbofuran	Metalaxyl-d_6	9.40E-02	3.40E-02	0.9779	5		107.2	95.8		12.3	11.3	SQ

Continued on next page

Table A.11: CBS-MS/MS figures of merit of pesticides extracted from apple juice matrix – continued from previous page

Compound	Internal Standard	Slope	Intercept	R^2	LOQ (ng/g)	Accuracy, % (ng/g) 3	Accuracy, % (ng/g) 30	Accuracy, % (ng/g) 90	Precision, % (ng/g) 3	Precision, % (ng/g) 30	Precision, % (ng/g) 90	Class
Carboxin	Atrazine-d_5	2.80E-02	2.44E-02	0.9859	2.5	83.3	108.1	106.7	18.1	13.1	13.2	SQ
Carfentrazone-ethyl	Azoxystrobin-d_4	1.20E-03	2.75E-03	0.975	5		101.1	101.9		25.5	19.7	SQ
Chlorantraniliprole	Azoxystrobin-d_4	1.09E-03	-1.79E-03	0.9824	5		97.4	105.9		27.5	11.7	SQ
Chloroxuron	Atrazine-d_5	1.47E-03	2.91E-03	0.9578	5		99.8	98.7		18.1	14.2	SQ
Clothianidin	Metalaxyl-d_6	7.65E-03	-8.87E-03	0.964	5		86.7	92.5		6.7	6.8	SQ
Cyprodinil	Metalaxyl-d_6	1.49E-02	8.55E-03	0.9831	5		95.3	94		26.6	13	SQ
Dicrotophos	Metalaxyl-d_6	6.84E-02	-8.76E-03	0.9409	1	85.9	96.7	84.5	10.3	19.9	20	SQ
Diethofencarb	Azoxystrobin-d_4	1.85E-03	4.21E-03	0.9864	5		108.2	94.6		19	2	SQ
Diflubenzuron	Azoxystrobin-d_4	1.42E-03	5.87E-04	0.942	5		108.9	116.8		21	34.4	SQ
Dimethomorph	Azoxystrobin-d_4	2.66E-03	-4.52E-03	0.9755	5		97.1	106.1		21	8.1	SQ
Epoxiconazole	Azoxystrobin-d_4	5.27E-03	-2.54E-03	0.9777	5		104.4	112.7		20.8	4.5	SQ
Etaconazole	Azoxystrobin-d_4	6.94E-03	-2.30E-03	0.9812	1	104.3	99.2	107.2	25.7	20.9	6.8	SQ
Fenbuconazole	Atrazine-d_5	6.40E-03	3.73E-03	0.9541	10		102.5	110.6		23.8	7.8	SQ
Fenpropimorph	Imazalil-d_5	2.90E-01	1.69E-02	0.9749	5		98.8	112.7		9.9	23.6	SQ
Flubendiamide	Azoxystrobin-d_4	1.49E-04	3.69E-05	0.9719	5		111.7	116.2		28.3	12.5	SQ
Flufenacet	Azoxystrobin-d_4	4.57E-03	1.42E-03	0.9897	1	100.2	106	103.4	16.3	20.6	7.3	SQ
Fluometuron	Atrazine-d_5	2.68E-02	3.81E-02	0.9893	2.5	78.5	108.3	94.2	13.3	2.3	2.3	SQ
Fluoxastrobin	Azoxystrobin-d_4	5.49E-03	-1.61E-03	0.9828	1	106.7	94.1	106.6	17.3	11	4.3	SQ
Flusilazole	Atrazine-d_5	2.96E-02	-1.92E-02	0.9737	5		98.6	109.8		14.3	2.3	SQ
Flutolanil	Atrazine-d_5	5.62E-02	7.06E-02	0.973	1	118	114.2	98.3	9.7	12	6.6	SQ
Furathiocarb	Azoxystrobin-d_4	2.11E-03	9.47E-04	0.967	5		98.6	109.9		18.9	15.7	SQ
Imidacloprid	Metalaxyl-d_6	1.24E-02	2.44E-03	0.9664	5		98.1	104.9		8.7	6.4	SQ
Ipconazole	Atrazine-d_5	1.94E-03	8.85E-04	0.9647	5		103.3	107.9		17.5	2.9	SQ
Iprovalicarb	Metalaxyl-d_6	5.18E-02	1.64E-02	0.9867	5		103	97.3		12.4	2.8	SQ
Isocarbophos	Azoxystrobin-d_4	8.52E-04	7.65E-04	0.9743	10		110.2	98.9		17.7	9	SQ
Linuron	Atrazine-d_5	1.61E-02	2.82E-02	0.9687	2.5	108.8	119.1	103.1	21.7	14.4	11.9	SQ
Mepronil	Azoxystrobin-d_4	1.45E-02	3.52E-02	0.9878	5		111.9	105.3		18.3	8.7	SQ
Metconazole	Atrazine-d_5	2.83E-03	-1.59E-03	0.9783	5		97.2	104.6		17.3	6.3	SQ
Nuarimol	Atrazine-d_5	9.62E-03	-1.64E-03	0.9824	1	119.1	106.1	109.7	16.7	13.6	6	SQ
Omethoate	Metalaxyl-d_6	1.48E-02	8.04E-03	0.9313	5		102.1	102.9		15.2	8.8	SQ
Oxamyl	Metalaxyl-d_6	8.74E-03	1.67E-03	0.9858	5		108.5	97.3		5.3	10.5	SQ
Penconazole	Atrazine-d_5	1.23E-02	4.77E-04	0.9824	1	103.4	106.6	109.6	18.6	10.7	8.3	SQ
Pencycuron	Metalaxyl-d_6	5.27E-03	6.26E-05	0.9778	5		99.4	108.3		16.4	10.7	SQ
Picoxystrobin	Azoxystrobin-d_4	4.38E-03	6.32E-04	0.9936	1	123.9	103.1	102.7	8.7	15.8	11.7	SQ
Piperonyl butoxide	Metalaxyl-d_6	5.64E-03	-1.52E-04	0.9703	1	130.6	103	123.8	21.1	28.4	28.2	SQ
Prochloraz	Azoxystrobin-d_4	2.07E-03	2.70E-04	0.9875	1	104.3	96.4	99.9	19.5	9.7	2.8	SQ
Prometon	Imazalil-d_5	7.09E-01	3.57E-02	0.986	1	103.1	95.9	100.1	7.2	8.6	16.5	SQ
Propoxur	Metalaxyl-d_6	1.92E-02	2.68E-02	0.988	5		107.2	92.4		9.9	16.9	SQ
Secbumeton	Imazalil-d_5	4.86E-01	-3.11E-02	0.983	1	102.4	99.1	111.3	3.6	6.7	19.8	SQ
Simetryn	Atrazine-d_5	2.69E-02	5.37E-02	0.9731	5		109.7	94.9		23	7.4	SQ
Spinetoram	Azoxystrobin-d_4	4.38E-04	-8.85E-04	0.9719	5		76.6	99.8		23.4	11.9	SQ
Spirotetramat	Azoxystrobin-d_4	4.31E-03	-8.11E-04	0.9857	1	94.2	99.8	97.9	13.7	24.5	10.5	SQ
Spiroxamine	Imazalil-d_5	6.65E-01	-1.61E-01	0.9886	1	80.4	93.3	124.4	14	8.5	25.1	SQ
Tebuconazole	Atrazine-d_5	2.01E-02	-2.65E-03	0.9818	1	110.5	104.4	103.4	19.1	12.4	6.8	SQ
Tebufenozide	Atrazine-d_5	6.01E-03	1.62E-02	0.9755	2.5	99	106.8	94.5	17.3	11.5	15.5	SQ
Terbumeton	Imazalil-d_5	1.55E+00	1.68E-02	0.9888	1	108.7	98.9	104.3	13.6	7.9	16.5	SQ
Triadimefon	Atrazine-d_5	1.05E-02	4.67E-03	0.9923	1	114.4	105.6	104.2	22.9	13.6	7.8	SQ
Trifloxystrobin	Azoxystrobin-d_4	3.59E-03	5.54E-04	0.9909	1	127.3	93.4	101.6	28	19.8	16.5	SQ
Triflumizole	Azoxystrobin-d_4	1.92E-03	1.04E-04	0.9812	1	103.6	96.5	103.4	4.6	14.6	3.6	SQ
Vamidothion	Metalaxyl-d_6	7.62E-02	-7.05E-03	0.9835	1	93.1	100.4	100.6	13.1	9	10.9	SQ
Zoxamide	Azoxystrobin-d_4	3.48E-03	5.38E-03	0.9765	5		106.4	111.4		19.8	10.4	SQ
Mexacarbate	Metalaxyl-d_6	9.52E-02	-2.24E-02	0.9871	1	93.4	103.1	100.2	7.7	4.1	6.9	SQ
Pyrimethanil	Pyrimethanil-d_5	1.08E-01	1.39E-01	0.9907	1	97.5	92.9	104.5	17	4.1	8.7	SQ

A.3 Chapter 3

Table A.12: CBS-MS/MS figures of merit of pesticides extracted from apple matrix.

[Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	8.38E-03	8.01E-03	0.9869	2.5		96.6	87.4	115.9		11.5	5.1	11.7
2	acetamiprid	carbofuran-d_3	1.64E-02	1.55E-03	0.9937	1		116.7	99.2	105.1		13.3	4.7	6.9
3	aldicarb	dimethoate-d_6	1.43E-02	-2.28E-02	0.9873	5			84.9	100.8			4.2	3.7
4	ametryn	metalaxyl-d_6	6.06E-02	-2.27E-02	0.9812	1		76.4	86.7	100.2		6.4	5.1	1.5
5	aminocarb	dimethoate-d_6	2.44E-01	6.08E-03	0.9833	1		86.8	90.3	95.3		11.6	6.4	21.4
6	amitraz	spirotetramat-d_6	1.50E-02	5.36E-03	0.9911	5			96.3	95.9			11.0	5.4
7	azoxystrobin	malathion-d_6	3.56E-01	7.76E-02	0.9924	1		105.0	101.1	113.6		6.0	11.0	8.7
8	benalaxyl	metalaxyl-d_6	1.79E-02	3.62E-03	0.9854	5			97.2	95.7			5.4	9.7
9	bendiocarb	carbofuran-d_3	3.97E-02	-5.09E-03	0.9988	0.5	100.1	104.7	99.6	100.1	4.6	5.7	2.9	3.5
10	boscalid	carbofuran-d_3	1.19E-02	4.61E-02	0.9638	10			108.6	98.1			9.0	16.8
11	bromucanozole	carbofuran-d_3	9.04E-03	-5.47E-03	0.9606	5			106.0	97.5			11.3	12.1
12	bupirimate	kresoxim-methyl-d_7	1.49E+00	9.22E-02	0.9948	1		109.4	101.0	113.8		15.6	8.6	8.0
13	buprofenzin	malathion-d_6	9.08E-02	-4.35E-02	0.9951	1		89.9	100.1	111.5		10.4	12.1	1.1
14	butafenacil	trifloxystrobin-d_6	1.46E-01	3.94E-02	0.9963	1		113.3	107.2	97.5		10.6	8.1	3.9
15	butoxycarboxim	carbofuran-d_3	5.60E-02	-1.47E-02	0.9905	1		89.7	102.2	99.3		2.4	7.3	11.4
16	carbaryl	atrazine-d_5	1.27E-02	2.52E-02	0.9979	5			93.4	99.4			5.0	9.5
17	carbendazim	carbofuran-d_3	8.27E-02	-8.15E-03	0.9917	0.5	85.9	88.1	85.6	106.8	16.4	11.4	14.1	13.4
18	carbetamide	dimethoate-d_6	1.77E-02	-7.77E-04	0.9894	2.5		88.0	96.2	100.9		8.6	4.9	4.0
19	carbofuran	dimethoate-d_6	1.24E-01	-1.55E-02	0.9938	0.5	85.7	78.7	92.8	97.7	11.0	10.6	8.6	5.8
20	carfentrazone-ethyl	trifloxystrobin-d_6	1.82E-02	9.01E-04	0.9926	1		99.4	103.5	95.5		15.4	7.0	6.0
21	chlorantraniliprole	atrazine-d_5	1.16E-02	-3.29E-03	0.9939	1		102.3	90.0	112.3		1.8	2.3	7.1
22	chlorotoluron	carbofuran-d_3	1.28E-02	-4.78E-04	0.9917	0.5	81.4	91.6	98.1	100.7	14.7	12.1	5.7	5.5
23	chloroxuron	kresoxim-methyl-d_7	6.31E-01	-1.52E-01	0.9928	2.5		111.4	97.1	101.9		15.2	8.5	13.4
24	clothianidin	dimethoate-d_6	6.73E-03	-1.25E-04	0.9865	1		97.1	102.5	105.8		19.3	9.2	7.0
25	cyazofamid	spirotetramat-d_6	5.78E-03	-2.43E-03	0.9836	2.5		113.0	94.6	97.5		12.7	9.0	1.1
26	cycluron	dimethoate-d_6	8.60E-02	-9.55E-02	0.9926	2.5		93.6	95.0	90.2		17.1	6.8	8.0
27	cyproconazole	atrazine-d_5	2.28E-02	-1.75E-03	0.9937	1		96.3	106.5	103.4		16.4	10.1	6.2
28	cyprodinil	carbofuran-d_3	9.07E-03	4.10E-03	0.9843	2.5		101.4	90.7	97.8		10.8	11.7	3.1
29	desmedipham	methiocarb-d_3	4.97E-02	-1.10E-02	0.9938	1		87.4	108.1	103.9		9.0	21.7	3.4
30	diclobutrazol	atrazine-d_5	1.87E-02	-3.39E-03	0.9871	5			106.4	109.9			3.3	1.8
31	diethofencarb	methiocarb-d_3	5.60E-02	-1.64E-04	0.9945	0.5	102.8	98.4	110.6	98.5	3.8	9.9	17.3	4.6
32	difenoconazole	kresoxim-methyl-d_7	3.65E-01	-3.64E-01	0.9852	5			89.4	106.9			9.7	9.1
33	dimethoate	dimethoate-d_6	2.96E-02	-4.13E-03	0.9971	0.5	100.0	101.2	88.0	101.0	4.8	8.6	10.0	2.3
34	dimethomorph	methiocarb-d_3	1.08E-01	-9.10E-02	0.9877	2.5		102.1	107.6	106.3		10.2	15.9	3.5
35	dimoxystrobin	malathion-d_6	8.73E-02	6.45E-03	0.9952	0.5	93.6	104.2	100.5	105.5	15.2	15.0	2.4	2.9
36	dioxacarb	carbofuran-d_3	3.91E-02	-2.42E-03	0.9988	0.5	94.1	100.0	97.6	100.3	3.3	8.7	2.5	3.1
37	diuron	atrazine-d_5	6.36E-02	4.44E-02	0.9943	5			96.8	103.7			5.2	9.2
38	epoxiconazole	methiocarb-d_3	2.64E-02	-1.76E-02	0.9857	5			116.6	104.8			19.3	4.4
39	etaconazole	atrazine-d_5	3.18E-02	1.13E-02	0.9945	1		89.0	104.6	104.1		9.6	4.7	2.0
40	ethiprole	atrazine-d_5	2.45E-02	2.48E-02	0.9902	2.5		100.0	106.7	106.7		12.9	5.8	2.7
41	ethirimol	dimethoate-d_6	3.58E-02	-6.79E-02	0.9915	2.5		98.3	80.8	107.4		9.3	6.6	7.6
42	ethofumesate	atrazine-d_5	1.07E-02	2.63E-02	0.9882	5			102.8	99.7			11.7	4.7
43	etoxazole	malathion-d_6	9.82E-03	-8.81E-03	0.9854	2.5		113.4	87.2	111.7		17.6	4.0	10.0
44	fenamidone	atrazine-d_5	1.28E-02	1.58E-03	0.9927	1		91.1	105.5	107.9		7.0	9.1	1.3
45	fenarimol	atrazine-d_5	5.21E-03	1.94E-04	0.9759	5			114.5	109.7			8.4	6.9
46	fenbuconazole	methiocarb-d_3	1.34E-02	-1.33E-02	0.9806	5			109.2	104.7			19.5	9.2
47	fenobucarb	carbofuran-d_3	4.26E-02	-2.64E-02	0.9913	2.5		102.8	92.5	92.4		4.1	6.7	4.9
48	fenpropimorph	imazalil-d_5	1.82E-01	-3.49E-01	0.9698	2.5		112.7	95.8	91.2		11.4	18.2	14.5
49	fenuron	dimethoate-d_6	5.78E-02	-1.80E-02	0.9956	1		92.6	95.9	95.9		9.1	11.4	5.4
50	flufenacet	methiocarb-d_3	6.19E-02	5.84E-03	0.9940	0.5	96.9	102.8	107.3	104.3	14.1	6.6	9.6	2.5
51	fluometuron	atrazine-d_5	3.67E-02	8.50E-03	0.9942	5			97.9	100.7			8.4	11.4
52	fluoxastrobin	kresoxim-methyl-d_7	1.85E+00	-7.63E-01	0.9935	2.5		102.9	91.0	108.2		10.4	16.2	14.0
53	flusilazole	atrazine-d_5	2.69E-02	-2.01E-02	0.9884	2.5		88.4	101.0	108.6		7.0	4.8	4.0
54	flutolanil	methiocarb-d_3	1.32E-01	3.30E-03	0.9957	0.25	98.0	114.2	98.6	105.3	13.3	5.3	2.2	4.4
55	flutriafol	atrazine-d_5	2.43E-02	1.55E-03	0.9915	1		106.3	104.2	106.6		25.3	3.5	6.6
56	forchlorfenuron	carbofuran-d_3	2.88E-02	-7.02E-02	0.9723	5			98.7	94.5			5.7	4.5

Continued on next page

Table A.12: CBS-MS/MS figures of merit of pesticides extracted from apple matrix – continued from previous page

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
57	fuberidazole	metalaxyl-d_6	4.91E-02	-1.47E-01	0.9829	5			85.4	95.7			19.1	5.5
58	furalaxyl	metalaxyl-d_6	7.08E-02	-1.35E-03	0.9905	0.5	86.7	97.6	99.2	96.4	4.4	12.2	9.5	3.3
59	furathiocarb	malathion-d_6	4.53E-02	9.65E-03	0.9883	1		91.4	97.2	112.8		19.2	7.2	3.6
60	hexaconazole	atrazine-d_5	1.10E-02	-2.79E-03	0.9848	5			104.5	105.2			1.7	6.1
61	imazalil	imazalil-d_5	6.76E-02	8.77E-02	0.9927	1		118.2	98.5	97.1		25.4	9.2	5.0
62	imidacloprid	carbofuran-d_3	5.26E-03	9.30E-03	0.9915	2.5		103.7	102.2	101.4		16.4	4.1	1.9
63	ipconazole	carbofuran-d_3	1.45E-03	-1.90E-03	0.9363	10			98.5	98.5			3.2	11.2
64	iprovalicarb	metalaxyl-d_6	2.39E-02	1.54E-03	0.9945	0.5	94.1	102.0	101.6	95.5	20.8	17.1	5.2	6.4
65	isoprocarb	carbofuran-d_3	3.79E-02	-4.47E-02	0.9923	2.5		102.5	89.4	93.5		8.6	13.2	6.6
66	isoproturon	carbofuran-d_3	2.62E-02	-8.36E-03	0.9891	1		88.1	98.0	90.3		13.1	2.1	7.9
67	linuron	carbofuran-d_3	1.15E-02	-6.26E-03	0.9895	5			98.9	86.7			4.6	4.0
68	mandipropamid	trifloxystrobin-d_6	8.99E-02	3.74E-02	0.9958	2.5		100.9	105.1	98.0		10.8	3.8	3.8
69	mefenacet	malathion-d_6	1.11E-01	-1.73E-02	0.9946	1		104.0	101.7	106.6		15.1	9.3	2.7
70	mepanipyrim	carbofuran-d_3	3.86E-03	-2.10E-03	0.9730	5			94.2	108.7			5.6	12.5
71	mepronil	methiocarb-d_3	1.23E-01	6.41E-02	0.9918	1		93.1	109.1	98.7		13.5	18.3	6.2
72	metalaxyl	metalaxyl-d_6	5.17E-02	3.39E-03	0.9987	0.25	94.6	104.2	96.6	101.6	6.4	2.3	5.4	3.1
73	metconazole	atrazine-d_5	1.97E-02	-1.97E-02	0.9876	2.5		96.8	103.8	108.7		10.2	8.7	2.3
74	methabenzthiazuron	carbofuran-d_3	1.12E-01	-1.86E-02	0.9950	0.5	89.7	91.3	94.4	98.7	9.4	1.6	11.1	5.9
75	methiocarb	atrazine-d_5	9.09E-03	-2.27E-03	0.9953	1		113.9	88.0	96.2		21.4	0.5	2.0
76	methomyl	dimethoate-d_6	6.61E-03	-2.19E-04	0.9799	2.5		120.3	92.5	98.7		9.0	10.1	9.9
77	methoprotryne	metalaxyl-d_6	4.27E-02	-5.02E-02	0.9904	2.5		98.6	90.4	94.5		7.0	10.8	3.9
78	methoxyfenozide	carbofuran-d_3	8.64E-03	4.72E-04	0.9876	1		97.6	103.0	97.2		13.6	6.0	6.4
79	metobromuron	methiocarb-d_3	4.16E-02	2.71E-03	0.9960	0.5	92.5	105.5	107.0	102.1	15.8	3.4	11.1	5.7
80	mevinphos	metalaxyl-d_6	1.44E-02	-6.73E-02	0.9718	10			81.8	93.5			7.7	1.7
81	mexacarbate	carbofuran-d_3	6.15E-02	-4.66E-02	0.9892	2.5		98.1	103.0	98.8		5.9	9.2	12.4
82	monolinuron	carbofuran-d_3	6.04E-03	1.32E-03	0.9694	2.5		88.5	91.4	90.9		12.2	15.4	2.9
83	myclobutanil	methiocarb-d_3	3.50E-02	-8.02E-03	0.9893	5			119.8	101.8			18.3	7.3
84	neburon	carbofuran-d_3	4.45E-03	-2.74E-03	0.9813	5			92.7	83.9			2.4	6.7
85	nuarimol	atrazine-d_5	1.12E-02	1.84E-03	0.9800	5			113.4	108.5			6.2	2.7
86	oxadixyl	dimethoate-d_6	2.33E-02	3.63E-03	0.9831	1		86.5	98.0	107.1		15.3	12.3	7.5
87	paclobutrazol	atrazine-d_5	4.72E-03	-2.51E-06	0.9940	5			104.8	103.5			14.9	5.5
88	penconazole	atrazine-d_5	1.10E-02	2.05E-03	0.9798	1		81.9	103.6	102.7		21.9	3.1	8.5
89	pencycuron	trifloxystrobin-d_6	1.08E-01	5.36E-02	0.9966	2.5		97.6	110.0	100.9		9.3	6.1	0.5
90	picoxystrobin	metalaxyl-d_6	1.17E-02	-9.30E-03	0.9940	2.5		85.8	90.7	95.6		10.4	12.9	12.1
91	piperonyl butoxide	metalaxyl-d_6	2.59E-03	-1.32E-03	0.9926	5			82.2	96.2			8.4	17.6
92	pirimicarb	metalaxyl-d_6	2.83E-02	-1.17E-02	0.9911	1		83.8	92.4	95.5		7.2	11.5	7.7
93	prochloraz	kresoxim-methyl-d_7	2.77E-01	-2.04E-01	0.9935	2.5		110.1	85.2	109.5		23.2	17.3	8.4
94	promecarb	atrazine-d_5	3.00E-02	9.29E-04	0.9973	1		90.6	94.6	98.7		5.9	2.4	5.8
95	prometon	metalaxyl-d_6	8.99E-02	-1.28E-01	0.9925	2.5		104.0	89.4	96.1		6.9	9.5	5.4
96	prometryne	malathion-d_6	2.17E-01	-8.49E-02	0.9871	1		101.0	91.7	103.7		16.2	4.6	5.7
97	propham	carbofuran-d_3	4.14E-03	-6.72E-03	0.9639	5			104.4	94.3			19.5	4.5
98	propiconazole	atrazine-d_5	1.80E-02	4.25E-03	0.9900	1		71.0	102.1	106.4		8.6	6.4	5.2
99	propoxur	dimethoate-d_6	3.36E-02	-3.67E-02	0.9889	2.5		96.6	87.1	91.5		10.9	3.8	6.9
100	pyracarbolid	carbofuran-d_3	6.14E-02	1.78E-03	0.9944	0.5	89.7	92.5	97.8	96.1	16.5	6.5	6.3	8.4
101	pyraclostrobin	metalaxyl-d_6	2.92E-03	-6.71E-03	0.9892	5			75.4	96.1			12.9	15.1
102	pyrimethanil	atrazine-d_5	1.63E-02	-1.69E-02	0.9932	2.5		95.0	86.2	101.6		15.0	6.4	4.4
103	secbumeton	metalaxyl-d_6	9.66E-02	-3.98E-02	0.9908	0.5	112.4	85.4	86.2	95.9	3.0	8.3	10.5	8.8
104	siduron	methiocarb-d_3	8.34E-02	1.69E-02	0.9917	1		101.4	110.9	102.1		17.8	17.0	2.8
105	simetryn	carbofuran-d_3	4.76E-02	-6.83E-02	0.9848	2.5		100.5	89.1	97.5		7.7	9.4	13.2
106	spinetoram	metalaxyl-d_6	6.15E-03	-1.31E-02	0.9837	2.5		106.8	77.7	96.6		11.2	12.5	4.2
107	spinosyn A	metalaxyl-d_6	8.03E-03	-1.61E-02	0.9815	5			78.1	99.2			13.9	2.7
108	spirotetramat	spirotetramat-d_6	4.61E-02	-6.28E-04	0.9991	0.5	97.2	99.6	100.3	100.1	15.1	1.1	0.7	3.0
109	spiroxamine	imazalil-d_5	5.89E-01	-5.06E-01	0.9634	1		89.6	96.2	95.5		7.6	18.5	16.1
110	tebuconazole	atrazine-d_5	1.85E-02	-5.82E-03	0.9887	1		79.2	104.6	106.2		17.7	3.6	0.6
111	tebuthiuron	carbofuran-d_3	5.09E-02	-7.54E-03	0.9952	1		92.1	106.3	103.4		16.3	1.6	5.6
112	terbumeton	metalaxyl-d_6	2.25E-01	-4.95E-02	0.9904	0.25	88.6	77.5	91.0	98.6	3.0	7.2	8.4	5.5
113	terbutryn	malathion-d_6	4.47E-01	-3.67E-02	0.9926	1		102.2	93.6	108.6		12.1	3.9	4.6
114	tetraconazole	carbofuran-d_3	1.49E-02	-1.10E-02	0.9551	5			109.0	99.8			4.6	12.2
115	thiabendazole	dimethoate-d_6	1.53E-01	-4.68E-01	0.9816	5			83.4	92.6			8.2	2.5

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Table A.12: CBS-MS/MS figures of merit of pesticides extracted from apple matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	thiacloprid	carbofuran-d_3	3.65E-02	-2.94E-04	0.9927	0.5	105.6	105.6	97.1	94.4	11.4	17.7	6.7	4.4
117	thiamethoxam	dimethoate-d_6	1.04E-02	8.67E-03	0.9926	1		105.2	87.9	102.2		19.4	13.5	12.4
118	triadimefon	methiocarb-d_3	2.51E-02	7.07E-03	0.9933	1		102.3	107.0	100.4		22.6	12.3	9.7
119	triadimenol	carbofuran-d_3	9.01E-03	7.09E-03	0.9680	5			113.0	95.8			2.5	8.9
120	tricyclazole	carbofuran-d_3	4.84E-02	-1.44E-03	0.9966	0.25	88.3	94.7	97.7	98.7	8.8	14.9	11.5	3.6
121	trifloxystrobin	trifloxystrobin-d_6	7.61E-02	-2.35E-02	0.9980	2.5		105.3	104.2	103.0		12.8	8.3	1.9
122	triflumizole	carbofuran-d_3	5.03E-03	-2.75E-04	0.9784	5			97.4	95.0			3.9	8.5
123	triflumuron	methiocarb-d_3	7.19E-03	1.26E-02	0.9563	10			114.3	112.6			1.5	8.1
124	triticonazole	atrazine-d_5	1.52E-02	-5.22E-03	0.9906	2.5		90.8	101.0	110.4		19.3	5.5	3.5
125	vamidothion	imazalil-d_5	7.48E-02	-2.69E-03	0.9876	5			99.1	120.2			10.9	1.8
126	zoxamide	methiocarb-d_3	3.71E-02	-1.36E-03	0.9883	0.5	94.2	98.2	113.8	106.7	1.3	7.9	19.1	6.9

Table A.13: LC-MS/MS figures of merit of pesticides extracted from apple matrix.

[Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	8.07E-03	1.07E-03	0.9884	2.5		92.7	120.6	94.3		18.3	6.3	12.8
2	acetamiprid	dimethoate-d_6	6.47E-02	1.29E-02	0.9923	1		114.8	105.2	104.0		17.9	5.6	8.8
3	aldicarb	fludioxonil-$^{13}C_2$	8.17E-02	-3.35E-02	0.9894	5			121.9	90.8			3.6	13.9
4	ametryn	atrazine-d_5	9.40E-02	-1.15E-02	0.9915	1		98.0	101.2	98.9		11.0	8.5	7.8
5	aminocarb	dimethoate-d_6	7.43E-02	-6.66E-03	0.9758	2.5		109.5	100.2	98.9		20.0	4.0	15.5
6	amitraz	malathion-d_6	5.34E-02	4.83E-03	0.9904	2.5		95.2	102.1	103.7		15.6	19.3	8.7
7	azoxystrobin	metalaxyl-d_6	7.83E-02	1.07E-02	0.9851	0.5	85.9	110.6	94.2	109.0	13.4	13.2	14.0	5.2
8	benalaxyl	cyprodinil-d_5	8.87E-01	-2.06E-02	0.9933	1		122.7	94.8	95.7		3.3	2.5	13.8
9	bendiocarb	imazalil-d_5	8.19E-02	-3.12E-03	0.9916	2.5		93.6	101.2	101.4		13.0	13.8	9.5
10	boscalid	atrazine-d_5	1.90E-02	2.00E-03	0.9926	1		97.6	93.1	94.3		13.4	6.9	7.7
11	bromucanozole	atrazine-d_5	6.66E-03	1.23E-03	0.9918	2.5		89.3	88.0	92.6		13.1	7.4	9.0
12	bupirimate	atrazine-d_5	6.43E-03	-3.11E-03	0.9871	5			97.9	101.4			5.8	15.2
13	buprofenzin	carbofuran-d_3	2.44E-02	-1.18E-02	0.9852	2.5		120.3	92.9	103.6		4.4	9.2	10.9
14	butafenacil	atrazine-d_5	1.69E-02	-1.09E-02	0.9831	2.5		109.1	87.2	92.7		13.3	13.0	7.3
15	butoxycarboxim	carbofuran-d_3	3.51E-02	-8.89E-03	0.9911	2.5		100.3	98.8	101.0		13.2	7.3	7.5
16	carbaryl	atrazine-d_5	8.51E-03	2.41E-04	0.9862	2.5		89.7	100.0	95.1		17.7	5.1	13.7
17	carbendazim	dimethoate-d_6	2.21E-01	-9.35E-03	0.9890	0.5	91.8	103.4	94.7	95.2	11.0	8.5	7.9	7.5
18	carbetamide	carbofuran-d_3	5.92E-03	-4.40E-03	0.9834	5			108.2	92.8			12.8	10.4
19	carbofuran	carbofuran-d_3	2.98E-02	-8.39E-04	0.9946	0.5	109.7	104.0	102.3	110.4	16.3	20.0	5.0	11.7
20	carfentrazone-ethyl	imazalil-d_5	3.06E-02	-1.66E-02	0.9854	2.5		112.9	89.7	104.8		12.0	14.9	11.8
21	chlorantraniliprole	dimethoate-d_6	2.56E-02	-9.81E-03	0.9893	2.5		110.8	90.5	104.7		15.3	15.1	5.0
22	chlorotoluron	imazalil-d_5	6.67E-02	-1.11E-02	0.9927	1		110.1	93.0	96.0		8.2	10.4	14.2
23	chloroxuron	imazalil-d_5	9.95E-02	-1.45E-01	0.9898	5			91.8	103.3			14.1	6.7
24	clothianidin	dimethoate-d_6	1.12E-02	7.11E-03	0.9739	5			95.8	96.8			12.1	8.9
25	cyazofamid	cyprodinil-d_5	1.05E+04	-1.17E+04	0.9950	5			98.9	106.4			6.0	1.9
26	cycluron	methiocarb-d_3	6.19E-02	-5.76E-03	0.9928	1		102.1	98.1	97.1		14.2	9.1	2.8
27	cyproconazole	carbofuran-d_3	2.25E-02	-2.09E-03	0.9939	1		110.4	106.6	101.4		6.5	3.6	10.6
28	cyprodinil	fludioxonil-$^{13}C_2$	2.07E-01	1.54E-01	0.9916	2.5		93.5	104.5	113.0		17.9	15.1	11.7
29	desmedipham	cyprodinil-d_5	2.26E-01	-8.72E-02	0.9930	2.5		113.8	103.4	101.9		16.7	12.8	13.6
30	diclobutrazol	imazalil-d_5	6.41E-02	-3.63E-02	0.9913	5			99.1	97.9			10.1	14.9
31	diethofencarb	imazalil-d_5	7.57E-02	2.92E-03	0.9907	1		103.6	96.9	102.3		8.9	4.9	14.1
32	difenoconazole	fludioxonil-$^{13}C_2$	1.68E-01	-1.50E-01	0.9889	5			96.8	106.9			19.6	15.8
33	dimethoate	dimethoate-d_6	2.66E-02	-1.35E-02	0.9872	2.5		100.0	104.7	91.9		13.9	7.8	9.8
34	dimethomorph	imazalil-d_5	1.00E-01	5.44E-02	0.9864	5			104.8	107.4			11.7	16.7
35	dimoxystrobin	atrazine-d_5	1.37E-02	-3.51E-03	0.9905	2.5		95.1	97.9	100.2		20.1	10.2	15.9
36	dioxacarb	imazalil-d_5	8.20E-02	-1.21E-02	0.9928	1		96.2	101.3	101.4		12.6	13.8	9.5
37	diuron	imazalil-d_5	6.53E-02	-8.82E-03	0.9940	1		101.3	93.2	93.6		12.2	10.3	11.5
38	epoxiconazole	carbofuran-d_3	2.75E-02	5.72E-04	0.9888	2.5		116.8	95.3	106.9		14.0	7.4	16.0
39	etaconazole	imazalil-d_5	1.44E-01	-1.92E-02	0.9929	1		116.7	94.2	94.3		8.0	8.6	15.2
40	ethiprole	imazalil-d_5	1.56E-01	7.26E-02	0.9922	2.5		107.8	107.2	90.0		16.1	11.5	12.4
41	ethirimol	carbofuran-d_3	1.16E-02	-1.63E-02	0.9873	5			118.2	111.1			11.8	5.9
42	ethofumesate	imazalil-d_5	4.62E-02	8.97E-03	0.9904	2.5		102.0	94.3	97.0		19.9	8.2	17.2
43	etoxazole	trifloxystrobin-d_6	2.18E-02	9.41E-03	0.9688	5			95.7	114.0			16.0	10.2
44	fenamidone	imazalil-d_5	1.25E-01	1.51E-02	0.9913	2.5		98.7	104.6	106.5		11.8	9.7	19.8
45	fenarimol	imazalil-d_5	3.38E-02	-1.16E-02	0.9903	2.5		111.0	93.9	97.2		21.0	13.9	17.1
46	fenbuconazole	atrazine-d_5	6.05E-03	-2.15E-03	0.9899	2.5		101.2	93.6	96.0		15.6	8.7	11.7
47	fenobucarb	imazalil-d_5	2.50E-01	1.90E-02	0.9936	1		93.0	90.6	101.5		6.6	9.7	16.6
48	fenpropimorph	imazalil-d_5	1.54E-01	-4.96E-02	0.9958	1		101.4	102.8	96.0		16.8	15.5	7.8
49	fenuron	carbofuran-d_3	1.46E-02	-1.25E-02	0.9898	2.5		117.9	104.4	93.9		8.2	8.7	8.1
50	flufenacet	fludioxonil-$^{13}C_2$	5.81E-01	-3.56E-02	0.9939	1		91.1	101.0	94.7		20.2	9.7	18.1
51	fluometuron	cyprodinil-d_5	3.91E-01	3.36E-02	0.9916	1		115.6	99.0	91.0		11.7	4.0	6.3
52	fluoxastrobin	imazalil-d_5	1.56E-01	-4.04E-02	0.9930	1		106.7	92.8	93.2		8.4	11.9	13.0
53	flusilazole	carbofuran-d_3	3.63E-02	-5.12E-03	0.9900	1		108.2	89.0	101.2		12.6	3.0	16.3
54	flutolanil	atrazine-d_5	5.85E-02	7.04E-04	0.9913	1		95.0	96.4	95.6		17.4	10.1	11.0
55	flutriafol	carbofuran-d_3	1.83E-02	-3.04E-03	0.9904	2.5		119.4	97.8	97.0		6.4	10.2	14.7
56	forchlorfenuron	imazalil-d_5	1.51E-01	1.25E-01	0.9902	2.5		88.2	104.3	96.7		12.8	13.8	11.9

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Table A.13: LC-MS/MS figures of merit of pesticides extracted from apple matrix – continued from previous page

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
57	fuberidazole	carbofuran-d_3	7.79E-02	-2.48E-02	0.9935	1		90.2	94.9	97.6		10.8	6.9	7.9
58	furalaxyl	trifloxystrobin-d_6	3.46E-01	2.43E-02	0.9695	2.5		117.3	119.1	111.0		20.8	17.4	12.8
59	furathiocarb	atrazine-d_5	7.66E-03	-5.03E-03	0.9865	2.5		94.2	79.3	92.9		19.2	15.0	16.7
60	hexaconazole	atrazine-d_5	9.05E-03	-2.99E-03	0.9950	2.5		109.3	92.5	90.8		9.0	11.8	11.1
61	imazalil	imazalil-d_5	6.19E-02	2.83E-02	0.9926	1		97.8	117.5	98.6		11.7	11.3	12.4
62	imidacloprid	atrazine-d_5	6.15E-03	-3.88E-03	0.9881	2.5		109.4	112.3	96.9		16.2	13.1	22.1
63	ipconazole	imazalil-d_5	4.82E-02	3.28E-03	0.9920	2.5		89.0	94.6	105.8		4.2	16.2	15.3
64	iprovalicarb	cyprodinil-d_5	3.44E-01	1.02E-02	0.9889	1		103.2	91.6	95.9		7.5	18.2	6.1
65	isoprocarb	atrazine-d_5	3.34E-02	-2.29E-02	0.9956	1		104.9	93.1	94.0		10.2	10.5	11.7
66	isoproturon	imazalil-d_5	9.61E-02	2.51E-03	0.9941	2.5		102.3	102.8	101.9		12.1	14.0	21.5
67	linuron	cyprodinil-d_5	1.87E-01	-9.12E-03	0.9931	1		102.4	99.5	98.5		12.5	23.7	5.3
68	mandipropamid	imazalil-d_5	8.36E-02	5.70E-04	0.9893	1		96.9	92.7	98.8		24.0	15.4	17.5
69	mefenacet	imazalil-d_5	1.38E-01	-4.17E-02	0.9883	2.5		118.0	94.9	98.0		18.8	21.9	17.7
70	mepanipyrim	trifloxystrobin-d_6	4.07E-02	8.02E-02	0.9314	10			100.5	108.4			22.2	10.8
71	mepronil	imazalil-d_5	3.20E-01	-2.75E-02	0.9884	1		112.3	92.1	96.1		18.6	8.8	14.9
72	metalaxyl	imazalil-d_5	2.43E-01	2.07E-02	0.9904	0.5	88.3	112.1	99.7	95.4	22.4	5.9	15.0	7.0
73	metconazole	imazalil-d_5	1.26E-02	-3.62E-03	0.9930	2.5		109.7	106.8	104.2		18.4	9.9	20.6
74	methabenzthiazuron	atrazine-d_5	2.20E-02	-2.59E-03	0.9948	1		102.9	95.6	96.0		12.3	6.4	3.4
75	methiocarb	methiocarb-d_3	7.21E-03	7.74E-03	0.9837	5			92.5	94.4			14.2	8.2
76	methomyl	dimethoate-d_6	5.00E-03	-4.34E-03	0.9856	5			100.1	101.2			17.5	10.9
77	methoprotryne	fludioxonil-$^{13}C_2$	1.32E+00	1.09E-01	0.9929	0.5	78.7	85.8	98.6	95.9	14.9	14.8	14.2	18.9
78	methoxyfenozide	metalaxyl-d_6	3.77E-03	-6.10E-04	0.9740	5			99.9	116.8			5.0	7.9
79	metobromuron	imazalil-d_5	1.18E-01	-2.85E-02	0.9954	1		103.6	94.0	94.6		7.7	8.3	16.6
80	mevinphos	imazalil-d_5	5.34E-02	-2.59E-02	0.9879	2.5		101.0	98.4	89.3		15.1	7.8	11.5
81	mexacarbate	carbofuran-d_3	4.35E-02	-7.35E-03	0.9930	1		101.5	96.1	98.0		13.9	7.3	11.5
82	monolinuron	imazalil-d_5	1.87E-02	-1.17E-02	0.9814	5			93.9	93.9			19.9	9.4
83	myclobutanil	atrazine-d_5	1.06E-02	-2.89E-03	0.9920	1		101.4	97.0	92.3		18.8	4.4	7.4
84	neburon	atrazine-d_5	6.44E-03	-1.74E-03	0.9940	2.5		99.3	89.8	95.0		11.6	8.1	5.0
85	nuarimol	imazalil-d_5	6.02E-02	1.37E-02	0.9905	1		89.2	98.8	98.5		2.6	12.0	20.2
86	oxadixyl	carbofuran-d_3	1.41E-02	-6.27E-03	0.9923	2.5		100.6	114.3	100.2		9.9	9.7	22.3
87	paclobutrazol	imazalil-d_5	1.47E-01	6.36E-02	0.9897	2.5		100.9	100.6	101.5		10.2	13.0	18.7
88	penconazole	atrazine-d_5	1.47E-02	-7.98E-04	0.9942	1		101.2	99.2	96.2		15.6	5.1	10.2
89	pencycuron	atrazine-d_5	2.18E-02	-4.36E-03	0.9923	0.5	95.1	100.5	89.8	101.6	6.8	12.2	18.1	14.5
90	picoxystrobin	malathion-d_6	5.06E-02	-1.72E-02	0.9851	1		107.7	91.5	90.0		13.8	12.3	4.7
91	piperonyl butoxide	carbofuran-d_3	1.14E-02	-9.22E-03	0.9881	2.5		108.8	77.9	105.0		6.0	9.5	15.5
92	pirimicarb	carbofuran-d_3	2.83E-02	-7.67E-03	0.9914	1		108.0	93.8	103.5		12.6	2.4	7.3
93	prochloraz	atrazine-d_5	5.32E-03	-5.83E-03	0.9816	5			90.5	93.0			9.8	13.9
94	promecarb	imazalil-d_5	1.67E-01	-1.68E-02	0.9932	1		104.9	92.8	99.3		21.2	9.6	14.4
95	prometon	carbofuran-d_3	1.09E-01	-9.62E-03	0.9942	0.5	92.2	100.8	94.0	101.4	15.4	4.7	4.9	2.7
96	prometryne	imazalil-d_5	5.62E-01	2.87E-04	0.9914	0.25	78.2	103.2	98.5	94.9	21.9	10.9	8.6	11.4
97	propham	atrazine-d_5	1.46E-03	1.32E-03	0.9815	5			97.1	90.5			6.3	9.7
98	propiconazole	methiocarb-d_3	4.78E-02	-1.98E-02	0.9958	2.5		110.1	93.3	99.6		13.6	8.1	11.9
99	propoxur	carbofuran-d_3	1.03E-02	-5.88E-03	0.9924	2.5		113.1	94.9	107.6		15.5	7.8	10.9
100	pyracarbolid	imazalil-d_5	2.78E-01	8.57E-02	0.9905	1		108.0	104.9	91.8		9.7	10.6	13.1
101	pyraclostrobin	metalaxyl-d_6	3.19E-03	-6.36E-03	0.9889	5			74.8	98.7			17.7	13.6
102	pyrimethanil	atrazine-d_5	1.63E-02	-1.66E-03	0.9925	1		90.3	94.6	91.9		12.1	7.6	12.3
103	secbumeton	atrazine-d_5	5.34E-02	-5.75E-03	0.9942	0.5	92.3	100.4	98.1	94.4	7.1	8.8	6.8	12.2
104	siduron	imazalil-d_5	1.80E-01	-2.03E-03	0.9919	2.5		108.0	95.9	99.2		16.0	7.1	13.0
105	simetryn	imazalil-d_5	2.25E-01	1.81E-02	0.9900	1		95.1	97.0	95.5		6.0	14.4	21.5
106	spinetoram	spirotetramat-d_6	1.79E-02	-1.70E-02	0.9843	5			74.0	103.4			18.9	10.8
107	spinosyn A	trifloxystrobin-d_6	1.55E+04	1.25E+04	0.9848	5			109.7	123.6			13.2	13.8
108	spirotetramat	atrazine-d_5	1.51E-02	-1.19E-02	0.9811	2.5		112.1	96.8	94.2		11.4	10.4	16.8
109	spiroxamine	imazalil-d_5	2.48E-01	1.95E-02	0.9932	1		99.8	97.6	96.2		6.4	9.3	6.8
110	tebuconazole	atrazine-d_5	1.23E-02	-3.97E-03	0.9942	1		97.4	91.3	97.3		15.6	5.1	12.8
111	tebuthiuron	atrazine-d_5	4.75E-02	-2.41E-02	0.9869	2.5		104.2	99.0	89.0		7.8	18.0	9.5
112	terbumeton	carbofuran-d_3	2.58E-01	-2.08E-02	0.9956	0.5	96.7	103.7	96.5	102.4	10.2	9.4	6.8	8.5
113	terbutryn	imazalil-d_5	6.62E-01	-1.36E-02	0.9852	1		104.3	97.8	99.3		18.9	10.6	20.7
114	tetraconazole	atrazine-d_5	1.35E-02	-1.01E-03	0.9891	1		105.3	96.8	98.1		18.0	3.7	5.6
115	thiabendazole	carbofuran-d_3	5.60E-02	4.45E-02	0.9874	5			109.2	101.3			10.9	11.1

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Table A.13: LC-MS/MS figures of merit of pesticides extracted from apple matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	thiacloprid	carbofuran-d_3	7.03E-02	-9.59E-03	0.9928	2.5		105.3	108.0	97.1		7.6	11.8	10.2
117	thidiazuron	carbofuran-d_3	8.52E-03	-2.39E-03	0.9898	2.5		108.5	98.0	96.0		9.7	4.8	7.6
118	thiobencarb	fludioxonil-$^{13}C_2$	2.96E-01	-1.32E-01	0.9918	2.5		96.7	92.4	109.4		10.5	12.8	2.9
119	triadimefon	atrazine-d_5	8.39E-03	-8.73E-04	0.9942	1		107.7	95.7	91.2		21.1	3.1	13.4
120	tricyclazole	carbofuran-d_3	7.61E-02	-2.36E-02	0.9908	1		103.5	99.8	98.7		7.4	5.3	6.7
121	trifloxystrobin	cyprodinil-d_5	2.02E-01	-8.57E-02	0.9913	2.5		97.1	85.2	92.2		4.9	15.3	12.3
122	triflumizole	atrazine-d_5	4.22E-03	7.40E-03	0.9852	5			104.0	110.8			15.0	18.4
123	triflumuron	atrazine-d_5	2.74E-03	-3.72E-03	0.9889	5			80.6	92.3			7.0	13.5
124	triticonazole	imazalil-d_5	4.50E-02	-1.45E-03	0.9906	1		111.9	94.9	99.2		23.6	11.9	14.6
125	vamidothion	dimethoate-d_6	6.07E-02	-1.80E-03	0.9876	5			111.5	98.0			9.0	9.1
126	zoxamide	atrazine-d_5	1.74E-02	-1.53E-03	0.9914	1		110.5	87.7	106.3		14.8	15.3	17.5

Table A.14: CBS-MS/MS figures of merit of pesticides extracted from blueberry matrix.

[Take me back!]

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
1	3-hydroxycarbofuran	dimethoate-d_6	1.26E-03	1.84E-04	0.9824	2.5		91.4	91.9	98.3		3.5	4.8	3.5
2	acetamiprid	carbofuran-d_3	2.02E-03	-6.32E-04	0.9964	1		91.9	94.1	102.4		8.1	3.7	1.4
3	aldicarb-insource	spirotetramat-d_6	5.53E-04	-1.63E-03	0.9527	5			85.3	96.6			7.1	5.2
4	ametryn	atrazine-d_5	1.85E-02	2.91E-03	0.9940	1		99.6	106.3	100.6		13.0	17.0	6.4
5	aminocarb	oxamyl-d_6	2.04E-01	5.99E-01	0.9788	5			102.8	100.5			15.6	5.4
6	amitraz	atrazine-d_5	1.89E-03	8.62E-03	0.9827	5			116.4	101.3			21.0	11.1
7	azoxystrobin	malathion-d_6	2.36E-02	5.16E-04	0.9953	0.5	90.1	93.9	104.0	103.4	2.0	4.4	8.5	5.5
8	benalaxyl	malathion-d_6	8.44E-03	3.89E-03	0.9963	0.5	73.8	100.3	105.6	101.8	13.3	2.8	7.4	7.2
9	bendiocarb	carbofuran-d_3	3.41E-03	-2.14E-05	0.9977	0.5	91.5	90.4	98.3	96.7	6.3	8.2	0.8	3.4
10	boscalid	spirotetramat-d_6	9.92E-04	1.14E-03	0.9709	5			91.3	102.2			17.9	10.6
11	bromucanozole	methiocarb-d_3	2.11E-03	8.22E-04	0.9887	2.5		97.2	97.3	110.7		16.6	7.7	3.6
12	bupirimate	malathion-d_6	1.10E-02	8.49E-04	0.9951	1		93.8	101.9	101.4		7.6	6.8	4.8
13	buprofenzin	malathion-d_6	9.13E-03	-1.63E-04	0.9957	0.5	99.6	85.7	103.8	102.4	6.5	4.1	6.4	3.4
14	butafenacil	malathion-d_6	6.82E-03	9.05E-04	0.9949	1		101.6	110.5	102.2		3.1	7.2	6.3
15	butoxycarboxim	carbofuran-d_3	5.12E-03	-5.86E-04	0.9907	1		95.7	93.0	92.3		5.4	5.1	2.6
16	carbaryl	atrazine-d_5	1.39E-03	1.08E-03	0.9909	1		91.0	106.4	101.8		11.9	6.0	8.4
17	carbendazim	dimethoate-d_6	2.29E-02	-1.80E-04	0.9907	0.25	90.7	95.6	94.3	101.9	15.7	4.1	4.9	3.7
18	carbetamide	carbofuran-d_3	7.29E-04	3.43E-04	0.9960	1		84.9	92.9	99.9		5.0	4.6	1.0
19	carbofuran	carbofuran-d_3	6.37E-03	-1.49E-05	0.9969	0.25	80.7	89.7	100.3	94.1	5.1	3.5	1.9	4.0
20	carfentrazone-ethyl	trifloxystrobin-d_6	3.83E-03	7.59E-04	0.9932	1		114.4	104.7	98.0		10.6	4.5	4.9
21	chlorantraniliprole	atrazine-d_5	8.63E-04	-7.03E-05	0.9902	1		94.9	97.1	109.5		5.8	6.1	7.0
22	chlorotoluron	atrazine-d_5	2.07E-03	6.11E-04	0.9965	1		92.7	100.3	99.9		10.2	5.2	2.6
23	chloroxuron	methiocarb-d_3	3.27E-03	1.36E-04	0.9911	2.5		97.1	103.1	107.3		10.3	9.9	5.8
24	clothianidin	atrazine-d_5	3.79E-04	-3.45E-04	0.9791	5			81.5	93.3			9.4	2.0
25	cyazofamid	trifloxystrobin-d_6	2.33E-03	4.01E-04	0.9930	1		111.7	100.7	98.4		10.3	11.8	6.6
26	cycluron	metalaxyl-d_6	1.76E-03	1.24E-06	0.9962	1		95.4	95.5	102.8		2.6	6.6	2.0
27	cyproconazole	atrazine-d_5	2.13E-03	6.40E-04	0.9948	1		93.6	101.6	105.0		2.0	6.5	2.5
28	cyprodinil	carbofuran-d_3	1.03E-03	1.91E-03	0.9571	2.5		79.4	86.9	99.9		7.7	10.3	9.6
29	desmedipham	methiocarb-d_3	4.58E-03	8.31E-04	0.9945	2.5		101.5	104.7	111.2		8.4	10.5	5.4
30	diclobutrazol	spirotetramat-d_6	1.53E-03	6.75E-04	0.9683	5			98.8	104.5			12.5	6.5
31	dicrotophos	oxamyl-d_6	9.63E-02	2.48E-02	0.9836	5			105.6	91.7			7.4	4.3
32	diethofencarb	methiocarb-d_3	5.62E-03	1.93E-03	0.9963	2.5		97.8	106.4	96.4		8.5	10.2	3.7
33	difenoconazole	trifloxystrobin-d_6	2.33E-03	-1.62E-03	0.9830	2.5		102.2	92.7	100.8		7.9	7.4	3.0
34	dimethoate	dimethoate-d_6	3.39E-03	-1.15E-04	0.9977	1		83.5	94.1	93.9		2.7	3.3	3.3
35	dimethomorph	methiocarb-d_3	8.96E-03	-7.60E-05	0.9962	0.5	85.8	94.2	100.7	107.1	7.4	7.5	7.6	5.7
36	dimoxystrobin	malathion-d_6	7.03E-03	6.00E-04	0.9975	1		100.3	104.0	99.9		7.3	8.0	4.2
37	dioxacarb	carbofuran-d_3	3.38E-03	-8.87E-05	0.9978	0.5	97.6	89.5	98.4	97.8	5.7	8.9	2.0	4.2
38	diuron	atrazine-d_5	6.95E-03	2.27E-04	0.9972	0.5	85.9	96.9	100.1	100.9	4.2	0.9	3.5	1.9
39	epoxiconazole	methiocarb-d_3	2.22E-03	6.28E-05	0.9909	1		99.6	101.0	108.3		5.0	3.5	2.8
40	etaconazole	malathion-d_6	5.54E-03	1.02E-02	0.9862	2.5		91.0	99.3	102.9		9.3	12.9	9.2
41	ethiprole	atrazine-d_5	2.22E-03	1.73E-03	0.9960	1		97.3	97.5	100.7		1.1	9.8	5.7
42	ethirimol	dimethoate-d_6	3.76E-03	-1.07E-03	0.9783	2.5		99.2	91.9	99.7		10.8	10.6	4.4
43	ethofumesate	atrazine-d_5	1.01E-03	5.74E-03	0.9729	5			104.0	101.4			5.4	5.4
44	etoxazole	malathion-d_6	2.42E-03	6.90E-04	0.9826	2.5		85.6	97.3	107.9		6.9	13.7	3.6
45	fenamidone	methiocarb-d_3	7.78E-03	4.90E-04	0.9957	1		94.6	100.2	102.3		10.2	7.2	5.1
46	fenarimol	methiocarb-d_3	9.77E-04	2.03E-04	0.9759	5			90.3	100.5			6.3	10.4
47	fenbuconazole	methiocarb-d_3	1.28E-03	8.70E-04	0.9816	2.5		103.3	99.7	109.3		16.0	7.2	5.5
48	fenhexamid	carbofuran-d_3	3.95E-04	4.48E-03	0.9616	10			92.4	103.5			13.5	8.3
49	fenobucarb	atrazine-d_5	6.00E-03	3.77E-03	0.9956	1		99.3	105.3	100.3		4.9	3.3	2.3
50	fenoxycarb	kresoxim-methyl-d_7	9.40E-03	1.95E-02	0.9693	5			89.4	94.4			2.9	7.8
51	fenpropimorph	imazalil-d_5	1.59E-02	3.48E-03	0.9881	1		94.1	103.6	96.6		3.4	3.4	4.0
52	fenuron	dimethoate-d_6	6.78E-03	2.53E-04	0.9918	0.5	87.8	95.3	105.1	94.5	5.7	10.1	2.1	6.9
53	flufenacet	methiocarb-d_3	5.98E-03	1.09E-03	0.9969	1		107.3	107.7	101.4		3.7	5.4	1.6
54	fluometuron	carbofuran-d_3	3.37E-03	2.27E-06	0.9901	1		97.0	102.4	103.6		9.0	7.2	2.3
55	fluoxastrobin	trifloxystrobin-d_6	1.79E-02	-8.47E-04	0.9935	0.5	108.1	93.9	102.2	97.4	13.8	0.9	4.6	1.9
56	flusilazole	kresoxim-methyl-d_7	9.08E-02	-1.54E-02	0.9910	2.5		95.3	94.9	103.8		7.5	6.6	7.7

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Table A.14: CBS-MS/MS figures of merit of pesticides extracted from blueberry matrix – continued from previous page

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ (ng/g)	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
							0.8	4	40	80	0.8	4	40	80
57	flutolanil	malathion-d_6	1.26E-02	-5.13E-04	0.9921	0.5	100.7	100.3	103.7	107.3	5.9	2.9	14.3	8.0
58	flutriafol	atrazine-d_5	2.24E-03	4.66E-03	0.9975	2.5		95.3	96.2	101.3		7.7	4.5	5.4
59	forchlorfenuron	methiocarb-d_3	7.17E-03	2.68E-03	0.9895	1		84.1	97.0	109.5		7.3	4.8	4.1
60	fuberidazole	carbofuran-d_3	7.47E-03	-3.88E-05	0.9862	2.5		82.1	93.5	105.5		10.7	8.3	3.1
61	furalaxyl	carbofuran-d_3	1.36E-02	3.85E-03	0.9937	0.5	79.9	110.1	105.2	97.4	18.8	2.3	7.5	7.9
62	furathiocarb	malathion-d_6	3.16E-03	1.15E-03	0.9910	1		105.7	99.1	104.3		4.2	3.4	6.2
63	hexaconazole	methiocarb-d_3	2.09E-03	2.34E-03	0.9889	2.5		90.2	97.0	105.5		9.3	3.0	6.1
64	imazalil	imazalil-d_5	6.83E-03	5.32E-03	0.9944	1		93.5	102.2	97.8		3.4	3.9	9.6
65	imidacloprid	atrazine-d_5	7.28E-04	4.30E-04	0.9848	1		90.3	84.5	94.4		8.2	7.4	1.3
66	ipconazole	malathion-d_6	3.09E-04	3.42E-04	0.9608	5			97.6	108.1			9.2	13.3
67	iprovalicarb	spirotetramat-d_6	5.23E-03	1.63E-03	0.9942	0.5	97.5	94.5	103.6	93.6	6.5	5.1	6.1	3.1
68	isoprocarb	atrazine-d_5	5.54E-03	3.24E-03	0.9934	1		102.2	107.4	100.0		4.7	4.5	4.9
69	isoproturon	carbofuran-d_3	3.25E-03	2.96E-04	0.9968	0.5	82.2	97.1	108.8	99.9	7.4	4.6	7.9	2.0
70	kresoxim-methyl	spirotetramat-d_6	1.00E-04	1.41E-06	0.9636	5			97.5	101.3			13.5	6.9
71	linuron	methiocarb-d_3	3.31E-03	3.99E-03	0.9935	2.5		107.7	105.0	102.6		11.2	4.8	4.5
72	mandipropamid	kresoxim-methyl-d_7	9.35E-02	-8.81E-03	0.9949	1		97.3	97.0	100.7		8.5	7.0	2.0
73	mefenacet	malathion-d_6	7.88E-03	-9.16E-04	0.9923	0.5	102.3	87.4	98.1	102.5	6.4	9.4	5.0	7.1
74	mepanipyrim	trifloxystrobin-d_6	2.46E-03	1.63E-02	0.9741	5			90.9	94.0			6.1	4.1
75	mepronil	methiocarb-d_3	1.32E-02	5.12E-03	0.9953	1		102.6	110.6	103.9		11.5	8.5	2.8
76	metalaxyl	metalaxyl-d_6	5.30E-03	4.82E-04	0.9990	0.25	95.2	103.6	99.5	100.5	7.4	2.4	3.4	1.5
77	metconazole	methiocarb-d_3	4.10E-03	7.09E-04	0.9932	0.5	103.8	92.3	104.7	111.2	11.9	10.7	3.1	5.6
78	methabenzthiazuron	carbofuran-d_3	1.13E-02	-1.14E-03	0.9947	0.5	93.5	93.3	98.8	94.1	10.7	6.2	1.0	4.3
79	methiocarb	methiocarb-d_3	3.05E-03	2.75E-04	0.9977	1		97.9	104.2	102.7		15.4	5.1	2.0
80	methomyl	dimethoate-d_6	8.34E-04	3.14E-06	0.9814	2.5		102.1	101.6	89.0		12.5	8.7	4.4
81	methoprotryne	spirotetramat-d_6	1.34E-02	-3.46E-03	0.9878	1		85.2	95.2	94.3		7.0	7.5	7.3
82	methoxyfenozide	spirotetramat-d_6	8.43E-04	9.25E-06	0.9971	1		94.0	104.5	104.2		2.3	2.3	2.6
83	metobromuron	methiocarb-d_3	4.69E-03	9.42E-04	0.9954	2.5		95.0	105.6	98.8		9.1	6.8	5.5
84	metribuzin	atrazine-d_5	8.38E-04	2.38E-03	0.9940	5			99.6	99.2			3.3	4.5
85	mevinphos	dimethoate-d_6	7.51E-03	-6.53E-04	0.9842	2.5		96.0	98.3	89.7		10.6	14.1	5.2
86	mexacarbate	metalaxyl-d_6	2.55E-03	-2.99E-04	0.9876	1		91.5	90.7	99.1		4.4	13.3	2.6
87	monocrotophos	oxamyl-d_6	1.94E-02	4.03E-02	0.9692	5			102.1	100.8			6.7	5.3
88	monolinuron	atrazine-d_5	1.77E-03	3.52E-04	0.9938	1		99.8	104.7	96.8		7.7	2.7	4.8
89	myclobutanil	methiocarb-d_3	2.93E-03	7.16E-04	0.9929	2.5		90.1	101.0	101.7		11.8	5.0	7.6
90	neburon	trifloxystrobin-d_6	1.92E-03	7.32E-04	0.9906	2.5		103.7	104.6	96.0		11.7	5.0	7.8
91	nuarimol	atrazine-d_5	9.53E-04	3.86E-04	0.9871	1		90.3	91.4	96.1		19.5	10.4	3.8
92	oxadixyl	dimethoate-d_6	4.82E-03	1.30E-02	0.9903	5			101.9	95.8			11.4	3.4
93	oxamyl	dimethoate-d_6	9.70E-04	1.44E-05	0.9903	1		97.6	100.7	92.6		13.8	14.1	5.8
94	paclobutrazol	carbofuran-d_3	3.53E-04	1.35E-04	0.9757	5			101.8	105.2			7.8	7.5
95	penconazole	methiocarb-d_3	2.07E-03	1.19E-03	0.9905	2.5		100.1	99.5	106.7		13.6	3.6	4.6
96	pencycuron	atrazine-d_5	2.55E-03	1.07E-02	0.9624	5			103.3	105.8			8.5	10.1
97	phenmedipham	malathion-d_6	3.61E-04	2.35E-04	0.9639	5			102.1	100.2			10.6	12.6
98	picoxystrobin	malathion-d_6	5.60E-03	1.51E-03	0.9954	1		94.1	102.8	103.6		5.6	10.7	3.2
99	piperonyl butoxide	kresoxim-methyl-d_7	1.09E-01	9.01E-02	0.9856	1		96.4	94.0	95.7		4.2	15.0	7.3
100	pirimicarb	imazalil-d_5	9.92E-03	6.12E-04	0.9935	0.5	87.3	90.1	99.1	87.2	6.2	2.5	5.2	9.4
101	prochloraz	malathion-d_6	1.12E-03	1.64E-04	0.9932	2.5		84.8	91.3	114.5		8.1	6.7	4.2
102	promecarb	methiocarb-d_3	7.72E-03	2.00E-03	0.9958	1		91.2	104.3	102.5		4.8	7.3	3.3
103	prometon	metalaxyl-d_6	1.03E-02	-1.27E-03	0.9944	0.5	101.0	89.5	96.8	102.1	3.0	13.3	6.3	5.4
104	prometryne	atrazine-d_5	2.07E-02	3.08E-03	0.9888	1		100.6	105.0	100.7		6.5	17.5	5.4
105	propham	malathion-d_6	1.13E-03	5.78E-04	0.9895	1		99.6	95.8	96.1		9.5	17.1	4.5
106	propiconazole	methiocarb-d_3	3.77E-03	7.19E-04	0.9881	1		94.9	99.8	106.8		6.2	4.8	5.3
107	propoxur	carbofuran-d_3	1.56E-03	5.07E-04	0.9957	1		88.1	97.9	96.9		4.0	4.2	3.5
108	pyracarbolid	atrazine-d_5	8.42E-03	7.50E-04	0.9982	0.5	88.9	99.5	100.8	95.8	6.3	1.0	6.6	2.3
109	pyraclostrobin	trifloxystrobin-d_6	1.73E-03	4.48E-04	0.9867	2.5		92.6	97.9	100.0		22.1	4.7	6.2
110	pyrimethanil	methiocarb-d_3	4.39E-03	8.45E-04	0.9872	0.5	101.2	89.1	96.0	105.3	14.0	4.3	6.9	4.5
111	secbumeton	metalaxyl-d_6	1.40E-02	-1.00E-03	0.9963	0.25	87.3	86.5	96.5	103.8	10.3	13.7	4.0	6.9
112	siduron	atrazine-d_5	3.68E-03	6.19E-03	0.9919	1		92.7	107.5	102.2		3.2	3.6	2.2
113	simetryn	atrazine-d_5	7.22E-03	5.79E-04	0.9923	1		91.5	99.7	98.1		5.3	15.1	2.8
114	spinetoram	atrazine-d_5	1.02E-03	-4.81E-04	0.9745	5			107.3	107.7			16.0	8.6
115	spinosyn A	atrazine-d_5	1.14E-03	-6.43E-06	0.9832	2.5		94.4	117.2	110.7		12.1	17.6	5.3

Continued on next page

Table A.14: CBS-MS/MS figures of merit of pesticides extracted from blueberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	spinosyn D	atrazine-d_5	2.50E-04	5.88E-05	0.9687	2.5		90.9	119.4	111.1		21.7	22.9	8.9
117	spirotetramat	spirotetramat-d_6	4.75E-03	1.87E-03	0.9982	0.5	76.2	97.3	103.5	99.8	5.9	2.8	2.0	1.4
118	spiroxamine	imazalil-d_5	4.95E-02	-3.52E-03	0.9920	0.25	84.1	82.9	94.9	94.3	10.4	7.2	6.8	9.9
119	sulfentrazone	spirotetramat-d_6	1.61E-04	1.56E-04	0.9757	5			91.2	96.5			11.4	10.5
120	tebuconazole	methiocarb-d_3	4.08E-03	3.29E-04	0.9953	1		94.2	100.9	108.1		6.2	4.5	5.1
121	tebufenozide	atrazine-d_5	1.48E-03	3.44E-03	0.9916	2.5		109.4	112.8	105.6		2.8	7.8	4.1
122	tebuthiuron	carbofuran-d_3	6.37E-03	9.01E-04	0.9963	0.1	83.9	88.3	92.0	99.3	10.9	5.7	4.8	1.8
123	terbumeton	metalaxyl-d_6	2.63E-02	-8.00E-04	0.9941	0.1	85.7	90.6	98.7	103.5	10.0	14.2	5.5	5.7
124	terbutryn	atrazine-d_5	2.43E-02	4.30E-03	0.9891	0.5	80.7	98.6	105.0	101.8	9.6	8.8	22.3	8.2
125	tetraconazole	methiocarb-d_3	3.54E-03	9.84E-04	0.9904	1		89.8	99.6	106.5		10.2	10.6	6.6
126	thiabendazole	carbofuran-d_3	4.83E-03	-1.14E-03	0.9869	0.5	90.2	69.7	86.2	108.8	2.2	4.3	3.9	1.9
127	thiacloprid	atrazine-d_5	4.19E-03	-3.75E-04	0.9930	0.5	120.2	90.7	96.1	104.2	9.7	2.0	4.2	6.3
128	thiamethoxam	spirotetramat-d_6	5.07E-04	1.74E-03	0.9801	5			91.4	102.3			7.2	9.9
129	thidiazuron	atrazine-d_5	7.90E-04	2.68E-04	0.9837	2.5		78.2	97.5	102.8		4.7	6.8	9.9
130	thiobencarb	methiocarb-d_3	2.28E-03	1.30E-03	0.9755	5			100.6	102.5			13.5	6.4
131	triadimefon	methiocarb-d_3	2.42E-03	1.66E-03	0.9906	1		104.5	103.7	97.8		6.7	3.6	6.6
132	triadimenol	methiocarb-d_3	2.58E-03	7.30E-03	0.9876	5			98.0	98.7			2.2	6.8
133	tricyclazole	atrazine-d_5	6.28E-03	-3.55E-04	0.9920	0.5	86.2	87.4	92.4	102.0	9.7	9.5	3.6	5.0
134	trifloxystrobin	trifloxystrobin-d_6	7.52E-03	-2.39E-04	0.9955	0.5	105.4	92.8	99.0	100.4	9.6	9.4	6.2	2.6
135	triflumizole	kresoxim-methyl-d_7	2.26E-02	1.79E-02	0.9854	5			94.4	106.4			12.5	1.7
136	triflumuron	atrazine-d_5	2.14E-04	2.95E-04	0.9482	5			97.3	112.1			4.9	5.9
137	triticonazole	atrazine-d_5	1.38E-03	2.83E-04	0.9951	0.5	83.8	94.5	101.0	107.1	7.3	6.1	7.7	1.3
138	vamidothion	oxamyl-d_6	3.13E-02	-8.32E-04	0.9817	2.5		90.7	93.9	98.2		33.6	20.1	8.2
139	zoxamide	malathion-d_6	2.78E-03	1.90E-03	0.9848	1		94.8	100.5	108.0		25.2	13.6	5.0

Table A.15: LC-MS/MS figures of merit of pesticides extracted from blueberry matrix. [Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ (ng/g)	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
							0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	carbofuran-d_3	3.39E-04	1.42E-04	0.9936	2.5		109.9	94.8	99.0		6.4	14.2	3.2
2	acetamiprid	atrazine-d_5	2.11E-03	6.24E-05	0.9971	1		109.2	110.9	98.3		9.0	13.2	3.8
3	aldicarb-insource	atrazine-d_5	2.99E-04	-2.45E-04	0.9830	2.5		100.0	94.9	96.8		7.6	18.2	4.9
4	ametryn	malathion-d_6	3.24E-02	2.42E-03	0.9954	1		105.0	101.4	98.5		5.5	10.6	10.1
5	aminocarb	dimethoate-d_6	9.70E-03	-2.13E-03	0.9958	2.5		97.8	97.3	99.1		5.5	4.1	7.5
6	amitraz	methiocarb-d_3	3.37E-03	1.11E-03	0.9905	2.5		105.4	96.8	104.7		14.6	4.1	16.9
7	azoxystrobin	carbofuran-d_3	7.87E-03	2.56E-04	0.9924	0.5	91.4	89.2	90.4	91.8	15.2	15.4	4.2	8.6
8	benalaxyl	fludioxonil-$^{13}C_2$	1.03E-01	6.92E-03	0.9931	0.5	86.5	93.5	99.7	97.1	18.1	14.8	17.2	17.7
9	bendiocarb	atrazine-d_5	1.42E-03	5.87E-05	0.9938	1		103.3	100.0	97.3		13.5	4.2	5.4
10	boscalid	methiocarb-d_3	5.84E-03	1.07E-03	0.9956	2.5		99.9	99.3	102.9		11.1	7.4	12.3
11	bromucanozole	atrazine-d_5	5.47E-04	7.74E-05	0.9924	2.5		91.4	95.2	108.6		3.1	8.3	14.6
12	bupirimate	malathion-d_6	2.48E-03	4.27E-04	0.9930	1		95.0	98.1	100.1		6.8	16.4	4.3
13	buprofenzin	malathion-d_6	8.64E-03	2.69E-04	0.9943	0.5	95.1	94.8	100.2	96.5	8.6	7.8	14.4	9.5
14	butafenacil	malathion-d_6	4.91E-03	2.28E-03	0.9892	2.5		81.6	110.9	103.0		8.4	16.8	6.7
15	butoxycarboxim	dimethoate-d_6	9.39E-03	1.35E-04	0.9956	1		94.6	101.2	104.1		16.8	7.1	4.3
16	carbaryl	atrazine-d_5	1.04E-03	6.71E-05	0.9948	1		93.9	103.1	98.9		9.1	4.8	10.7
17	carbendazim	dimethoate-d_6	1.86E-02	-2.62E-04	0.9952	1		96.0	100.5	97.4		7.5	6.3	4.3
18	carbetamide	atrazine-d_5	5.16E-04	6.15E-05	0.9928	2.5		98.0	98.3	101.8		5.9	8.6	2.5
19	carbofuran	carbofuran-d_3	4.06E-03	-1.47E-04	0.9924	0.5	93.3	100.4	97.9	91.2	19.7	5.2	2.9	10.7
20	carfentrazone-ethyl	methiocarb-d_3	3.22E-03	-7.95E-04	0.9906	2.5		97.2	95.0	100.0		8.7	8.5	20.4
21	chlorantraniliprole	malathion-d_6	1.88E-03	4.60E-04	0.9853	5			94.4	106.3			8.8	9.8
22	chlorotoluron	atrazine-d_5	1.26E-03	-5.58E-05	0.9929	1		92.5	100.8	99.5		7.3	3.5	7.0
23	chloroxuron	cyprodinil-d_5	2.00E-02	-2.93E-04	0.9906	1		106.2	105.7	93.9		6.2	2.3	2.8
24	clothianidin	dimethoate-d_6	1.14E-03	-6.99E-05	0.9912	1		95.3	99.8	100.6		6.9	7.0	4.3
25	cyazofamid	cyprodinil-d_5	5.42E-03	-1.51E-03	0.9932	2.5		105.7	104.4	88.7		12.8	11.6	8.8
26	cycluron	atrazine-d_5	1.92E-03	2.83E-05	0.9927	0.5	87.0	95.0	99.8	98.0	22.8	4.6	7.8	7.2
27	cyproconazole	atrazine-d_5	1.37E-03	-7.18E-05	0.9941	2.5		110.6	98.9	100.4		10.2	9.4	8.8
28	cyprodinil	cyprodinil-d_5	1.71E-02	-1.84E-03	0.9959	1		99.8	99.2	91.1		7.6	9.8	5.1
29	desmedipham	cyprodinil-d_5	1.52E-02	9.93E-04	0.9919	2.5		103.4	107.6	92.3		15.2	12.6	6.5
30	diclobutrazol	malathion-d_6	2.76E-03	1.48E-03	0.9923	2.5		96.5	98.3	100.2		11.0	14.9	7.3
31	dicrotophos	dimethoate-d_6	2.67E-03	-2.12E-04	0.9916	1		111.2	97.6	97.3		12.8	12.3	7.2
32	diethofencarb	atrazine-d_5	1.23E-03	7.60E-06	0.9927	2.5		93.4	102.7	99.4		8.3	4.7	12.6
33	difenoconazole	trifloxystrobin-d_6	3.10E-03	-1.81E-03	0.9903	2.5		123.3	99.9	91.1		17.7	8.9	10.9
34	dimethoate	dimethoate-d_6	2.95E-03	-5.50E-04	0.9934	1		99.9	101.1	95.9		18.3	10.9	4.8
35	dimethomorph	atrazine-d_5	1.52E-03	2.71E-05	0.9875	1		109.1	95.8	110.6		15.6	7.7	16.8
36	dimoxystrobin	malathion-d_6	5.05E-03	3.11E-04	0.9939	2.5		94.1	99.9	98.4		12.1	7.7	12.2
37	dioxacarb	atrazine-d_5	1.42E-03	5.87E-05	0.9938	1		103.3	100.0	97.3		13.5	4.2	5.4
38	diuron	malathion-d_6	3.45E-03	8.24E-04	0.9960	1		97.9	102.4	98.7		16.4	9.9	4.5
39	epoxiconazole	malathion-d_6	5.85E-03	2.99E-03	0.9912	2.5		85.7	106.5	103.6		3.3	13.6	3.5
40	etaconazole	atrazine-d_5	1.64E-03	3.35E-04	0.9933	2.5		101.9	105.8	102.0		7.0	3.6	8.9
41	ethiprole	atrazine-d_5	2.46E-03	1.43E-04	0.9943	0.5	105.0	91.3	99.5	95.4	6.8	15.4	3.5	4.8
42	ethirimol	dimethoate-d_6	3.25E-03	3.59E-05	0.9937	2.5		98.2	97.4	99.2		10.0	4.9	6.2
43	ethofumesate	malathion-d_6	2.39E-03	8.22E-04	0.9908	2.5		107.9	102.6	107.3		5.4	11.2	5.8
44	etoxazole	cyprodinil-d_5	4.43E-03	-3.05E-03	0.9776	2.5		97.7	99.1	92.7		5.4	5.3	3.9
45	fenamidone	atrazine-d_5	1.99E-03	-3.98E-04	0.9925	1		79.7	88.7	100.4		19.8	1.9	9.7
46	fenarimol	cyprodinil-d_5	5.37E-03	1.01E-03	0.9922	2.5		74.6	105.7	95.9		27.1	9.7	5.2
47	fenbuconazole	methiocarb-d_3	1.67E-03	-4.57E-04	0.9912	1		102.3	93.6	104.2		13.2	3.9	8.8
48	fenhexamid	imazalil-d_5	3.30E-03	-1.91E-04	0.9938	2.5		110.6	94.1	89.3		26.9	20.9	14.8
49	fenobucarb	methiocarb-d_3	1.27E-02	2.76E-04	0.9944	1		100.8	99.3	97.0		2.3	3.3	6.3
50	fenoxycarb	trifloxystrobin-d_6	1.46E-03	1.08E-04	0.9799	2.5		90.3	113.8	93.7		21.7	18.7	4.5
51	fenpropimorph	cyprodinil-d_5	3.19E-02	4.23E-04	0.9935	1		108.7	99.1	93.6		20.3	7.7	15.0
52	fenuron	dimethoate-d_6	4.63E-03	3.55E-04	0.9957	1		103.8	102.0	102.3		6.8	7.8	4.1
53	flufenacet	dimethoate-d_6	8.94E-03	-1.47E-03	0.9901	1		94.2	89.7	100.6		7.2	13.0	3.7
54	fluometuron	atrazine-d_5	2.42E-03	-1.20E-04	0.9930	0.5	87.4	102.0	98.2	97.5	13.1	8.6	2.1	6.7
55	fluoxastrobin	malathion-d_6	9.14E-03	1.32E-03	0.9843	1		84.8	99.4	94.0		18.7	8.1	14.5
56	flusilazole	malathion-d_6	6.84E-03	7.17E-04	0.9955	2.5		93.7	98.2	99.6		1.2	9.4	7.7

Continued on next page

Table A.15: LC-MS/MS figures of merit of pesticides extracted from blueberry matrix – continued from previous page

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ (ng/g)	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
							0.8	4	40	80	0.8	4	40	80
57	flutolanil	imazalil-d_5	4.23E-02	-3.14E-03	0.9947	0.5	88.7	107.0	91.5	89.5	13.3	15.4	13.9	15.7
58	flutriafol	spirotetramat-d_6	3.80E-03	4.26E-04	0.9968	1		87.5	95.3	107.4		9.7	4.6	5.2
59	forchlorfenuron	malathion-d_6	6.18E-03	1.50E-03	0.9934	1		89.6	99.6	102.7		8.2	9.2	6.0
60	fuberidazole	dimethoate-d_6	1.64E-02	-5.28E-03	0.9968	1		97.2	95.6	107.6		7.8	5.6	5.9
61	furalaxyl	atrazine-d_5	6.25E-03	-2.74E-04	0.9931	0.5	99.9	93.0	89.8	99.9	18.0	2.2	1.9	9.9
62	furathiocarb	cyprodinil-d_5	1.00E-02	-1.46E-03	0.9860	2.5		103.1	107.6	100.7		10.7	8.0	8.8
63	hexaconazole	cyprodinil-d_5	8.87E-03	1.67E-03	0.9915	2.5		92.7	106.0	95.1		2.9	3.0	8.9
64	imazalil	imazalil-d_5	6.73E-03	7.19E-04	0.9932	1		99.7	92.6	97.9		14.7	15.7	8.3
65	imidacloprid	dimethoate-d_6	2.54E-03	7.71E-04	0.9929	2.5		98.7	102.3	102.3		20.3	4.7	4.6
66	ipconazole	cyprodinil-d_5	8.47E-03	-3.78E-04	0.9932	2.5		107.0	105.5	96.4		11.0	5.7	2.8
67	iprovalicarb	atrazine-d_5	1.90E-03	-2.48E-04	0.9949	1		106.0	93.5	98.4		9.5	6.3	10.4
68	isoprocarb	atrazine-d_5	3.39E-03	-1.21E-04	0.9963	0.5	102.8	102.1	102.1	97.3	15.1	8.3	4.4	10.1
69	isoproturon	atrazine-d_5	1.86E-03	-1.02E-04	0.9963	1		94.9	101.7	95.5		1.2	6.6	7.9
70	kresoxim-methyl	kresoxim-methyl-d_7	7.26E-03	-4.70E-03	0.9767	10			115.5	115.6			7.4	16.1
71	linuron	methiocarb-d_3	4.17E-03	2.29E-04	0.9942	2.5		100.6	98.9	98.5		8.2	4.6	11.4
72	mandipropamid	cyprodinil-d_5	1.76E-02	-3.92E-03	0.9930	2.5		93.3	101.4	91.8		13.5	10.2	13.9
73	mefenacet	cyprodinil-d_5	3.34E-02	-1.83E-03	0.9952	0.5	89.3	92.8	104.6	94.7	9.5	13.0	7.7	6.4
74	mepanipyrim	malathion-d_6	3.78E-03	2.94E-03	0.9802	10			95.8	100.9			11.7	4.9
75	mepronil	malathion-d_6	1.86E-02	5.04E-03	0.9950	1		100.6	95.7	104.4		9.5	9.1	7.4
76	metalaxyl	dimethoate-d_6	1.34E-02	2.13E-04	0.9938	0.5	95.6	98.2	99.6	102.5	19.5	6.8	3.1	6.0
77	metconazole	fludioxonil-$^{13}C_2$	3.09E-03	3.98E-03	0.9814	10			92.5	97.1			19.6	11.2
78	methabenzthiazuron	spirotetramat-d_6	8.74E-03	-1.11E-03	0.9967	1		93.4	94.2	102.7		3.6	3.1	6.0
79	methiocarb	methiocarb-d_3	1.94E-03	9.29E-04	0.9911	2.5		107.5	106.9	100.5		2.9	7.5	6.3
80	methomyl	dimethoate-d_6	5.57E-04	7.08E-07	0.9930	2.5		106.7	101.4	100.9		21.4	4.8	5.8
81	methoprotryne	carbofuran-d_3	7.36E-03	-1.47E-04	0.9933	0.5	96.3	89.4	100.8	102.4	3.2	6.9	4.2	10.0
82	methoxyfenozide	carbofuran-d_3	3.26E-04	-1.33E-04	0.9550	5			93.8	100.6			22.1	17.5
83	metobromuron	atrazine-d_5	2.14E-03	-1.10E-04	0.9964	1		93.2	95.0	102.3		2.1	4.8	7.1
84	metribuzin	atrazine-d_5	9.69E-04	2.82E-04	0.9955	2.5		93.5	99.2	98.6		5.0	8.1	8.3
85	mevinphos	dimethoate-d_6	3.34E-03	-5.88E-04	0.9943	1		97.4	94.8	100.5		4.4	6.9	5.7
86	mexacarbate	dimethoate-d_6	1.12E-02	3.41E-04	0.9966	1		100.2	104.2	104.3		12.8	7.9	6.4
87	monocrotophos	dimethoate-d_6	5.49E-04	2.42E-04	0.9891	5			97.4	92.6			9.5	13.1
88	monolinuron	atrazine-d_5	1.24E-03	1.47E-04	0.9925	1		98.2	98.3	98.2		7.6	6.7	7.8
89	myclobutanil	malathion-d_6	3.25E-03	9.43E-04	0.9947	2.5		90.0	107.2	106.6		2.6	13.9	8.9
90	neburon	cyprodinil-d_5	8.61E-03	5.99E-04	0.9933	2.5		97.4	105.2	96.6		17.6	14.9	5.3
91	nuarimol	imazalil-d_5	5.07E-03	8.54E-04	0.9956	2.5		116.1	95.5	91.0		6.8	15.6	6.1
92	oxadixyl	dimethoate-d_6	3.87E-03	1.87E-03	0.9970	2.5		101.2	98.0	99.0		10.7	6.9	6.6
93	oxamyl	oxamyl-d_6	2.88E-03	-1.77E-03	0.9902	10			91.3	106.1			1.8	8.2
94	paclobutrazol	malathion-d_6	6.41E-03	4.49E-03	0.9931	2.5		93.1	104.8	106.1		11.0	13.1	3.8
95	penconazole	malathion-d_6	4.36E-03	-2.83E-04	0.9937	2.5		93.6	100.7	107.5		15.4	13.0	7.5
96	pencycuron	cyprodinil-d_5	2.54E-02	1.80E-03	0.9911	1		91.5	108.1	101.9		17.3	4.6	3.8
97	phenmedipham	imazalil-d_5	4.56E-04	-1.06E-04	0.9814	10			107.9	95.2			11.8	19.8
98	picoxystrobin	malathion-d_6	3.03E-03	7.17E-04	0.9924	1		83.7	107.2	105.4		8.4	9.5	8.9
99	piperonyl butoxide	fludioxonil-$^{13}C_2$	2.20E-02	-1.06E-02	0.9892	2.5		92.0	89.3	89.3		19.9	17.3	10.6
100	pirimicarb	dimethoate-d_6	6.98E-03	-5.01E-04	0.9949	2.5		106.6	101.3	97.9		5.3	5.8	5.6
101	prochloraz	malathion-d_6	1.29E-03	7.35E-04	0.9907	5			96.2	113.6			13.4	10.0
102	promecarb	malathion-d_6	8.90E-03	2.17E-03	0.9952	1		93.1	103.0	99.7		6.6	11.2	4.6
103	prometon	dimethoate-d_6	2.75E-02	-2.63E-04	0.9946	0.5	85.6	101.3	99.0	97.3	15.2	12.2	5.6	4.3
104	prometryne	methiocarb-d_3	3.13E-02	3.56E-04	0.9950	0.5	98.0	93.6	95.0	95.1	8.2	5.8	4.5	6.5
105	propham	spirotetramat-d_6	5.71E-04	1.04E-03	0.9897	5			95.7	110.5			7.7	6.1
106	propiconazole	methiocarb-d_3	4.03E-03	1.71E-04	0.9957	1		99.7	100.9	102.5		11.8	10.4	19.9
107	propoxur	atrazine-d_5	8.80E-04	1.48E-04	0.9924	2.5		103.7	100.0	101.8		7.0	4.1	4.8
108	pyracarbolid	dimethoate-d_6	1.72E-02	9.95E-04	0.9954	1		108.2	99.4	102.1		14.4	8.4	6.4
109	pyraclostrobin	trifloxystrobin-d_6	9.83E-04	-1.03E-03	0.9761	10			99.4	93.9			14.2	10.8
110	pyrimethanil	malathion-d_6	6.56E-03	2.71E-04	0.9942	0.5	103.5	92.4	99.8	102.1	21.4	7.3	9.2	3.4
111	secbumeton	atrazine-d_5	9.08E-03	-3.97E-04	0.9959	0.5	90.7	103.0	101.0	96.7	4.9	1.0	9.8	8.3
112	siduron	spirotetramat-d_6	1.10E-02	-8.27E-04	0.9938	0.5	97.6	105.7	99.4	107.9	15.8	11.8	3.9	4.5
113	simetryn	dimethoate-d_6	1.29E-02	-1.98E-03	0.9922	1		105.6	96.4	94.7		10.3	7.6	2.1
114	spinetoram	fludioxonil-$^{13}C_2$	5.48E-03	-2.27E-03	0.9820	5			92.5	72.6			19.7	21.4
115	spinosyn A	fludioxonil-$^{13}C_2$	7.39E-03	-7.09E-03	0.9809	5			92.9	120.0			20.5	16.7

Continued on next page

Table A.15: LC-MS/MS figures of merit of pesticides extracted from blueberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	spinosyn D	cyprodinil-d_5	1.20E-03	-2.02E-03	0.9731	5			114.4	97.5			11.9	12.7
117	spirotetramat	dimethoate-d_6	5.18E-03	8.67E-04	0.9936	2.5		101.7	88.2	96.0		5.5	7.5	5.8
118	spiroxamine	imazalil-d_5	2.60E-02	-1.02E-03	0.9952	1		101.1	94.4	93.9		8.7	10.2	10.1
119	sulfentrazone	dimethoate-d_6	4.16E-04	4.06E-04	0.9797	5			99.8	103.5			12.5	14.2
120	tebuconazole	malathion-d_6	3.19E-03	6.96E-04	0.9946	1		96.3	98.1	102.3		19.8	11.9	6.5
121	tebufenozide	malathion-d_6	7.34E-04	9.48E-05	0.9806	5			95.0	99.5			9.6	17.8
122	tebuthiuron	atrazine-d_5	4.99E-03	-1.78E-05	0.9939	0.25	101.8	100.0	97.4	93.2	5.8	7.7	8.4	7.0
123	terbumeton	metalaxyl-d_6	2.82E-02	-9.05E-04	0.9961	0.5	97.5	106.4	97.4	102.3	6.3	10.5	5.2	7.9
124	terbutryn	atrazine-d_5	1.18E-02	-5.01E-04	0.9962	0.25	96.3	98.6	101.4	102.3	4.0	7.0	11.2	6.2
125	tetraconazole	malathion-d_6	3.49E-03	9.26E-04	0.9951	1		90.8	98.5	102.2		7.9	12.4	5.8
126	thiabendazole	cyprodinil-d_5	4.51E-02	5.00E-04	0.9942	2.5		92.4	103.0	103.5		1.9	9.5	18.2
127	thiacloprid	dimethoate-d_6	2.12E-02	-4.85E-04	0.9926	0.25	111.3	97.4	101.5	106.2	11.6	8.5	8.9	5.3
128	thiamethoxam	dimethoate-d_6	1.64E-03	3.46E-05	0.9910	5			92.4	95.7			13.9	6.7
129	thidiazuron	atrazine-d_5	5.47E-04	-8.61E-05	0.9939	1		98.8	99.1	100.0		12.2	4.0	9.1
130	thiobencarb	cyprodinil-d_5	1.88E-02	-7.11E-03	0.9925	2.5		98.0	107.0	91.5		4.7	12.5	6.4
131	triadimefon	methiocarb-d_3	2.60E-03	-2.53E-04	0.9908	2.5		107.1	94.5	101.4		7.4	3.1	6.4
132	triadimenol	dimethoate-d_6	5.10E-04	1.39E-03	0.9683	10			93.9	107.3			17.3	7.1
133	tricyclazole	malathion-d_6	1.83E-02	3.39E-03	0.9942	1		96.6	98.8	96.3		8.2	17.7	8.1
134	trifloxystrobin	cyprodinil-d_5	1.55E-02	-6.69E-04	0.9866	2.5		95.0	108.3	90.5		12.6	11.8	6.4
135	triflumizole	methiocarb-d_3	1.14E-03	1.00E-03	0.9675	10			99.1	111.2			14.2	7.0
136	triflumuron	cyprodinil-d_5	3.03E-03	-1.90E-04	0.9802	10			103.4	96.0			9.1	3.6
137	triticonazole	imazalil-d_5	3.88E-03	-3.58E-04	0.9925	1		95.6	99.1	88.8		13.2	14.5	11.4
138	vamidothion	dimethoate-d_6	4.48E-03	-2.86E-03	0.9821	10			100.9	98.6			7.7	6.8
139	zoxamide	cyprodinil-d_5	2.22E-02	4.53E-03	0.9946	5			111.7	101.2			7.7	7.4

Table A.16: CBS-MS/MS figures of merit of pesticides extracted from grape matrix.

[Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	1.21E-02	-2.73E-03	0.9920	2.5		102.6	99.5	107.5		24.0	6.7	3.9
2	acetamiprid	carbofuran-d_3	2.11E-02	-3.14E-03	0.9904	1		99.2	101.6	93.7		14.7	13.5	3.9
3	aldicarb-insource	atrazine-d_5	4.66E-03	-1.05E-02	0.9823	5			113.2	117.5			21.8	10.3
4	ametryn	kresoxim-methyl-d_7	4.44E+00	-4.20E-01	0.9931	1		93.5	113.1	105.7		6.9	20.7	8.7
5	aminocarb	metalaxyl-d_6	4.23E-02	5.16E-03	0.9937	2.5		97.7	93.6	107.7		29.0	2.4	10.6
6	amitraz	malathion-d_6	3.29E-02	5.23E-06	0.9917	1		94.8	103.2	104.2		12.3	3.7	4.0
7	azoxystrobin	malathion-d_6	2.63E-01	-7.12E-02	0.9960	1		97.1	102.5	107.4		3.5	6.9	7.0
8	benalaxyl	malathion-d_6	8.12E-02	-9.45E-03	0.9957	0.5	113.4	101.0	103.9	105.6	8.5	9.7	4.3	4.8
9	bendiocarb	carbofuran-d_3	3.92E-02	-4.38E-03	0.9959	0.5	95.8	98.1	96.9	96.2	5.0	8.1	3.5	1.9
10	boscalid	methiocarb-d_3	4.57E-02	6.50E-03	0.9900	2.5		83.2	93.4	96.8		11.0	7.9	4.2
11	bromucanozole	kresoxim-methyl-d_7	4.39E-01	-5.68E-01	0.9861	5			86.0	97.3			9.9	6.3
12	bupirimate	trifloxystrobin-d_6	1.37E-01	-2.70E-03	0.9957	0.5	105.7	104.1	107.6	112.5	8.2	18.9	11.6	7.1
13	buprofenzin	malathion-d_6	8.65E-02	-3.18E-02	0.9958	2.5		92.3	96.0	101.4		6.2	5.3	6.2
14	butafenacil	malathion-d_6	7.19E-02	-1.04E-02	0.9956	0.5	102.3	88.1	96.4	105.2	8.6	12.3	13.5	5.0
15	butoxycarboxim	imazalil-d_5	9.70E-02	4.69E-02	0.9936	2.5		104.5	108.7	97.1		15.4	18.3	6.6
16	carbaryl	methiocarb-d_3	2.83E-02	-1.08E-02	0.9927	2.5		111.0	100.7	108.6		20.7	10.5	6.4
17	carbendazim	imazalil-d_5	1.90E-01	5.96E-03	0.9910	1		103.5	101.6	105.7		19.2	36.3	8.9
18	carbetamide	carbofuran-d_3	6.81E-03	5.47E-04	0.9977	0.5	114.3	102.1	94.8	107.0	6.8	5.6	6.4	5.5
19	carbofuran	carbofuran-d_3	4.63E-02	-2.35E-03	0.9960	0.5	93.9	101.8	109.3	101.5	4.9	14.6	11.0	6.0
20	carfentrazone-ethyl	trifloxystrobin-d_6	3.64E-02	-1.06E-04	0.9932	0.5	117.5	94.2	93.9	103.0	8.0	10.7	5.6	4.9
21	chlorantraniliprole	kresoxim-methyl-d_7	3.70E-01	-8.43E-01	0.9915	5			91.9	104.5			6.8	4.8
22	chlorotoluron	methiocarb-d_3	3.66E-02	4.36E-04	0.9907	2.5		106.5	106.9	111.3		8.4	11.9	2.4
23	chloroxuron	trifloxystrobin-d_6	5.51E-02	8.22E-04	0.9962	0.5	106.1	96.5	100.4	109.6	2.7	10.5	3.5	5.4
24	clothianidin	atrazine-d_5	3.91E-03	-1.72E-03	0.9945	2.5		98.7	101.6	101.8		13.8	18.1	10.5
25	cyazofamid	malathion-d_6	1.44E-02	-7.79E-04	0.9925	2.5		93.8	95.3	101.3		9.8	14.9	5.7
26	cycluron	metalaxyl-d_6	1.89E-02	-1.04E-03	0.9971	1		101.6	101.6	100.5		14.0	12.0	6.1
27	cyproconazole	atrazine-d_5	2.38E-02	-1.73E-03	0.9940	2.5		83.7	87.2	98.1		9.2	15.3	3.2
28	cyprodinil	trifloxystrobin-d_6	3.66E-02	1.13E-02	0.9926	1		99.2	95.5	113.9		17.9	2.5	4.9
29	desmedipham	trifloxystrobin-d_6	7.56E-02	-1.27E-02	0.9964	1		90.1	104.2	117.1		9.1	6.5	5.9
30	diclobutrazol	atrazine-d_5	2.32E-02	-5.33E-02	0.9910	5			84.2	90.4			12.5	3.2
31	diethofencarb	methiocarb-d_3	5.66E-02	7.96E-03	0.9951	1		106.1	103.2	102.1		10.2	4.6	5.5
32	difenoconazole	trifloxystrobin-d_6	2.91E-02	-7.85E-02	0.9853	5			81.7	101.9			17.2	6.4
33	dimethoate	dimethoate-d_6	2.97E-02	-5.07E-03	0.9968	1		91.4	100.4	99.5		7.3	1.3	4.8
34	dimethomorph	atrazine-d_5	4.99E-02	-7.28E-02	0.9872	5			92.0	87.2			11.7	2.7
35	dimoxystrobin	malathion-d_6	6.87E-02	-3.87E-03	0.9956	0.5	105.2	98.2	105.7	102.1	2.6	6.3	8.1	4.4
36	dioxacarb	carbofuran-d_3	3.90E-02	-3.51E-03	0.9956	0.5	103.3	98.0	97.1	95.9	6.4	5.0	3.7	3.2
37	diuron	atrazine-d_5	6.23E-02	1.12E-02	0.9925	1		103.7	107.3	100.3		9.4	12.3	3.1
38	epoxiconazole	methiocarb-d_3	6.62E-02	-7.60E-03	0.9894	2.5		86.7	84.9	99.2		12.3	14.8	5.5
39	etaconazole	atrazine-d_5	3.46E-02	-2.91E-04	0.9918	1		89.3	89.0	89.6		14.3	11.9	3.1
40	ethiprole	atrazine-d_5	2.69E-02	7.07E-03	0.9954	1		82.8	96.7	105.8		8.1	8.3	8.2
41	ethirimol	imazalil-d_5	2.93E-02	-1.38E-02	0.9865	2.5		100.2	103.6	109.7		13.2	23.0	6.5
42	ethofumesate	methiocarb-d_3	1.42E-02	2.38E-02	0.9917	2.5		109.3	89.5	94.8		14.1	15.4	2.0
43	etoxazole	malathion-d_6	2.46E-02	-5.15E-02	0.9958	5			92.5	96.9			17.4	6.9
44	fenamidone	atrazine-d_5	1.44E-02	-2.38E-03	0.9927	1		91.4	91.4	91.8		13.5	11.7	4.3
45	fenarimol	kresoxim-methyl-d_7	2.22E-01	-5.33E-01	0.9880	5			85.7	99.4			20.2	7.6
46	fenbuconazole	methiocarb-d_3	2.32E-02	-5.39E-02	0.9867	5			82.8	89.1			14.2	3.0
47	fenhexamid	atrazine-d_5	8.64E-03	-1.50E-03	0.9831	5			89.2	93.9			9.7	4.4
48	fenobucarb	methiocarb-d_3	1.18E-01	-6.99E-02	0.9942	2.5		106.8	102.8	112.3		9.0	5.9	3.0
49	fenoxycarb	trifloxystrobin-d_6	1.20E-02	-6.87E-03	0.9775	5			91.3	100.2			14.7	11.3
50	fenpropimorph	imazalil-d_5	1.40E-01	-2.79E-02	0.9897	2.5		95.1	117.6	91.8		16.2	6.7	8.1
51	fenuron	dimethoate-d_6	5.93E-02	-9.68E-03	0.9938	0.5	106.8	93.6	107.1	93.2	7.0	16.5	8.6	7.2
52	flufenacet	methiocarb-d_3	6.62E-02	-4.68E-04	0.9974	0.25	108.9	100.6	100.4	98.6	6.5	12.6	5.1	4.4
53	fluometuron	atrazine-d_5	3.19E-02	1.88E-03	0.9944	0.5	93.8	107.7	106.1	103.8	11.6	7.5	9.3	3.3
54	fluoxastrobin	trifloxystrobin-d_6	1.44E-01	-2.02E-02	0.9944	1		87.8	98.4	109.9		6.0	3.3	3.9
55	flusilazole	kresoxim-methyl-d_7	1.00E+00	-2.69E+00	0.9893	5			84.5	96.1			11.4	7.9
56	flutolanil	methiocarb-d_3	1.52E-01	1.01E-02	0.9978	0.5	101.0	98.8	103.0	100.5	6.2	8.0	4.9	2.5

Continued on next page

Table A.16: CBS-MS/MS figures of merit of pesticides extracted from grape matrix – continued from previous page

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
57	flutriafol	atrazine-d_5	2.53E-02	2.10E-03	0.9929	0.5	93.4	83.6	88.7	105.1	7.1	9.5	8.7	5.1
58	forchlorfenuron	methiocarb-d_3	9.33E-02	-1.57E-01	0.9877	5			84.0	109.8			12.9	8.3
59	fuberidazole	imazalil-d_5	2.12E-01	-2.46E-01	0.9886	5			100.7	95.8			17.5	4.9
60	furalaxyl	metalaxyl-d_6	8.07E-02	-3.17E-04	0.9938	0.25	111.3	95.3	97.0	91.3	13.0	19.6	8.0	3.0
61	furathiocarb	trifloxystrobin-d_6	5.20E-02	6.74E-03	0.9950	1		104.1	103.3	103.8		9.1	4.7	8.2
62	hexaconazole	atrazine-d_5	1.31E-02	-1.78E-02	0.9866	5			85.1	91.0			14.4	3.8
63	imazalil	imazalil-d_5	3.00E-02	2.98E-02	0.9966	1		100.3	95.6	101.5		9.5	3.5	6.8
64	imidacloprid	carbofuran-d_3	8.26E-03	-6.46E-03	0.9920	2.5		112.0	105.5	93.4		15.2	21.6	4.9
65	ipconazole	atrazine-d_5	2.15E-03	-1.47E-04	0.9696	10			76.0	81.7			20.1	5.0
66	iprovalicarb	methiocarb-d_3	1.19E-01	1.45E-01	0.9714	5			118.0	102.8			20.7	8.4
67	isoprocarb	atrazine-d_5	4.53E-02	9.38E-04	0.9945	1		96.7	104.6	100.6		7.5	11.4	5.0
68	isoproturon	imazalil-d_5	6.73E-02	3.36E-02	0.9934	2.5		103.1	105.4	92.9		18.4	17.6	5.9
69	linuron	methiocarb-d_3	3.49E-02	1.64E-02	0.996842	1		101.6	94.1	99.1		11.1	7.8	1.9
70	mandipropamid	trifloxystrobin-d_6	7.87E-02	-4.69E-03	0.9965	0.5	109.2	95.9	102.9	110.8	9.5	3.9	4.2	3.0
71	mefenacet	trifloxystrobin-d_6	1.47E-01	-5.57E-03	0.9940	0.25	90.2	108.6	105.6	106.1	9.8	18.0	8.7	5.4
72	mepanipyrim	trifloxystrobin-d_6	2.35E-02	-2.37E-02	0.9906	5			89.5	105.9			2.9	5.7
73	mepronil	methiocarb-d_3	1.41E-01	9.80E-03	0.9947	0.25	104.3	103.6	98.3	94.1	4.3	12.7	8.2	3.1
74	metalaxyl	metalaxyl-d_6	5.24E-02	-5.47E-04	0.9993	0.25	101.6	104.2	99.7	99.3	9.1	3.3	2.8	3.4
75	metconazole	atrazine-d_5	2.33E-02	-5.27E-02	0.9846	5			84.9	88.4			17.3	6.9
76	methabenzthiazuron	methiocarb-d_3	3.03E-01	-3.00E-02	0.9896	1		95.3	110.3	109.1		13.5	16.0	8.3
77	methiocarb	methiocarb-d_3	1.31E-02	-1.02E-02	0.9930	2.5		99.9	94.1	98.4		2.7	6.2	4.4
78	methomyl	dimethoate-d_6	6.56E-03	8.57E-04	0.9895	2.5		94.8	121.7	95.2		15.2	18.0	10.3
79	methoprotryne	imazalil-d_5	2.20E-01	7.02E-02	0.9918	2.5		101.3	102.1	85.5		18.8	16.3	8.9
80	methoxyfenozide	spirotetramat-d_6	1.04E-02	8.98E-03	0.9952	5			112.1	103.5			6.7	3.4
81	metobromuron	methiocarb-d_3	4.43E-02	1.03E-03	0.9977	0.25	86.3	99.0	99.5	102.5	4.5	5.5	2.5	3.0
82	metribuzin	atrazine-d_5	8.97E-03	-9.54E-04	0.9944	5			89.5	101.3			4.5	2.7
83	mevinphos	imazalil-d_5	5.52E-02	9.80E-03	0.9945	2.5		94.4	125.5	104.6		19.8	22.6	6.6
84	mexacarbate	metalaxyl-d_6	2.65E-02	-2.20E-03	0.9943	0.5	86.8	98.7	98.2	99.3	20.4	14.0	12.6	5.6
85	monocrotophos	metalaxyl-d_6	2.22E-03	-3.31E-05	0.9917	5			121.4	108.3			42.9	8.1
86	monolinuron	methiocarb-d_3	1.04E-02	-7.93E-04	0.9940	1		95.9	93.7	103.1		13.1	7.0	3.4
87	myclobutanil	atrazine-d_5	1.74E-02	-3.15E-03	0.9914	2.5		89.2	89.2	93.9		17.8	13.8	4.7
88	neburon	malathion-d_6	1.22E-02	3.40E-03	0.9887	2.5		127.4	95.7	105.2		8.3	13.3	4.7
89	nuarimol	atrazine-d_5	1.34E-02	-1.20E-03	0.9882	1		82.5	83.2	97.1		16.3	14.2	2.6
90	oxadixyl	dimethoate-d_6	4.81E-02	5.10E-02	0.9901	2.5		89.8	93.8	93.3		15.4	19.0	7.4
91	paclobutrazol	atrazine-d_5	4.95E-03	-9.73E-04	0.9924	2.5		89.9	84.6	99.2		10.7	16.5	5.3
92	penconazole	trifloxystrobin-d_6	3.88E-02	-4.02E-03	0.9887	0.5	101.8	92.3	86.4	121.7	1.4	19.7	5.7	9.5
93	pencycuron	trifloxystrobin-d_6	9.74E-02	4.49E-03	0.9969	0.5	99.8	98.0	99.6	106.2	2.8	6.5	1.1	6.7
94	phenmedipham	trifloxystrobin-d_6	7.20E-03	-5.28E-03	0.9785	5			102.1	102.6			14.6	13.9
95	picoxystrobin	malathion-d_6	5.77E-02	-4.50E-05	0.9943	0.5	106.0	94.0	106.2	102.7	7.7	5.6	13.4	8.3
96	piperonyl butoxide	trifloxystrobin-d_6	8.38E-02	3.35E-02	0.9911	1		116.3	108.0	101.9		4.5	22.9	12.8
97	pirimicarb	imazalil-d_5	1.14E-01	1.69E-03	0.9971	0.5	83.2	105.8	116.6	92.4	6.2	7.2	11.0	2.6
98	prochloraz	trifloxystrobin-d_6	1.65E-02	-4.95E-03	0.9934	2.5		102.4	94.6	107.3		10.6	1.0	4.5
99	promecarb	methiocarb-d_3	7.03E-02	-1.96E-03	0.9945	0.5	98.4	92.8	99.7	104.7	4.7	8.4	6.2	1.9
100	prometon	imazalil-d_5	3.75E-01	7.59E-03	0.9958	0.25	82.4	101.6	106.5	95.3	4.3	8.9	5.9	5.4
101	prometryne	trifloxystrobin-d_6	4.80E-01	-4.09E-02	0.9880	0.5	95.2	114.6	111.4	116.4	8.5	31.2	16.1	4.6
102	propham	methiocarb-d_3	1.29E-02	-1.86E-02	0.9824	5			84.3	106.4			10.3	5.4
103	propiconazole	trifloxystrobin-d_6	6.58E-02	-1.26E-02	0.9914	1		81.0	86.5	111.1		12.0	9.2	8.6
104	propoxur	carbofuran-d_3	1.23E-02	-1.38E-04	0.9961	0.5	99.2	95.6	97.7	100.2	11.2	0.3	3.9	4.6
105	pyracarbolid	spirotetramat-d_6	8.44E-02	6.10E-03	0.9888	0.5	83.9	109.7	96.9	99.9	2.5	19.5	5.8	2.6
106	pyraclostrobin	trifloxystrobin-d_6	1.84E-02	-1.73E-03	0.9922	2.5		108.3	97.7	108.2		6.6	6.6	12.1
107	pyrimethanil	methiocarb-d_3	3.95E-02	-2.21E-02	0.9882	2.5		92.0	96.4	106.6		7.2	6.4	2.2
108	quinoxyfen	methiocarb-d_3	3.39E-03	-1.57E-02	0.9771	10			71.8	85.4			21.1	10.0
109	secbumeton	imazalil-d_5	3.19E-01	-8.43E-03	0.9917	1		101.6	102.6	91.4		11.6	5.4	7.3
110	siduron	methiocarb-d_3	7.44E-02	1.53E-02	0.9908	1		105.0	101.9	104.9		8.4	6.3	3.4
111	simetryn	imazalil-d_5	1.23E-01	2.79E-03	0.9901	1		101.0	99.0	89.8		16.8	17.4	5.7
112	spinetoram	imazalil-d_5	1.50E-02	-1.26E-02	0.9810	10			101.2	93.1			17.0	12.4
113	spinosyn A	imazalil-d_5	2.01E-02	-5.85E-02	0.9878	5			103.6	88.6			20.0	9.2
114	spinosyn D	trifloxystrobin-d_6	5.79E-03	-1.36E-02	0.9899	5			108.0	120.2			12.2	13.0
115	spirotetramat	spirotetramat-d_6	4.70E-02	1.08E-02	0.9971	0.5	91.1	94.4	92.7	97.3	12.7	9.0	3.2	0.3

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Table A.16: CBS-MS/MS figures of merit of pesticides extracted from grape matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	spiroxamine	imazalil-d_5	4.18E-01	-4.33E-02	0.9922	0.5	85.7	89.1	108.7	92.5	4.6	11.4	4.0	10.2
117	tebuconazole	atrazine-d_5	2.19E-02	-1.19E-02	0.9870	2.5		88.5	84.8	90.1		15.2	15.4	6.8
118	tebufenozide	spirotetramat-d_6	1.68E-02	3.31E-02	0.9942	1		95.1	103.7	98.5		17.0	5.6	2.8
119	tebuthiuron	atrazine-d_5	6.13E-02	-3.48E-04	0.9934	0.5	94.8	111.9	105.5	110.3	4.9	24.7	16.7	7.5
120	terbumeton	imazalil-d_5	9.89E-01	7.66E-03	0.9934	0.1	83.8	102.5	107.3	94.4	9.6	11.1	8.6	5.8
121	terbutryn	trifloxystrobin-d_6	5.98E-01	-8.49E-02	0.9903	1		109.5	106.7	111.0		25.9	15.1	5.4
122	tetraconazole	methiocarb-d_3	5.80E-02	-1.49E-01	0.9885	5			81.5	102.4			14.3	1.6
123	thiacloprid	methiocarb-d_3	1.04E-01	-6.02E-03	0.9927	0.5	94.4	97.6	107.7	108.9	6.2	9.2	13.5	5.5
124	thiamethoxam	carbofuran-d_3	4.83E-03	3.12E-03	0.9899	5			104.1	98.4			21.3	4.6
125	thidiazuron	trifloxystrobin-d_6	4.79E-02	-1.28E-01	0.9833	5			88.4	114.6			8.1	11.3
126	thiobencarb	trifloxystrobin-d_6	4.28E-02	1.46E-03	0.9927	2.5		99.6	87.8	100.6		4.4	14.2	4.4
127	triadimefon	methiocarb-d_3	3.00E-02	-4.09E-03	0.9920	0.5	118.4	92.4	91.3	98.9	10.2	21.2	10.0	6.8
128	triadimenol	atrazine-d_5	1.28E-02	-2.05E-03	0.9934	2.5		89.0	87.5	100.9		14.3	12.1	3.5
129	trichlorfon	carbofuran-d_3	4.11E-03	8.69E-03	0.9896	5			103.2	123.4			32.0	8.5
130	tricyclazole	imazalil-d_5	1.26E-01	2.11E-03	0.9915	1		111.5	110.0	97.8		20.6	31.5	4.9
131	trifloxystrobin	trifloxystrobin-d_6	7.35E-02	1.16E-02	0.9973	0.5	94.8	97.7	98.2	104.4	10.9	7.4	2.9	4.8
132	triflumizole	trifloxystrobin-d_6	1.25E-02	2.49E-03	0.9937	2.5		103.1	94.4	109.5		9.5	5.3	7.1
133	triflumuron	trifloxystrobin-d_6	1.27E-02	-1.10E-02	0.9865	5			80.5	110.8			29.3	5.2
134	triticonazole	atrazine-d_5	1.62E-02	-4.23E-03	0.9949	2.5		117.2	89.4	93.9		14.8	12.4	5.6
135	vamidothion	imazalil-d_5	7.44E-02	-6.18E-02	0.9839	5			116.9	111.4			19.8	3.0
136	zoxamide	trifloxystrobin-d_6	5.64E-02	1.03E-02	0.9945	1		96.5	107.1	111.0		3.8	11.7	2.5

Table A.17: LC-MS/MS figures of merit of pesticides extracted from grape matrix.

[Take me back!]

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	Compound	Internal Standard	Slope	Intercept	R^2	(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	7.51E-03	3.18E-03	0.9753	5			112.1	89.0			11.9	8.8
2	acetamiprid	dimethoate-d_6	7.85E-02	-3.41E-03	0.9913	1		90.1	101.0	99.9		8.6	6.8	13.6
3	aldicarb-insource	cyprodinil-d_5	3.47E-02	-7.52E-02	0.9752	5			88.4	79.6			10.8	5.3
4	ametryn	cyprodinil-d_5	1.38E+00	2.77E-01	0.9939	1		93.4	92.4	89.8		18.5	12.4	9.0
5	aminocarb	dimethoate-d_6	5.89E-02	-3.64E-04	0.9916	2.5		114.0	99.1	105.5		8.4	14.7	11.5
6	amitraz	metalaxyl-d_6	2.00E-02	-2.99E-03	0.9860	5			100.6	116.1			14.9	3.8
7	azoxystrobin	methiocarb-d_3	1.66E-01	-4.76E-04	0.9955	1		98.1	97.4	100.5		14.6	15.2	13.4
8	benalaxyl	malathion-d_6	1.86E-01	-1.81E-02	0.9952	0.5	124.1	100.9	100.4	95.3	9.8	12.9	4.7	7.2
9	bendiocarb	cyprodinil-d_5	1.83E-01	1.76E-02	0.9914	2.5		103.3	98.8	81.8		26.4	12.7	8.4
10	boscalid	malathion-d_6	7.38E-02	1.05E-02	0.9932	2.5		96.3	95.5	95.3		16.5	6.1	11.0
11	bromucanozole	methiocarb-d_3	1.85E-02	1.15E-03	0.9905	5			100.7	93.3			6.4	5.1
12	bupirimate	carbofuran-d_3	1.18E-02	-1.23E-02	0.9910	2.5		107.5	92.1	118.2		9.0	13.5	7.4
13	buprofenzin	cyprodinil-d_5	3.32E-01	4.69E-02	0.9956	1		110.8	95.7	85.8		23.8	12.0	11.5
14	butafenacil	methiocarb-d_3	4.58E-02	-8.45E-03	0.9874	2.5		107.1	94.0	98.7		6.9	11.2	10.0
15	butoxycarboxim	atrazine-d_5	2.04E-02	6.96E-04	0.9920	1		102.7	102.5	90.7		7.3	7.0	11.9
16	carbaryl	cyprodinil-d_5	1.24E-01	-7.85E-03	0.9925	5			93.6	86.3			11.1	5.8
17	carbendazim	dimethoate-d_6	1.83E-01	7.20E-03	0.9937	0.5	90.4	104.2	100.3	102.1	7.8	15.5	12.0	8.7
18	carbetamide	metalaxyl-d_6	6.13E-03	-1.45E-03	0.9888	5			100.8	90.8			5.7	9.3
19	carbofuran	metalaxyl-d_6	3.54E-02	-4.20E-05	0.9935	1		94.4	100.5	102.6		14.0	11.9	1.4
20	carfentrazone-ethyl	atrazine-d_5	1.05E-02	-4.88E-03	0.9904	2.5		89.1	81.0	101.0		14.7	7.3	11.7
21	chlorantraniliprole	metalaxyl-d_6	9.60E-03	-3.99E-03	0.9825	2.5		101.6	102.2	92.1		17.7	23.2	13.0
22	chlorotoluron	atrazine-d_5	1.05E-02	-9.86E-04	0.9918	0.5	110.2	89.8	97.8	100.3	18.1	6.1	8.4	6.5
23	chloroxuron	cyprodinil-d_5	2.38E-01	5.04E-02	0.9899	5			99.4	96.8			11.1	5.0
24	clothianidin	imazalil-d_5	1.53E-02	4.35E-03	0.9768	5			97.1	90.2			15.9	7.1
25	cyazofamid	methiocarb-d_3	1.29E-02	-7.44E-03	0.9954	2.5		114.8	101.0	103.8		13.5	6.9	15.4
26	cycluron	methiocarb-d_3	4.86E-02	1.07E-02	0.9931	1		95.4	94.6	92.3		4.2	6.4	13.0
27	cyproconazole	methiocarb-d_3	4.24E-02	-2.84E-03	0.9899	2.5		109.7	100.1	93.1		12.2	15.8	9.5
28	cyprodinil	cyprodinil-d_5	1.68E-01	9.93E-03	0.9925	2.5		103.9	97.6	99.2		10.9	6.8	13.6
29	desmedipham	cyprodinil-d_5	1.83E-01	2.22E-02	0.9871	2.5		103.2	104.8	99.3		16.0	7.7	4.0
30	diclobutrazol	malathion-d_6	3.52E-02	-4.56E-03	0.9947	1		114.6	98.8	90.3		11.8	6.0	18.1
31	diethofencarb	malathion-d_6	4.53E-02	-1.29E-02	0.9929	2.5		108.8	95.6	92.5		3.6	11.4	15.1
32	difenoconazole	metalaxyl-d_6	1.05E-02	-7.70E-03	0.9922	5			88.5	105.9			9.9	6.1
33	dimethoate	dimethoate-d_6	2.45E-02	1.58E-03	0.9903	2.5		100.6	101.7	104.8		7.9	16.3	6.7
34	dimethomorph	metalaxyl-d_6	4.06E-02	-2.12E-02	0.9875	2.5		105.8	93.6	106.1		12.3	11.9	4.8
35	dimoxystrobin	malathion-d_6	5.26E-02	-2.53E-03	0.9910	2.5		101.0	95.5	97.5		10.6	7.1	15.6
36	dioxacarb	cyprodinil-d_5	1.83E-01	2.06E-03	0.9908	5			98.8	81.8			12.7	8.4
37	diuron	atrazine-d_5	1.12E-02	-2.41E-03	0.9903	1		107.8	91.4	95.7		14.4	10.7	5.7
38	epoxiconazole	atrazine-d_5	2.15E-02	-3.22E-03	0.9911	1		92.5	98.1	102.1		13.6	14.0	8.3
39	etaconazole	cyprodinil-d_5	2.85E-01	-4.62E-03	0.9924	1		95.9	97.6	92.6		18.5	11.2	6.5
40	ethiprole	atrazine-d_5	2.36E-02	1.59E-03	0.9921	0.5	94.8	107.0	100.7	90.5	11.4	14.1	7.2	11.2
41	ethirimol	metalaxyl-d_6	1.06E-02	2.79E-03	0.9860	5			105.1	79.5			17.3	13.9
42	ethofumesate	atrazine-d_5	8.32E-03	-4.30E-03	0.9913	2.5		109.8	91.1	99.0		4.2	3.9	6.0
43	etoxazole	metalaxyl-d_6	5.89E-03	-5.13E-03	0.9903	2.5		102.9	87.3	113.6		18.2	8.2	11.0
44	fenamidone	malathion-d_6	7.10E-02	6.47E-03	0.9887	1		94.1	101.8	90.1		9.4	9.9	14.1
45	fenarimol	atrazine-d_5	5.17E-03	-2.50E-03	0.9905	2.5		114.0	96.1	104.4		11.7	2.7	4.1
46	fenbuconazole	cyprodinil-d_5	8.00E-02	8.47E-03	0.9913	2.5		93.1	93.7	99.1		10.2	11.1	11.7
47	fenhexamid	atrazine-d_5	5.66E-03	3.17E-03	0.9923	2.5		91.0	94.5	103.6		10.4	6.9	4.0
48	fenobucarb	cyprodinil-d_5	5.93E-01	8.57E-02	0.9938	1		101.4	98.3	88.2		24.5	8.8	7.5
49	fenoxycarb	cyprodinil-d_5	3.83E-02	-1.25E-02	0.9910	5			99.5	100.1			9.4	10.2
50	fenpropimorph	methiocarb-d_3	6.42E-02	3.55E-03	0.9911	2.5		110.8	101.6	104.2		15.6	10.2	4.5
51	fenuron	metalaxyl-d_6	1.49E-02	-8.57E-04	0.9947	2.5		108.7	101.9	95.0		7.4	10.5	8.3
52	flufenacet	carbofuran-d_3	3.74E-02	-6.62E-03	0.9927	1		104.8	101.3	113.7		16.7	9.2	8.9
53	fluometuron	metalaxyl-d_6	3.97E-02	-1.12E-02	0.9913	1		92.7	100.5	102.6		10.1	15.8	7.8
54	fluoxastrobin	imazalil-d_5	1.92E-01	-2.31E-01	0.9879	5			91.0	126.1			21.8	13.5
55	flusilazole	methiocarb-d_3	7.69E-02	-2.70E-03	0.9941	2.5		98.4	103.0	108.7		7.7	14.7	8.7
56	flutolanil	atrazine-d_5	6.53E-02	-6.06E-03	0.9952	0.5	104.7	106.1	93.9	109.5	1.8	8.6	11.9	2.3

Continued on next page

Table A.17: LC-MS/MS figures of merit of pesticides extracted from grape matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	Compound	Internal Standard	Slope	Intercept	R^2	(ng/g)	0.8	4	40	80	0.8	4	40	80
57	flutriafol	metalaxyl-d_6	1.97E-02	-4.47E-03	0.9923	2.5		111.1	102.8	96.8		13.7	15.1	4.1
58	forchlorfenuron	atrazine-d_5	2.53E-02	-3.30E-04	0.9966	1		108.4	93.8	95.1		6.7	10.7	2.7
59	fuberidazole	metalaxyl-d_6	7.31E-02	-7.59E-03	0.9927	1		93.2	105.2	93.8		8.5	7.1	4.1
60	furalaxyl	carbofuran-d_3	9.69E-02	-2.58E-02	0.9928	1		106.9	86.2	105.1		11.9	3.7	7.9
61	furathiocarb	metalaxyl-d_6	1.27E-02	-7.13E-03	0.9913	5			90.7	115.6			13.6	7.2
62	hexaconazole	atrazine-d_5	8.52E-03	-1.26E-03	0.9942	1		92.8	103.0	101.8		13.4	7.0	13.6
63	imazalil	metalaxyl-d_6	2.20E+04	-2.18E+03	0.9886	2.5		111.4	100.8	94.7		9.0	3.8	14.9
64	imidacloprid	dimethoate-d_6	2.46E-02	7.22E-03	0.9929	2.5		102.7	100.9	95.1		18.5	17.2	9.6
65	ipconazole	carbofuran-d_3	1.22E-02	-2.03E-03	0.9929	1		79.4	94.7	118.6		15.5	6.8	7.6
66	iprovalicarb	methiocarb-d_3	5.30E-02	3.74E-03	0.9955	1		85.7	100.0	101.1		7.8	16.5	9.2
67	isoprocarb	cyprodinil-d_5	4.45E-01	1.56E-01	0.9959	1		94.8	95.6	91.2		13.3	11.2	15.6
68	isoproturon	malathion-d_6	5.26E-02	9.93E-03	0.9865	2.5		101.2	102.9	94.1		12.8	12.2	15.4
69	linuron	malathion-d_6	4.27E-02	6.97E-03	0.9898	1		86.4	93.5	95.7		10.7	9.8	11.8
70	mandipropamid	cyprodinil-d_5	1.92E-01	2.27E-02	0.9908	5			92.3	90.9			15.0	10.8
71	mefenacet	methiocarb-d_3	7.58E-02	-4.81E-02	0.9933	5			95.9	105.2			7.8	13.0
72	mepanipyrim	atrazine-d_5	1.10E-02	-4.05E-03	0.9926	5			90.0	104.9			8.0	16.5
73	mepronil	atrazine-d_5	5.89E-02	-8.47E-03	0.9913	0.5	113.2	94.3	103.1	106.2	1.9	17.4	10.1	5.6
74	metalaxyl	carbofuran-d_3	5.26E-02	-1.42E-03	0.9915	0.5	115.3	106.9	94.5	100.4	6.6	6.0	9.0	5.5
75	metconazole	metalaxyl-d_6	3.16E-03	-1.16E-03	0.9917	5			92.3	112.3			18.3	3.0
76	methabenzthiazuron	atrazine-d_5	2.34E-02	-1.37E-02	0.9938	2.5		109.7	88.9	100.4		7.3	5.6	10.5
77	methiocarb	methiocarb-d_3	5.30E-03	1.92E-03	0.9752	5			97.3	111.3			3.1	20.0
78	methomyl	imazalil-d_5	6.90E-03	-6.98E-03	0.9774	10			101.1	93.8			9.8	11.4
79	methoprotryne	carbofuran-d_3	7.81E-02	-1.07E-02	0.9933	0.5	108.4	92.1	94.2	108.5	9.8	11.8	5.8	8.9
80	methoxyfenozide	metalaxyl-d_6	4.66E-03	6.05E-04	0.9841	10			94.0	110.3			12.7	10.9
81	metobromuron	malathion-d_6	7.11E-02	-4.56E-04	0.9936	0.5	100.8	97.2	94.1	92.6	11.4	12.3	8.4	15.6
82	metribuzin	metalaxyl-d_6	1.24E-02	1.42E-03	0.9894	5			98.8	105.2			7.7	4.0
83	mevinphos	cyprodinil-d_5	1.03E-01	-2.82E-02	0.9900	5			98.4	91.2			23.9	12.6
84	mexacarbate	metalaxyl-d_6	4.21E-02	2.45E-03	0.9928	1		105.2	104.8	95.3		10.3	6.6	8.8
85	monocrotophos	dimethoate-d_6	2.64E-03	-5.72E-03	0.9656	5			93.1	93.1			17.9	6.1
86	monolinuron	cyprodinil-d_5	4.34E-02	-1.23E-01	0.9819	10			88.2	90.4			13.0	16.7
87	myclobutanil	atrazine-d_5	1.08E-02	-8.28E-04	0.9930	2.5		95.3	90.5	98.7		7.2	8.3	7.9
88	neburon	methiocarb-d_3	2.16E-02	-4.52E-03	0.9920	2.5		98.5	97.6	102.9		3.4	13.5	8.7
89	nuarimol	metalaxyl-d_6	1.45E-02	-2.82E-03	0.9928	2.5		112.5	100.8	111.9		13.2	8.7	1.5
90	oxadixyl	dimethoate-d_6	3.96E-02	1.25E-02	0.9918	5			106.4	91.2			9.0	13.2
91	paclobutrazol	atrazine-d_5	2.19E-02	-1.49E-03	0.9924	2.5		100.5	91.8	102.9		10.4	5.8	3.6
92	penconazole	atrazine-d_5	1.56E-02	-1.89E-03	0.9944	1		89.6	93.5	108.7		8.5	3.3	8.9
93	pencycuron	cyprodinil-d_5	3.18E-01	-2.04E-02	0.9917	5			92.5	107.0			9.5	12.6
94	phenmedipham	cyprodinil-d_5	1.06E-02	-1.69E-02	0.9711	10			102.7	96.5			16.7	12.9
95	picoxystrobin	cyprodinil-d_5	1.50E-01	-5.05E-02	0.9852	2.5		99.5	100.4	100.9		12.8	7.2	17.9
96	piperonyl butoxide	metalaxyl-d_6	1.50E-02	-6.20E-03	0.9914	2.5		86.2	103.6	118.8		8.2	22.0	8.3
97	pirimicarb	cyprodinil-d_5	2.46E-01	4.18E-02	0.9930	2.5		96.2	95.3	82.0		25.2	16.6	9.3
98	prochloraz	metalaxyl-d_6	6.27E-03	-2.71E-03	0.9887	5			106.2	119.5			15.6	5.2
99	promecarb	cyprodinil-d_5	4.12E-01	1.06E-01	0.9943	1		93.3	93.4	92.1		8.8	7.8	8.8
100	prometon	imazalil-d_5	5.10E-01	-7.46E-02	0.9955	0.5	105.4	97.9	95.4	116.2	8.5	16.0	11.4	10.5
101	prometryne	methiocarb-d_3	2.86E-01	1.87E-02	0.9919	1		98.2	92.3	100.2		7.7	8.1	12.7
102	propham	metalaxyl-d_6	2.76E-03	-4.54E-03	0.9887	5			95.3	107.2			15.3	5.8
103	propiconazole	methiocarb-d_3	4.45E-02	2.53E-04	0.9924	1		94.5	90.3	101.4		9.5	8.5	6.3
104	propoxur	metalaxyl-d_6	1.21E-02	-8.61E-03	0.9884	2.5		114.9	106.0	102.4		11.8	10.4	5.3
105	pyracarbolid	metalaxyl-d_6	7.21E-02	4.24E-03	0.9930	1		108.4	93.6	107.1		6.0	15.3	7.7
106	pyraclostrobin	metalaxyl-d_6	3.42E-03	-4.21E-03	0.9920	2.5		102.7	102.6	113.5		9.5	10.6	11.8
107	pyrimethanil	cyprodinil-d_5	2.89E-01	1.91E-02	0.9907	2.5		89.8	91.5	90.4		7.9	8.1	7.5
108	quinoxyfen	malathion-d_6	4.45E-03	-3.63E-03	0.9891	5			84.6	94.6			10.7	3.4
109	secbumeton	metalaxyl-d_6	7.80E-02	-2.01E-02	0.9856	1		86.3	90.4	99.2		6.8	8.9	6.1
110	siduron	atrazine-d_5	2.87E-02	-2.35E-03	0.9920	0.5	117.0	108.1	97.9	101.2	4.7	15.2	5.0	6.0
111	simetryn	metalaxyl-d_6	5.86E-02	-2.32E-03	0.9944	1		87.2	106.6	106.6		8.0	11.5	3.5
112	spinetoram	imazalil-d_5	1.91E-02	-7.91E-03	0.9828	5			87.5	117.8			28.1	17.2
113	spinosyn A	dimethoate-d_6	1.65E-02	-3.43E-02	0.9798	5			83.2	93.9			15.3	15.8
114	spinosyn D	imazalil-d_5	5.22E-03	-1.11E-02	0.9680	10			85.1	118.3			16.9	10.2
115	spirotetramat	spirotetramat-d_6	5.05E-02	-3.33E-02	0.9915	2.5		95.9	95.2	113.5		14.5	11.0	5.5

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Table A.17: LC-MS/MS figures of merit of pesticides extracted from grape matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	spiroxamine	dimethoate-d_6	1.62E-01	-1.72E-02	0.9919	0.5	112.6	93.7	93.5	109.9	15.8	12.2	15.1	10.1
117	tebuconazole	malathion-d_6	3.96E-02	-1.16E-03	0.9908	1		110.9	98.9	94.8		17.1	9.9	14.1
118	tebufenozide	spirotetramat-d_6	1.14E-02	2.65E-03	0.9807	5			87.6	125.2			20.7	14.6
119	tebuthiuron	imazalil-d_5	2.63E-01	-1.12E-02	0.9925	5		108.5	92.2	98.7		4.0	5.9	9.9
120	terbumeton	cyprodinil-d_5	2.34E+00	1.94E+00	0.9931	5			98.3	86.9			13.1	7.3
121	terbutryn	metalaxyl-d_6	2.10E-01	-3.86E-02	0.9954	0.5	110.5	94.4	93.5	101.7	4.1	6.2	9.2	4.5
122	tetraconazole	carbofuran-d_3	2.10E-02	-6.63E-03	0.9923	2.5		103.6	93.9	108.4		18.0	5.0	9.6
123	thiacloprid	metalaxyl-d_6	8.58E-02	-1.31E-03	0.9887	0.5	107.8	111.0	102.8	95.8	9.7	10.9	8.5	10.7
124	thiamethoxam	dimethoate-d_6	1.26E-02	2.89E-03	0.9867	2.5		103.4	109.4	90.8		15.9	13.6	17.0
125	thidiazuron	methiocarb-d_3	1.79E-02	1.53E-03	0.9932	2.5		109.2	101.8	90.8		17.2	16.7	12.5
126	thiobencarb	atrazine-d_5	1.34E-02	-4.29E-03	0.9930	1		75.6	92.6	110.5		9.3	4.2	1.9
127	triadimefon	methiocarb-d_3	2.47E-02	2.00E-03	0.9916	2.5		96.7	98.4	106.2		17.8	13.4	8.5
128	triadimenol	atrazine-d_5	1.51E-03	-5.27E-04	0.9893	5			94.9	112.1			15.8	9.4
129	trichlorfon	dimethoate-d_6	1.04E-02	-3.40E-03	0.9500	10			111.7	86.9			25.6	10.0
130	tricyclazole	metalaxyl-d_6	8.44E-02	-3.64E-03	0.9915	2.5		100.6	98.2	94.9		12.4	6.4	8.8
131	trifloxystrobin	carbofuran-d_3	2.02E-02	-1.98E-02	0.9883	2.5		110.7	90.7	114.7		12.3	9.1	18.1
132	triflumizole	fludioxonil-$^{13}C_2$	7.55E-02	3.24E-02	0.9832	10			94.1	91.3			19.1	21.8
133	triflumuron	malathion-d_6	7.99E-03	-7.76E-03	0.9890	5			97.9	105.7			3.8	14.9
134	triticonazole	imazalil-d_5	4.62E-02	-4.05E-03	0.9872	2.5		110.0	100.2	113.1		13.9	21.6	10.8
135	vamidothion	dimethoate-d_6	4.35E-02	-2.11E-02	0.9875	2.5		98.8	95.5	95.2		28.0	11.4	9.0
136	zoxamide	methiocarb-d_3	5.29E-02	-4.31E-03	0.9949	1		94.6	99.9	104.8		19.1	8.2	11.3

Table A.18: CBS-MS/MS figures of merit of pesticides extracted from strawberry matrix. [Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	1.15E-02	-8.72E-03	0.9704	2.5		104.1	88.2	94.1		19.4	14.1	17.3
2	acetamiprid	dimethoate-d_6	4.04E-02	-3.18E-02	0.9904	2.5		104.8	93.3	92.4		4.3	15.5	10.1
3	aldicarb-insource	carbofuran-d_3	5.10E-03	-9.20E-03	0.9881	5			89.7	97.2			16.1	10.3
4	ametryn	carbofuran-d_3	1.19E-01	-3.56E-02	0.9933	0.5	114.2	98.1	97.4	91.8	5.1	6.2	8.4	11.8
5	aminocarb	dimethoate-d_6	1.43E-01	6.15E-02	0.9935	1		109.3	113.5	109.6		8.2	14.5	12.4
6	amitraz	malathion-d_6	3.90E-02	6.59E-02	0.9953	2.5		125.4	113.5	95.9		19.9	9.9	1.7
7	azoxystrobin	malathion-d_6	2.76E-01	-4.84E-02	0.9969	0.5	110.8	102.0	102.0	95.2	8.1	6.4	7.9	3.2
8	benalaxyl	malathion-d_6	9.62E-02	1.14E-02	0.9930	0.5	99.1	104.5	109.3	94.0	7.2	5.8	10.7	3.4
9	bendiocarb	carbofuran-d_3	3.00E-02	-1.42E-02	0.9954	1		100.3	93.8	96.2		7.1	8.1	5.2
10	boscalid	atrazine-d_5	9.43E-03	5.19E-03	0.9857	2.5		106.2	105.0	86.5		4.8	12.9	3.2
11	bromucanozole	atrazine-d_5	8.67E-03	1.63E-03	0.9864	2.5		108.5	98.2	91.0		7.8	10.7	11.7
12	bupirimate	malathion-d_6	2.51E-02	3.56E-03	0.9923	2.5		102.4	102.4	98.2		8.2	8.4	4.0
13	buprofenzin	malathion-d_6	1.04E-01	-5.88E-02	0.9904	1		95.8	98.2	96.7		9.1	11.9	5.6
14	butafenacil	malathion-d_6	8.52E-02	-7.60E-03	0.9887	1		108.4	106.5	89.9		10.4	13.5	7.2
15	butoxycarboxim	dimethoate-d_6	1.10E-01	-2.83E-02	0.9906	1		109.0	110.4	105.2		7.1	10.7	8.3
16	carbaryl	malathion-d_6	2.66E-02	2.72E-02	0.9913	2.5		118.2	96.0	98.8		22.6	15.5	8.6
17	carbendazim	dimethoate-d_6	1.74E-01	-1.27E-01	0.9878	2.5		117.5	103.8	111.0		8.0	4.8	7.6
18	carbetamide	dimethoate-d_6	1.48E-02	5.34E-04	0.9937	1		110.1	96.3	99.4		10.1	6.6	2.3
19	carbofuran	carbofuran-d_3	3.68E-02	3.08E-03	0.9933	0.5	100.6	88.5	92.1	96.5	6.7	6.4	4.5	4.3
20	carfentrazone-ethyl	malathion-d_6	1.85E-02	-2.40E-02	0.9833	5			86.2	83.4			18.9	21.7
21	chlorantraniliprole	malathion-d_6	1.70E-02	-1.42E-02	0.9940	2.5		106.6	84.1	90.0		15.1	7.3	6.4
22	chlorotoluron	atrazine-d_5	1.29E-02	-2.05E-03	0.9931	1		110.3	107.3	102.2		12.8	5.3	3.6
23	chloroxuron	malathion-d_6	3.11E-02	-2.49E-02	0.9915	2.5		115.2	103.1	96.0		9.5	13.0	12.1
24	clothianidin	dimethoate-d_6	5.16E-03	1.64E-03	0.9896	2.5		96.9	97.2	93.3		14.8	15.0	6.9
25	cyazofamid	malathion-d_6	1.35E-02	-1.16E-02	0.9846	2.5		115.5	89.3	91.0		15.3	12.9	5.4
26	cycluron	carbofuran-d_3	3.15E-02	-8.06E-03	0.9919	1		103.3	99.5	90.0		11.2	6.9	3.9
27	cyproconazole	atrazine-d_5	1.96E-02	-1.11E-03	0.9950	1		93.3	99.0	99.0		3.1	2.8	3.9
28	cyprodinil	malathion-d_6	2.44E-02	-4.83E-02	0.9887	5			96.3	99.8			6.6	2.7
29	desmedipham	malathion-d_6	6.12E-02	-1.21E-01	0.9921	5			92.1	92.1			12.8	8.3
30	diclobutrazol	atrazine-d_5	1.69E-02	2.51E-04	0.9924	1		92.6	91.9	92.0		11.4	10.9	10.3
31	dicrotophos	oxamyl-d_6	2.62E-01	-7.39E-02	0.9599	5			80.7	105.9			16.4	17.2
32	diethofencarb	malathion-d_6	5.54E-02	-1.49E-02	0.9929	1		102.3	111.9	99.6		7.9	4.2	4.7
33	difenoconazole	malathion-d_6	1.91E-02	-8.04E-03	0.9866	2.5		103.8	94.4	93.5		25.0	21.1	13.8
34	dimethoate	dimethoate-d_6	2.01E-02	-3.23E-03	0.9930	1		98.2	99.7	105.2		6.0	6.7	5.6
35	dimethomorph	atrazine-d_5	1.34E-02	6.94E-03	0.9887	1		96.3	89.2	91.5		6.9	10.7	13.9
36	dimoxystrobin	malathion-d_6	8.37E-02	-3.02E-03	0.9935	0.25	99.7	101.5	109.0	95.5	13.2	8.6	9.9	3.9
37	dioxacarb	carbofuran-d_3	3.01E-02	-1.36E-02	0.9966	1		99.2	96.3	96.0		10.6	6.3	5.0
38	diuron	atrazine-d_5	6.48E-02	6.83E-03	0.9953	0.25	101.9	97.1	100.6	102.6	9.7	9.8	8.8	2.7
39	epoxiconazole	atrazine-d_5	1.81E-02	8.20E-02	0.9815	2.5		111.0	101.4	88.0		16.5	13.2	10.3
40	etaconazole	atrazine-d_5	2.69E-02	4.59E-02	0.9933	1		96.6	100.9	93.2		14.4	7.4	10.7
41	ethiprole	atrazine-d_5	1.87E-02	8.00E-03	0.9922	2.5		103.9	96.7	92.8		17.0	7.1	6.5
42	ethirimol	imazalil-d_5	3.28E-02	-3.52E-02	0.9629	2.5		105.5	98.2	109.7		8.3	17.3	13.9
43	ethofumesate	malathion-d_6	1.21E-02	3.90E-02	0.9889	5			108.2	95.9			10.8	1.7
44	etoxazole	malathion-d_6	2.26E-02	-2.09E-03	0.9887	2.5			101.9	99.7			10.3	3.9
45	fenamidone	malathion-d_6	8.44E-02	-8.06E-02	0.9917	2.5		108.6	97.3	91.2		12.2	9.8	3.2
46	fenarimol	atrazine-d_5	3.84E-03	-9.30E-04	0.9863	5			97.6	87.2			5.2	12.3
47	fenbuconazole	atrazine-d_5	4.12E-03	4.24E-03	0.9821	2.5		96.9	96.1	90.3		8.3	19.7	14.5
48	fenhexamid	atrazine-d_5	4.39E-03	1.13E-02	0.9926	2.5		106.5	115.3	92.0		7.7	9.6	12.7
49	fenobucarb	malathion-d_6	1.43E-01	-1.21E-01	0.9922	2.5		108.8	99.0	102.2		14.1	6.0	8.0
50	fenoxycarb	atrazine-d_5	2.02E-03	-1.66E-03	0.9647	5			102.1	93.2			13.9	10.6
51	fenpropimorph	imazalil-d_5	1.76E-01	-1.30E-01	0.9800	1		96.7	103.6	94.2		11.6	4.8	10.4
52	fenuron	carbofuran-d_3	2.13E-02	-2.09E-02	0.9914	2.5		110.7	97.7	94.8		6.4	11.0	2.3
53	flufenacet	atrazine-d_5	2.37E-02	-4.16E-03	0.9929	1		106.4	103.9	97.2		13.4	9.1	8.8
54	fluometuron	atrazine-d_5	3.29E-02	3.36E-03	0.9932	1		94.7	94.8	104.4		9.4	4.2	5.9
55	fluoxastrobin	malathion-d_6	9.53E-02	-1.47E-02	0.9900	1		92.2	95.5	96.4		9.9	11.7	10.6
56	flusilazole	atrazine-d_5	1.98E-02	-7.93E-03	0.9890	2.5		105.2	99.2	97.5		13.5	7.7	9.2

Continued on next page

Table A.18: CBS-MS/MS figures of merit of pesticides extracted from strawberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	Compound	Internal Standard	Slope	Intercept	R^2	(ng/g)	0.8	4	40	80	0.8	4	40	80
57	flutolanil	malathion-d_6	1.74E-01	-1.72E-02	0.9941	0.5	92.0	100.3	101.4	96.8	7.4	8.6	9.1	4.0
58	flutriafol	atrazine-d_5	2.15E-02	-1.25E-02	0.9955	2.5		104.6	95.7	93.2		2.6	3.6	3.1
59	forchlorfenuron	malathion-d_6	6.61E-02	-4.58E-02	0.9873	2.5		105.9	95.5	92.3		14.3	15.4	5.2
60	fuberidazole	dimethoate-d_6	1.63E-01	-6.80E-02	0.9918	1		92.6	99.4	98.0		7.6	12.1	7.5
61	furalaxyl	carbofuran-d_3	1.38E-01	1.34E-03	0.9933	0.1	103.0	115.0	103.1	87.0	15.7	11.7	11.8	5.4
62	furathiocarb	malathion-d_6	3.07E-02	-1.99E-02	0.9872	5			107.0	96.4			6.7	4.2
63	hexaconazole	atrazine-d_5	8.01E-03	-1.73E-03	0.9909	1		100.2	98.3	94.1		6.5	7.0	8.2
64	imazalil	imazalil-d_5	7.24E-02	-1.05E-02	0.9906	1		96.9	98.2	90.8		1.7	6.2	7.7
65	imidacloprid	carbofuran-d_3	3.81E-03	-1.44E-03	0.9934	1		97.6	86.3	92.6		12.8	16.3	8.7
66	ipconazole	atrazine-d_5	7.36E-03	-1.11E-03	0.9910	2.5		105.4	96.4	96.3		20.8	15.4	17.9
67	iprovalicarb	carbofuran-d_3	4.51E-02	6.72E-03	0.9955	1		112.9	107.9	89.1		11.8	3.7	8.3
68	isoprocarb	atrazine-d_5	5.09E-02	4.63E-03	0.9940	0.5	117.4	99.0	100.0	106.0	4.3	8.6	4.0	2.2
69	isoproturon	carbofuran-d_3	2.54E-02	-4.77E-03	0.9926	0.5	117.4	103.6	101.8	93.9	10.5	8.1	6.9	6.8
70	kresoxim-methyl	malathion-d_6	2.60E-03	-1.01E-02	0.9938	10			90.3	83.1			15.5	5.3
71	linuron	malathion-d_6	3.30E-02	-4.24E-04	0.9910	2.5		98.6	102.7	93.9		19.2	11.0	8.2
72	mandipropamid	malathion-d_6	4.80E-02	-1.51E-02	0.9896	1		97.7	95.9	93.4		8.0	16.0	10.1
73	mefenacet	malathion-d_6	9.02E-02	-1.46E-02	0.9912	0.5	106.0	99.2	108.4	96.3	12.9	6.6	7.7	4.8
74	mepanipyrim	malathion-d_6	2.54E-02	1.84E-02	0.9824	1		90.5	95.6	96.1		11.6	6.2	4.5
75	mepronil	malathion-d_6	1.47E-01	2.02E-01	0.9920	1		103.4	109.6	94.8		11.4	9.7	5.9
76	metalaxyl	metalaxyl-d_6	2.99E-01	1.37E-02	0.9902	0.5	97.1	121.4	113.1	88.9	6.0	13.9	12.3	6.1
77	metconazole	atrazine-d_5	1.54E-02	-2.47E-03	0.9883	1		93.8	95.6	95.8		11.0	9.9	9.6
78	methabenzthiazuron	atrazine-d_5	1.85E-02	-9.54E-04	0.9907	0.5	118.1	91.7	96.0	90.7	8.5	5.8	13.2	14.2
79	methiocarb	malathion-d_6	4.41E-03	-4.55E-03	0.9863	2.5		109.5	117.7	103.7		10.3	17.7	3.4
80	methomyl	dimethoate-d_6	7.64E-03	-2.44E-03	0.9925	2.5		123.7	114.6	97.9		13.6	17.6	4.8
81	methoprotryne	malathion-d_6	2.86E-01	-1.00E-01	0.9943	2.5		113.2	110.8	97.8		9.2	17.7	6.0
82	methoxyfenozide	dimethoate-d_6	2.05E-02	8.15E-03	0.9905	1		124.4	101.6	89.1		18.5	13.3	10.0
83	metobromuron	atrazine-d_5	1.86E-02	-1.36E-03	0.9933	1		96.5	104.3	102.5		4.7	5.9	5.0
84	metribuzin	atrazine-d_5	6.56E-03	1.22E-02	0.9921	2.5		119.1	95.2	97.4		11.3	7.7	8.7
85	mevinphos	dimethoate-d_6	7.96E-02	-5.21E-04	0.9906	2.5		118.0	100.2	93.9		5.8	11.2	8.9
86	mexacarbate	carbofuran-d_3	4.20E-02	-3.89E-02	0.9916	2.5		110.0	92.7	97.7		6.4	3.3	5.6
87	monolinuron	malathion-d_6	2.89E-03	1.20E-03	0.9855	5			103.0	113.8			11.9	12.4
88	myclobutanil	atrazine-d_5	5.83E-03	3.45E-03	0.9921	2.5		98.3	106.2	91.0		10.4	8.0	8.3
89	neburon	malathion-d_6	1.19E-02	-2.30E-03	0.9837	2.5		111.9	103.3	92.0		12.7	12.0	5.3
90	nuarimol	atrazine-d_5	9.29E-03	3.00E-04	0.9924	1		92.9	104.6	89.7		6.8	10.3	8.1
91	oxadixyl	imazalil-d_5	5.42E-02	4.95E-02	0.9860	2.5		107.1	102.2	96.0		23.7	17.3	6.5
92	paclobutrazol	malathion-d_6	1.10E-02	-9.10E-03	0.9915	2.5		110.6	102.5	97.0		17.0	15.6	5.2
93	penconazole	atrazine-d_5	7.73E-03	-2.05E-03	0.9900	2.5		103.0	97.8	88.5		15.1	12.8	8.9
94	pencycuron	malathion-d_6	6.35E-02	6.43E-03	0.9916	2.5		109.1	94.6	90.8		12.9	17.3	12.4
95	picoxystrobin	malathion-d_6	6.37E-02	-5.03E-02	0.9906	2.5		115.0	102.2	93.7		6.9	11.3	4.4
96	piperonyl butoxide	malathion-d_6	5.11E-02	-6.03E-02	0.9781	5			106.6	98.5			14.9	5.6
97	pirimicarb	dimethoate-d_6	1.05E-01	-8.89E-02	0.9880	2.5		118.7	108.1	94.0		13.5	17.3	14.0
98	prochloraz	malathion-d_6	1.05E-02	3.13E-03	0.9806	2.5		110.1	94.0	95.7		17.2	7.7	14.9
99	promecarb	malathion-d_6	8.14E-02	-6.25E-02	0.9918	2.5		105.9	103.1	99.4		10.4	7.3	4.9
100	prometon	carbofuran-d_3	1.62E-01	-1.33E-01	0.9922	2.5		111.9	99.5	91.0		7.8	11.3	8.3
101	prometryne	malathion-d_6	4.19E-01	-1.41E-01	0.9934	1		106.7	102.9	94.5		10.5	10.8	6.1
102	propham	atrazine-d_5	4.88E-03	-3.47E-03	0.9866	5			98.7	97.0			6.7	9.0
103	propiconazole	atrazine-d_5	1.45E-02	4.33E-03	0.9856	1		97.7	97.4	89.8		20.1	10.6	11.5
104	propoxur	carbofuran-d_3	1.08E-02	-7.03E-03	0.9942	2.5		102.9	96.0	99.0		3.4	4.0	2.6
105	pyracarbolid	atrazine-d_5	6.86E-02	-1.31E-02	0.9956	1		105.8	105.1	100.8		12.5	6.0	2.3
106	pyraclostrobin	malathion-d_6	1.05E-02	-4.96E-03	0.9822	2.5		105.2	85.8	95.0		10.0	13.5	10.5
107	pyrimethanil	malathion-d_6	4.56E-02	-5.11E-02	0.9853	2.5		105.5	87.9	98.0		15.0	12.0	4.9
108	quinoxyfen	malathion-d_6	2.97E-03	-1.68E-02	0.9759	10			90.8	93.3			13.1	12.3
109	secbumeton	carbofuran-d_3	1.03E-01	-1.04E-01	0.9912	2.5		117.9	102.7	95.4		8.8	13.8	8.8
110	siduron	atrazine-d_5	3.45E-02	2.36E-02	0.9963	1		109.0	100.5	93.0		10.7	1.3	3.0
111	simetryn	carbofuran-d_3	4.59E-02	-5.06E-02	0.9928	2.5		112.1	98.1	94.8		6.7	8.5	9.6
112	spinetoram	malathion-d_6	5.98E-03	-2.52E-02	0.9689	10			154.5	146.8			10.6	4.4
113	spirotetramat	atrazine-d_5	4.02E-02	1.79E-02	0.9952	1		119.4	106.7	92.6		11.0	11.6	5.9
114	spiroxamine	imazalil-d_5	4.59E-01	-5.74E-01	0.9889	2.5		105.9	99.5	90.7		5.3	10.0	11.9
115	tebuconazole	malathion-d_6	4.08E-02	-6.23E-02	0.9898	5			100.1	91.3			12.0	5.3

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Table A.18: CBS-MS/MS figures of merit of pesticides extracted from strawberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	tebufenozide	malathion-d_6	3.75E-02	1.86E-02	0.9931	2.5		110.5	101.9	91.4		8.5	6.6	8.8
117	tebuthiuron	carbofuran-d_3	4.01E-02	-2.85E-02	0.9950	2.5		105.6	93.4	95.2		9.9	5.4	2.6
118	terbumeton	carbofuran-d_3	4.04E-01	-1.63E-01	0.9903	1		109.2	99.0	93.4		8.2	14.6	7.8
119	terbutryn	malathion-d_6	4.69E-01	-1.10E-01	0.9933	0.5	97.2	104.4	104.9	96.4	10.5	10.3	8.7	5.8
120	tetraconazole	atrazine-d_5	1.52E-02	-5.43E-04	0.9903	2.5		99.2	99.9	90.1		14.8	17.2	6.8
121	thiabendazole	dimethoate-d_6	6.13E-02	-3.07E-02	0.9753	1		110.2	109.9	117.0		13.9	13.5	32.8
122	thiacloprid	malathion-d_6	8.28E-02	-6.00E-02	0.9936	2.5		95.8	93.1	100.0		9.9	12.1	8.8
123	thiamethoxam	imazalil-d_5	8.95E-03	-8.61E-04	0.9867	5			91.2	92.6			22.8	19.7
124	thidiazuron	atrazine-d_5	7.89E-03	1.21E-04	0.9940	2.5		110.2	91.2	85.9		9.4	10.4	8.5
125	thiobencarb	malathion-d_6	1.64E-02	-2.01E-03	0.9863	2.5		124.2	104.6	98.8		16.5	17.4	9.5
126	triadimefon	atrazine-d_5	9.44E-03	3.60E-03	0.9923	1		108.3	107.5	89.3		10.2	10.8	9.4
127	triadimenol	atrazine-d_5	1.01E-02	2.83E-03	0.9949	1		100.4	99.6	95.0		6.8	8.4	4.0
128	trichlorfon	dimethoate-d_6	1.09E-02	1.06E-01	0.9730	10			98.0	103.3			4.8	11.2
129	tricyclazole	carbofuran-d_3	3.66E-02	-3.16E-02	0.9964	2.5		103.2	90.7	93.0		5.4	9.0	7.9
130	trifloxystrobin	malathion-d_6	4.37E-02	-4.47E-02	0.9886	2.5		113.8	87.4	90.8		13.9	12.6	8.5
131	triflumizole	malathion-d_6	1.10E-02	-7.48E-03	0.9858	5			103.4	102.9			5.8	10.7
132	triflumuron	atrazine-d_5	2.34E-03	-4.78E-03	0.9680	5			102.0	87.1			15.6	9.8
133	triticonazole	atrazine-d_5	1.16E-02	-2.68E-03	0.9938	1		110.0	95.0	94.1		11.7	5.4	5.5
134	vamidothion	imazalil-d_5	1.07E-01	-1.78E-01	0.9379	2.5		110.5	93.1	91.4		19.5	27.0	12.8
135	zoxamide	malathion-d_6	3.74E-02	-2.05E-02	0.9894	2.5		102.4	97.6	93.7		13.1	16.0	7.0

Table A.19: LC-MS/MS figures of merit of pesticides extracted from strawberry matrix.

[Take me back!]

n	Compound	Internal Standard	Slope	Intercept	R^2	LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
						(ng/g)	0.8	4	40	80	0.8	4	40	80
1	3-hydroxycarbofuran	dimethoate-d_6	6.84E-03	-4.86E-03	0.9748	5			85.9	95.7			7.5	13.1
2	acetamiprid	dimethoate-d_6	8.02E-02	-1.13E-02	0.9923	1		101.0	97.6	102.3		8.2	8.2	12.0
3	aldicarb-insource	carbofuran-d_3	4.22E-03	-8.84E-03	0.9854	5			80.3	88.4			11.8	5.3
4	ametryn	atrazine-d_5	9.49E-02	-6.17E-03	0.9967	0.5	104.3	101.0	98.1	97.4	9.8	4.2	6.7	3.2
5	aminocarb	dimethoate-d_6	7.73E-02	-7.97E-02	0.9912	5			106.6	107.1			2.6	5.0
6	amitraz	atrazine-d_5	1.05E-02	-7.76E-04	0.9897	1		91.7	91.5	93.7		13.7	6.9	6.7
7	azoxystrobin	atrazine-d_5	4.32E-02	-5.20E-04	0.9960	0.5	96.7	94.3	88.3	88.6	15.7	4.6	4.3	6.8
8	benalaxyl	methiocarb-d_3	1.54E-01	-9.09E-03	0.9941	0.5	98.6	93.3	96.2	87.9	13.8	5.7	3.3	4.3
9	bendiocarb	atrazine-d_5	1.22E-02	-7.66E-03	0.9966	2.5		116.2	102.6	98.4		8.4	2.5	2.5
10	boscalid	atrazine-d_5	1.65E-02	1.51E-03	0.9947	2.5		93.9	92.8	93.2		9.3	9.5	6.2
11	bromucanozole	atrazine-d_5	4.86E-03	-1.01E-03	0.9940	2.5		102.4	88.7	91.2		3.3	10.0	5.1
12	bupirimate	malathion-d_6	2.82E-02	-2.41E-03	0.9909	1		115.3	114.6	102.6		16.2	4.7	9.1
13	buprofenzin	malathion-d_6	1.05E-01	-3.57E-02	0.9933	2.5		96.5	97.7	93.0		7.0	10.2	2.0
14	butafenacil	methiocarb-d_3	4.84E-02	-2.18E-02	0.9907	2.5		101.6	89.6	86.6		2.5	5.6	6.5
15	butoxycarboxim	dimethoate-d_6	9.85E-02	2.29E-03	0.9926	0.5	99.0	98.5	104.6	106.8	15.3	14.0	9.0	8.3
16	carbaryl	atrazine-d_5	8.79E-03	-3.14E-03	0.9954	2.5		114.1	101.7	103.6		7.6	7.3	2.7
17	carbendazim	dimethoate-d_6	1.49E-01	1.89E-02	0.9963	1		111.0	103.2	103.5		7.4	2.7	5.2
18	carbetamide	carbofuran-d_3	5.86E-03	-2.58E-03	0.9818	2.5		108.1	91.0	83.9		12.1	15.9	9.0
19	carbofuran	carbofuran-d_3	3.72E-02	-7.53E-03	0.9970	1		102.3	97.0	91.8		12.9	8.1	9.3
20	carfentrazone-ethyl	methiocarb-d_3	2.96E-02	-9.93E-03	0.9895	2.5		93.1	84.5	77.2		9.4	4.7	4.6
21	chlorantraniliprole	dimethoate-d_6	2.23E-02	-7.78E-03	0.9939	1		94.8	92.6	91.8		20.6	8.3	9.9
22	chlorotoluron	atrazine-d_5	1.09E-02	-4.88E-04	0.9955	0.5	104.8	96.1	100.0	99.1	12.1	6.9	4.3	6.6
23	chloroxuron	atrazine-d_5	1.34E-02	-3.71E-04	0.9905	1		102.0	87.8	88.7		9.7	8.0	4.7
24	clothianidin	dimethoate-d_6	7.66E-03	-6.75E-03	0.9916	5			96.7	90.7			8.5	8.4
25	cyazofamid	atrazine-d_5	2.84E-03	-5.21E-04	0.9864	2.5		90.8	91.7	90.7		13.6	10.4	10.4
26	cycluron	metalaxyl-d_6	2.94E-02	-6.23E-03	0.9967	1		109.4	98.7	99.1		2.1	6.1	7.3
27	cyproconazole	atrazine-d_5	1.22E-02	1.93E-03	0.9973	1		107.3	99.2	96.4		2.4	6.6	0.9
28	cyprodinil	cyprodinil-d_5	1.66E-01	-1.25E-02	0.9935	2.5		109.6	115.0	104.1		12.9	10.3	10.3
29	desmedipham	atrazine-d_5	1.05E-02	-5.75E-03	0.9929	2.5		106.3	97.3	98.4		2.0	1.7	10.3
30	diclobutrazol	atrazine-d_5	8.31E-03	-4.92E-04	0.9945	2.5		89.1	96.0	98.1		11.5	2.7	4.4
31	dicrotophos	dimethoate-d_6	2.37E-02	-2.30E-02	0.9959	5			92.9	95.6			7.2	6.0
32	diethofencarb	atrazine-d_5	1.10E-02	-1.28E-03	0.9932	2.5		99.1	100.7	98.3		13.5	3.6	6.4
33	difenoconazole	trifloxystrobin-d_6	2.55E-02	1.88E-03	0.9913	1		104.8	107.3	112.4		16.9	12.1	13.8
34	dimethoate	dimethoate-d_6	2.96E-02	-1.74E-02	0.9942	2.5		109.3	99.7	100.2		6.3	10.3	4.2
35	dimethomorph	atrazine-d_5	1.11E-02	4.15E-03	0.9942	2.5		89.8	90.9	87.1		5.2	7.3	5.6
36	dimoxystrobin	methiocarb-d_3	4.68E-02	-2.16E-02	0.9934	2.5		104.6	91.9	84.4		13.6	6.6	3.1
37	dioxacarb	metalaxyl-d_6	2.02E-02	-1.45E-02	0.9935	2.5		111.2	101.3	102.1		4.5	4.7	4.2
38	diuron	atrazine-d_5	9.79E-03	-4.40E-03	0.9969	2.5		107.0	101.8	94.8		9.2	1.9	3.2
39	epoxiconazole	atrazine-d_5	1.60E-02	4.98E-03	0.9959	1		88.2	92.1	91.3		10.0	2.6	4.0
40	etaconazole	atrazine-d_5	1.49E-02	3.08E-03	0.9947	1		98.0	101.8	94.2		6.5	5.4	5.8
41	ethiprole	metalaxyl-d_6	3.40E-02	-2.36E-03	0.9956	1		103.3	99.2	95.4		13.1	6.2	3.7
42	ethirimol	dimethoate-d_6	3.17E-02	-1.02E-02	0.9911	2.5		107.9	97.6	98.9		6.2	1.5	6.5
43	ethofumesate	malathion-d_6	3.14E-02	-3.13E-03	0.9879	2.5		118.2	118.6	104.7		7.6	7.0	2.7
44	etoxazole	trifloxystrobin-d_6	4.27E-03	5.48E-04	0.9700	10			92.5	80.4			12.3	18.3
45	fenamidone	atrazine-d_5	1.57E-02	-1.63E-03	0.9953	1		97.3	98.2	93.1		13.4	8.2	6.7
46	fenarimol	atrazine-d_5	3.69E-03	-5.96E-04	0.9923	5			92.9	88.6			7.0	9.0
47	fenbuconazole	methiocarb-d_3	1.37E-02	1.52E-03	0.9931	1		102.6	88.7	85.7		17.7	6.8	4.5
48	fenhexamid	atrazine-d_5	4.67E-03	-3.08E-04	0.9949	1		107.1	101.6	98.3		8.5	4.3	7.5
49	fenobucarb	atrazine-d_5	3.66E-02	-3.74E-03	0.9960	0.5	119.4	98.5	103.9	103.6	14.3	6.1	2.8	6.0
50	fenoxycarb	malathion-d_6	1.11E-02	-1.13E-02	0.9787	5			91.3	79.6			11.8	13.5
51	fenpropimorph	methiocarb-d_3	7.35E-02	1.01E-02	0.9962	1		105.3	112.3	97.3		9.7	3.3	4.6
52	fenuron	imazalil-d_5	1.02E-01	-1.08E-01	0.9903	2.5		114.0	97.6	97.9		5.7	9.1	7.8
53	flufenacet	atrazine-d_5	2.04E-02	-2.71E-03	0.9929	1		95.4	94.6	96.5		6.8	3.9	7.9
54	fluometuron	atrazine-d_5	2.11E-02	1.04E-04	0.9945	2.5		100.8	106.9	102.9		3.6	3.4	2.1
55	fluoxastrobin	atrazine-d_5	2.06E-02	8.05E-04	0.9896	1		85.0	84.0	84.0		2.8	3.1	4.7
56	flusilazole	atrazine-d_5	2.00E-02	-1.48E-03	0.9949	0.5	101.5	97.5	88.7	91.8	12.5	12.5	5.9	6.5

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Table A.19: LC-MS/MS figures of merit of pesticides extracted from strawberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
57	flutolanil	atrazine-d_5	6.00E-02	-1.20E-03	0.9928	0.5	90.0	99.3	101.6	95.3	7.3	2.9	4.2	3.6
58	flutriafol	spirotetramat-d_6	4.15E-02	-7.72E-04	0.9954	1		99.8	104.1	94.0		7.2	14.0	13.2
59	forchlorfenuron	atrazine-d_5	1.59E-02	1.39E-03	0.9974	1		98.2	95.8	92.1		6.9	6.4	2.2
60	fuberidazole	imazalil-d_5	2.93E-01	-1.67E-01	0.9921	2.5		107.4	99.5	100.4		8.4	7.0	6.2
61	furalaxyl	methiocarb-d_3	2.05E-01	1.63E-03	0.9980	0.25	101.4	107.4	105.5	94.8	7.4	4.6	3.0	3.1
62	furathiocarb	methiocarb-d_3	1.95E-02	-3.56E-03	0.9866	1		99.2	74.7	67.4		10.0	11.2	10.2
63	hexaconazole	methiocarb-d_3	2.16E-02	-1.27E-03	0.9937	2.5		107.9	103.7	91.3		6.9	8.7	5.0
64	imazalil	carbofuran-d_3	1.17E-02	5.85E-04	0.9935	1		109.1	90.5	89.6		19.4	7.3	8.9
65	imidacloprid	dimethoate-d_6	1.72E-02	4.76E-03	0.9911	5			93.5	97.6			5.0	8.9
66	ipconazole	methiocarb-d_3	2.11E-02	-8.22E-03	0.9893	2.5		102.5	87.5	86.3		10.1	2.2	4.5
67	iprovalicarb	atrazine-d_5	1.79E-02	-5.95E-03	0.9948	2.5		96.3	98.1	99.1		8.8	2.7	4.8
68	isoprocarb	atrazine-d_5	3.06E-02	-6.34E-03	0.9942	1		100.2	104.8	103.0		11.5	2.9	5.0
69	isoproturon	atrazine-d_5	1.68E-02	-3.42E-03	0.9949	1		95.3	102.0	100.5		8.2	3.7	3.5
70	kresoxim-methyl	atrazine-d_5	4.13E-04	-6.57E-04	0.9771	5			91.3	79.0			12.2	7.6
71	linuron	atrazine-d_5	1.20E-02	-2.67E-03	0.9923	1		80.1	93.0	103.6		15.4	5.0	5.8
72	mandipropamid	atrazine-d_5	1.05E-02	8.01E-04	0.9904	1		84.1	83.1	89.5		8.6	3.5	3.6
73	mefenacet	atrazine-d_5	1.96E-02	-1.44E-03	0.9916	0.5	99.2	89.8	87.3	86.7	13.2	6.1	6.2	5.7
74	mepanipyrim	methiocarb-d_3	3.64E-02	6.55E-03	0.9864	5			85.8	78.0			10.2	8.9
75	mepronil	atrazine-d_5	5.27E-02	-4.34E-03	0.9934	0.5	94.0	92.0	95.5	95.7	6.4	3.2	3.6	7.0
76	metalaxyl	metalaxyl-d_6	5.71E-02	-2.74E-03	0.9979	0.5	104.7	99.3	98.8	99.5	16.0	4.8	3.2	4.2
77	metconazole	malathion-d_6	6.63E-03	7.16E-04	0.9758	2.5		103.2	105.5	96.3		12.9	5.5	5.4
78	methabenzthiazuron	atrazine-d_5	2.10E-02	-5.35E-04	0.9958	1		88.9	99.1	97.5		11.0	4.2	3.9
79	methiocarb	atrazine-d_5	5.26E-03	-9.06E-03	0.9885	5			96.4	95.7			8.8	7.3
80	methomyl	dimethoate-d_6	5.26E-03	-2.92E-03	0.9836	10			97.5	98.0			14.5	3.2
81	methoprotryne	metalaxyl-d_6	7.83E-02	-3.81E-03	0.9949	0.5	110.5	107.8	95.7	99.2	8.4	6.0	2.0	5.3
82	methoxyfenozide	metalaxyl-d_6	2.65E-03	1.65E-04	0.9826	5			96.8	93.8			9.5	12.0
83	metobromuron	atrazine-d_5	1.96E-02	-1.23E-02	0.9961	2.5		111.5	103.8	95.7		8.3	4.8	1.5
84	metribuzin	atrazine-d_5	8.11E-03	-2.59E-03	0.9935	2.5		102.6	97.3	90.8		25.8	3.9	4.9
85	mevinphos	carbofuran-d_3	1.34E-02	-6.75E-03	0.9948	2.5		97.3	95.6	95.4		12.2	4.5	8.2
86	mexacarbate	dimethoate-d_6	1.21E-01	-3.31E-03	0.9882	2.5		111.5	103.7	109.7		5.5	14.4	9.6
87	monolinuron	malathion-d_6	4.55E-02	-9.52E-02	0.9825	5			115.8	106.6			7.0	5.9
88	myclobutanil	atrazine-d_5	8.00E-03	9.14E-04	0.9937	1		96.6	106.7	101.2		7.5	4.1	6.0
89	neburon	atrazine-d_5	6.40E-03	-1.39E-03	0.9893	2.5		86.4	91.6	89.9		11.3	4.2	8.5
90	nuarimol	atrazine-d_5	6.60E-03	-2.60E-03	0.9964	2.5		105.0	96.8	95.0		10.7	4.0	6.6
91	oxadixyl	dimethoate-d_6	3.78E-02	1.16E-02	0.9946	2.5		115.6	93.7	94.4		9.3	5.5	5.7
92	paclobutrazol	atrazine-d_5	1.73E-02	-1.23E-03	0.9976	0.5	109.5	97.0	99.5	97.1	7.0	8.9	3.8	3.1
93	penconazole	methiocarb-d_3	4.35E-02	-5.31E-03	0.9936	1		98.0	102.7	92.5		7.4	8.3	3.6
94	pencycuron	malathion-d_6	9.19E-02	-1.17E-02	0.9902	1		91.2	81.1	77.2		7.8	3.3	6.5
95	picoxystrobin	malathion-d_6	3.63E-02	-3.33E-02	0.9869	5			99.1	87.9			8.9	11.2
96	piperonyl butoxide	trifloxystrobin-d_6	4.38E-02	1.22E-02	0.9913	2.5		93.9	102.8	111.7		24.2	14.3	10.8
97	pirimicarb	imazalil-d_5	1.58E-01	-1.10E-01	0.9900	2.5		112.2	99.4	97.3		5.7	9.1	6.3
98	prochloraz	methiocarb-d_3	1.07E-02	8.68E-04	0.9898	5			83.9	81.0			5.4	2.1
99	promecarb	atrazine-d_5	2.54E-02	-4.41E-03	0.9949	0.5	103.6	101.6	99.5	101.3	7.2	4.0	2.5	2.1
100	prometon	metalaxyl-d_6	1.13E-01	3.26E-03	0.9970	0.5	83.0	100.3	104.1	101.9	8.4	9.4	7.1	4.7
101	prometryne	atrazine-d_5	9.23E-02	-7.40E-04	0.9952	0.25	100.8	102.3	100.8	98.4	8.7	8.4	2.1	3.4
102	propham	malathion-d_6	6.19E-03	1.60E-03	0.9741	10			125.8	106.5			15.7	7.1
103	propiconazole	atrazine-d_5	1.13E-02	5.02E-04	0.9935	2.5		100.6	93.7	94.7		14.0	4.5	3.2
104	propoxur	atrazine-d_5	7.62E-03	-2.39E-03	0.9930	1		94.5	100.8	95.8		8.0	5.9	2.6
105	pyracarbolid	atrazine-d_5	4.10E-02	5.18E-04	0.9977	0.5	97.4	97.6	103.8	98.6	9.8	8.8	2.0	2.6
106	pyraclostrobin	trifloxystrobin-d_6	9.04E-03	-1.20E-02	0.9877	5			102.6	99.3			10.1	7.5
107	pyrimethanil	atrazine-d_5	1.65E-02	-4.04E-03	0.9932	1		96.6	95.4	95.7		3.1	4.3	4.6
108	quinoxyfen	trifloxystrobin-d_6	8.18E-03	-4.87E-03	0.9821	10			116.0	95.4			12.9	19.3
109	secbumeton	atrazine-d_5	7.96E-02	-8.16E-03	0.9956	0.5	112.3	103.9	101.1	97.5	9.7	3.9	5.6	5.9
110	siduron	atrazine-d_5	2.85E-02	-1.56E-03	0.9972	0.5	110.2	98.7	97.4	92.0	8.3	9.0	3.3	1.9
111	simetryn	atrazine-d_5	3.04E-02	-4.83E-03	0.9956	0.5	103.0	98.1	99.4	96.9	9.5	5.5	4.8	3.3
112	spinetoram	carbofuran-d_3	2.54E-03	-7.24E-04	0.9860	5			78.0	94.0			10.6	12.0
113	spirotetramat	spirotetramat-d_6	4.83E-02	-1.62E-02	0.9924	2.5		100.2	102.7	96.6		5.7	9.3	12.2
114	spiroxamine	metalaxyl-d_6	4.43E-02	3.46E-03	0.9944	1		107.4	103.0	101.3		6.4	5.9	4.3
115	tebuconazole	atrazine-d_5	8.88E-03	-1.27E-03	0.9910	2.5		91.5	95.5	94.1		10.1	4.9	7.9

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Table A.19: LC-MS/MS figures of merit of pesticides extracted from strawberry matrix – continued from previous page

						LOQ	Accuracy, % (n = 4, ng/g)				Precision, % (n = 4, ng/g)			
n	**Compound**	**Internal Standard**	**Slope**	**Intercept**	**R^2**	**(ng/g)**	**0.8**	**4**	**40**	**80**	**0.8**	**4**	**40**	**80**
116	tebufenozide	atrazine-d_5	2.07E-03	-6.66E-04	0.9864	5			97.9	94.7			4.4	8.5
117	tebuthiuron	imazalil-d_5	4.10E-01	-3.61E-01	0.9930	2.5		110.7	95.9	95.8		7.3	7.7	6.2
118	terbumeton	atrazine-d_5	1.68E-01	-6.26E-04	0.9966	0.5	109.3	105.2	102.4	97.7	4.3	3.0	4.9	4.6
119	terbutryn	atrazine-d_5	1.09E-01	-3.69E-03	0.9958	0.25	105.4	96.8	95.9	95.5	6.3	2.8	5.2	4.4
120	tetraconazole	atrazine-d_5	9.08E-03	-4.29E-05	0.9926	2.5		101.2	99.8	104.2		17.1	7.9	6.3
121	thiabendazole	imazalil-d_5	2.16E-01	-1.61E-01	0.9884	2.5		110.7	98.9	99.6		3.8	6.6	5.3
122	thiacloprid	carbofuran-d_3	6.39E-02	2.56E-03	0.9952	0.5	100.4	99.2	92.4	93.8	12.7	9.4	11.0	8.9
123	thiamethoxam	dimethoate-d_6	1.02E-02	-2.24E-03	0.9860	5			95.2	100.0			6.7	14.1
124	thidiazuron	carbofuran-d_3	6.09E-03	-2.78E-03	0.9953	2.5		111.8	89.5	87.3		11.7	1.3	9.0
125	thiobencarb	trifloxystrobin-d_6	8.48E-02	-1.22E-02	0.9894	1		112.3	116.3	114.1		7.0	4.4	13.2
126	triadimefon	malathion-d_6	3.55E-02	1.67E-03	0.9889	2.5		108.9	112.5	100.8		13.6	5.3	3.2
127	triadimenol	atrazine-d_5	1.30E-03	-1.19E-03	0.9780	5			101.5	98.8			7.8	4.7
128	trichlorfon	dimethoate-d_6	1.23E-02	3.29E-03	0.9719	5			87.6	86.6			10.1	7.9
129	tricyclazole	carbofuran-d_3	6.64E-02	-3.26E-03	0.9925	1		96.0	92.8	90.4		15.7	9.0	10.9
130	trifloxystrobin	trifloxystrobin-d_6	6.03E-02	-3.54E-02	0.9927	2.5		110.9	104.6	103.9		7.8	10.9	18.5
131	triflumizole	atrazine-d_5	1.91E-03	1.01E-03	0.9753	5			89.6	86.4			8.4	6.9
132	triflumuron	trifloxystrobin-d_6	1.59E-02	-1.98E-02	0.9816	5			113.8	108.9			10.3	12.5
133	triticonazole	atrazine-d_5	4.94E-03	-5.74E-04	0.9917	1		98.2	95.9	93.5		14.6	5.1	4.3
134	vamidothion	dimethoate-d_6	4.11E-02	-2.55E-02	0.9845	5			86.3	93.6			15.5	6.1
135	zoxamide	atrazine-d_5	1.70E-02	-2.33E-03	0.9902	1		85.3	83.2	84.3		12.9	3.6	7.2

Table A.20: Compiled summary of real sample results via CBS-MS/MS and LC-MS/MS.

Matrix	Compound	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		CBS ± SD	LC ± SD	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD	CBS ± SD	LC ± SD
Apple	chlorantraniliprole					1.7 ± 0.1	2 ± 0.3				
	pyrimethanil			3319 ± 657.5	3630.1 ± 315.8						
	thiacloprid			21 ± 2	25.6 ± 3.6						
Blueberry	azoxystrobin					18 ± 2.5	17.4 ± 0.7				
	fenbuconazole			4.9 ± 0.9	5.1 ± 0.8						
Grape	boscalid	63.6 ± 10.4	67.4 ± 6.7							184.3 ± 34.2	199 ± 22.4
	buprofenzin	10.9 ± 0.5	12.5 ± 0.6	2.3 ± 0.2	2.7 ± 0.3						
	chlorantraniliprole			7.4 ± 0.4	7.3 ± 0.2						
	cyprodinil			1.9 ± 0.2	3.7 ± 0.5						
	etoxazole			6.9 ± 0.6	6.1 ± 1						
	imidacloprid	34 ± 1.9	28 ± 7.3			7.3 ± 1.4	6.7 ± 1.5	10.8 ± 1.4	14.6 ± 1	46.8 ± 13	47.8 ± 5.6
	methoxyfenozide	84.1 ± 6	55.8 ± 9								
	myclobutanil									38 ± 4.7	34.5 ± 3.8
	pyraclostrobin	19 ± 2.1	17.3 ± 2.6							97.2 ± 8.4	87 ± 19.2
	pyrimethanil	211.5 ± 12.3	260.8 ± 34.3	202.4 ± 12.4	308.2 ± 32.7						
	quinoxyfen	16.2 ± 2	16.4 ± 2.6								
	spirotetramat							85.5 ± 3.1	73.9 ± 8.3	21.7 ± 0.7	20.6 ± 2.6
	tebuconazole							35.4 ± 6.5	51.3 ± 9		
	trifloxystrobin							50.6 ± 0.7	38.7 ± 7.1	1.9 ± 0.2	2.6 ± 0.3
Strawberry	acetamiprid			573.5 ± 41.7	606.9 ± 44						
	azoxystrobin			80.8 ± 6.4	95.7 ± 3.2						
	boscalid	13.2 ± 1.6	8.2 ± 0.8	5.2 ± 0.8	2.9 ± 0.3	7.1 ± 1.9	4.2 ± 0.3	3.4 ± 0.7	2.6 ± 0.2		
	chlorantraniliprole	3.6 ± 0.2	4.4 ± 1			3.7 ± 0.9	3.7 ± 0.4	3.1 ± 0.4	4.3 ± 0.1		
	cyprodinil			346.7 ± 24.7	485.9 ± 52.1			391.8 ± 29.8	537 ± 39.3		
	difenoconazole			97.9 ± 14	108.3 ± 6.2						
	fludioxonil			N/A	291.3 ± 18.4			N/A	270.3 ± 20.4		
	imidacloprid			5.7 ± 0.5	6.3 ± 1.3						
	metalaxyl	1.3 ± 0.2	1.2 ± 0.1					13.5 ± 2.5	14.4 ± 0.7		
	mevinphos			6.2 ± 0.1	8 ± 0.7						
	myclobutanil			18.6 ± 1.8	20.2 ± 0.7			2.7 ± 0.7	1.5 ± 0.1		
	propiconazole			51.7 ± 7.2	51.1 ± 3.6						
	pyraclostrobin	4.4 ± 0.9	3.7 ± 1	770 ± 63	849.8 ± 45.9	4.1 ± 2.1	2.5 ± 0.3	4.9 ± 0.8	5.3 ± 2		
	pyrimethanil	140.5 ± 4.1	162 ± 9			11.7 ± 2.1	13.8 ± 1.1				
	quinoxyfen			186.4 ± 18.8	161 ± 7.6						
	spinetoram			15.2 ± 1.3	14.4 ± 1.2						

A.4 Chapter 4

Table A.21: Details and characteristics of pesticides and plant growth regulators under study. [Take me back!]

Compound	Molecular formula	M_{mi} (Da)	LogP	MRL (mg/kg)	RT (min)	Adduct	Q1 (m/z)	Q3 (m/z)	
Abamectin	$C_{48}H_{72}O_{14}$	872.49219	5.94	0.25	7	$[M+NH_4]^+$	891	567	305
Acephate	$C_4H_{10}NO_3PS$	183.0119	-0.85	0.05	1.88	$[M+H]^+$	184	125	143
Acetamiprid	$C_{10}H_{11}ClN_4$	222.06723	0.62	0.05	3.02	$[M+H]^+$	223	99	126
Aldicarb	$C_7H_{14}N_2O_2S$	190.07759	1.13	0.5	3.34	$[M-C_2H_5NO_2+H]^+$	116	61	89
Azoxystrobin	$C_{22}H_{17}N_3O_5$	403.11682	5.13	0.01	4.4	$[M+H]^+$	404	344	372
Benzovindiflupyr	$C_{18}H_{15}Cl_2F_2N_3O$	397.05603	3.95	0.01	5.33	$[M+H]^+$	398	342	378
Bifenazate	$C_{17}H_{20}N_2O_3$	300.1474	3.12	0.01	4.79	$[M+H]^+$	301	170	198
Boscalid	$C_{18}H_{12}Cl_2N_2O$	342.03265	4.31	0.01	4.53	$[M+H]^+$	343	140	307
Buprofezin	$C_{16}H_{23}N_3OS$	305.15619	4.29	-	6.25	$[M+H]^+$	306	116	201
Carbaryl	$C_{12}H_{11}NO_2$	201.07898	3.35	0.025	3.69	$[M+H]^+$	202	127	145
Carbofuran	$C_{12}H_{15}NO_3$	221.10519	1.76	0.01	3.62	$[M+H]^+$	222	123	165
Chlorantraniliprole	$C_{18}H_{14}BrCl_2N_5O_2$	480.9708	5.55	-	4.18	$[M+H]^+$	484	286	453
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	348.92627	4.77	0.5	6.32	$[M+H]^+$	350	97	198
Clofentezine	$C_{14}H_8Cl_2N_4$	302.0126	3.27	0.01	5.57	$[M+H]^+$	303	138	102
Clothianidin	$C_6H_8ClN_5O_2S$	249.00873	0.4	0.025	2.82	$[M+H]^+$	250	132	169
Coumaphos	$C_{14}H_{16}ClO_5PS$	362.01447	3.86	0.01	5.48	$[M+H]^+$	363	227	307
Cyantraniliprole	$C_{19}H_{14}BrClN_6O_2$	472.00501	4.63	0.01	3.73	$[M+H]^+$	475	286	444
Cyprodinil	$C_{14}H_{15}N_3$	225.1266	4	0.01	4.44	$[M+H]^+$	226	77	93
Daminozide	$C_6H_{12}N_2O_3$	160.08479	-1.14	-	0.59	$[M+H]^+$	161	101	143
Diazinon	$C_{12}H_{21}N_2O_3PS$	304.10104	3.81	-	5.5	$[M+H]^+$	305	153	169
Dichlorvos	$C_4H_7Cl_2O_4P$	219.94591	0.71	0.05	3.56	$[M+H]^+$	221	79	109
Dimethoate	$C_5H_{12}NO_3PS_2$	228.99962	1.32	0.01	2.95	$[M+H]^+$	230	125	199
Dimethomorph	$C_{21}H_{22}ClNO_4$	387.12375	3.71	-	4.67	$[M+H]^+$	388	165	301
Dinotefuran	$C_7H_{14}N_4O_3$	202.10658	-0.7	0.05	2.2	$[M+H]^+$	203	129	157
Dodemorph	$C_{18}H_{35}NO$	281.27185	6.1	-	4.42	$[M+H]^+$	282	98	116
Ethoprophos	$C_8H_{19}O_2PS_2$	242.05641	3.59	0.01	5.08	$[M+H]^+$	243	131	173
Etofenprox	$C_{25}H_{28}O_3$	376.20386	7.34	-	7.13	$[M+NH4]^+$	394	107	177
Etoxazole	$C_{21}H_{23}F_2NO_2$	359.16968	5.85	-	6.52	$[M+H]^+$	360	141	304
Fenoxycarb	$C_{17}H_{19}NO_4$	301.13141	3.83	0.01	5.16	$[M+H]^+$	302	88	116
Fenpyroximate	$C_{24}H_{27}N_3O_4$	421.20017	6.44	-	6.71	$[M+H]^+$	422	135	366
Fensulfothion	$C_{11}H_{17}O_4PS_2$	308.03058	2.23	0.01	4.09	$[M+H]^+$	309	157	173
Fenthion	$C_{10}H_{15}O_3PS_2$	278.02002	3.21	0.01	5.3	$[M+H]^+$	279	169	247
Fipronil	$C_{12}H_4Cl_2F_6N_4OS$	435.93869	4.76	0.01	5.07	$[M-H]^-$	435	250	330
Flonicamid	$C_9H_6F_3N_3O$	229.0463	0.84	0.025	2.5	$[M+H]^+$	230	148	203
Fludioxonil	$C_{12}H_6F_2N_2O_2$	248.03973	3.67	0.01	4.4	$[M-H]^-$	247	126	169
Fluopyram	$C_{16}H_{11}ClF_6N_2O$	396.04642	4.36	0.01	4.83	$[M+H]^+$	397	173	208
Hexythiazox	$C_{17}H_{21}ClN_2O_2S$	352.10123	3.41	-	6.36	$[M+H]^+$	353	168	228
Imazalil	$C_{14}H_{14}Cl_2N_2O$	296.04831	3.58	0.01	4.17	$[M+H]^+$	297	159	201
Imidacloprid	$C_9H_{10}ClN_5O_2$	255.05231	-0.43	0.01	2.82	$[M+H]^+$	256	175	209
Iprodione	$C_{13}H_{13}Cl_2N_3O_3$	329.03339	2.8	0.5	4.75	$[M+H]^+$	330	245	
Kresoxim-methyl	$C_{18}H_{19}NO_4$	313.13141	4.34	0.15	5.3	$[M+H]^+$	314	116	206
Malathion	$C_{10}H_{19}O_6PS_2$	330.03607	2.92	0.01	4.61	$[M+H]^+$	331	99	127
Metalaxyl	$C_{15}H_{21}NO_4$	279.14706	2.15	0.01	4.14	$[M+H]^+$	280	160	220
Methiocarb	$C_{11}H_{15}NO_2S$	225.08235	2.88	0.01	4.43	$[M-C_2H_3NO+H]^+$	169	121	107
Methomyl	$C_5H_{10}N_2O_2S$	162.0463	0.6	0.025	2.53	$[M+H]^+$	163	88	106
Mevinphos	$C_7H_{13}O_6P$	224.04497	0.28	0.025	3.22	$[M+H]^+$	225	127	193
Myclobutanil	$C_{15}H_{17}ClN_4$	288.11417	2.82	0.01	4.68	$[M+H]^+$	289	70	125
Naled	$C_4H_7Br_2Cl_2O_4P$	377.78256	1.86	-	4.13	$[M+H]^+$	381	383	127
Novaluron	$C_{17}H_9ClF_8N_2O_4$	492.0123	6.78	0.025	5.89	$[M+H]^+$	493	141	158
Oxamyl	$C_7H_{13}N_3O_3S$	219.06776	-0.47	1.5	2.43	$[M+NH4]^+$	237	72	90
Paclobutrazol	$C_{15}H_{20}ClN_3O$	293.12949	2.99	0.01	4.6	$[M+H]^+$	294	70	125

Continued on next page

Compound	Molecular formula	M_{mi} (Da)	LogP	MRL (mg/kg)	RT (min)	Adduct	Q1 (m/z)	Q3 (m/z)	
Phosmet	$C_{11}H_{12}NO_4PS_2$	316.99454	2.84	-	4.2	$[M+H]^+$	318	160	77
Piperonyl butoxide	$C_{19}H_{30}O_5$	338.20932	4.23	1.25	4.75	$[M+NH4]^+$	356	177	119
Pirimicarb	$C_{11}H_{18}N_4O_2$	238.14298	1.7	0.01	3.88	$[M+H]^+$	239	72	182
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	341.06979	3.88	-	5.54	$[M+H]^+$	342	69	159
Propoxur	$C_{11}H_{15}NO_3$	209.10519	1.6	0.01	3.59	$[M+H]^+$	210	111	168
Pyraclostrobin	$C_{19}H_{18}ClN_3O_4$	387.09857	4.25	0.01	5.56	$[M+H]^+$	388	163	194
Pyridaben	$C_{19}H_{25}ClN_2OS$	364.1376	4.73	0.02	6.89	$[M+H]^+$	365	309	147
Spinetoram J	$C_{42}H_{69}NO_{10}$	747.49215	5.51	0.01	6.21	$[M+H]^+$	749	98	142
Spinetoram L	$C_{43}H_{69}NO_{10}$	759.49215	5.92	0.01	6.42	$[M+H]^+$	761	98	142
Spinosyn A	$C_{41}H_{65}NO_{10}$	731.46085	4.8	0.01	6.14	$[M+H]^+$	733	98	
Spinosyn D	$C_{42}H_{67}NO_{10}$	745.4765	5.39	0.01	5.9	$[M+H]^+$	747	98	
Spirodiclofen	$C_{21}H_{24}Cl_2O_4$	410.10516	6.36	-	6.71	$[M+H]^+$	411	71	313
Spiromesifen	$C_{23}H_{30}O_4$	370.21442	6.07	-	6.56	$[M+H]^+$	371	255	273
Spirotetramat	$C_{21}H_{27}NO_5$	373.18893	4.59	0.01	4.99	$[M+H]^+$	374	216	302
Spiroxamine	$C_{18}H_{35}NO_2$	297.26679	4.88	-	4.63	$[M+H]^+$	298	100	144
Tebuconazole	$C_{16}H_{22}ClN_3O$	307.14514	3.58	0.01	5.32	$[M+H]^+$	308	70	125
Tebufenozide	$C_{22}H_{28}N_2O_2$	352.21509	4.24	0.01	5.22	$[M+H]^+$	353	105	133
Teflubenzuron	$C_{14}H_6Cl_2F_4N_2O_2$	379.97424	5.49	0.025	6.05	$[M+H]^+$	381	141	158
Tetrachlorvinphos	$C_{10}H_9Cl_4O_4P$	363.89926	3.86	0.01	5.27	$[M+H]^+$	365	127	239
Thiacloprid	$C_{10}H_9ClN_4S$	252.02365	0.55	0.01	3.17	$[M+H]^+$	253	99	126
Thiamethoxam	$C_8H_{10}ClN_5O_3S$	291.01929	-1.16	0.01	2.56	$[M+H]^+$	292	181	211
Thiophanate-methyl	$C_{12}H_{14}N_4O_4S_2$	342.04565	1.16	-	3.49	$[M+H]^+$	343	151	268
Trifloxystrobin	$C_{20}H_{19}F_3N_2O_4$	408.1297	5.11	0.01	5.88	$[M+H]^+$	409	145	186

Table A.22: Internal standard compound details.

Compound	M_{mi} (Da)	RT (min)1	Adduct	Q1 (m/z)	Q3 (m/z)	
Acephate-d_3	186.03073	1.87	$[M+H]^+$	187	125	143
Atrazine-d_5	220.12516	3.99	$[M+H]^+$	221	137	179
Carbofuran-d_3	224.12402	3.62	$[M+H]^+$	225	123	165
Chlorpyrifos-d_{10}	358.98905	6.31	$[M+H]^+$	360	199	-
Cyprodinil-d_5	230.15798	4.42	$[M+H]^+$	231	94	109
Dimethoate-d_6	235.03728	2.94	$[M+H]^+$	236	131	205
Fludioxonil-$^{13}C_2$	250.04644	4.4	$[M-H]^-$	249	182	183
Imazalil-d_5	301.07971	4.14	$[M+H]^+$	302	1589	203
Kresoxim-methyl-d_7	320.17535	5.27	$[M+H]^+$	321	228	273
Malathion-d_6	336.07373	4.59	$[M+H]^+$	337	99	127
Metalaxyl-d_6	285.18472	4.12	$[M+H]^+$	286	166	226
Oxamyl-d_6	225.10542	2.42	$[M+NH_4]^+$	243	78	96
Spirotetramat-d_5	378.22031	4.97	$[M+H]^+$	379	303	335
Trifloxystrobin-d_6	414.16735	5.86	$[M+H]^+$	415	145	186

Table A.23: Central composite design coded and uncoded levels.

Shorthand label	Temperature	Time	Temperature	Time
a0	-1.414213562	0	18.8	35
a0	-1.414213562	0	18.8	35
a0	-1.414213562	0	18.8	35
	-1	-1	25	15
	-1	-1	25	15
	-1	-1	25	15
+	-1	1	25	55
+	-1	1	25	55
+	-1	1	25	55
0a	0	-1.414213562	40	6.7
0a	0	-1.414213562	40	6.7
0a	0	-1.414213562	40	6.7
0	0	0	40	35
0	0	0	40	35
0	0	0	40	35
0	0	0	40	35
0	0	0	40	35
0	0	0	40	35
0A	0	1.414213562	40	63.3
0A	0	1.414213562	40	63.3
0A	0	1.414213562	40	63.3
+	1	-1	55	15
+	1	-1	55	15
+	1	-1	55	15
++	1	1	55	55
++	1	1	55	55
++	1	1	55	55
A0	1.414213562	0	61.2	35
A0	1.414213562	0	61.2	35
A0	1.414213562	0	61.2	35

Table A.24: LC-MS/MS figures of merit of pesticides extracted from cannabis oil matrix.

n	Compound	Internal Standard	Slope	Intercept	R^2	MRL Health Canada (ng/g)	LOQ (ng/g)	Accuracy, ng/g (%)			Precision, ng/g (%)		
								15	80	150	15	80	150
1	acephate	atrazine-d_5	2.45E-02	1.03E-01	0.9864	50	10	92	103	101	11	4	5
2	acetamiprid	dimethoate-d_6	1.17E-02	4.47E-03	0.9920	50	5	86	103	96	21	5	13
3	aldicarb	carbofuran-d_3	3.27E-03	5.75E-03	0.9846	500	25		92	88		14	10
4	azoxystrobin	acephate-d_3	1.35E+04	1.62E+03	0.9954	10	2.5	87	98	95	9	17	2
5	benzovindiflupyr	acephate-d_3	2.12E+03	-1.45E+03	0.9896	10	10	90	98	90	29	7	2
6	boscalid	dimethoate-d_6	3.01E-02	2.30E-02	0.9939	10	5	77	95	93	10	6	12
7	carbaryl	carbofuran-d_3	3.78E-03	-4.52E-03	0.9796	25	10	95	95	91	1	7	4
8	carbofuran	carbofuran-d_3	3.78E-03	4.99E-03	0.9737	10	10	68	89	87	24	7	4
9	chlorantraniliprole	dimethoate-d_6	1.67E-02	-5.21E-03	0.9938	-	5	86	97	92	4	7	9
10	clofentezine	carbofuran-d_3	3.48E-03	1.07E-02	0.9623	10	25		97	84		14	25
11	clothianidin	dimethoate-d_6	4.02E-02	9.10E-03	0.9955	25	2.5	83	103	99	10	8	4
12	coumaphos	dimethoate-d_6	2.19E-02	1.27E-03	0.9920	10	5	90	96	92	13	16	4
13	cyantraniliprole	dimethoate-d_6	2.62E-02	-1.04E-02	0.9946	10	2.5	86	97	96	8	4	4
14	daminozide	acephate-d_3	1.93E+04	-2.00E+04	0.9874	-	5	94	105	90	6	5	9
15	diazinon	carbofuran-d_3	1.03E-02	-1.11E-03	0.9900	-	10	88	84	95	15	13	12
16	dichlorvos	dimethoate-d_6	6.96E-03	1.81E-02	0.9906	50	10	84	79	97	35	11	7
17	dimethoate	dimethoate-d_6	1.25E-03	2.83E-03	0.9635	10	10	106	95	104	35	17	9
18	dimethomorph	dimethoate-d_6	1.70E-02	-1.30E-03	0.9945	-	10	83	97	100	4	14	8
19	dinotefuran	trifloxystrobin-d_6	2.25E-02	2.88E-02	0.9878	50	25		111	110		18	14
20	dodemorph	atrazine-d_5	8.71E-02	3.47E-02	0.9867	-	2.5	92	94	82	14	9	10
21	etoxazole	atrazine-d_5	1.75E-02	6.71E-03	0.9857	-	10	86	95	98	11	8	20
22	fenoxycarb	dimethoate-d_6	8.73E-03	4.66E-03	0.9859	10	10	80	99	100	12	10	4
23	fenpyroximate	acephate-d_3	1.82E+03	7.40E+03	0.9897	-	10	72	91	91	16	3	5
24	fensulfothion	dimethoate-d_6	1.39E-02	9.20E-04	0.9926	10	5	94	93	98	12	11	3
25	fipronil	acephate-d_3	7.33E+02	3.01E+02	0.9769	10	25		107	97		11	2
26	flonicamid	spirotetramat-d_6	7.77E-03	5.69E-02	0.9382	25	25		112	114		5	19
27	fludioxonil	dimethoate-d_6	2.38E-03	3.24E-03	0.9736	10	10	91	97	94	16	17	2
28	fluopyram	carbofuran-d_3	1.25E-02	1.09E-02	0.9920	10	5	101	87	90	19	9	9
29	imazalil	imazalil-d_5	3.85E-02	5.07E-03	0.9950	10	2.5	81	103	98	4	7	3
30	imidacloprid	atrazine-d_5	5.69E-02	-1.24E-02	0.9941	10	2.5	91	102	98	9	10	6
31	metalaxyl	metalaxyl-d_6	3.43E-02	3.11E-02	0.9913	10	5	88	101	90	18	15	10
32	methiocarb	atrazine-d_5	2.00E-02	1.50E-02	0.9958	10	5	85	99	102	13	12	6
33	methomyl	carbofuran-d_3	9.49E-03	-4.41E-03	0.9843	25	10	102	97	97	27	10	5
34	mevinphos	acephate-d_3	1.51E+03	2.66E+03	0.9881	25	10	82	102	89	21	10	3
35	myclobutanil	imazalil-d_5	7.27E-03	7.51E-03	0.9665	10	5	89	110	96	15	13	15
36	naled	carbofuran-d_3	9.73E-04	8.26E-05	0.9606	-	50		106	93		22	11
37	oxamyl	carbofuran-d_3	6.15E-03	-5.85E-03	0.9838	1500	10	97	97	97	24	7	12
38	paclobutrazol	imazalil-d_5	6.07E-02	2.24E-02	0.9810	10	2.5	95	105	101	22	16	23
39	phosmet	acephate-d_3	3.87E+03	-4.36E+02	0.9944	-	5	85	99	97	9	12	6
40	prophos	metalaxyl-d_6	1.40E-02	4.78E-02	0.9795	10	25		96	87		19	17
41	propiconazole	imazalil-d_5	7.28E-03	2.11E-02	0.9636	-	5	99	117	106	22	16	21
42	pyraclostrobin	dimethoate-d_6	7.51E-03	5.71E-03	0.9871	10	10	74	84	93	25	5	2
43	pyridaben	carbofuran-d_3	5.80E-03	2.01E-02	0.9730	20	25		89	84		7	13
44	spinetoram	imazalil-d_5	3.20E-02	-1.58E-02	0.9935	10	2.5	79	98	110	9	7	14
45	spinetoram isomer b	acephate-d_3	1.89E+03	-2.74E+03	0.9862		5	94	111	94	20	11	13
46	spinosyn A	imazalil-d_5	3.56E-02	-2.14E-02	0.9945	10	2.5	82	89	99	9	14	12
47	spirotetramat	acephate-d_3	4.17E+03	4.60E+03	0.9943	10	5	79	100	101	4	4	7
48	spiroxamine	acephate-d_3	4.18E+04	-6.30E+03	0.9955	-	2.5	87	101	91	8	11	3
49	tebuconazole	imazalil-d_5	1.09E-02	1.17E-02	0.9690	10	10	107	103	101	25	14	15
50	tebufenozide	acephate-d_3	2.75E+03	7.85E+02	0.9862	10	10	86	102	95	5	6	7
51	tetrachlovinphos	dimethoate-d_6	1.91E+03	7.43E+02	0.9910	10	5	97	97	96	13	8	8
52	thiacloprid	dimethoate-d_6	3.76E-02	-1.93E-03	0.9917	10	2.5	83	96	102	9	10	6
53	thiamethoxam	dimethoate-d_6	3.75E-02	-8.81E-03	0.9906	10	2.5	85	97	95	4	5	4
54	thiophanate-methyl	imazalil-d_5	5.67E-02	-1.24E-01	0.9488	-	10	75	97	118	20	17	13
55	trifloxystrobin	carbofuran-d_3	9.97E-03	1.28E-02	0.9932	10	10	84	83	84	10	13	13

Table A.25: CBS-MS/MS figures of merit of pesticides extracted from cannabis oil matrix.

						MRL Health Canada	LOQ	Accuracy, ng/g (%)			Precision, ng/g (%)		
n	Compound	Internal Standard	Slope	Intercept	R^2	(ng/g)	(ng/g)	15	80	150	15	80	150
1	acephate	dimethoate-d_6	4.75E-02	5.34E-03	0.9821	50	10	114	102	85	8	6	6
2	acetamiprid	imazalil-d_5	1.24E-03	5.52E-03	0.9899	50	5	97	110	111	27	12	10
3	aldicarb	atrazine-d_5	1.68E-03	6.58E-03	0.9630	500	25	83	116	83	43	14	13
4	azoxystrobin	spirotetramat-d_6	4.40E-02	4.23E-01	0.9904	10	5	75	98	108	10	16	10
5	buprofenzin	cyprodinil-d_5	1.24E-02	3.32E-02	0.9727	25	10	71	90	82	26	21	29
6	carbofuran	dimethoate-d_6	5.41E-03	7.55E-02	0.9278	10	25	105	107	77	27	16	20
7	chlorantraniliprole	spirotetramat-d_6	5.99E-03	5.29E-03	0.9889	-	10	89	99	109	17	7	16
8	cyantraniliprole	atrazine-d_5	3.39E-03	4.44E-02	0.9677	-	10	111	116	91	9	18	16
9	cyprodinil	cyprodinil-d_5	4.56E-02	8.39E-02	0.9827	10	2.5	93	97	97	16	15	15
10	daminozide	carbofuran-d_3	7.17E-02	7.48E-01	0.9746	-	10	87	111	123	26	20	18
11	dimethoate	dimethoate-d_6	4.73E-03	3.47E-04	0.9461	10	25	99	89	94	71	14	20
12	dimethomorph	atrazine-d_5	1.04E-02	2.05E-01	0.9880	-	5	98	105	92	40	8	25
13	dodemorph	imazalil-d_5	4.01E-02	-2.17E-03	0.9892	-	1	76	95	88	12	8	16
14	etoxazole	oxamyl-d_6	3.60E-02	1.04E-01	0.9830	-	2.5	87	99	96	36	3	19
15	fipronil	fludioxonil-$^{13}C_2$	2.15E-02	2.23E-01	0.9694	10	25	90	109	112	45	20	8
16	fludioxonil	fludioxonil-$^{13}C_2$	3.84E-02	1.37E-01	0.9785	10	10	127	105	94	36	6	9
17	fluopyram	atrazine-d_5	9.67E-03	4.22E-02	0.9727	10		68	108	89	20	9	7
18	imazalil	imazalil-d_5	3.93E-02	2.08E-02	0.9987	10	2.5	88	97	96	3	2	4
19	imidacloprid	dimethoate-d_6	1.28E-02	2.58E-01	0.9597	10	25	102	106	89	92	25	22
20	metalaxyl	metalaxyl-d_6	2.10E-02	3.98E-02	0.9938	10	2.5	79	92	92	9	9	5
21	methiocarb	dimethoate-d_6	3.27E-03	9.75E-02	0.9085	10	25	148	109	99	73	22	9
22	methomyl	atrazine-d_5	3.92E-03	2.46E-03	0.9727	25	25	114	111	108	45	26	8
23	mevinphos	oxamyl-d_6	1.10E-02	5.72E-02	0.9326	25	25	61	92	98	38	15	8
24	oxamyl	oxamyl-d_6	2.56E-02	1.96E-02	0.9884	1500	2.5	82	96	98	12	14	7
25	pirimicarb	cyprodinil-d_5	9.28E-02	-1.98E-01	0.9644	10	10	91	89	77	17	17	16
26	spinetoram J	carbofuran-d_3	3.56E-02	6.09E-03	0.9886	10	2.5	89	106	90	14	24	18
27	spinetoram L	carbofuran-d_3	4.09E-02	1.08E-02	0.9878	10	2.5	88	105	88	14	18	23
28	spinosyn A	carbofuran-d_3	3.79E-02	2.42E-02	0.9897	10	2.5	84	105	90	12	23	27
29	spinosyn D	carbofuran-d_3	6.16E-02	9.97E-03	0.9876	10	2.5	87	103	86	11	24	26
30	spirotetramat	spirotetramat-d_6	3.14E-02	1.11E-01	0.9934	10	5	87	96	95	3	10	4
31	spiroxamine	imazalil-d_5	5.79E-02	-3.57E-03	0.9945	-	1	83	97	96	7	4	8
32	tebuconazole	atrazine-d_5	2.30E-02	1.59E-01	0.9709	10	10	103	109	114	16	10	15
33	tebufenozide	atrazine-d_5	5.24E-03	7.83E-02	0.9752	10	10	95	121	101	24	8	20
34	thiacloprid	imazalil-d_5	9.00E-04	5.91E-03	0.9746	10	10	75	110	115	24	14	16
35	thiamethoxam	imazalil-d_5	2.17E-04	1.19E-03	0.9680	10	25	89	121	105	25	10	13
36	trifloxystrobin	atrazine-d_5	1.52E-03	1.57E-02	0.9631	10	25	84	128	99	72	18	19
37	fensulfothion	fludioxonil-$^{13}C_2$	6.75E+02	1.49E+04	0.9765	10	25	59	116	105	56	29	9

Table A.26: CBS-MS/MS figures of merit of pesticides extracted from cannabis oil matrix, compounds meeting screening criteria.

Compound	MRL Health Canada (ng/g)	SDL (ng/g)
benzovindiflupyr	10	75
clothianidin	25	50
diazinon	-	50
dinotefuran	50	100
flonicamid	25	25
myclobutanil	10	50
paclobutrazol	10	25
phosmet	-	100
propiconazole	-	100
propoxur	10	75
pyraclostrobin	10	25

Table A.27: CBS-MS/MS S/N of compounds of interest upon extraction from cannabis-extract infused MCT oil compared with extraction of MCT oil.

Compound	LogP	MCT oil	Cannabis oil (MCT carrier oil)	Supp./Enhanc. (%)
acephate	-0.85	18	89	396
acetamiprid	0.62	844	716	-15
aldicarb	1.13	21	60	179
azoxystrobin	5.13	959	88	-91
carbofuran	1.76	141	30	-79
chlorantraniliprole	5.55	535	53	-90
clothianidin	0.40	236	96	-59
cyantraniliprole	4.63	14	12	-14
cyprodinil	4.00	45	27	-40
diazinon	3.81	43	5	-87
dimethoate	1.32	1605	122	-92
dimethomorph	3.71	1729	70	-96
dodemorph	6.10	4031	3123	-23
etoxazole	5.85	2229	128	-94
fensulfothion	2.23	372	36	-90
fipronil	4.76	74055	572	-99
flonicamid	0.84	1445	198	-86
fluopyram	4.36	837	141	-83
imazalil	3.58	2384	107	-95
imidacloprid	-0.43	531	36	-93
metalaxyl	2.15	621	269	-57
methiocarb	2.88	65	18	-72
methomyl	0.60	193	139	-28
mevinphos	0.28	310	54	-82
myclobutanil	2.82	66	39	-41
paclobutrazol	2.99	215	130	-40
pirimicarb	1.70	2260	745	-67
propiconazole	3.88	30	5	-82
propoxur	1.60	101	23	-77
pyraclostrobin	4.25	80	23	-71
spinosyn A	4.80	1344	149	-89
spirotetramat	4.59	474	97	-80
spiroxamine	4.88	52334	8743	-83
tebuconazole	3.58	380	168	-56
thiacloprid	0.55	1707	328	-81
thiamethoxam	-1.16	422	61	-86
thiophanate-methyl	1.16	70	5	-93
trifloxystrobin	5.11	48	11	-78