Strategies for the multi-residue analysis of 100 pesticides by liquid chromatography – triple quadrupole mass spectrometry

Oscar Núñez[1,*], Héctor Gallart-Ayala[1], Imma Ferrer[2], Encarnación Moyano[1], Maria Teresa Galceran[1]

[1] Department of Analytical Chemistry, University of Barcelona. Martí i Franquès, 1-11, E-08028, Barcelona, Spain.

[2] Center for Environmental Mass Spectrometry, Department of Environmental Engineering, University of Colorado. ECOT 441, Boulder, CO 08309, USA.

* Corresponding author: Oscar Núñez
Department of Analytical Chemistry, University of Barcelona.
Martí i Franquès, 1-11, E-08028, Barcelona, Spain.
Phone: 34-93-403-3706
Fax: 34-93-402-1233
e-mail: oscar.nunez@ub.edu

Keywords: pesticides; multi-residue analysis; triple quadrupole; enhanced mass spectrometry; accurate mass measurements

Abstract

Analytical strategies for screening, quantitation and confirmation of a group of 100 pesticides in fruit and vegetable samples by LC-MS and LC-MS/MS were developed. The pesticides studied belong to different chemical families of herbicides, insecticides and fungicides. A selection of some degradation products was also included. Chromatographic separation was performed using a Zorbax Eclipse XDB-C8 column (150 mm ×~~x~~ 4.6 mm and 5 µm particle size), and gradient elution with acetonitrile-water (both with 0.1% formic acid) as mobile phase. LC-MS/MS using highly-selective selected reaction monitoring (H-SRM) acquisition mode monitoring two transitions for each compound showed to be the most sensitive methodology. Quantitation was carried out using matrix-matched standard calibration and good linearity of response was demonstrated ($r > 0.998$). Limits of detection (by acquiring two transitions and with the ion-ratio requirements) ranged between 0.01 and 20 µg/kg were obtained. So, in general, the sensitivity achieved meets the maximum residue levels (MRLs) established by the European Union regulation for food monitoring programs. Pesticide confirmation was carried out following European Union guidelines. In order to prevent false-positives, further confirmatory strategies were proposed. LC-MS in highly-selective selected ion monitoring (H-SIM) mode with accurate mass measurement was used to obtain an orthogonal criterion (exact mass) for confirmation. Accurate mass measurements were always bellow 0.9 mDa for almost all pesticides studied (similar to those described with TOF instruments). A user reversed energy ramp (RER) product ion scan spectra library was generated by means of a data dependent analysis for routine library searching of pesticides. The combination of LC-MS/MS in H-SRM mode and the generation of the RER product ion scan spectra and library search were then used to achieve further confirmation on pesticide analysis. The LC-MS and LC-MS/MS strategies developed were successfully applied for the analysis and confirmation of pesticides ~~indifferent types~~in different types of fruit and vegetables

samples, and examples of the screening, quantitation and confirmation of pesticides in these samples are shown in this work.

1. Introduction

Liquid chromatography – tandem mass spectrometry (LC-MS/MS) methods based on triple quadrupole (QqQ) analyzers are frequently used in environmental and food analysis because of the high sensitivity achieved using selected reaction monitoring (SRM) acquisition mode. As a compromise between sensitivity, acceptable chromatographic peak shape, and confirmation purposes established by 2002/657/EC directive [1] two SRM transitions are currently monitored. However, in some cases the use of only two transitions could result in false-positive or false-negative confirmations when the compound coelutes with an interfering matrix compound with ions in the MS/MS matching with those of the analyte [2-4]. In these cases, false-positive results can be dealt with by further confirmatory analysis, e.g. using of a third transition or an orthogonal criterion like accurate mass. In this context, time-of-flight (TOF) and Orbitrap analyzers present some advantages related to their high resolution capability and the possibility of accurate mass measurements providing *m/z* values with errors between 2 and 10 mDa depending on the mass of the compound.

Pesticides are used worldwide to a broad variety of crops to control pests and prevent diseases in order to increase agricultural production. The monitoring of pesticide residues in food is nowadays a priority objective in order to get extensive evaluation of food quality and to avoid possible risks to human health. The setting of low EU-harmonized MRLs for unregistered pesticide/sample combinations and the introduction of very low residue limits (10 μg kg^{-1}) in fruits and vegetables intended for baby food production [5-8] have increased the necessity of developing analytical methodologies to monitor pesticides at low levels [9]. Traditionally, the analysis of pesticides in food has been accomplished by gas chromatography-mass spectrometry (GC-MS) [10-20] where the use of conventional library searching routines is well established. Nevertheless, today LC-MS/MS has become a powerful tool for pesticides-residue analysis in a variety of complex matrices [13,17,21-30], due to its selectivity and sensitivity, a substantial reduction of sample-

treatment steps compared with other methodologies such as GC-MS, and its reliable quantification and confirmation at the low concentration levels required.

LC coupled to high resolution mass spectrometry (HRMS) has been proven to be a sensitive and selective method for the determination and confirmation of pesticide residues in vegetables and fruits [31-38]. These methods provide high specificity (because of both high mass accuracy and mass resolution), without limiting the number of simultaneously observed target compounds. Its high full-scan speed and acceptable sensitivity have made TOF and Orbitrap instruments an attractive alternative to quadrupole LC-MS/MS instruments. Moreover, the use of elemental database searching as an accurate mass library for pesticides in food using HRMS has also been described [31,39-42] as a powerful tool for unequivocal identification.

Whereas LC-HRMS seem the best option for multi-residue analysis these instruments showed some disadvantages ~~such as its high cost~~such as their high cost. The aim of this paper is to discuss and evaluate the capabilities of a triple quadrupole instrument which allow working in enhanced mass resolution (up to 12500 mass resolving power measured at *m/z* 500) and accurate mass measurements for the multi-residue analysis and confirmation of pesticides. A group of 100 pesticides with several chemical uses (insecticides, herbicides and fungicides) was selected as a family test. Different acquisition strategies to guarantee pesticide confirmation following the 2002/657/EC EU directive will be evaluated. The strength of this kind of instrument to perform reliable MS/MS experiments will be combined with the enhanced mass resolution of precursor ions (H-SRM on Q1) to increase sensitivity and selectivity while acquiring two MS/MS transitions for each target compound, and with accurate mass (AM) measurements (errors within ±5 mDa) to prevent false-positives confirmation. Moreover, a product ion scan spectra library useful as a routine library search engine in pesticide analysis has been developed. For this purpose, spectra obtained by data dependent scan combining H-SRM and product ion scan in a reversed energy ramp (RER) acquisition modes have been proposed. All the acquisition strategies presented in this work

will be evaluated and discussed by analyzing the target pesticides in different fruit and vegetable samples obtained from commercial markets and a private farm.

2. Experimental

2.1. Chemicals

Pesticide analytical standards were purchased from Sigma (St. Louis, MO, USA), Chem Service (West Chester, PA, USA), and Dr. Ehrenstorfer (Ausburg. Germany). Water and acetonitrile LC-MS grade were obtained from Fluka (Steinheim, Sweden). Formic acid (98-100%) was purchased from Merck (Darmstadt, Germany). Anhydrous magnesium sulfate was obtained from Sigma, sodium chloride from Fluka, and propylamino (PSA) bonded silica SPE bulk from Supelco (Gland, Switzerland). Diethylamine, bisphenol F-diglycidylether (BFDGE), and the antibiotic narasin (NAR) purchased from Sigma, mepiquat (1,1´-dimethylpyperidinium ion, MQ) from Riedel-de Haën, difenzoquat (1,2-dimethyl-3,5-diphenylpyrazolium ion, DF) from Chem Service, and polytirosina 3 and 6 from CS Bio Co. (Menlo Park, CA, USA) were used for triple quadrupole instrument calibration and as internal lock mass standards for accurate mass measurements.

Individual pesticide stock solutions (1000 µg mL^{-1}) were prepared in pure acetonitrile and stored at -18 ^{0}C. From these stock solutions, working standard solutions were prepared by dilution with acetonitrile:water (1:1) solution.

Nitrogen (99.98% pure) supplied by Claind Nitrogen Generator N_2 FLO (Lenno, Italy) was used for the API source. High-purity Argon (Ar_1) obtained from Air Liquide (Madrid, Spain) was used as a collision-induced gas (CID gas) in the triple quadrupole instrument.

2.2. Instrumentation

A liquid chromatography instrument (Accela system; Thermo Fisher Scientific, San José, CA, USA), equipped with a low-pressure quaternary pump, an autosampler and a column oven was used for the chromatographic separation using a reversed phase C_8 analytical column (150 mm × 4.6 mm and 5 µm particles size) (Zorbax Eclipse XDB-C8, Agilent, Frankfurt, Germany). Column temperature was maintained at 25 ^{o}C. The injected sample volume was 10 µL. Mobile phases A and B were acetonitrile and water with 0.1% formic acid, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A for 30 min. The flow-rate used was 0.6 mL min^{-1}. A 15 min post-run time was used after each analysis.

The liquid chromatography system was coupled to a triple quadrupole mass spectrometer instrument, TSQ Quantum Ultra AM (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an electrospray ionization (ESI) source and hyperbolic quadrupoles that can operate in enhanced mass spectrometry mode (Q1 and/or Q3 with a full width half maximum (FWHM) value of 0.1 *m/z*) and performing accurate mass (AM) measurements (Q1 or Q3 at a FWHM value of 0.04 *m/z*) with errors lower than 5 mDa. Nitrogen (purity > 99.98%) was used as sheath gas, ion sweep gas, and auxiliary gas at flow rates of 60, 40 and 40 a.u. (arbitrary units), respectively. Ion transfer tube temperature was set at 350 ^{o}C and electrospray voltage at +3.5 kV.

MS experiments were performed in full-scan (*m/z* 50-1000) and selected ion monitoring (SIM) modes on Q1 using a FWHM value of 0.7 *m/z* (scan time of 0.5 s in full-scan mode or 10 ms in SIM mode) for low resolution, and a FWHM value of 0.1 *m/z* (scan time of 1.5 s in full-scan or 5 ms in SIM mode) for enhanced mass resolution. MS/MS experiments were carried-out in selected reaction monitoring (SRM, FWHM value of 0.7 *m/z* on Q1 and Q3) and highly selective-selected reaction monitoring (H-SRM, FWHM values of 0.1 *m/z* on Q1 and of 0.7 *m/z* on Q3) modes. A scan width of 0.01 Da was used for SIM, SRM and H-SRM, and all acquisitions were performed using 1 µscan.

Data dependent scan mode ~~was used to home make~~was used to build a product ion scan spectra library. H-SRM (Q1 at 0.1 *m/z* FWHM and Q3 at 0.7 *m/z* FWHM) mode was selected as first scan event for the data dependent scan analysis. A threshold of 10^3 was established for the activation of the second scan event, where product ion scan spectra were obtained using a reversed energy ramp (RER, from 90 to 25 eV).

Xcalibur software version 2.0 was used to control the LC-MS system and to process data.

2.3. MS and accurate mass (AM) calibrations

A full mass calibration of the triple quadrupole mass spectrometer is necessary before working in enhanced mass resolution mode (FWHM of 0.1 or 0.04 *m/z*) and to perform accurate mass (AM) measurements. For this purpose, a calibration mixture of 7 compounds: diethylamine (*m/z* 74.0964), MQ (*m/z* 114.1280), DF (*m/z* 249.1390), BFDGE (*m/z* 330.1700), polytirosina 3 (*m/z* 508.2080), narasin antibiotic (*m/z* 787.4970) and polytirosina 6 (*m/z* 997.3980), prepared in acetonitrile (0.1% formic acid) was used. The accurate mass calibration and all the accurate mass measurements were carried out in internal calibration mode using the above mentioned compounds as internal lock masses. The calibration mixture was infused using the syringe pump integrated in the TSQ instrument (2 µL/min) and mixed with the analytes from the chromatographic column by means of a zero-dead volume Valco T-piece. For the accurate mass measurements, mass at the average of the chromatographic peak was obtained

2.4. Sample preparation

A QuEchERS method (quick, easy, cheap, effective, rugged and safe) was used for the extraction of food samples following a procedure previously described [38,43]. Briefly, food samples were ground and homogenised using a supermixer blender system (Moulinex, Lyon, France) and an Ultraturrax T25 basic (Ika-Werke, Staufen, Germany). Sub-samples of 15 g were

weighed into a 50 mL PTFE centrifuge tube. Then, 15 mL of acetonitrile were added and the tube was vigorously shaken for 1 min. After this time, 1.5 g of NaCl and 4 g of $MgSO_4$ were added repeating the shaking process for 1 min to prevent coagulation of $MgSO_4$. The extract was then centrifuged at 3700 rpm for 1 min with a Selecta Centronic centrifuge (Selecta, Barcelona, Spain). A 5 mL aliquot of the supernatant (acetonitrile phase) was transferred to a 15 mL graduated centrifuge tube, that contained 250 mg of PSA (propylamino bonded silica SPE bulk) and 750 mg of $MgSO_4$. The mixture was energetically shaken for 20 s and then centrifuged at 3700 rpm for 1 min. Finally, 2 mL of supernatant were evaporated to dryness under a stream of nitrogen, and reconstituted using 1 mL of ACN:Water (1:1) containing both 0.1% formic acid. Prior to analysis, the extract was filtered through a 0.45 µm nylon filter and transferred into an injection vial. Matrix extracts were used for validation of the method by appropriate spiking with the pesticide mix.

The scope of this work was simply to evaluate the capabilities of a hyperbolic triple quadrupole instrument in the screening and confirmation of 100 pesticides in vegetable and fruit matrices, so recovery of the compounds from raw samples was not taken into account here. Vegetables and fruit samples included tomatoes, cucumbers, green-peppers, red-peppers, carrots, green beans, spinaches, plums, peaches, pears, apples and oranges.

3. Results and discussion

3.1. LC-MS analysis *of 100 pesticides.*

The pesticides included in this work were selected among different classes of compounds (triazines, organophosphates, carbamates, phenylureas, etc.) and several chemical uses (insecticides, herbicides and fungicides). Most of them are currently analyzed by hundreds of laboratories all over the world performing target analysis of pesticides in both food and water samples. Table 1 compiles the chemical formulae as well as the accurate mass of the protonated ion $[M+H]^+$, except for aldicarb, for which sodium adduct $[M+Na]^+$ is given. These ions were used as primary ions in SIM

mode and as precursor ions in tandem MS studies. Some of the most frequently detected degradation products have been also included in this study (e.g. degradation products for atrazine, aldicarb, etc.) for more complete and detailed information.

As an example, Figure 1 shows the LC-MS separation (H-SIM mode) of a standard solution of the 100 pesticides (~100 µg/kg). As can be seen, most of the compounds elute from 15 to 30 min, due to the similarity in polarity among the group of pesticides studied (retention times are also included in Table 1).

As a preliminary study, instrumental limits of detection (ILODs) in full scan MS mode (*m/z* 50-1000) and SIM mode (100 *m/z* values monitored with dwell time of 10 ms) were determined at low resolution (Q1 0.7 *m/z* FWHM) and enhanced mass resolution mode (Q1 0.1 *m/z* FWHM), and the results are summarized in Table 1. ILODs of acetochlor and alachlor were not determined because of isobaric masses (*m/z* 270.1255) and coelution (at 27.2 min). The best sensitivity was achieved with H-SIM as expected, with ILOD values between 0.1 and 100 µg/kg, with a total of 87 pesticide compounds with ILODs lower than 10 µg/kg. From these results we can see that H-SIM can be used as a preliminary acquisition strategy for multi-residue screening of pesticides by LC-MS, because an important number of pesticides were detected at concentrations lower than the residue limits established by the EU legislation [5-8]. However, this acquisition strategy can only be used as a preliminary one for screening purposes because pesticide confirmation cannot be achieved following the identification point system of EU legislation [1]. To achieve this confirmation as well as to decrease LODs other acquisition strategies must be considered.

3.2. Accurate mass (AM) *measurements in LC-MS (H-SIM acquisition mode).*

Another acquisition strategy that we have evaluated for the multi-residue analysis and confirmation of pesticides by LC-MS is H-SIM acquisition mode (Q1 at 0.04 *m/z* FWHM) by performing AM measurements through all the analysis. For this purpose, 107 *m/z* target values

(those corresponding to the 100 pesticides and the 7 internal lock masses) were monitored simultaneously while performing the internal lock mass correction for AM measurements. ILODs working under these conditions were determined and the results are summarized in Table 2. Again, no ILOD values are given with AM H-SIM mode for acetochlor and alachlor pesticides because of isobaric masses (*m/z* 270.1255) and coelution (t_R 27.2 min). The exact mass for each monitored ion, as well as the accurate *m/z* value measured and the mass error achieved are also included in Table 2. In general, ILODs obtained by H-SIM with AM measurements are similar or only slightly higher than those achieved by H-SIM (Table 1). The small increase in ILODs observed for some of the pesticides is expected because the QqQ instrument is not only monitorizing the target masses of the pesticides but also performing simultaneously the AM correction of these masses. A total of 61 pesticides showed an ILOD lower than 10 µg/kg, 30 pesticides between 20 and 50 µg/kg, and only 7 pesticides presented an ILOD values higher than 50 µg/kg. Regarding mass accuracy on the mass determination good results were achieved (see Table 2). Mass errors for most of the pesticides were lower than 0.9 mDa, with only three pesticides (cartap, fluroxypyr, and teflubenzuron) with slightly higher values (up to 1.7 mDa). So, in general, similar mass accuracies than those achieved with TOF instruments for this group of pesticides can be obtained with the QqQ instrument TSQ Quantum Ultra AM [38]. However, this does not mean that it is possible to get two identification points for confirmation following the identification point system of EU directive 96/23/EC [1], as mass resolution is not always be higher than 10000 with the QqQ instrument. For instance, the mass resolution power of the hyperbolic QqQ instrument is 12500 for an ion at *m/z* 500, but only around 5000 for an ion at *m/z* 200. Even though the exact mass can be used as an orthogonal criterion for identification in order to prevent false positives, and this acquisition strategy can be useful when other confirmation strategies failed, for instance for compounds showing only one SRM transition, as it will be demonstrated later.

The applicability of LC-MS in H-SIM mode with AM measurements for multi-residue analysis of pesticides was evaluated by analyzing some fruit and vegetable samples. Sample extraction was performed by using a previously established QuEChERS procedure (see experimental section). All the fruit and vegetable samples analysed were positive for some of the pesticides, so method limits of detection (MLODs) were determined using two samples, orange and green pepper, and the values are given in Table 3 (no MLOD value is given for the pesticides found in each sample). In general similar MLODs were observed for each pesticide in both matrices, with around 50 pesticides with MLOD values lower than 10 µg/kg, while MLODs in the range of 15-350 µg/kg were observed for the other compounds. So, LC-MS in AM measurements H-SIM mode could be useful as a suitable method for the screening and analysis of an important number of pesticides at the levels established by EU legislation [5-8]. Figure 2 shows, as an example, the analysis of a tomato sample by LC-MS in AM H-SIM mode. As can be seen, three pesticides, azoxystrobin, imazalil and spiromesifen, were detected. However, only for azoxystrobin and imazalil the AM measurement can be performed, with mass errors of 0.2 mDa and 0.4 mDa respectively (the Figure also shows the two lock masses used in the internal correction of the pesticide *m/z*). In the case of spiromesifen, with a signal corresponding to MLOD, the determination of the exact mass was not possible. In this case, alternative confirmation and quantitation strategies are necessary.

3.3. Liquid chromatography - tandem mass spectrometry

A common strategy for the multi-residue analysis of pesticides using triple quadrupole instruments is to perform the determination by liquid chromatography-tandem mass spectrometry, using two SRM transitions (corresponding to one precursor ion and two product ions) in order to achieve four identification points according to EU directive 96/23/EC [1]. In this work the optimal SRM conditions for each pesticide was established by using a 100 µg/kg standard solution of all

pesticides. The SRM transitions monitored for each pesticide and the optimum collision energy value for each transition is given in Table 4. For all pesticides two transitions were monitored except for spinosad A and spinosad D where only one SRM transition was obtained, a fact that will make necessary alternative confirmation strategies.

Under these optimal LC-MS/MS conditions, ILODs were determined in SRM and H-SRM acquisition modes and the values are also given in Table 4. Again, enhanced mass resolution provided similar or slightly better sensitivity than low mass resolution. Under these conditions all pesticides presented a LOD lower than 10 µg/kg, except for aldicarb sulfoxide and bensultap that gave a LOD of 25 µg/kg. For some of the pesticides, LODs down to 5 ng/kg were obtained. H-SRM mode was also used to determine MLODs in real samples (orange and green pepper) and the results are indicated in Table 3. Although slightly higher than the instrumental LODs, all pesticides gave values in real samples lower than 10 µg/kg (except bensultap with a value of 20 µg/kg), being the lowest LOD observed 0.01 µg/kg for some of them. These MLODs are considerably lower than those previously reported in green pepper matrix using conventional QqQ instruments [23], achieving a 4- to 200-fold improvement with the hyperbolic QqQ instrument. So, the LC-MS/MS in H-SRM mode method reported in this work is very sensitive and can be proposed as an useful acquisition strategy for the multi-residue analysis of pesticides in fruits and vegetables at the levels established by EU [5-8]. As an example, Figure 3 shows the analysis of an apple sample by LC-MS/MS in H-SRM mode. A total of 8 pesticides were identified and confirmation was achieved following two H-SRM transitions. The confirmation of positive identifications in real samples requires not only the additional second SRM transition but the evaluation of ion ratios between the two monitored transitions as compared to a reference standard. The confirmation criteria using tandem mass spectrometry cover a range of maximum permitted tolerances for relative ion intensity, expressed as a percentage of the intensity of the most intense transition [1]. It should be noted that for all pesticides identified in real samples ion ratios were similar to those of standards and within

the tolerances (lower than 20-25% for ion intensities higher than 20% of base peak) specified by the EU directive [1].

Although LC-MS/MS in a triple quadrupole instrument is very sensitive for the multi-residue analysis of pesticides, as commented before, in some cases confirmation cannot be achieved following the identification points system of EU directive 96/23/EC [1]. That is the case when only one SRM transition obtained (for instance for the pesticides spinosad A and spinosad D studied in this work). In other situations, the use of two SRM transitions could result in a false-positive confirmation. For instance, Schürmann *et al.* [2] reported a false-positive LC-MS/MS confirmation of sebuthylazine residues using the identification points system of EU directive 2002/657/EC because of the presence of a biogenic insecticide. This can usually be prevented with the ion-ratio criteria as reported by Ferrer *et al.* [23] for the pesticide carbofuran. But in other cases, the ion-ratio criteria cannot prevent false-positive identification if, for instance, the second SRM transition is not sensitive enough. As an example, Figure 4a shows the analysis of a celery sample by the proposed LC-MS/MS using H-SRM acquisition mode monitoring two transitions for each compound. As can be seen, initially four pesticides (carbaryl, DEET, diazinon and imidacloprid) were found in the sample. However, only three of these pesticides could be confirmed following the ion-ratio criteria of EU legislation [1]. In the case of DEET, although this pesticide is present in the celery sample in a relatively high concentration, the second transition is not sensitive enough in this sample matrix and it does not satisfy the ion-ratio criteria. This lack of confirmation or in some cases false-positive results can be dealt with by further confirmatory analysis, e.g. with the use of a third transition (when possible) or using an orthogonal criterion like accurate mass measurements, as commented in section 3.2. For example, Figure 4b shows the signal obtained for DEET when the same celery sample was analysed by LC-MS in AM H-SIM mode. Although sensitivity with this method is lower than that of LC-MS/MS in H-SRM mode, the peak signal for DEET (close to LOD) was enough to perform the *m/z* correction using two lock masses, and then the AM measurement with a

mass error of 0.3 mDa, allowing to confirm the presence of DEET in the celery sample. Obviously, if detection by LC-MS in AM H-SIM mode is not good enough, other confirmatory strategies are necessary.

3.4. Spectra library search using data dependent analysis.

Data dependent analysis can also be used as a complementary acquisition strategy for the analysis of pesticides in fruits and vegetables. In fact, two of any of the acquisition modes previously described in this work, can be combined with the data dependent analysis. In this section we are going to describe the results obtained using data dependent analysis when H-SRM mode is combined with a product ion scan mode where spectra are obtained using a reversed energy ramp (RER). These spectra will then be used to implement a product ion MS/MS spectra library useful for routine library searching for pesticide screening and confirmation.

H-SRM mode, which provided high sensitivity, was selected as the first scan event. Only when ions were detected with a signal higher than a threshold value of 10^3 the second scan event was activated. This threshold prevented performing data dependent experiments of background noise ions. Moreover, high intensity ions detected on the first scan due to solvent or contaminant ions were eliminated from the data dependent experiment by including a list of rejected masses. On the other hand, to detect co-elution, a dynamic exclusion time is defined. Dynamic exclusion is a process whereby the software recognises that an MS/MS experiment has already been carried out for a particular *m/z* value. The software then ignores this ion even if it remains the most intense ion and will instead perform the data dependent experiment on the next most intense ion (not included in the reject mass list).

Product ion scan mode was used as second scan event for the data dependent experiments performed in this work. However, product ion spectra were not obtained with defined collision energies but by using reversed energy ramp (RER) mode and applying collision energies from 90 to

25 eV. The result is then a product ion scan spectrum average of spectra at the different collision energies. The advantage of this product ion scan spectrum with RER is that it provides higher structural information than a simple product ion scan spectrum obtained at specific collision energy. Since it is well known that low collision energies are too weak to adequately fragment the precursor ions, while at high collision energies few product ions are generated, the use of RER is more likely to generate fragment-rich MS/MS spectra that will be optimal for library entries and searching purposes.

So first, in order to set up a product ion scan spectra library, a standard containing 100 µg/kg of each target pesticide was analyzed using the described data dependent experiment using LC-MS/MS with H-SRM mode in the first scan and a threshold of 10^3 to activate the product ion scan with RER of the second scan event. Once the spectrum for each pesticide standard was obtained it was loaded into the Quantum Library of the Xcalibur software, and a user library for routine library searching was generated. This data dependent analysis was then used for the analysis of pesticides in fruit and vegetable samples. As an example, Figure 5 shows the analysis of an orange sample. Three pesticides were detected in H-SRM mode, and their product ion scan spectra with RER were obtained in the second scan event (to simplify, the figure only shows that of imazalil pesticide). Then a library search is performed using the user library previously generated. Figure 6 shows the results generated by the software library search engine. The software compares RER product ion scan spectra of the target sample with those of the library, and as can be seen, a match (with a probability of 98.61) was found, allowing the confirmation of the presence of imazalil pesticide in the orange sample. Following this procedure all the other pesticides were also confirmed with matching probabilities higher than 95.0%. So, data dependent scan with the acquisition of RER product ion scan spectra and a library search can be proposed as further confirmatory strategy in the multi-residue analysis of pesticides in fruits and vegetables.

3.5. Quantitation of pesticides in fruit and vegetable samples

A total of 17 fruit and vegetable samples obtained from commercial markets and a farm were analyzed in this work. In order to quantify the target pesticides the most sensitive LC-MS/MS strategy using H-SRM mode and monitoring two transitions was used. However, to prevent false-positives and to guarantee pesticide confirmation the different alternative acquisition strategies described in this work were applied. Table 5 shows the samples analyzed as well as the pesticides identified in each sample and their concentration levels. As no blank fruit or vegetable matrices were found during this study, quantitation was performed by pseudomatrix matched calibration using an orange sample as matrix to prepare the standards. Pseudomatrix-matched standards where prepared by spiking raw orange sample at concentrations ranging from limit of quantitation (LOQ) to 1 mg/kg. The same QuEChERS procedure used for fruit and vegetable samples was then applied to the pseudomatrix-matched standards. Calibration curves based on peak area for all pesticides were then obtained and good linearity, with correlation coefficients higher than 0.998, was observed.

As can be seen in Table 5 all fruit and vegetable samples were positive for some pesticides, and in some samples relatively high concentrations were observed for some of them, such as the pesticide imidacloprid in a green pepper sample obtained from a farm (217 µg/kg), imazalil in oranges and apples (250 µg/kg and 235 µg/kg, respectively) and azoxystrobin in tomatoes (364 µg/kg), obtained from a commercial market. Of all the samples analyzed only six of them, two from a farm (lettuce and Swiss chard) and four from the market (red pepper, pear, plum, and peach) complies with the maximum residue levels established by EU legislation [5-8]. The concentration levels of all the others pesticides found at levels higher than those legislated are between 10 µg/kg and 66 µg/kg. In general, the pesticides identified on these samples agree with data described in the literature by other authors [34,38,41]. For instance, it has been reported the presence of imidacloprid in green pepper samples [41] and in some cases also at relatively high concentration (170 µg/kg) [34]. The presence of imazalil has also been described in fruits [38,44], especially citric

ones, pointing out the importance of carrying out the identification of fungicides in citrus fruits. Finally, it should be noted that all samples obtained from the farm were positive for imidacloprid, with concentrations ranging between 3 µg/kg and 217 µg/kg. It seems that for this pesticide concentration is lower in green leaves vegetables compared to other vegetables such as tomatoes, peppers or eggplants, showing that probably this pesticide is quite adsorbed into the vegetable.

4. Concluding remarks

Several acquisition strategies for the multi-residue analysis of 100 pesticides by LC-MS and LC-MS/MS using a hyperbolic QqQ instrument were evaluated. LC-MS/MS in H-SRM acquisition mode monitoring two transitions showed to be one of the most sensitive methodologies described till now for the analysis of several families of pesticides in fruit and vegetable samples below the levels established by EU legislation [5-8]. Limits of detection in green pepper matrix were 4 to 200 times lower than those previously described with conventional QqQ instruments [23]. In general, confirmation was also achieved by LC-MS/MS in H-SRM mode following the identification point systems of EU legislation [1] by monitoring two transitions. However, to prevent false-positives such as in the case of pesticides with only one transition or when second transition is not good enough (ion-ratio criterion not achieved), further confirmatory analysis is still necessary. LC-MS in H-SIM (Q1 at 0.04 *m/z* FWHM) acquisition mode with AM measurements can be proposed as a complementary acquisition strategy to obtain an orthogonal confirmatory criterion. With the triple quadrupole instrument used in this work, similar mass accuracies (with mass errors lower than 0.9 mDa for almost all pesticides) than those described with a TOF instrument for the same family of pesticides [38] were obtained.

A user RER product ion scan spectra library was generated by means of a data dependent analysis for routine library searching of pesticides to be used as an alternative strategy for confirmation purposes. Samples were then analyzed by a data dependent experiment consisting of a

very sensitive H-SRM acquisition mode as first scan event, and the acquisition of a product ion scan spectra with a reversed energy ramp as second scan event. Spectra match with probabilities higher than 95.0 were obtained for all pesticides. So, data dependent analyses with RER product ion scan spectra searching library engine can be proposed as a simple and useful acquisition strategy to achieve further confirmatory information in the screening and analysis of pesticides in fruit and vegetable samples.

Finally, the analysis of pesticides in 17 fruit and vegetable samples obtained from a farm and a commercial market was carried out. Quantitation was performed by matrix-matched calibration with good results (linearity with correlation coefficients higher than 0.998), and the confirmation of all target pesticides found in the samples was performed by combining the different acquisition strategies described in this work in order to prevent false-positives. All samples showed to be positive for some pesticides, and only 6 of these samples comply the requirements established by EU legislation [5-8]. In some cases, relatively high concentrations of some pesticides, such as the case of imazalil in citrus fruits, was observed.

In conclusion, the multi-residue analysis of a high number of pesticides in fruit and vegetable samples sometimes requires the combination of different acquisition and confirmatory strategies in order to prevent false-positives and false-negatives. The triple hyperbolic quadrupole instruments, as the one used in this work, give a number of acquisition possibilities to perform additional acquisition strategies helping in the confirmation of target pesticides following the guidelines established by the EU legislation [1], without the necessity of combining information from different MS analyzers.

Acknowledgements

The authors gratefully acknowledge financial support from the Spanish Ministry of Science and Innovation through project ref. CTQ2009-09253.

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Figure captions

Figure 1. Chromatographic separation of a standard of 100 pesticides (100 µg/kg) by LC-MS in H-SIM mode.

Figure 2. Analysis of a tomato sample by LC-MS with accurate mass measurements in H-SIM (Q1 at 0.04 Th FWHM) mode and internal lock mass calibration.

Figure 3. Analysis of an apple sample by LC-MS/MS in H-SRM mode with two transitions.

Figure 4. (a) Analysis of a celery sample by LC-MS/MS in H-SRM mode with two transitions. (b) Signal of DEET pesticide in the celery sample by LC-MS in AM H-SRM mode.

Figure 5. Analysis of an orange sample by data dependent analysis. Pesticides detected in H-SRM mode (first scan event) and, as an example, the RER product ion scan spectrum of imazalil (second scan event).

Figure 6. Results generated by the library search engine with the RER product ion scan spectrum of imazalil in an orange sample.

Figure 1

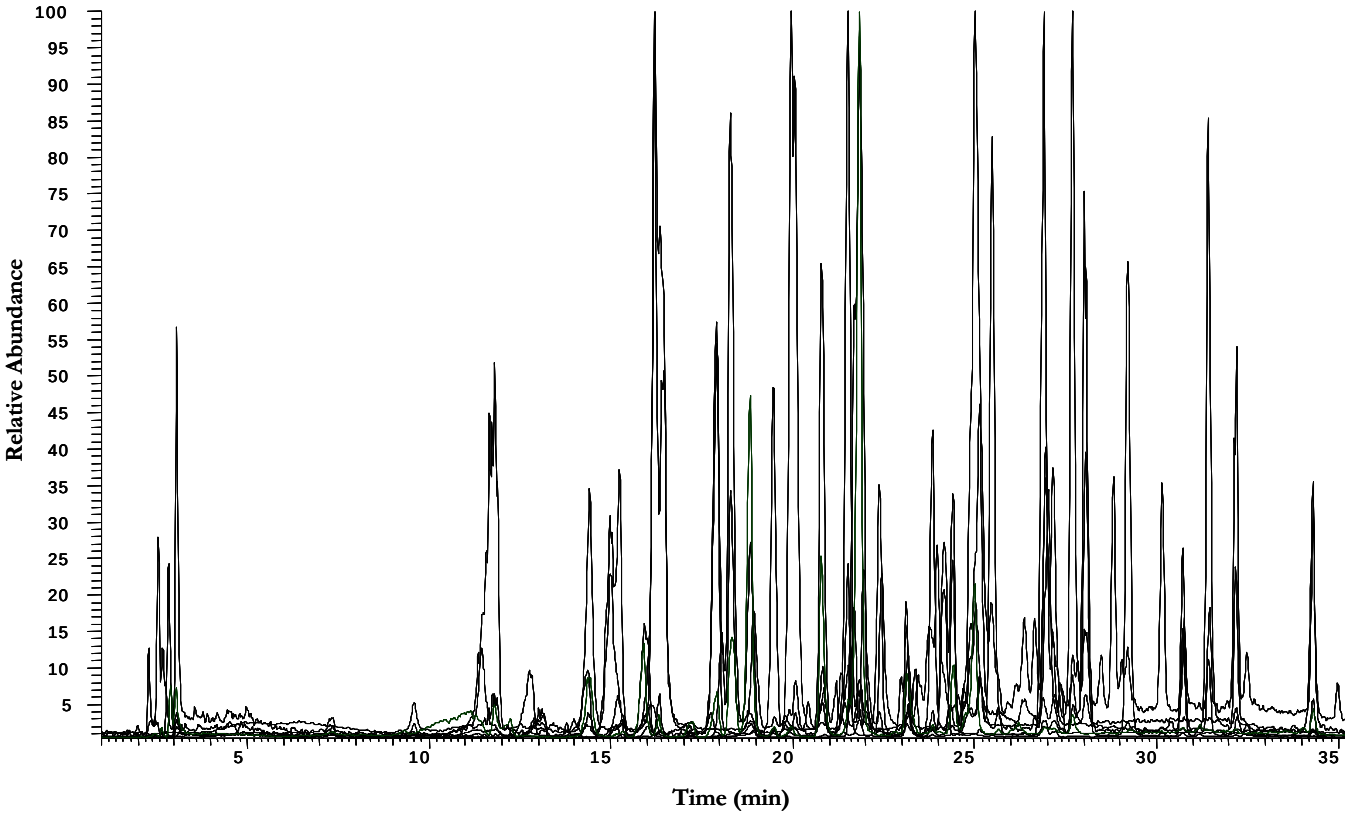
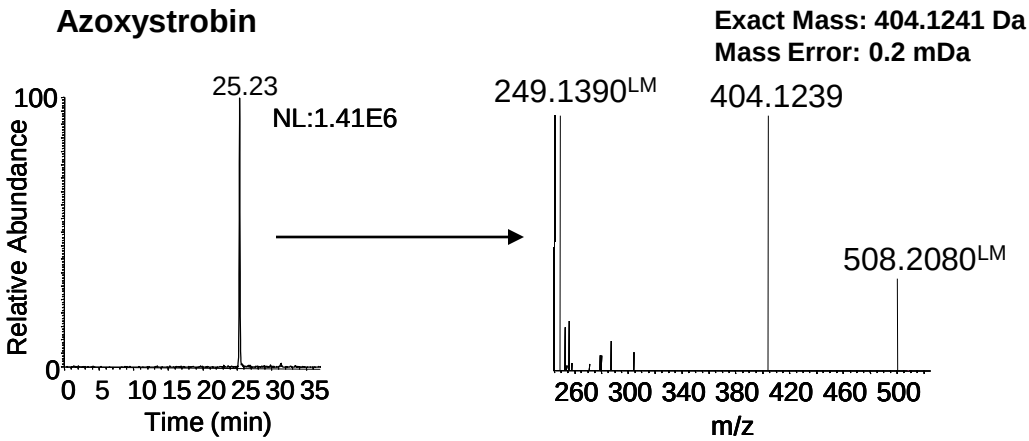
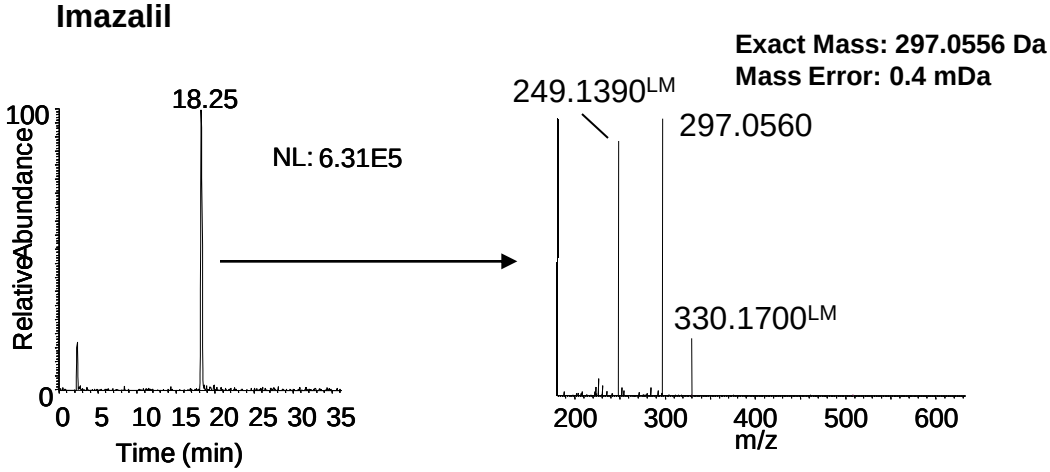

Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
5
10
15
20
25
30
35
Time (min)

Figure 2


Azoxystrobin
Exact Mass: 404.1241 Da
Mass Error: 0.2 mDa
25.23
NL:1.41E6
249.1390LM
404.1239
508.2080LM
Relative Abundance
100
0
0 5 10 15 20 25 30 35
Time (min)
260 300 340 380 420 460 500
m/z


Imazalil
Exact Mass: 297.0556 Da
Mass Error: 0.4 mDa
18.25
NL: 6.31E5
249.1390LM
297.0560
330.1700LM
Relative Abundance
100
0
0 5 10 15 20 25 30 35
Time (min)
200 300 400 500 600
m/z

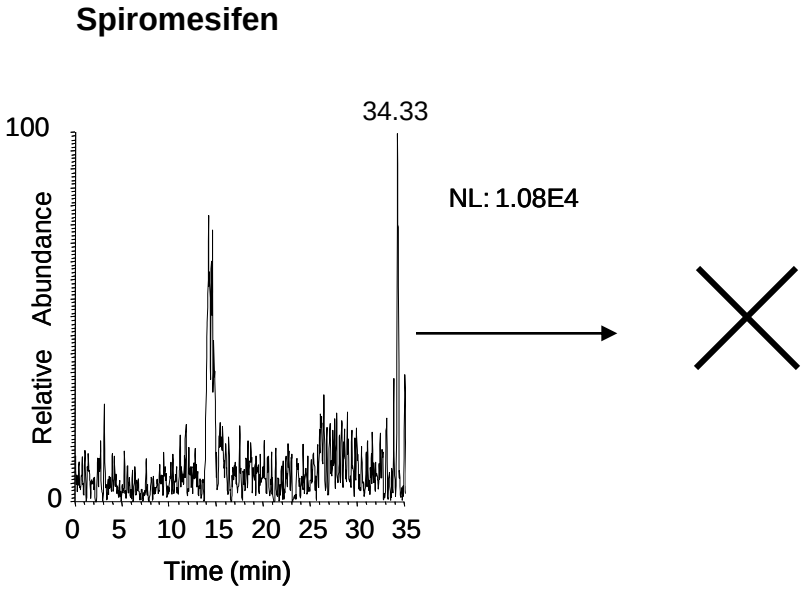

Spiromesifen
34.33
NL: 1.08E4
Relative Abundance
100
0
0 5 10 15 20 25 30 35
Time (min)

Figure 3

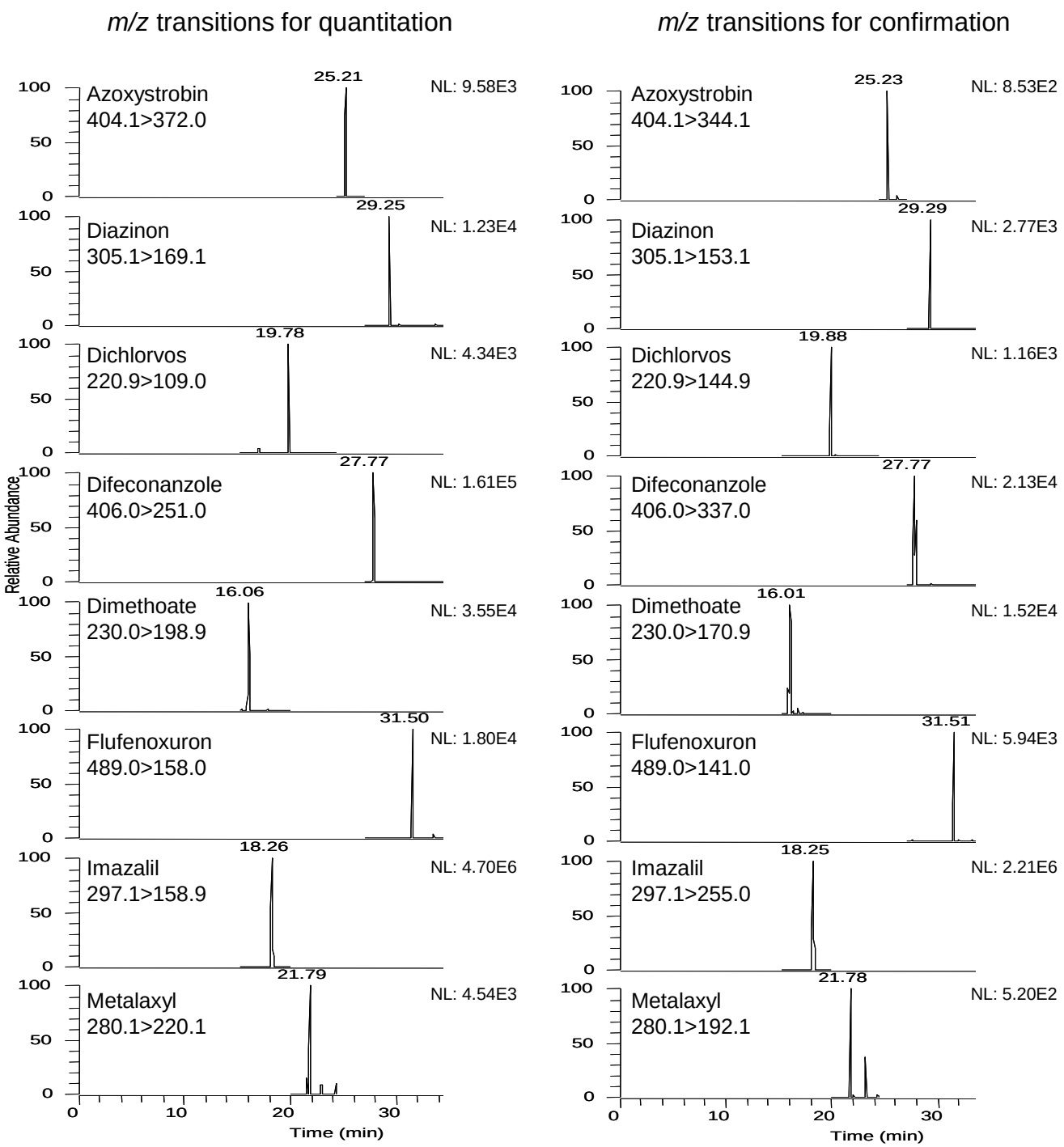

m/z transitions for quantitation
m/z transitions for confirmation
Relative Abundance
Time (min)
Azoxystrobin
404.1>372.0
NL: 9.58E3
25.21
Azoxystrobin
404.1>344.1
NL: 8.53E2
25.23
Diazinon
305.1>169.1
NL: 1.23E4
29.25
Diazinon
305.1>153.1
NL: 2.77E3
29.29
Dichlorvos
220.9>109.0
NL: 4.34E3
19.78
Dichlorvos
220.9>144.9
NL: 1.16E3
19.88
Difeconanzole
406.0>251.0
NL: 1.61E5
27.77
Difeconanzole
406.0>337.0
NL: 2.13E4
27.77
Dimethoate
230.0>198.9
NL: 3.55E4
16.06
Dimethoate
230.0>170.9
NL: 1.52E4
16.01
Flufenoxuron
489.0>158.0
NL: 1.80E4
31.50
Flufenoxuron
489.0>141.0
NL: 5.94E3
31.51
Imazalil
297.1>158.9
NL: 4.70E6
18.26
Imazalil
297.1>255.0
NL: 2.21E6
18.25
Metalaxyl
280.1>220.1
NL: 4.54E3
21.79
Metalaxyl
280.1>192.1
NL: 5.20E2
21.78

Figure 4

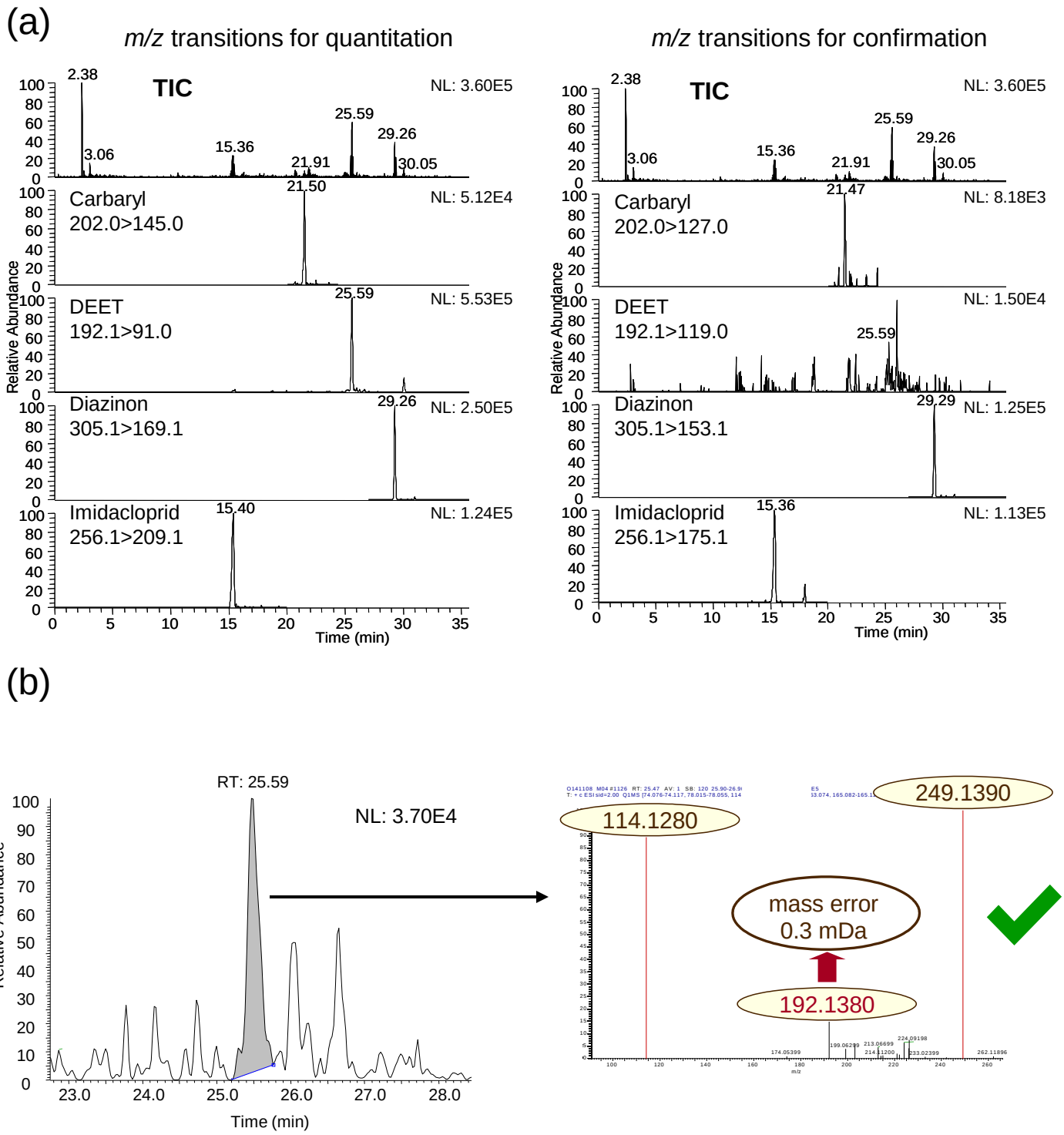

(a)
m/z transitions for quantitation
m/z transitions for confirmation
TIC
NL: 3.60E5
2.38
3.06
15.36
21.91
25.59
29.26
30.05
Carbaryl
202.0>145.0
NL: 5.12E4
21.50
DEET
192.1>91.0
NL: 5.53E5
Diazinon
305.1>169.1
NL: 2.50E5
29.26
Imidacloprid
256.1>209.1
NL: 1.24E5
15.40
Relative Abundance
Time (min)
Carbaryl
202.0>127.0
NL: 8.18E3
21.47
DEET
192.1>119.0
NL: 1.50E4
Diazinon
305.1>153.1
NL: 1.25E5
29.29
Imidacloprid
256.1>175.1
NL: 1.13E5
15.36
(b)
RT: 25.59
NL: 3.70E4
249.1390
114.1280
mass error
0.3 mDa
192.1380

Figure 5

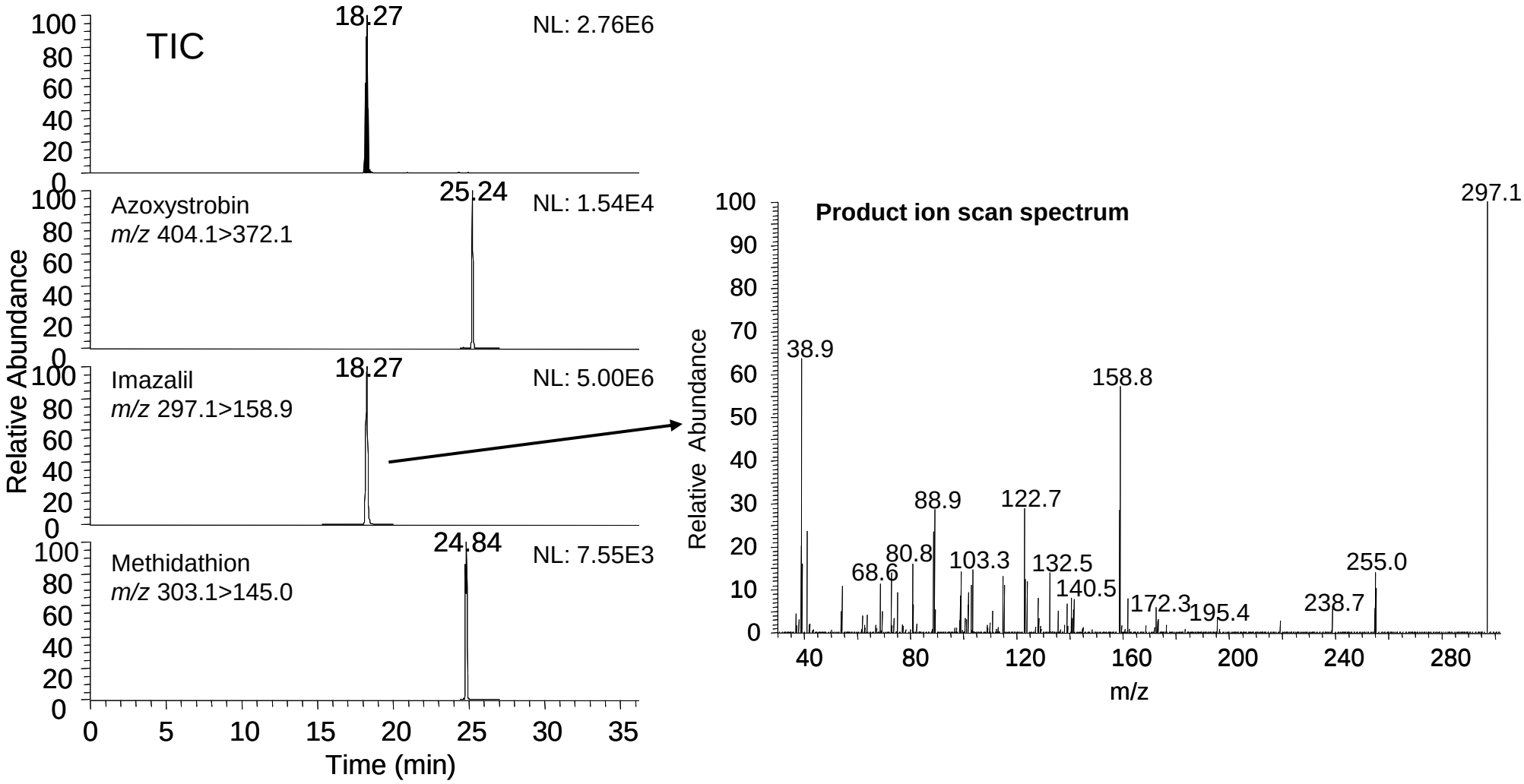

TIC
18.27
NL: 2.76E6
Azoxystrobin
m/z 404.1>372.1
25.24
NL: 1.54E4
Imazalil
m/z 297.1>158.9
18.27
NL: 5.00E6
Methidathion
m/z 303.1>145.0
24.84
NL: 7.55E3
Relative Abundance
Time (min)
Product ion scan spectrum
297.1
38.9
158.8
88.9
122.7
80.8
103.3
68.6
132.5
140.5
255.0
172.3
195.4
238.7
m/z

Figure 6

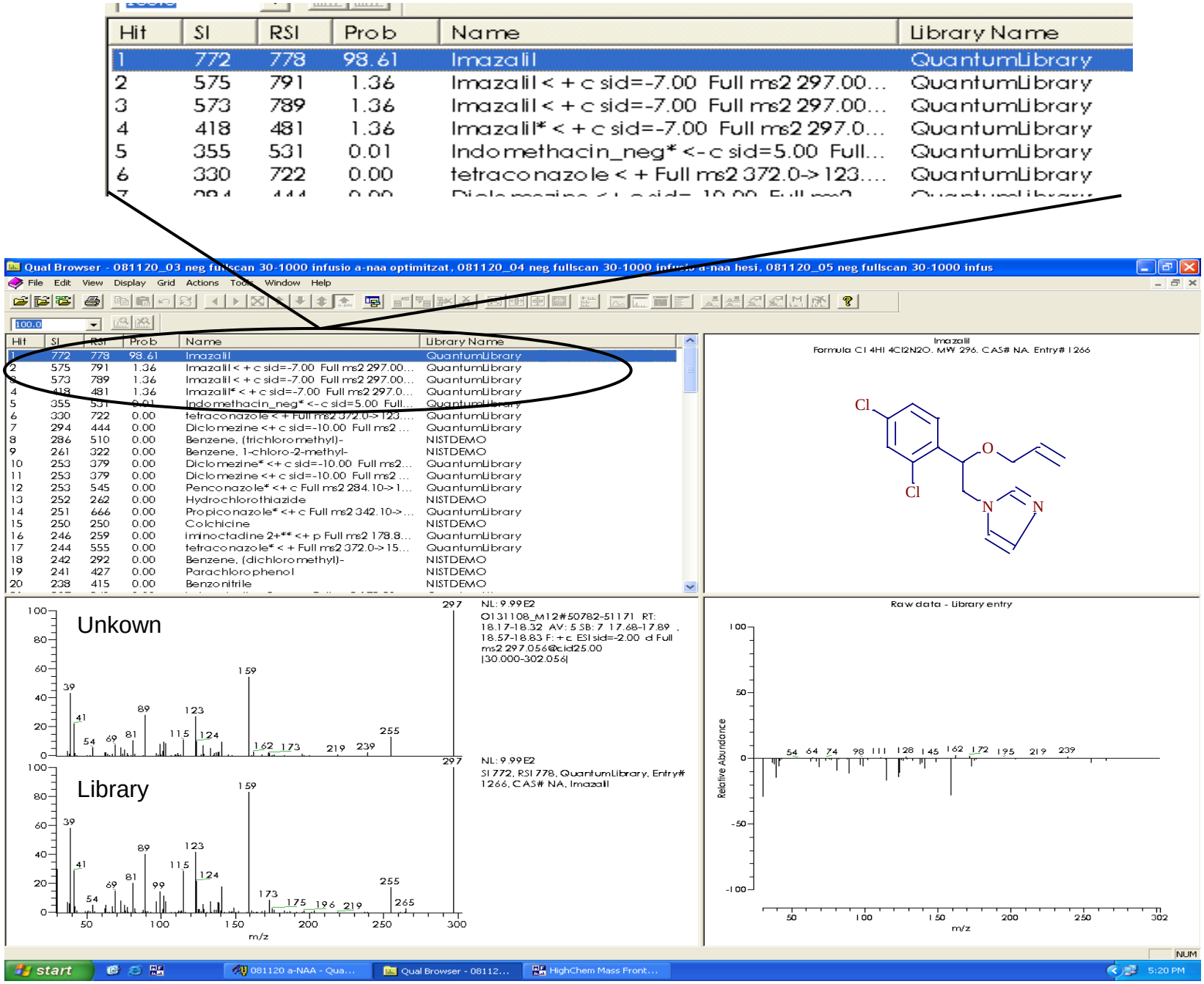

Hit SI RSI Prob Name Library Name
1 772 778 98.61 Imazalil QuantumLibrary
2 575 791 1.36 Imazalil < + c sid=-7.00 Full ms2 297.00... QuantumLibrary
3 573 789 1.36 Imazalil < + c sid=-7.00 Full ms2 297.00... QuantumLibrary
4 418 481 1.36 Imazalil* < + c sid=-7.00 Full ms2 297.0... QuantumLibrary
5 355 531 0.01 Indomethacin_neg* <- c sid=5.00 Full... QuantumLibrary
6 330 722 0.00 tetraconazole < + Full ms2 372.0-> 123.... QuantumLibrary
Qual Browser - 081120_03 neg fullscan 30-1000 infusio a-naa optimitzat, 081120_04 neg fullscan 30-1000 infusio a-naa hesi, 081120_05 neg fullscan 30-1000 infus
File Edit View Display Grid Actions Tools Window Help
Hit SI RSI Prob Name Library Name
1 772 778 98.61 Imazalil QuantumLibrary
2 575 791 1.36 Imazalil < + c sid=-7.00 Full ms2 297.00... QuantumLibrary
3 573 789 1.36 Imazalil < + c sid=-7.00 Full ms2 297.00... QuantumLibrary
4 418 481 1.36 Imazalil* < + c sid=-7.00 Full ms2 297.0... QuantumLibrary
5 355 531 0.01 Indomethacin_neg* <- c sid=5.00 Full... QuantumLibrary
6 330 722 0.00 tetraconazole < + Full ms2 372.0-> 123.... QuantumLibrary
7 294 444 0.00 Diclomezine <+ c sid=-10.00 Full ms2 ... QuantumLibrary
8 286 510 0.00 Benzene, (trichloromethyl)- NISTDEMO
9 261 322 0.00 Benzene, 1-chloro-2-methyl- NISTDEMO
10 253 379 0.00 Diclomezine* <+ c sid=-10.00 Full ms2... QuantumLibrary
11 253 379 0.00 Diclomezine <+ c sid=-10.00 Full ms2 ... QuantumLibrary
12 253 545 0.00 Penconazole* <+ c Full ms2 284.10-> 1... QuantumLibrary
13 252 262 0.00 Hydrochlorothiazide NISTDEMO
14 251 666 0.00 Propiconazole* <+ c Full ms2 342.10->... QuantumLibrary
15 250 250 0.00 Colchicine NISTDEMO
16 246 259 0.00 iminoctadine 2+** <+ p Full ms2 178.8... QuantumLibrary
17 244 555 0.00 tetraconazole* < + Full ms2 372.0-> 15... QuantumLibrary
18 242 292 0.00 Benzene, (dichloromethyl)- NISTDEMO
19 241 427 0.00 Parachlorophenol NISTDEMO
20 238 415 0.00 Benzonitrile NISTDEMO
Imazalil
Formula C14H14Cl2N2O, MW 296, CAS# NA, Entry# 1266
Cl
O
Cl
N
N
Unkown
NL: 9.99E2
O131108_M12#50782-51171 RT: 18.17-18.32 AV: 5 SB: 7 17.68-17.89 , 18.57-18.83 F: + c ESI sid=-2.00 d Full ms2 297.056@cid25.00 [30.000-302.056]
Library
NL: 9.99E2
SI 772, RSI 778, QuantumLibrary, Entry# 1266, CAS# NA, Imazalil
m/z
Raw data - Library entry
Relative Abundance
m/z
start
081120 a-NAA - Qua...
Qual Browser - 08112...
HighChem Mass Front...
5:20 PM

Table 1

Table 1. Instrumental limits of detection in LC-MS.

Compound	Elemental composition[a]	Accurate mass $[M+H]^+$	Retention time (min)	ILODs in full scan mode (µg/kg)		ILODs in SIM mode (µg/kg)	
				Low resolution[d]	Enhanced resolution[d]	Low resolution[d]	Enhanced resolution[d]
Acetamiprid	$C_{10}H_{11}N_4Cl$	223.0745	16.2	11	6	3	3
Acetochlor	$C_{14}H_{20}NO_2Cl$	270.1255	27.2	-[b]	-[b]	-[b]	-[b]
Alachlor	$C_{14}H_{20}NO_2Cl$	270.1255	27.2	-[b]	-[b]	-[b]	-[b]
Aldicarb	$C_7H_{14}N_2O_2S$	213.0668[c]	18.4	15	15	10	10
Aldicarb sulfone	$C_7H_{14}N_2O_4S$	223.0747	11.2	150	100	30	10
Aldicarb sulfoxide	$C_7H_{14}N_2O_3S$	207.0798	7.35	500	500	200	100
Atrazine	$C_8H_{14}N_5Cl$	216.1010	21.5	15	10	1	0.5
Azoxystrobin	$C_{22}H_{17}N_3O_5$	404.1241	25.2	10	10	3	0.5
Benalaxyl	$C_{20}H_{23}NO_3$	326.1751	28.0	4	1	1	0.6
Bendiocarb	$C_{11}H_{13}NO_4$	224.0917	20.9	100	100	20	10
Bensultap	$C_{17}H_{21}NO_4S_4$	432.0426	21.2	20	15	10	1
Bromoxynil	$C_7H_3NOBr_2$	275.8654	22.7	100	100	50	50
Bromuconazole	$C_{13}H_{12}N_3OCl_2Br$	375.9614	24.8+25.7	20	10	10	1
Buprofezin	$C_{16}H_{23}N_3OS$	306.1635	26.9	20	15	0.5	0.3
Butylate	$C_{11}H_{23}NOS$	218.1573	31.5	15	10	1	1
Captan	$C_9H_8NO_2SCl_3$	299.9414	26.1	100	100	50	50
Carbaryl	$C_{12}H_{11}NO_2$	202.0863	21.4	100	100	10	10
Carbendazim	$C_9H_9N_3O_2$	192.0768	7.8	100	100	10	10
Carbofuran	$C_{12}H_{15}NO_3$	222.1125	20.8	10	5	1	1
Cartap	$C_7H_{15}N_3O_2S_2$	237.0606	3.0	20	10	4	1
Chlorfenvinphos	$C_{12}H_{14}O_4PCl_3$	358.9768	27.7	25	25	10	10
Chlorpyrifos methyl	$C_7H_7NO_3PSCl_3$	321.9023	29.7	200	200	100	50
Cyanazine	$C_9H_{13}N_6Cl$	241.0963	19.9	100	100	50	50
Cyproconazole	$C_{15}H_{18}N_3OCl$	292.1211	24.2	10	3	1	0.6
Cyromazine	$C_6H_{10}N_6$	167.1040	2.9	5	5	1	0.5
DEET	$C_{12}H_{17}NO$	192.1383	21.7	50	50	10	5
Deethylatrazine	$C_6H_{10}N_5Cl$	188.0697	15.3	50	50	5	5
Deethylterbuthylazine	$C_7H_{12}N_5Cl$	202.0854	19.0	10	10	2	1
Deisopropylatrazine	$C_5H_8N_5Cl$	174.0541	12.2	100	100	30	15
Diazinon	$C_{12}H_{21}N_2O_3PS$	305.1083	29.2	3	1	1	0.3
Dichlorvos	$C_4H_7O_4PCl_2$	220.9532	19.8	50	50	10	10
Difeconazole	$C_{19}H_{17}N_3O_3Cl_2$	406.0720	27.7+27.9	10	10	3	0.5
Difenoxuron	$C_{16}H_{18}N_2O_3$	287.1390	21.9	10	10	0.3	0.1
Diflubenzuron	$C_{14}H_9N_2O_2F_2Cl$	311.0393	26.2	100	60	20	12
Dimethenamide	$C_{12}H_{18}NO_2SCl$	276.0820	25.0	10	10	5	1
Dimethoate	$C_5H_{12}NO_3PS_2$	230.0069	16.0	10	10	3	1
Dimethomorph	$C_{21}H_{22}NO_4Cl$	388.1310	23.0+23.4	50	50	5	0.5
Diuron	$C_9H_{10}N_2OCl_2$	233.0243	21.9	10	3	3	2
Ethiofencarb	$C_{11}H_{15}NO_2S$	226.0896	22.0	50	50	10	10
Fenamiphos	$C_{13}H_{22}NO_3PS$	304.1131	24.9	25	10	10	0.5
Fenuron	$C_9H_{12}N_2O$	165.1022	14.9	10	10	0.5	0.5
Flufenacet	$C_{14}H_{13}N_3O_2F_4S$	364.0737	27.4	30	20	5	2
Flufenoxuron	$C_{21}H_{11}N_2O_3F_6Cl$	489.0435	31.5	100	50	10	1
Fluoroacetamide	C_2H_4NOF	78.0350	2.8	100	50	10	6
Fluroxypyr	$C_7H_5N_2O_3FCl_2$	254.9734	19.0	200	50	50	15
Hexaflumuron	$C_{16}H_8N_2O_3F_6Cl_2$	460.9889	29.0	150	50	50	10
Hydroxyatrazine	$C_8H_{15}N_5O$	198.1349	11.3	30	30	10	5
Imazalil	$C_{14}H_{14}N_2OCl_2$	297.0556	18.2	3	1	0.5	0.1
Imazapyr	$C_{13}H_{15}N_3O_3$	262.1186	12.8	10	10	3	1
Imazaquin	$C_{17}H_{17}N_3O_3$	312.1343	18.8	3	1	0.5	0.5
Imidacloprid	$C_9H_{10}N_5O_2Cl$	256.0596	15.3	10	10	5	3
Ioxynil	$C_7H_3NOI_2$	371.8377	25.1	250	250	10	10
Iprodione	$C_{13}H_{13}N_3O_3Cl_2$	330.0407	26.7	100	100	50	10
Irgarol 1051	$C_{11}H_{19}N_5S$	254.1434	20.7	5	3	0.3	0.1
Irgarol metabolite	$C_8H_{15}N_5S$	214.1121	16.3	5	5	1	1
Isoproturon	$C_{12}H_{18}N_2O$	207.1492	21.8	6	1	1	0.8

Compound	Elemental composition[a]	Accurate mass $[M+H]^+$	Retention time (min)	ILODs in full scan mode (µg/kg)		ILODs in SIM mode (µg/kg)	
				Low resolution[d]	Enhanced Resolution[d]	Low resolution[d]	Enhanced resolution[d]
Lenacil	$C_{13}H_{18}N_2O_2$	235.1441	19.6	100	100	10	10
Lufenuron	$C_{17}H_8N_2O_3F_8Cl_2$	510.9857	30.8	200	100	10	10
Malathion	$C_{10}H_{19}O_6PS_2$	331.0433	26.4	50	50	10	5
Mebendazole	$C_{16}H_{13}N_3O_3$	296.1030	18.0	10	10	0.5	0.5
Metalaxyl	$C_{15}H_{21}NO_4$	280.1543	21.7	7	5	1	0.3
Metamitron	$C_{10}H_{10}N_4O$	203.0927	14.3	10	10	2	1
Methidathion	$C_6H_{12}N_2O_4PS_3$	302.9691	24.9	100	100	50	50
Methiocarb	$C_{11}H_{15}NO_2S$	226.0896	24.4	50	50	10	10
Methiocarb sulfone	$C_{11}H_{15}NO_4S$	258.0795	17.2	50	50	10	10
Methomyl	$C_5H_{10}N_2O_2S$	163.0536	11.7	50	50	10	10
Metolachlor	$C_{15}H_{22}NO_2Cl$	284.1412	26.9	10	10	5	1
Metolcarb	$C_9H_{11}NO_2$	166.0863	19.5	50	50	10	5
Metribuzin	$C_8H_{14}N_4OS$	215.0961	19.8	10	10	1	1
Molinate	$C_9H_{17}NOS$	188.1104	25.5	10	8	3	2
Monuron	$C_9H_{11}N_2OCl$	199.0633	19.1	100	100	50	10
Nicosulfuron	$C_{15}H_{18}N_6O_6S$	411.1081	17.8	20	5	4	3
Nitenpyram	$C_{11}H_{15}N_4O_2Cl$	271.0956	14.0	100	10	20	1
Oxadixyl	$C_{14}H_{18}N_2O_4$	279.1339	18.9	10	10	1	1
Parathion ethyl	$C_{10}H_{14}NO_5PS$	292.0403	32.2	10	3	3	2
Pendimethalin	$C_{13}H_{19}N_3O_4$	282.1448	32.2	25	25	10	10
Phosmet	$C_{11}H_{12}NO_4PS_2$	318.0018	25.2	100	50	50	10
Prochloraz	$C_{15}H_{16}N_3O_2Cl_3$	376.0381	23.1	5	5	1	1
Profenofos	$C_{11}H_{15}O_3PSClBr$	372.9424	30.2	50	20	15	10
Promecarb	$C_{12}H_{17}NO_2$	208.1332	25.2	100	50	50	10
Prometon	$C_{10}H_{19}N_5O$	226.1662	16.2	10	10	1	0.5
Prometryn	$C_{10}H_{19}N_5S$	242.1434	19.9	2	0.5	0.5	0.2
Propachlor	$C_{11}H_{14}NOCl$	212.0837	23.2	25	25	10	10
Propanil	$C_9H_9NOCl_2$	218.0134	23.9	30	30	5	5
Propiconazole	$C_{15}H_{17}N_3O_2Cl_2$	342.0771	27.0+27.2	10	10	3	1
Prosulfocarb	$C_{14}H_{21}NOS$	252.1417	30.8	10	10	1	1
Simazine	$C_7H_{12}N_5Cl$	202.0854	18.9	10	10	2	1
Spinosad A	$C_{41}H_{65}NO_{10}$	732.4681	22.3	50	50	10	10
Spinosad D	$C_{42}H_{67}NO_{10}$	746.4838	22.8	50	50	10	10
Spiromesifen	$C_{23}H_{30}O_4$	371.2217	30.7	100	50	10	6
Spiroxamine	$C_{18}H_{35}NO_2$	298.2741	18.2	20	20	10	10
Teflubenzuron	$C_{14}H_6N_2O_2F_4Cl_2$	380.9815	29.4	100	100	80	50
Terbuthylazine	$C_9H_{16}N_5Cl$	230.1167	24.4	10	10	2	1
Terbutryn	$C_{10}H_{19}N_5S$	242.1434	20.0	1	1	0.3	0.1
Thiabendazole	$C_{10}H_7N_3S$	202.0433	9.6	100	100	10	10
Thiacloprid	$C_{10}H_9N_4SCl$	253.0309	17.9	50	50	5	5
Thiocyclam	$C_5H_{11}NS_3$	182.0126	3.1	100	100	10	10
Thiosultap	$C_5H_{13}NO_6S_4$	311.9698	2.7	200	200	50	15
Triclocarban	$C_{13}H_9N_2OCl_3$	314.9853	28.9	50	20	10	10
Triflumizole	$C_{15}H_{15}N_3OF_3Cl$	346.0929	29.2	100	100	25	10

[a] Elemental compositions correspond to the neutral molecule.

[b] Values not given because of isobaric masses and coelution.

[c] Ion corresponding to the sodium adduct $[M+Na]^+$

[d] Low resolution: Q1 at 0.7 *m/z* FWHM; Enhanced resolution: Q1 at 0.1 *m/z* FWHM

Table 2. Accurate mass measurements in LC-MS H-SIM mode.

Compound	Retention time (min)	Accurate mass $[M+H]^+$	Measured *m/z*	Mass error (mDa)	ILOD (µg/kg)
Acetamiprid	16.2	223.0745	223.0750	-0.5	10
Acetochlor	27.2	270.1255	270.1249	0.6	-[b]
Alachlor	27.2	270.1255	270.1249	0.6	-[b]
Aldicarb	18.4	213.0668[c]	213.0670	-0.2	20
Aldicarb sulfone	11.2	223.0747	223.0750	-0.3	50
Aldicarb sulfoxide	7.35	207.0798	207.0800	-0.2	300
Atrazine	21.5	216.1010	216.1010	0	3
Azoxystrobin	25.2	404.1241	404.1240	0.1	5
Benalaxyl	28.0	326.1751	326.1749	0.2	1
Bendiocarb	20.9	224.0917	224.0920	-0.3	10
Bensultap	21.2	432.0426	432.0424	0.2	20
Bromoxynil	22.7	275.8654	275.8656	-0.2	50
Bromuconazole	24.8+25.7	375.9614	375.9617	-0.3	10
Buprofezin	26.9	306.1635	306.1640	-0.5	5
Butylate	31.5	218.1573	218.1570	0.3	10
Captan	26.1	299.9414	299.9419	-0.5	50
Carbaryl	21.4	202.0863	202.0850	1.3	10
Carbendazim	7.8	192.0768	192.0770	-0.2	25
Carbofuran	20.8	222.1125	222.1130	-0.5	3
Cartap	3.0	237.0606	150.0412	1.3	5
Chlorfenvinphos	27.7	358.9768	358.9770	-0.2	10
Chlorpyrifos methyl	29.7	321.9023	321.9020	0.3	150
Cyanazine	19.9	241.0963	241.0960	0.3	80
Cyproconazole	24.2	292.1211	292.1209	0.2	5
Cyromazine	2.9	167.1040	167.1040	0	1
DEET	21.7	192.1383	192.1380	0.3	10
Deethylatrazine	15.3	188.0697	188.0692	0.5	10
Deethylterbuthylazine	19.0	202.0854	202.0850	0.4	2
Deisopropylatrazine	12.2	174.0541	174.0540	0.1	20
Diazinon	29.2	305.1083	305.1080	0.3	1
Dichlorvos	19.8	220.9532	220.9530	0.2	25
Difeconazole	27.7+27.9	406.0720	406.0724	-0.4	5
Difenoxuron	21.9	287.1390	287.1390	0	0.5
Diflubenzuron	26.2	311.0393	311.0389	0.4	25
Dimethenamide	25.0	276.0820	276.0820	0	5
Dimethoate	16.0	230.0069	230.0070	-0.1	3
Dimethomorph	23.0+23.4	388.1310	388.1308	0.2	5
Diuron	21.9	233.0243	233.0239	0.4	5
Ethiofencarb	22.0	226.0896	226.0900	-0.4	30
Fenamiphos	24.9	304.1131	304.1130	0.1	10
Fenuron	14.9	165.1022	165.1020	0.2	4
Flufenacet	27.4	364.0737	364.0745	-0.8	10
Flufenoxuron	31.5	489.0435	489.0430	0.5	10
Fluoroacetamide	2.8	78.0350	78.0353	-0.3	50
Fluroxypyr	19.0	254.9734	254.9751	-1.7	80
Hexaflumuron	29.0	460.9889	460.9885	0.4	80
Hydroxyatrazine	11.3	198.1349	198.1350	-0.1	10
Imazalil	18.2	297.0556	297.0560	-0.4	1
Imazapyr	12.8	262.1186	262.1192	-0.6	10
Imazaquin	18.8	312.1343	312.1340	0.3	1
Imidacloprid	15.3	256.0596	256.0590	0.6	10
Ioxynil	25.1	371.8377	371.8381	-0.4	10
Iprodione	26.7	330.0407	330.0403	0.4	60
Irgarol 1051	20.7	254.1434	254.1430	0.4	0.5
Irgarol metabolite	16.3	214.1121	214.1120	0.1	1
Isoproturon	21.8	207.1492	207.1483	0.9	4

Compound	Retention time (min)	Accurate mass $[M+H]^+$	Measured *m/z*	Mass error (mDa)	LOD (µg/~~L~~ kg)
Lenacil	19.6	235.1441	235.1440	0.1	30
Lufenuron	30.8	510.9857	510.9853	0.5	50
Malathion	26.4	331.0433	331.0430	0.3	25
Mebendazole	18.0	296.1030	296.1030	0	1
Metalaxyl	21.7	280.1543	280.1539	0.4	1
Metamitron	14.3	203.0927	203.0930	-0.3	2
Methidathion	24.9	302.9691	302.9689	0.2	10
Methiocarb	24.4	226.0896	226.0900	-0.4	25
Methiocarb sulfone	17.2	258.0795	258.0791	0.4	30
Methomyl	11.7	163.0536	163.0540	-0.4	10
Metolachlor	26.9	284.1412	284.1409	0.3	5
Metolcarb	19.5	166.0863	166.0860	0.3	30
Metribuzin	19.8	215.0961	215.0960	0.1	3
Molinate	25.5	188.1104	188.1077	2.7	10
Monuron	19.1	199.0633	199.0630	0.3	30
Nicosulfuron	17.8	411.1081	411.1080	0.1	20
Nitenpyram	14.0	271.0956	271.0959	-0.3	10
Oxadixyl	18.9	279.1339	279.1340	-0.1	3
Parathion ethyl	32.2	292.0403	292.0399	0.4	25
Pendimethalin	32.2	282.1448	282.1450	-0.2	50
Phosmet	25.2	318.0018	318.0011	0.7	50
Prochloraz	23.1	376.0381	376.0386	-0.5	10
Profenofos	30.2	372.9424	372.9434	-1.0	40
Promecarb	25.2	208.1332	208.1330	0.2	10
Prometon	16.2	226.1662	226.1660	0.2	1
Prometryn	19.9	242.1434	242.1430	0.4	0.5
Propachlor	23.2	212.0837	212.0840	-0.3	10
Propanil	23.9	218.0134	218.0130	0.4	10
Propiconazole	27.0+27.2	342.0771	342.0770	0.1	10
Prosulfocarb	30.8	252.1417	252.1420	-0.3	5
Simazine	18.9	202.0854	202.0851	0.3	5
Spinosad A	22.3	732.4681	732.4678	-0.3	20
Spinosad D	22.8	746.4838	742.4836	0.2	20
Spiromesifen	30.7	371.2217	371.2220	-0.3	50
Spiroxamine	18.2	298.2741	298.1746	0.5	20
Teflubenzuron	29.4	380.9815	380.9801	1.4	100
Terbuthylazine	24.4	230.1167	230.1170	-0.3	3
Terbutryn	20.0	242.1434	242.1431	0.3	0.5
Thiabendazole	9.6	202.0433	202.0430	0.3	10
Thiacloprid	17.9	253.0309	253.0315	-0.6	5
Thiocyclam	3.1	182.0126	182.0130	-0.4	10
Thiosultap	2.7	311.9698	311.9694	0.4	50
Triclocarban	28.9	314.9853	314.9849	0.4	50
Triflumizole	29.2	346.0929	346.0926	0.3	50

[a] Elemental compositions correspond to the neutral molecule.
[b] Values not given because of isobaric masses and coelution.
[c] Ion corresponding to the sodium adduct $[M+Na]^+$
AM H-SIM: Q1 at 0.04 *m/z* FWHM

Table 3. Method limits of detection in orange and green pepper matrices.

Compound	Retention time (min)	MLODs in AM H-SIM mode[c] (µg/kg)		MLODs in H-SRM mode[c] (µg/kg)	
		Orange	Green pepper	Orange	Green pepper
Acetamiprid	16.2	50	50	0.08	0.08
Acetochlor	27.2	-[a]	-[a]	0.08	0.08
Alachlor	27.2	-[a]	-[a]	0.1	0.1
Aldicarb	18.4	20	20	0.5	0.5
Aldicarb sulfone	11.2	100	100	1	1
Aldicarb sulfoxide	7.35	350	350	10	10
Atrazine	21.5	2	2	0.01	0.05
Azoxystrobin	25.2	-[b]	10	-[b]	0.05
Benalaxyl	28.0	1	2	0.008	0.01
Bendiocarb	20.9	10	10	0.3	0.2
Bensultap	21.2	50	50	20	20
Bromoxynil	22.7	100	100	0.5	0.5
Bromuconazole	24.8+25.7	10	10	0.05	0.5
Buprofezin	26.9	10	8	0.04	0.05
Butylate	31.5	20	10	0.1	0.5
Captan	26.1	80	80	5	5
Carbaryl	21.4	5	4	0.1	0.1
Carbendazim	7.8	80	40	3	3
Carbofuran	20.8	3	3	0.03	0.05
Cartap	3.0	10	10	0.5	0.5
Chlorfenvinphos	27.7	10	10	0.05	0.1
Chlorpyrifos methyl	29.7	200	200	1	1
Cyanazine	19.9	100	100	10	10
Cyproconazole	24.2	3	3	0.05	0.05
Cyromazine	2.9	10	10	0.5	0.5
DEET	21.7	30	30	10	10
Deethylatrazine	15.3	30	30	1	1
Deethylterbuthylazine	19.0	3	3	5	5
Deisopropylatrazine	12.2	60	60	10	10
Diazinon	29.2	3	-[b]	0.01	-[b]
Dichlorvos	19.8	30	25	0.5	0.5
Difeconazole	27.7+27.9	10	10	0.01	0.01
Difenoxuron	21.9	5	2	0.03	0.03
Diflubenzuron	26.2	50	50	0.5	0.5
Dimethenamide	25.0	3	3	0.1	0.1
Dimethoate	16.0	5	5	0.5	0.5
Dimethomorph	23.0+23.4	6	6	0.1	0.1
Diuron	21.9	10	10	0.5	0.5
Ethiofencarb	22.0	50	50	0.1	0.1
Fenamiphos	24.9	2	2	0.05	0.05
Fenuron	14.9	10	6	0.5	0.5
Flufenacet	27.4	10	10	0.08	0.08
Flufenoxuron	31.5	10	10	0.5	0.5
Fluoroacetamide	2.8	100	100	1	1
Fluroxypyr	19.0	120	120	0.06	0.06
Hexaflumuron	29.0	130	130	0.5	0.5
Hydroxyatrazine	11.3	10	10	5	5
Imazalil	18.2	-[b]	0.5	-[b]	0.05
Imazapyr	12.8	25	25	0.5	0.5
Imazaquin	18.8	10	10	0.5	0.5
Imidacloprid	15.3	20	-[b]	0.02	-[b]
Ioxynil	25.1	25	25	5	5
Iprodione	26.7	100	100	1	1
Irgarol 1051	20.7	1	1	0.02	0.02
Irgarol metabolite	16.3	3	3	0.2	0.2
Isoproturon	21.8	5	5	0.05	0.05

Compound	Retention time (min)	LODs in AM SIM mode[c] (µg/~~L~~kg)		LODs in H-SRM mode[c] (µg/~~L~~kg)	
		Orange	Green pepper	Orange	Green pepper
Lenacil	19.6	60	30	0.5	0.5
Lufenuron	30.8	100	100	5	5
Malathion	26.4	80	80	1	1
Mebendazole	18.0	1	0.5	0.1	0.1
Metalaxyl	21.7	3	-[b]	0.08	-[b]
Metamitron	14.3	10	6	1	0.5
Methidathion	24.9	-[b]	10	-[b]	0.5
Methiocarb	24.4	80	80	1	1
Methiocarb sulfone	17.2	100	100	1	1
Methomyl	11.7	50	50	1	1
Metolachlor	26.9	10	10	0.1	0.1
Metolcarb	19.5	10	10	0.5	0.5
Metribuzin	19.8	2	2	0.5	0.5
Molinate	25.5	5	5	0.5	0.5
Monuron	19.1	10	10	0.5	0.5
Nicosulfuron	17.8	15	30	1	1
Nitenpyram	14.0	10	10	1	1
Oxadixyl	18.9	10	10	1	1
Parathion ethyl	32.2	10	80	5	5
Pendimethalin	32.2	10	10	0.08	0.5
Phosmet	25.2	25	10	0.5	0.5
Prochloraz	23.1	1	2	0.01	0.03
Profenofos	30.2	10	10	0.5	0.5
Promecarb	25.2	10	10	0.5	0.1
Prometon	16.2	5	5	0.5	0.5
Prometryn	19.9	0.5	0.5	0.1	0.1
Propachlor	23.2	6	3	0.5	0.5
Propanil	23.9	30	15	0.5	0.5
Propiconazole	27.0+27.2	5	5	0.1	0.05
Prosulfocarb	30.8	10	4	0.01	0.01
Simazine	18.9	3	3	0.1	0.05
Spinosad A	22.3	30	30	0.1	0.1
Spinosad D	22.8	30	30	0.1	0.1
Spiromesifen	30.7	80	80	0.1	0.1
Spiroxamine	18.2	40	30	0.1	0.1
Teflubenzuron	29.4	100	100	10	10
Terbuthylazine	24.4	3	3	0.03	0.03
Terbutryn	20.0	0.5	0.5	0.03	0.03
Thiabendazole	9.6	100	100	10	10
Thiacloprid	17.9	10	10	0.5	0.5
Thiocyclam	3.1	25	25	1	0.5
Thiosultap	2.7	100	100	10	10
Triclocarban	28.9	80	80	1	1
Triflumizole	29.2	80	80	10	10

[a] Values not given because of isobaric masses and coelution.

[b] Value not given because sample is positive for this compound.

[c] AM H-SIM mode: Q1 at 0.04 *m/z* FWHM; H-SRM: Q1 at 0.1 *m/z* FWHM, Q3 at 0.7 *m/z* FWHM.

Table 4

Table 4. SRM transitions, MS/MS operating parameters and ILODs for LC-MS/MS analysis of 100 pesticides.

Compound	RT (min)	SRM transitions (*m/z*)	Collision energy (eV)	ILOD SRM[a] (µg/kg)	ILOD H-SRM[a] (µg/kg)
Acetamiprid	16.2	223.0745>126.0	20	0.08	0.08
		223.0745>56.1	20		
Acetochlor	27.2	270.1255>224.1	10	0.5	0.08
		270.1255>148.1	20		
Alachlor	26.7	270.1255>238.1	10	0.2	0.1
		270.1255>162.1	15		
Aldicarb	18.4	213.0668>89.0	15	1	1
		213.0668>116.0	15		
Aldicarb sulfone	11.2	223.0747>148.0	10	5	5
		223.0747>86.1	15		
Aldicarb sulfoxide	7.35	207.0798>89.0	15	50	25
		207.0798>132.0	10		
Atrazine	21.5	216.1010>174.0	20	0.01	0.01
		216.1010>132.0	25		
Azoxystrobin	25.2	404.1241>372.0	15	0.1	0.1
		404.1241>344.1	25		
Benalaxyl	28.0	326.1751>148.0	15	0.03	0.005
		326.1751>208.1	15		
Bendiocarb	20.9	224.0917>109.0	15	0.1	0.1
		224.0917>167.1	10		
Bensultap	21.2	432.0426>290.0	15	50	25
		432.0426>244.9	15		
Bromoxynil	22.7	275.8654>199.0	30	0.1	0.1
		275.8654>223.0	30		
Bromuconazole	24.8+25.7	375.9614>158.9	25	0.5	0.5
		375.9614>70.0	25		
Buprofezin	26.9	306.1635>201.1	15	0.05	0.05
		306.1635>116.0	20		
Butylate	31.5	218.1573>57.1	15	1	0.5
		218.1573>162.1	10		
Captan	26.1	299.9414>263.9	20	1	1
		299.9414>235.9	20		
Carbaryl	21.4	202.0863>145.0	10	0.1	0.1
		202.0863>127.0	20		
Carbendazim	7.8	192.0768>160.05	20	10	10
		192.0768>132.01	25		
Carbofuran	20.8	222.1125>165.0	15	0.1	0.1
		222.1125>123.0	20		
Cartap	3.0	150.0406>104.9	15	0.2	0.1
		150.0406>73.0	15		
Chlorfenvinphos	27.7	358.9768>155.0	15	0.1	0.1
		358.9768>127.0	20		
Chlorpyrifos methyl	29.7	321.9023>124.9	20	5	1
		321.9023>289.9	20		
Cyanazine	19.9	241.0963>214.0	20	10	10
		241.0963>174.0	20		
Cyproconazole	24.2	292.1211>70.0	25	0.05	0.05
		292.0153>125.0	25		
Cyromazine	2.9	167.1040>85.0	20	0.5	0.1
		167.1040>125.1	20		
DEET	21.7	192.1383>119.0	15	5	5
		192.1383>91.0	15		
Deethylatrazine	15.3	188.0697>146.0	20	1	1
		188.0697>104.0	25		
Deethylterbuthylazine	19.0	202.0854>146.0	20	1	1
		202.0854>110.0	25		
Deisopropylatrazine	12.2	174.0541>96.0	20	10	10
		174.0541>132.0	20		
Diazinon	29.2	305.1083>169.0	20	0.01	0.005
		305.1083>153.1	20		
Dichlorvos	19.8	220.9532>109.0	20	0.5	0.5
		220.9532>144.9	15		
Difeconazole	27.7+27.9	406.0720>251.0	25	0.1	0.1
		406.0720>337.0	20		
Difenoxuron	21.9	287.1390>123.0	20	0.1	0.1
		287.1390>72.0	20		
Diflubenzuron	26.2	311.0393>158.0	15	1	0.5
		311.0393>141.0	25		

Compound	RT (min)	SRM transitions (*m/z*)	Collision energy (eV)	LOD SRM (µg/kg)	LOD H-SRM (µg/kg)
Dimethenamide	25.0	276.0820>244.0	25	0.1	0.1
		276.0820>168.0	25		
Dimethoate	16.0	230.0069>198.9	10	0.5	0.1
		230.0069>170.9	15		
Dimethomorph	23.0+23.4	388.1310>301.0	20	0.5	0.1
		388.1310>165.0	30		
Diuron	21.9	233.0243>72.0	25	0.1	0.1
		233.0243>159.9	30		
Ethiofencarb	22.0	226.0896>107.0	10	0.5	0.1
		226.0896>164.0	10		
Fenamiphos	24.9	304.1131>217.0	25	0.1	0.05
		304.1131>234.0	15		
Fenuron	14.9	165.1022>72.0	15	0.3	0.1
		165.1022>120.0	15		
Flufenacet	27.4	364.0737>152.0	20	0.2	0.2
		364.0737>194.0	15		
Flufenoxuron	31.5	489.0435>158.0	25	0.5	0.5
		489.0435>141.0	25		
Fluoroacetamide	2.8	78.0350>61.0	10	1	1
		78.0350>58.2	15		
Fluroxypyr	19.0	254.9734>208.9	15	1	0.5
		254.9734>180.9	25		
Hexaflumuron	29.0	460.9889>158.0	20	1	1
		460.9889>141.0	20		
Hydroxyatrazine	11.3	198.1349>156.0	20	1	0.5
		198.1349>86.0	20		
Imazalil	18.2	297.0556>158.9	20	0.1	0.1
		297.0556>255.0	20		
Imazapyr	12.8	262.1186>217.0	20	0.1	0.05
		262.1186>234.1	20		
Imazaquin	18.8	312.1343>267.0	20	0.1	0.05
		312.1343>198.9	30		
Imidacloprid	15.3	256.0596>209.0	20	1	0.5
		256.0596>175.0	20		
Ioxynil	25.1	371.8377>118.0	30	1	1
		371.8377>245.0	30		
Iprodione	26.7	330.0407>244.9	20	1	0.5
		330.0407>288.0	20		
Irgarol 1051	20.7	254.1434>198.0	20	0.05	0.05
		254.1434>156.0	25		
Irgarol metabolite	16.3	214.1121>158.0	20	0.5	0.5
		214.1121>110.0	25		
Isoproturon	21.8	207.1492>72.0	20	0.1	0.1
		207.1492>165.1	20		
Lenacil	19.6	235.1441>153.0	15	5	0.5
		235.1441>136.0	20		
Lufenuron	30.8	510.9857>158.0	20	1	1
		510.9857>141.0	25		
Malathion	26.4	331.0433>127.0	15	1	0.5
		331.0433>99.0	20		
Mebendazole	18.0	296.1030>264.0	25	0.1	0.1
		296.1030>105.0	30		
Metalaxyl	21.7	280.1543>220.1	15	0.01	0.01
		280.1543>192.1	20		
Metamitron	14.3	203.0927>175.0	15	1	0.5
		203.0927>104.1	15		
Methidathion	24.9	302.9691>145.0	10	10	0.1
		302.9691>85.0	20		
Methiocarb	24.4	226.0896>169.0	15	20	10
		226.0896>121.0	20		
Methiocarb sulfone	17.2	258.0795>122.0	15	1	1
		258.0795>201.0	10		
Methomyl	11.7	163.0536>88.0	10	1	1
		163.0536>106.0	10		
Metolachlor	26.9	284.1412>252.1	25	0.1	0.1
		284.1412>176.0	25		
Metolcarb	19.5	166.0863>109.0	15	1	0.1
		166.0863>94.0	25		
Metribuzin	19.8	215.0961>187.1	20	0.5	0.1
		215.0961>131.0	20		
Molinate	25.5	188.1104>126.0	15	0.5	0.3
		188.1104>83.1	20		

Compound	RT (min)	SRM transitions (*m/z*)	Collision energy (eV)	LOD SRM (µg/kg)	LOD H-SRM (µg/kg)
Monuron	19.1	199.0633>72.0	15	0.5	0.5
		199.0633>126.0	25		
Nicosulfuron	17.8	411.1081>182.0	20	0.1	0.1
		411.1081>213.0	20		
Nitenpyram	14.0	271.0956>225.1	15	0.5	0.5
		271.0956>99.0	20		
Oxadixyl	18.9	279.1339>219.1	15	0.5	0.5
		279.1339>102.1	10		
Parathion ethyl	32.2	292.0403>236.0	15	1	1
		292.0403>235.9	15		
Pendimethalin	32.2	282.1448>212.0	15	1	0.5
		282.1448>194.0	20		
Phosmet	25.2	318.0018>160.0	10	0.5	0.5
		318.0018>133.1	30		
Prochloraz	23.1	376.0381>308.0	15	0.3	0.1
		376.0381>265.9	15		
Profenofos	30.2	372.9424>302.8	20	0.2	0.1
		372.9424>344.9	15		
Promecarb	25.2	208.1332>109.0	15	0.1	0.05
		208.1332>151.1	10		
Prometon	16.2	226.1662>184.1	20	0.1	0.1
		226.1662>142.0	25		
Prometryn	19.9	242.1434>158.0	25	0.05	0.05
		242.1434>200.0	20		
Propachlor	23.2	212.0837>170.0	20	0.5	0.5
		212.0837>152.0	20		
Propanil	23.9	218.0134>161.9	15	0.5	0.5
		218.0134>127.0	30		
Propiconazole	27.0+27.2	342.0771>158.9	25	0.3	0.1
		342.0771>69.0	20		
Prosulfocarb	30.8	252.1417>91.0	20	0.1	0.1
		252.1417>128.1	15		
Simazine	18.9	202.0854>132.0	20	0.5	0.5
		202.0854>124.0	20		
Spinosad A	22.3	732.4681>141.9	25	0.1	0.1
Spinosad D	22.8	746.4838>141.9	25	0.1	0.1
Spiromesifen	30.7	371.2217>273.0	10	0.1	0.1
		371.2217>255.	25		
Spiroxamine	18.2	298.2741>144.1	15	0.1	0.1
		298.2741>100.1	15		
Teflubenzuron	29.4	380.9815>158.0	20	5	5
		380.9815>141.0	25		
Terbuthylazine	24.4	230.1167>174.0	20	0.1	0.1
		230.1167>132.0	25		
Terbutryn	20.0	242.1434>186.0	20	0.1	0.1
		242.1434>71.1	30		
Thiabendazole	9.6	202.0433>175.0	30	5	1
		202.0433>131.0	30		
Thiacloprid	17.9	253.0309>126.0	25	0.5	0.5
		253.0309>186.0	15		
Thiocyclam	3.1	182.0126>136.9	15	0.1	0.1
		182.0126>73.0	25		
Thiosultap	2.7	311.9698>232.0	15	0.1	0.1
		311.9698>151.9	20		
Triclocarban	28.9	314.9853>161.9	20	0.5	0.5
		314.9853>127.0	20		
Triflumizole	29.2	346.0929>278.0	10	0.5	0.5
		346.0929>73.0	15		

[a] SRM: Q1 and Q3 at 0.7 *m/z* FWHM; H-SRM: Q1 at 0.1 *m/z* FWHM, Q3 at 0.7 *m/z* FWHM.

Table 5

Table 5. Concentration of the pesticides found and confirmed in fruit and vegetable samples.

Sample	Pesticides found	Concentration (µg/kg)
Green pepper [a]	Diazinon	0.6
	Imidacloprid	217
	Metalaxyl	~LOD
Tomato [a]	Fluroxypyr	27
	Imidacloprid	40
	Molinate	5
Eggplant [a]	Diazinon	0.06
	Imidacloprid	66
Celery [a]	Carbazyl	~LOD
	Diazinon	6
	Imidacloprid	15
	DEET	30
Lettuce [a]	Carbaryl	6
	Diazinon	1
	Dimethomorph	0.9
	Imidacloprid	13
	Methiocarb sulfone	~LOD
Escarole [a]	Carbaryl	~LOD
	Diazinon	3
	Dimethomorph	0.8
	Fluroxypyr	10
	Imidacloprid	33
	Methiocarb sulfone	5
Swiss chard [a]	Carbaryl	2
	Diazinon	0.1
	Dimethomorph	~LOD
	Imidacloprid	3
	Methiocarb sulfone	2
Red pepper [b]	Alachlor	~LOD
	Azoxystrobin	~LOD
	Fluroxypyr	~LOD
Green bean [b]	Azoxystrobin	26
	Diazinon	~LOD
	Methiocarb sulfone	~LOD
Green pepper [b]	Acetamiprid	24
	Azoxystrobin	1
	Diazinon	0.3
	Difeconazole	29
	Methiocarb sulfone	5
	Promecarb	0.9
Spinach [b]	Atrazine	0.2
	Imazalil	0.9
	Imidacloprid	21
	Lenacil	8
	Metalaxyl	0.3
	Methiocarb sulfone	~LOD
	Methomyl	21

Sample	Pesticides found	Concentration (μg/kg)
Orange [b]	Azoxystrobin	~LOD
	Imazalil	250
	Methidathion	~LOD
Pear [b]	Azoxystrobin	1.6
	Buprofezin	0.3
	Diazinon	0.8
	Difeconazole	4
	Imazalil	4
	Imidacloprid	12
	Terbuthylazine	~LOD
Apple [b]	Azoxystrobin	0.6
	Diazinon	0.2
	Dichlorvos	6
	Difeconazole	4
	Dimethoate	2
	Flufenoxuron	9
	Imazalil	235
	Metalaxyl	~LOD
Tomato [b]	Azoxystrobin	364
	Imazalil	12
	Spiromesifen	~LOD
Plum [b]	Azoxystrobin	1
Peach [b]	Azoxystrobin	~LOD
	Diazinon	0.1
	Ethiofencarb	1
	Imazalil	1
	Terbuthylazine	~LOD

[a] Samples collected from the same farm.
[b] Samples purchased from a commercial market.