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Critical assessment of extraction methods for the simultaneous determination of pesticide residues and mycotoxins in fruits, cereals, spices and oil seeds employing ultra-high performance liquid chromatography–tandem mass spectrometry

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ABSTRACT

This study addresses a current trend in chemical food safety control represented by an effort to integrate analyses of various groups of food contaminants/toxicants into a single, high-throughput method. The choice of optimal sample preparation step is one of the key conditions to achieve good performance characteristics. In this context, we investigated the possibility to expand the scope of the three multi-analyte extraction procedures employed earlier in other studies for rapid isolation of either pesticides or mycotoxins from plant matrices. Following procedures were tested: A – aqueous acetonitrile extraction followed by partition (QuEChERS-like method), B – aqueous acetonitrile extraction, and C – pure acetonitrile extraction. On the list of target analytes, we had 288 pesticides (including 'troublesome' acidic, basic and base-sensitive compounds) together with 38 mycotoxins (including all EU regulated ones and many 'emerging' toxins on the European Food Safety Authority (EFSA) list). The matrices selected for the experiments, apple baby food, wheat flour, spices and sunflower seeds, represented various composition categories in terms of moisture, fat and extractable compounds (*e.g.* pigments and essential oils) content. In preliminary experiments, acceptable recoveries (70–120%) for most of analytes were obtained by the analysis of spiked matrices, regardless which extraction procedure was used. However, when analysing dry samples with incurred pesticide residues/mycotoxins, the method C did not enable efficient extraction of some common contaminants. Procedure A, thanks to a higher matrix equivalent compared to the method B and relatively less pronounced matrix effects, enabled lower quantification limits for all analyte/matrix combinations, with the exception of polar mycotoxins and/or pesticides. Higher recoveries for the latter group of analytes could be achieved by the method B; on the other hand, extraction efficiency of non-polar pesticides from fatty matrix was rather poor by this method.

1. Introduction

Food crops and products thereof may contain a number of different groups of contaminants including pesticide residues and/or mycotoxins; for many of them, maximum limits have been established in the EU legislation [1–3]. The continuously growing number of regulated residues/toxins has increased the demands for development of 'new' laboratory procedures applicable for their effective control. During the recent years, several methods based on simple and rapid analytical approaches for the analysis of multiple food contaminant groups have been published [4–6]. The first comprehensive study by Mol et al. [4] introduced a simple 'dilute-and-shoot' approach based on a shaking of respective sample of plant and animal origin (horse feed, maize, egg, meat, honey and milk) with an acetonitrile (MeCN)/water/formic acid mixture (75:24:1, v/v/v); the scope involved 172 pesticides, veterinary drugs, mycotoxins and phytotoxins. In comparison with the well-established, 'traditional' multi-mycotoxin and multi-pesticide methods, only the proposed procedure provided acceptable performance characteristics for a wide range of analytes, with the exception of base-sensitive compounds (*e.g.* tolylfluanid and thiophanate-methyl).

Recently, a study assessing the possibility to use the existing broad scope approaches for the analysis of 90 pesticide residues and mycotoxins in cucumber, wheat flour and red wine has been conducted by Romero-González et al. [5]. Following sample

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preparation strategies were tested: (i) QuEChERS (quick, easy, cheap, rugged and safe) sample preparation method originally developed by Annastassiades et al. [7] for the isolation of pesticide residues and later on modified by Lehotay et al. [8]; (ii) a 'dilute-and-shoot' procedure proposed by Mol et al. [4] mentioned above; (iii) a multi-mycotoxin method [9] utilising an extraction mixture consisted of MeCN:water (8:2, v/v) and sonication. The latter multi-mycotoxin method was able to extract almost all analytes tested, but only a few of them with recoveries >70% and the 'dilute-and-shoot' method enabled quantitative extraction of only half of analytes. The relatively best method performances for most of selected pesticides and mycotoxins were achieved by the QuEChERS method, nevertheless, low recoveries (<70%) of acidic pesticides (*e.g.* picloram and quinmerac) were obtained. It should be mentioned that the most commonly occurring and regulated mycotoxins such as deoxynivalenol (DON), patulin and/or fumonisins were not included in this study, thus a possible use for the regulatory purpose was not fully documented.

Another multi-analyte method for the simultaneous determination of multiple analyte classes (pesticide residues, aflatoxins and dyes) in spices was introduced by Amate et al. [6]. Unfortunately, alike in previous case, several regulated mycotoxins as well as 'troublesome' compounds, such as base-sensitive, acidic and/or basic pesticides were missing in the target analyte list.

To fill a gap in the existing knowledge and sort out rather contradictory information on the performance of multi-analyte methods when employed for various matrices, an extensive study has been conducted for the analysis of 38 mycotoxins (all regulated in the EU) and 288 pesticide residues including acidic, basic and base-sensitive compounds. The experiments were carried out on matrices, which were found to have entries in the RASFF (Rapid Alert System for Food and Feed) for both pesticide residues and mycotoxins and also differing in their composition. The selected matrices were: (i) apple baby food (high moisture matrix); (ii) wheat flour (low moisture, high content of starch); (iii) paprika and black pepper (low moisture, high content of extractable compounds); (iv) sunflower seeds (low moisture, high content of lipids). Except the experiments on spiked matrices, methods performance on incurred pesticide residues and mycotoxins were evaluated by means of the analysis of certified reference materials and samples obtained within the inter-laboratory comparisons.

The extracts prepared by different extraction methods were analysed by ultra-high performance liquid chromatography–electrospray ionisation-tandem mass spectrometry (UHPLC–ESI-MS/MS). Although also gas chromatography (GC)-amenable pesticides are of possible interest, they were not considered due to the added complexity of the study. Since matrix interferences, especially in the black pepper and paprika extracts, were observed, we focused also on alternative ways to improve analyte identification and confirmation. In general, several solutions to overcome mass interferences in LC–MS/MS have been described in scientific literature and also in the Document SANCO/12495/2011 (paragraph 80) [10]. However, most of them are based on the acquisition of more than two multiple-reaction monitoring (MRM) transitions per analyte and/or the utilisation of instrumentation with different selectivity such as high-resolution mass spectrometry (HRMS) or gas chromatography–mass spectrometry (GC–MS) [11–14]. Since the interference has commonly different exact mass than that of the target analyte, HRMS provides sufficient selectivity for its removal. Thus, LC–HRMS permits the detection of the same scope of analytes as LC–MS/MS. In this work, we utilised both selection of different MRM transitions provided by MS/MS and increasing the mass resolving power by means of high-resolution/accurate mass time-of-flight MS (TOFMS) to avoid interferences at the analyte ions.

2. Experimental

2.1. Reagents and materials

Anhydrous magnesium sulphate ($MgSO_4$) was obtained from Fluka (Fluka; Steinheim, Germany), formic acid (95%), ammonium acetate (LCMS grade), ammonium formate (LCMS grade) and HPLC grade acetonitrile (MeCN) were from Sigma–Aldrich (Prague, Czech Republic). Methanol (MeOH) was obtained from Merck (Darmstadt, Germany). Sodium chloride was from Penta (Prague, Czech Republic) and Bondesil C_{18} sorbent (40 μm) for dispersive solid-phase extraction (dSPE) clean-up was obtained from Agilent Technologies (Santa Clara, CA, USA). Deionised water (18 MΩ) was produced by a Milli-Q system (Millipore; Bedford, MA, USA).

2.1.1. Standards

Certified standards of pesticides (altogether 288 compounds) were purchased from Dr. Ehrenstorfer GmbH (Darmstadt, Germany) or Riedel de Haen (Seelze, Germany); standards of mycotoxins (38 compounds) were from Biopure (Tulln, Austria) except for alternariol and alternatriol-methylether which were from Sigma–Aldrich (Taufkirchen, Germany) as well as triphenylphosphate (TPP) and nicarbazin used as internal standards. A mixture of TPP and nicarbazin was prepared in MeCN (2 $\mu g\,mL^{-1}$) and was used for the preparation of working calibration solutions and during the spiking procedure of the samples.

Individual pesticide stock solutions (concentrations in the range of 0.3–3 $mg\,mL^{-1}$) were prepared in MeOH, MeCN or acetone, depending on the solubility of particular pesticide. From these solutions the stock standard mixture in MeCN (each analyte at the concentration of 10 $\mu g\,mL^{-1}$) was prepared and stored at −20 °C.

Mycotoxins were dissolved in MeCN and stored at −20 °C. The stock solutions were used for preparation of a stock solution at the concentration of 10 $\mu g\,mL^{-1}$ except aflatoxins and ochratoxin A, which were at 10-times lower concentration (1 $\mu g\,mL^{-1}$).

The spiking solution (1 $\mu g\,mL^{-1}$) was prepared from the stock solutions of pesticides and mycotoxins and stored at −20 °C.

2.1.2. Samples

The extraction methods were tested on apple baby food, wheat flour, paprika, black pepper and sunflower seeds. All samples were obtained in local stores and tested by all three methods to be free of targeted pesticides and mycotoxins before their use.

2.2. Sample preparation

2.2.1. Method A: aqueous acetonitrile extraction followed by partition

This extraction procedure is based on the QuEChERS method [7]. An amount of 2.5 g of fine homogenised low moisture (<50%) matrix was weighed into a 50-mL polypropylene (PP) centrifugation tube, followed by the addition of 10 mL of water containing 2% (v/v) of formic acid. The tube was closed and the matrix was allowed to soak for 1 h. In case of apple baby food, which represents a high moisture matrix (>80%), an aliquot of 10 g was used without water addition.

The subsequent steps of the sample preparation were identical for all matrices tested. A volume of 10 mL of MeCN was added into the tube and vigorously shaken by hand for 1 min. In the next step, 4 g of $MgSO_4$ and 1 g NaCl were added and shaken immediately to prevent coagulation of $MgSO_4$. The mixture of internal standards (100 μL) was added and the tube was mixed again for 30 s and then centrifuged (Hettich; Tuttlingen, Germany) for 5 min (12,750 rcf).

The organic layer of the sample extracts were handled in following ways: (i) 0.25 mL of the paprika and black pepper extracts

were diluted with MeCN at a ratio of 1:5; (ii) 2 mL of the extracts of sunflower seeds including residual lipids was purified by dSPE (15-mL PP tube containing 0.1 g C_{18} silica sorbent and 0.3 g $MgSO_4$) and centrifuged (12,750 rcf) for 1 min. An aliquot of apple baby food and wheat extracts was not further treated. All extracts were finally filtered through a 0.2 μm PTFE filter (National Scientific; Rockwood, TN, USA) and transferred into a polypropylene vial (Sun Sri, Rockwood, TN, USA) for the LC–MS analysis. The matrix equivalents were as follows: apple baby food extracts 1 g mL^{-1}, wheat and sunflower seeds extracts 0.25 g mL^{-1}, and black pepper and paprika extracts 0.04 g mL^{-1}.

2.2.2. Method B: aqueous acetonitrile extraction

This extraction method employing acidified aqueous acetonitrile was based on the procedure developed by Mol et al. [4]. An amount of 2.5 g of the homogenised sample was weighed into a 50-mL PP centrifugation tube, followed by the addition of 5 mL of water containing 4% (v/v) of formic acid. The tube was mixed and the matrix was allowed to soak for 1 h. For a high moisture sample (apple baby food), 5 g of the sample was used without water addition.

Into the tube containing the sample, 15 mL of MeCN and internal standards (200 μL) were added and the tube was placed to a laboratory shaker for 30 min. Sonication for another 30 min followed and the tube was finally centrifuged (12,750 rcf) for 5 min.

The paprika and black pepper extracts were diluted with an extraction mixture (MeCN:water:formic acid, 74:25:1, v/v/v) at a ratio of 1:2. An aliquot of the apple baby food, wheat and sunflower seeds extracts and the diluted extracts of spices were filtered through a 0.2 μm PTFE filter (National Scientific; Rockwood, TN, USA) and transferred into a vial for the LC–MS analysis. The matrix equivalents were as follows: apple baby food extracts 0.25 g mL^{-1}, wheat and sunflower seeds extracts 0.125 g mL^{-1}, and black pepper and paprika extracts 0.04 g mL^{-1}.

2.2.3. Method C: acetonitrile extraction

This extraction procedure employing extraction of sample with pure acetonitrile was developed by Amate et al. [6] for the analysis of pesticide residues, mycotoxins and dyes in spices. The sample (1 g), 100 μL of internal standard and 10 mL of MeCN were added into a 50-mL PP tube and placed in an ultrasonic bath for 30 min. An aliquot of the final extract was filtered through a 0.2 μm PTFE filter (National Scientific; Rockwood, TN, USA) and transferred into a vial for the LC–MS analysis. The matrix equivalent of wheat, sunflower seeds, black pepper and paprika extracts was in all cases 0.1 g mL^{-1}. Since this procedure was originally developed mainly for dry samples, the apple baby food sample was not analysed by this method.

2.2.4. Method validation

An external matrix-matched calibration was prepared for each matrix/method combination using the above described procedures. The working calibration solutions were prepared from stock solutions, containing both pesticides and mycotoxins in the range of 0.010–2 μg mL^{-1} (aflatoxins and ochratoxin A in the range of 0.001–0.2 μg mL^{-1}), and the mixture of internal standards (2 μg mL^{-1}). The internal standards were used only for the correction of volume changes during the extraction. The matrix-matched calibration solutions were prepared by mixing of 900 μL of the blank matrix extract and 100 μL of the particular calibration solution to obtain matrix-matched standards corresponding to the concentration level 1, 2, 5, 10, 50, 100 and 200 ng mL^{-1}. Limits of quantifications (LOQs) were estimated as the lowest matrix-matched calibration standard which provided signal-to-noise ratio (S/N) higher than 10 and the second MS/MS transition had to provide S/N > 3. The S/N was determined as the peak-to-peak (PtP). Since most of the analytes were easily detectable at the lowest calibration point, which was low enough for a routine control, LOQs of such analytes were estimated as the lowest calibration level (LCL) and no S/N was determined. For some highly sensitive analytes the highest concentrations (100 and 200 ng mL^{-1}) were out of the instrument's linearity, thus, these calibration points had to be manually excluded.

The matrix effects (signal suppression or enhancement) during electrospray ionisation were evaluated by comparing of matrix-matched calibration slope (all combinations of matrix/method were tested) with the solvent calibration slope in the range from limit of quantification (LOQ) to 200 ng mL^{-1} or the highest concentration within linear range.

Extraction efficiency of all three tested methods was examined using spiking procedure of the blank materials (six replicates). Each sample was spiked 10–12 h before the extraction and left at 4 °C. The apple baby food was spiked at 10 μg kg^{-1} and 100 μg kg^{-1}, wheat and sunflower seeds were spiked at 20 and 200 μg kg^{-1} and spices (black pepper, paprika) at 50 and 500 μg kg^{-1}. To test extraction procedure at legislative limits, spike concentrations of aflatoxins and ochratoxin A were always 10-times lower. The methods trueness was verified by the analysis of: (i) certified reference materials (CRMs) maize containing ZON and DON from Biopure (Tulln, Austria); (ii) FAPAS proficiency testing materials no. 2237, 2252 and 2259 (matrices and analytes are listed in Table 3) obtained from the Food and Environmental Research Agency (FERA, York, UK); (iii) proficiency testing materials EUTP C2 (wheat flour, pesticides residues) and EUPT C3-SRM4 (oat flour, pesticide residues) (EU Reference Laboratories, EU) (analytes also listed in Table 3).

2.3. Detection

2.3.1. Liquid chromatography–tandem mass spectrometry

The LC–MS/MS analyses were performed using an Acquity Ultra-Performance LC system (Waters; Milford, MA, USA) equipped with an Acquity UPLC HSS T3 column (100 mm × 2.1 mm I.D., 1.8 μm particle size, Waters; Milford, MA, USA) maintained at 40 °C and a 10-μL sample loop. The mobile phases were different for ESI(+) and ESI(−) analysis. The 5 mM ammonium formate and 0.2% formic acid in both Milli-Q water and methanol was used in ESI(+). In ESI(−) 5 mM ammonium acetate in Milli-Q water and pure MeOH were used. The gradient was the same in both polarities: the starting mobile phase composition was 10% of organic phase (B) with flow 0.35 mL min^{-1} and linearly changed to 50% (B) in 1 min. A slower linear gradient from 50% (B) to 100% (B) in 10 min followed, simultaneously with flow rate change from 0.35 to 0.55 mL min^{-1}. The increased flow rate compensated the observed peak broadening caused by slow-down of the gradient. The column was washed for 2 min (flow 0.7 mL min^{-1}) with 100% organic and reconditioned for 2.5 min in the starting composition of 10% (B) (0.45 mL min^{-1}). A sample volume of 3 μL with the partial loop injection mode was used. Sample temperature was maintained at 4 °C.

The UHPLC system was connected to a 5500 QTRAP tandem mass spectrometer (AB SCIEX; Toronto, ON, Canada), equipped with an TurboIon™ electrospray (ESI) ion source operated in both positive and negative mode. The ESI(+) ion source parameters were as follows: needle voltage: 4.5 kV; curtain gas: 35 psi; nebuliser (Gas 1) and Turbo gas (Gas 2): 55 psi; turbo gas temperature: 500 °C. In the ESI(−) were needle voltage: −4.5 kV; curtain gas: 35 psi; nebuliser (Gas 1) and turbo gas (Gas 2): 55 psi; turbo gas temperature: 450 °C. Declustering potential (DP), collision (CE) and collision cell exit potential (CXP) were optimised during infusion of mixture of analytes (10–100 ng mL^{-1}) employing an automatic function of the Analyst software 1.5 (AB SCIEX). The instrument was operated in

MRM mode and the acquisition method used the scheduled MRM function. This function automatically optimised the dwell times according to the number of simultaneously detected MRM transitions. The time window of one MRM transition was 0.8 min and the cycle time (time for acquisition of one point) was 0.55 s. All analyte dependent parameters are summarised in Table S1 (Supplementary data).

2.3.2. Liquid chromatography–time-of-flight mass spectrometry

The chromatographic separation was the same as that described in Section 2.3.1 including the analytical column, mobile phases and injection volume. Acquity UHPLC system was connected to an orthogonal accelerated high-resolution/accurate mass time-of-flight mass spectrometer Waters LCT Premier XE (Waters; Milford, MA, USA) operated in both ESI(+) and ESI(−) modes. The parameters of ESI(+) mode were as follows: capillary voltage: 3.5 kV; cone voltage: 30 V; source temperature: 120 °C; desolvation gas temperature: 350 °C. Nitrogen was used as a desolvation and cone gas at a flow rate of 750 L h^{-1} and 10 L h^{-1}, respectively. The parameters of ESI(−) mode were follows: capillary voltage: −2.2 kV; cone voltage −30 V. Temperature of the ion source and desolvation gas and gas flow rates were the same as in ESI(+) mode. The instrument was tuned using a leucine–enkephalin solution to provide a mass resolving power >10,000 FWHM (full width at half maximum) (*m/z* 556.2672 in ESI(+) and *m/z* 554.2615 in ESI(−)) and the same solution was also used as a lock mass to correct small mass drifts during the measurement. Raw mass spectra were acquired in the *m/z* range 100–1000 and dynamic range enhancement (DRE) was used. The MassLynx 4.1 software (Waters) was used for data acquisition and data processing.

3. Results and discussion

3.1. Optimisation of the separation/detection system

In the first phase, separation and detection steps were optimised with the focus on sensitivity (expressed as limits of quantification, LOQs). Reversed phase (U)HPLC–MS/MS system employing a C18 separation column represents a 'gold standard' in both multimycotoxin [15,16] and multi-pesticide [17,18] analysis, however, in available literature many options of the mobile phase composition can be found. In most studies, mobile phases consist of either MeOH or MeCN and aqueous solution of some of following modifier: ammonium formate (AmF), ammonium acetate (AmAc), formic acid (FA) or acetic acid (AA). For instance, Sulyok et al. [19] used 5 mM AmAc with 1% (v/v) of AA in both aqueous and organic (MeOH) eluents to support formation of $[M+NH_4]^+$ adducts of A-trichothecenes in ESI(+) mode and $[M+CH_3COO]^-$ adducts of B-trichothecenes in ESI(−) mode. The 1% AA was added into eluents to focus fumonisin's peaks. Mol et al. [4] used AmF acidified by FA in both eluents (water and MeOH), which is a common mobile phase in the multi-pesticide analysis [5,17]. In the first stage of our study, both the two above mentioned mobile phases were tested for analytes detected in ESI(+) and ESI(−).

The majority of analytes detected in ESI(+) provided 2–4 times higher responses in the presence of AmF and some of them (including aflatoxins) were even more than 10 times intensive as compared to the use of AmAc with 1% AA. Initially, fumonisins were better detectable in the mobile phase consisted of AmAc with 1% AA, but increasing of FA up to 0.2% in AmF lead to more focused peaks and finally, the responses of target analytes were 2–3 times higher than in 5 mM AmAc with 1% AA. Signals of three pesticides (fomesafen, formetanate and picloram) were comparable in both mobile phases and a drop of the signal intensity of only HT-2 toxin was observed in acidified AmF. Keeping the same ionic strength over the gradient was essential to improve the peak shape as well as avoiding the retention time shifts of several compounds (*e.g.* fenpropidin, imazalil and spinosad). On this account, mobile phase consisting of acidified 5 mM AmF with FA (0.2%, v/v) in both eluents (water and MeOH) was employed for the subsequent LC–ESI(+)-MS(/MS) experiments.

Regarding acidic pesticides detected in ESI(−), their peak shapes were the same in both low pH and neutral mobile phases, contrary to analyte responses in ESI(+). The highest signal of these compounds was obtained in 5 mM AmAc without acidification. Another important group of compounds analysed in ESI(−) were B-trichothecenes known to form acetate adducts in the presence of AmAc, which are fragmented to $[M-H]^-$ followed by a neutral loss (CH_2O, 30 Da) from this deprotonated molecule [20]. Similarly, using the mobile phase containing AmF, B-trichothecenes produced $[M+HCOO]^-$ adducts, which were more intensive as compared to $[M+CH_3COO]^-$ adducts. However, these formate adducts were dominantly fragmented to formate ion and the neutral analyte molecule ($[M+HCOO]^- \rightarrow [M]^0 + [HCOO]^-$), thus sensitivity in MS/MS was very low. Since in ESI(−) no analyte was influenced by the different ion strength of the mobile phase, we added the buffer (5 mM AmAc) only into the aqueous part and used pure MeOH. This composition of mobile phases was used in all subsequent LC–ESI(−)-MS(/MS) experiments.

3.2. Optimisation of the extraction methods

3.2.1. Method A: aqueous acetonitrile extraction followed by a partition step

At present, three main variations of the QuEChERS method are in use: the original one employing only aqueous acetonitrile for the primary extraction [7] and two buffered ones known as the AOAC Official Method 2007.01 [8] and the CEN Standard Method EN 15662 [21]. Buffers were introduced to achieve constant pH value during the extraction of different matrices to improve stability of base-sensitive compounds (*e.g.* captan, folpet, dichlofluanid and tolylfluanid), which undergo hydrolysis at high pH. The comparison of all three QuEChERS methods has been recently published by Lehotay et al. [22]. The AOAC version utilising an acetate buffer was shown as the best choice, because neither the original nor the CEN standard method provided sufficient recoveries of pymetrozine and base-sensitive compounds. Worth to notice, also a number of widely used acidic herbicides (*e.g.* 2,4-D, 2,4-DB, clopyralid, dicamba, quinmerac and picloram) are usually analysed within a routine monitoring programs, unfortunately, these were not included in Lehotay's comparison.

Taking into account these facts, we compared the performance of the official buffered QuEChERS protocols for the analysis of a broad scope of pesticides and mycotoxins involved in our study on apple baby food and wheat flour (Table 1). The AOAC method gave poor recovery for most of acidic compounds (<70%) in both of tested matrices, which confirmed the results reported by other authors [4,5]. The recovery of these analytes obtained by the CEN method (with the exception of fumonisins and picloram in wheat) was in an acceptable range. Interestingly, a low recovery of base-sensitive analytes (and high recovery of their degradation products) was achieved by both methods for wheat flour. Trying to explain this phenomenon, we measured the pH value of aqueous phase during soaking of test matrices ('wetting' prior to the extraction is recommended in the Document SANCO/12495/2011 [10] whenever the matrix contains less than 40% of moisture). As shown in Table 2, an increase of pH value, as compared to added deionised water, occurred in case of wheat flour, black pepper and sunflower seeds. To our assumption, high pH during the soaking period was the cause of low recoveries of base-sensitive analytes. Since the use of acidified water for sample wetting is not mentioned in any of the buffered QuEChERS protocols, it was not used in our experiments.

Table 1
Recoveries of buffered QuEChERS variants and the method A for selected analytes.

	Average recovery (%) (RSD %) (n = 6)					
	Apple baby food (10 μg kg^{-1})			Wheat flour (20 μg kg^{-1})		
pH of aqueous extract Extraction method	3.7 Method A	3.7 CEN [21]	3.7 AOAC [8]	3.3 Method A	7.1 CEN [21]	7.1 AOAC [8]
Acidic analytes (pK_a)						
2-Naphthoxy acetic acid (3.55)	98 (2)	89 (4)	83 (3)	100 (4)	86 (3)	**66 (18)**
4-CPA (3.01)	105 (3)	90 (4)	78 (4)	105 (4)	84 (4)	**60 (14)**
Clopyralid (2.01)	96 (8)	86 (9)	**58 (12)**	93 (5)	74 (7)	**46 (18)**
Dicamba (1.87)	99 (8)	84 (3)	78 (4)	104 (2)	86 (6)	**67 (4)**
Imazapyr (1.9)	93 (5)	83 (16)	**49 (3)**	91 (4)	84 (6)	**50 (12)**
Ioxinyl (4.1)	97 (3)	83 (3)	**56 (8)**	95 (3)	77 (4)	**62 (6)**
MCPA (3.07)	103 (3)	87 (4)	**61 (11)**	101 (4)	79 (6)	**57 (9)**
MCPB (4.84)	99 (3)	91 (3)	**67 (8)**	98 (3)	83 (4)	**60 (6)**
Mecoprop (3.78)	97 (2)	88 (8)	**63 (7)**	102 (3)	83 (4)	**53 (8)**
Picloram (2.3)	95 (7)	76 (13)	**46 (7)**	83 (4)	**63 (7)**	**46 (13)**
Quinmerac (4.31)	90 (5)	88 (9)	**65 (5)**	84 (3)	80 (5)	**57 (12)**
Fumonisin B1 (3.63/9.24)	74 (9)	**42 (12)**	**14 (18)**	76 (5)	**18 (9)**	**7 (14)**
Fumonisin B2 (3.63/9.24)	77 (5)	**34 (16)**	**11 (22)**	78 (4)	**21 (11)**	**4 (19)**
Base sensitive analytes						
Clofentezine	97 (9)	98 (7)	93 (9)	93 (5)	**59 (4)**	**59 (17)**
Dichlofluanid	89 (4)	85 (7)	93 (9)	87 (7)	**15 (7)**	**21 (5)**
Naled	86 (10)	91 (10)	88 (9)	87 (11)	**18 (13)**	**28 (18)**
Thiodicarb	95 (5)	91 (4)	96 (5)	84 (2)	**26 (14)**	**33 (27)**
Thiophanate-methyl	93 (9)	90 (12)	93 (9)	87 (4)	**63 (8)**	**61 (9)**
Tolylfluanid	93 (3)	98 (4)	96 (3)	88 (6)	**24 (2)**	**23 (31)**
Degradation products (parent compound)						
DMSA (dichlofluanid)	97 (3)	91 (4)	97 (3)	98 (3)	**131 (11)**	**149 (26)**
DMST (tolylfluanid)	93 (2)	84 (5)	100 (3)	94 (3)	117 (9)	**150 (26)**
Methomyl (thiodicarb)	97 (3)	100 (4)	109 (4)	97 (2)	**131 (11)**	**139 (25)**
Bases (pK_a)						
Pymetrozine (4.06)	**9 (10)**	**39 (6)**	84 (6)	**10 (7)**	**57 (4)**	96 (12)
Propamocarb (9.05)	96 (2)	92 (6)	94 (7)	91 (3)	94 (3)	103 (4)
Spiroxamine (6.9)	94 (3)	91 (4)	96 (6)	93 (3)	96 (5)	97 (6)

Bold are recoveries out of the acceptable range 70–120%.

Table 2
pH of aqueous extracts of tested matrices.

Matrix	pH
Deionised water	6.1
Wheat flour	7.1
Sunflower	6.6
Black pepper	7.8
Paprika	5.2
Apple baby food	3.7

As no improvement of recoveries either of acidic or base-sensitive analytes during the buffered QuEChERS methods was observed, we followed the original QuEChERS procedure with an addition of FA to maintain low pH (method A). The addition of 0.5%, 1% and 2% (v/v) FA was tested. The amount of 0.5% FA provided lower recoveries of acidic compounds, but the method performance with the addition of 1% and 2% FA were comparable with the exception of fumonisins, for which the recoveries were more repeatable when 2% FA was used. This approach, adding of FA to the sample prior the extraction enables following benefits: (i) minimisation of losses of base-sensitive analytes and (ii) significant improvement of recoveries of polar, acidic analytes (especially clopyralid, dicamba and fumonisins) from high pH matrices (Table 1). Moreover, recoveries of basic analytes (except pymetrozine) were not compromised by low pH of the extract (all in the range 70–120%).

3.2.2. Method B: aqueous acetonitrile extraction

The 'dilute-and-shoot' multi-analyte approach [4] represents a rapid method suitable for various matrices; nevertheless, when employed by Romero-González et al. [5] poor recoveries for number of analytes were reported. In our preliminary experiments, in which combination of shaking and ultrasonication was used to enhance extraction efficiency, low recovery of base-sensitive compounds from dry matrices was observed. This observation was in line with the results reported for these compounds by Mol et al. [4] in a few matrices. The fact that FA was added into the extraction mixture *after* the soaking period may explain low recovery of base-sensitive compounds. When FA was added into the extraction mixture *before* a soaking, recovery of these compounds within acceptable range (70–120%) was achieved for all matrices.

3.3. Method C

Since spices are known to be a 'difficult' matrix in terms of the amount and kind of co-extracts, we were interested in applicability of the method introduced by Amate et al. [6], who reported relatively good extraction efficiency and low matrix effects in the LC–MS analysis of pesticides, aflatoxins and dyes extracted by pure acetonitrile. As expected, thanks to the absence of water, base-sensitive analytes were not hydrolysed during the extraction, hence their good recoveries (>90%) were obtained when analysing spiked wheat flour, spices and oilseeds. However, the recoveries of the most acidic polar compounds (clopyralid, dicamba, picloram, fumonisins, *etc.*) were in the range 40–70%. This was probably due to low polarity of pure acetonitrile, which was not able to extract the polar acids from basic matrices.

3.4. Methods trueness: analysis of materials with incurred analytes

In this phase of our study, we attempted to demonstrate the applicability of the extraction methods A, B and C on samples

Table 3
Results of the analysis of CRMs and samples from the proficiency tests by the tested methods.

Sample	Analyte		Assigned/certified value (μg kg^{-1})	σ_p[a] (μg kg^{-1})	Method A		Method B		Method C	
					μg kg^{-1}	*z*-Score	μg kg^{-1}	*z*-Score	μg kg^{-1}	*z*-Score
EUPT C2 – wheat flour	Azoxystrobin[c]	ESI(+)	239	60	252	0.2	264	0.4	86	−2.7
	Bifenthrin[b]	ESI(+)	87	22	84	−0.1	112	1.1	59	−1.2
	Carbendazim[b]	ESI(+)	570	143	624	0.4	648	0.5	126	−3.2
	Cypermethrin[b]	ESI(+)	98	25	108	0.4	136	1.6	63	−1.6
	Difenoconazole[d]	ESI(+)	169	42	176	0.2	184	0.4	61	−2.6
	Epoxyconazole[b]	ESI(+)	176	44	168	−0.2	176	0.0	64	−2.6
	Chlorpyrifos-methyl[b]	ESI(+)	130	33	136	0.2	144	0.4	41	−2.8
	Iprodione[b]	ESI(+)	289	72	344	0.8	312	0.3	ND	
	Malathion[d]	ESI(+)	162	41	184	0.5	200	0.9	44	−3.0
	Pirimicarb[b]	ESI(+)	38	10	32	−0.6	40	0.2	ND	
	Prochloraz[d]	ESI(+)	239	60	244	0.1	256	0.3	68	−2.8
	Spiroxamin[b]	ESI(+)	75	19	64	−0.6	88	0.7	ND	
	Trifloxystrobin[1]	ESI(+)	439	110	324	−1.0	392	−0.4	226	−2.0
	DON	*ESI(−)*	–	–	*196*	–	*224*	–	*ND*	–
	DON-3-Glc	*ESI(−)*	–	–	*21*	–	*56*	–	*ND*	–
	ZON	*ESI(−)*	–	–	*98*	–	*100*	–	*ND*	–
EUPT C3-SRM4 – oat flour	2,4-D[d]	ESI(−)	499	125	536	0.3	568	0.6	58	−3.5
	Azoxystrobin[b]	ESI(+)	175	44	180	0.1	192	0.4	60	−2.6
	Carbendazim[b]	ESI(+)	472	118	508	0.3	512	0.3	122	−3.0
	Cyproconazole[b]	ESI(+)	453	113	380	−0.6	424	−0.3	159	−2.6
	Cyprodinil[b]	ESI(+)	76	19	84	0.4	96	1.1	20	−2.9
	Dicamba[b]	ESI(−)	106	27	96	−0.4	120	0.5	ND	−4.0
	Fenbuconazole[b]	ESI(+)	508	127	492	−0.1	480	−0.2	138	−2.9
	Fenpropimorph[b]	ESI(+)	121	30	128	0.2	144	0.8	41	−2.7
	Fludioxonil[b]	ESI(−)	78	20	80	0.1	88	0.5	46	−2.5
	Flusilazole[b]	ESI(+)	728	182	784	0.3	760	0.2	278	−2.5
	Chlorpyrifos[b]	ESI(+)	1044	261	1120	0.3	984	−0.2	546	−1.9
	Lambda-cyhalothrin[b]	ESI(+)	50	31	68	1.4	64	1.1	ND	
	Metconazole[b]	ESI(+)	478	120	516	0.3	536	0.5	220	−2.2
	Pyraclostrobin[b]	ESI(+)	746	187	768	0.1	792	0.2	320	−2.3
	Tebuconazole[b]	ESI(+)	1230	308	1260	0.1	1290	0.2	512	−2.4
FAPAS 2259 – breakfast cereals	DON[d]	ESI(−)	522	92	456	−0.7	568	0.5	14	−4.2
	DON-3-Glc	*ESI(−)*			*8*	–	*26*	–	*ND*	–
FAPAS 2252 – oats	T2 toxin[c]	ESI(+)	194	40	196	0.1	208	0.4	96	−2.5
	HT2 toxin[c]	ESI(+)	125	27	116	−0.3	112	−0.5	60	−2.4
	T2-tetraol	*ESI(+)*	–	–	*40*	–	*44*	–	*ND*	–
	Ochratoxin A	*ESI(−)*	–	–	*36*	–	*42*	–	*ND*	–
	ZON	*ESI(−)*	–	–	*28*	–	*24*	–	*ND*	–
	NIV	*ESI(−)*	–	–	*24*	–	*32*	–	*ND*	–
	Fenazaquin	*ESI(+)*	–	–	*14*	–	*20*	–	*ND*	–
	Tolclofos-methyl	*ESI(+)*	–	–	*62*	–	*76*	–	*ND*	–
FAPAS 2237 – maize	FB1[b]	ESI(+)	759	193	45	−1.6	862	0.5	ND	–
	FB2[b]	ESI(+)	242	62	164	−1.3	212	−0.5	ND	–
	FB3	*ESI(+)*		–	*66*	–	*104*	–	*ND*	–
CRM ZON in maize	ZON	ESI(−)	60 ± 9	–	64	–	60	–	ND	–
	DON	*ESI(−)*		–	*548*	–	*560*	–	*138*	–
	DON-3-Glc	*ESI(−)*		–	*17*	–	*40*	–	*ND*	–
	15-ADON	*ESI(+)*		–	*76*	–	*88*	–	*ND*	–
	3-ADON	*ESI(−)*		–	*16*	–	*24*	–	*ND*	–
CRM DON in maize	DON	ESI(−)	474 ± 30	–	448		496	–	88	–
	15-ADON	*ESI(+)*		–	*96*		*104*	–	*ND*	–
	3-ADON	*ESI(−)*		–	*16*		*20*	–	*ND*	–
	DON-3-Glc	*ESI(−)*		–	*8*		*54*	–	*ND*	–

Analytes detected in the samples, but which were not targeted in the proficiency test or CRM are in italics. *ND*, not detected.
[a] Target standard deviation.
[b] Incurred pesticide residue/naturally contaminated sample.
[c] Spiked analyte.
[d] Incurred pesticide residue/naturally contaminated sample, but analyte was also added by test organisers.

with incurred analytes. Although spiking is a common approach in the development and validation of extraction methods, one should be aware that it enables only a rough simulation of the real-life conditions and the results in some extent may depend on respective spiking procedure. To verify method trueness, certified reference materials and well characterised samples from proficiency tests were analysed. Unfortunately, only cereals (maize, wheat and oat) were available for this purpose, thus the results obtained within these experiments indicated potential problems in the analysis of low moisture samples. Comparing the generated data (see Table 3) with assigned/certified values, both methods A and B achieved acceptable results (*z*-score <2). Low recoveries (10–60%) were obtained when employing the method C, although it was able to extract most of the tested compounds from spiked samples with recoveries in the range 70–120% and matrix effects were significantly lower compared to other two procedures. This

could be explained by contamination of only sample surface during the spiking procedure, thus, analytes not incorporated into the respective matrix are easily transferred in the organic solvent. In addition, lower matrix effects corresponded with low recoveries of incurred analytes. Although the method C achieved good performance using the spiked samples, with regards to these facts, it was classified as not suitable for subsequent experiments.

3.5. Analysis of troublesome analytes

Although for most of pesticides and mycotoxins involved in our study performance characteristics complying with the requirements laid down in the Document SANCO/12495/2011 [10] were achieved, some analytes were classified as troublesome. The problems experienced and conditions under which they can be minimised are discussed in the paragraphs below.

3.5.1. Basic analytes

Among the basic analytes, pymetrozine (recoveries achieved by the method A were between 10 and 31%) represents a typical example of troublesome compound which is difficult to extract by the QuEChERS method (method A), except of the AOAC version [22]. In more detail, pymetrozine is a highly polar, basic compound, which remains in the water layer as a protonated molecule due to the low pH during the phase separation. The only way to improve its recovery is maintaining of pH > 6. However, to meet this requirement is practically impossible with regards to the base-sensitive analytes and the worsened recovery of acidic analytes. The poor recoveries can be also expected for other polar, strong bases (*e.g.* nicotine and cyromazine). On the other hand, low pH during the extraction of the method A did not discriminate other basic analytes such as propamocarb ($pK_a \approx 9.5$), spiroxamine ($pK_a \approx 6.9$), thiabendazole ($pK_{a1} \approx 4.1$, $pK_{a2} \approx 12$) or ergopeptide alkaloids ($pK_a \approx 4.8$–6.2), which always provided recoveries above 70%. Thanks to the missing phase separation in the method B procedure, all bases including pymetrozine were easily dissolved in an extraction mixture and their recoveries were in the acceptable range for all matrices.

Another problem encountered in a quantitative analysis of basic analytes was epimerisation of ergot alkaloids on the carbon atom C8. Alike other authors [16,23], we observed, some conversion (10–25%) of natural *R*-forms (-ines) into *S*-form (-inines) even when using acidic extraction solvent mixtures (epimerisation rate increases at the higher pH values [24]). Epimerisation may explain low recoveries of ergot alkaloids reported by Mol et al. [4] who studied only the *R*-forms. A low stability of ergot alkaloids was also observed during 1 week storage at 4 °C, during which 40–60% of original *R*-epimers were transformed into *S*-forms in the method B extracts; somewhat lover extent of conversion (20–30%) was observed in the extracts of the method A.

3.5.2. Acidic analytes

Also some acidic analytes were found to be rather troublesome. For instance, fumonisins were rapidly lost in both solvent standard (MeCN) and the QuEChERS extract (matrix-matched standard) in glass vials. It is presumed that sorption of these compounds on active glass surface of employed vials occurred. This problem was not experienced when fumonisins were dissolved in aqueous solutions such as a water:MeCN (1:1, v/v) mixture or the method B extracts. The elimination of sorption effect by added water was documented by Zachariasova et al. [25] who extracted fumonisins together with other mycotoxins using the QuEChERS method, nevertheless, the MeCN layer was diluted with water before its transfer into the glass autosampler vial. Unfortunately, dilution with water before the LC–MS analysis was not feasible, since several pesticides such as sulphonylurea herbicides (imazosulfuron, metsulfuron-methyl, rimsulfuron and tribenuron-methyl), clofentezine, cycloxidim, formothion, naled, metribuzin, quinoxyfen or tepraloxydim degraded in aqueous solutions as compared to pure MeCN. The extent of observed degradation was 20–90% during 24 h. Moreover the extracts of paprika and black pepper were difficult to dilute since precipitation of relatively non-polar matrix co-extracts (discussed later) occurred as the result of increased solution polarity. Under these conditions the only feasible solution was using polypropylene vials instead of glass ones. The recoveries of fumonisins in the method A (QuEChERS) extracts were then (70–80%), nevertheless, higher values (80–110%) were still obtained by the method B.

Since the method B does not include a phase separation, higher recoveries of polar compounds as compared to the method A would be expectable. However, for the most polar acidic pesticides of this group such as clopyralid ($K_{OW} \approx -2$; $pK_a = 2$), dicamba ($K_{OW} \approx -0.6$; $pK_a = 2$) and picloram ($K_{OW} \approx 1$; $pK_a = 2.3$) the recoveries achieved by the extraction from black pepper, sunflower seeds and wheat flour realised according to the method B were in the range (50–70%). A possible explanation might be an unpredictable ionic binding of the most acidic analytes with basic matrix components. Thanks to the phase separation or a higher amount of water in the initial extraction step (approx. 1:1, v/v), these interactions were negligible in the method A.

3.5.3. Neutral analytes

Regarding neutral compounds, polarity was obviously the key characteristic associated with recoveries by particular extraction method. This was the case, for instance, for deoxynivalenol-3-glucoside (DON-3-Glc), recovery of which by the method A was relatively low (≈40%), since portion of this analyte remained in an aqueous layer during the partitioning step. For other polar trichothecenes represented by nivalenol (NIV) and T-2 tetraol, recoveries at the lowest acceptable level (≈70%) were obtained. Contrary to these results, recoveries ≈90% were achieved by the method B for these analytes in all of the examined matrices.

3.6. Assessment of methods performance on different matrices

3.6.1. Apple baby food

As documented in Fig. 1 (and Table S2–C in Supplementary data), LOQs of the method A for apple baby food allowed the control of all pesticide residues (except β-cyfluthrin with LOQ 20 μg kg^{-1}) and patulin at 10 μg kg^{-1}, which is the maximum level for baby food in the EU [1,26]. When analysing the extracts prepared by the method B, which contained 4-times lower matrix content (0.25 g mL^{-1}), LOQs of at least 26 analytes could not be controlled at 10 μg kg^{-1}. Matrix effects were negligible in both methods.

3.6.2. Wheat flour

In case of wheat flour, the difference in LOQs was less obvious compared to baby food (Fig. 1), nevertheless, the method A still allowed better detection of less sensitive analytes. On the other hand, performance characteristics for polar B-trichothecenes and fumonisins which represent important (regulated) analytes in cereals were better by the method B.

3.6.3. Sunflower seeds

Since sunflower seeds contain up to 50% of lipids, some transfer of these bulky components into the extract may occur, although the solvents used (both in methods A and B) were polar. In any case, presence of lipids needs to be carefully monitored at least during the method optimisation. For an easy lipids monitoring, we employed ambient mass spectrometry with a direct analysis in real time (DART) ion source coupled to a TOFMS instrument, which, as showed in our recent study [27], presents an ideal tool for the rapid monitoring of co-extracts prior to LC or GC analysis. During the

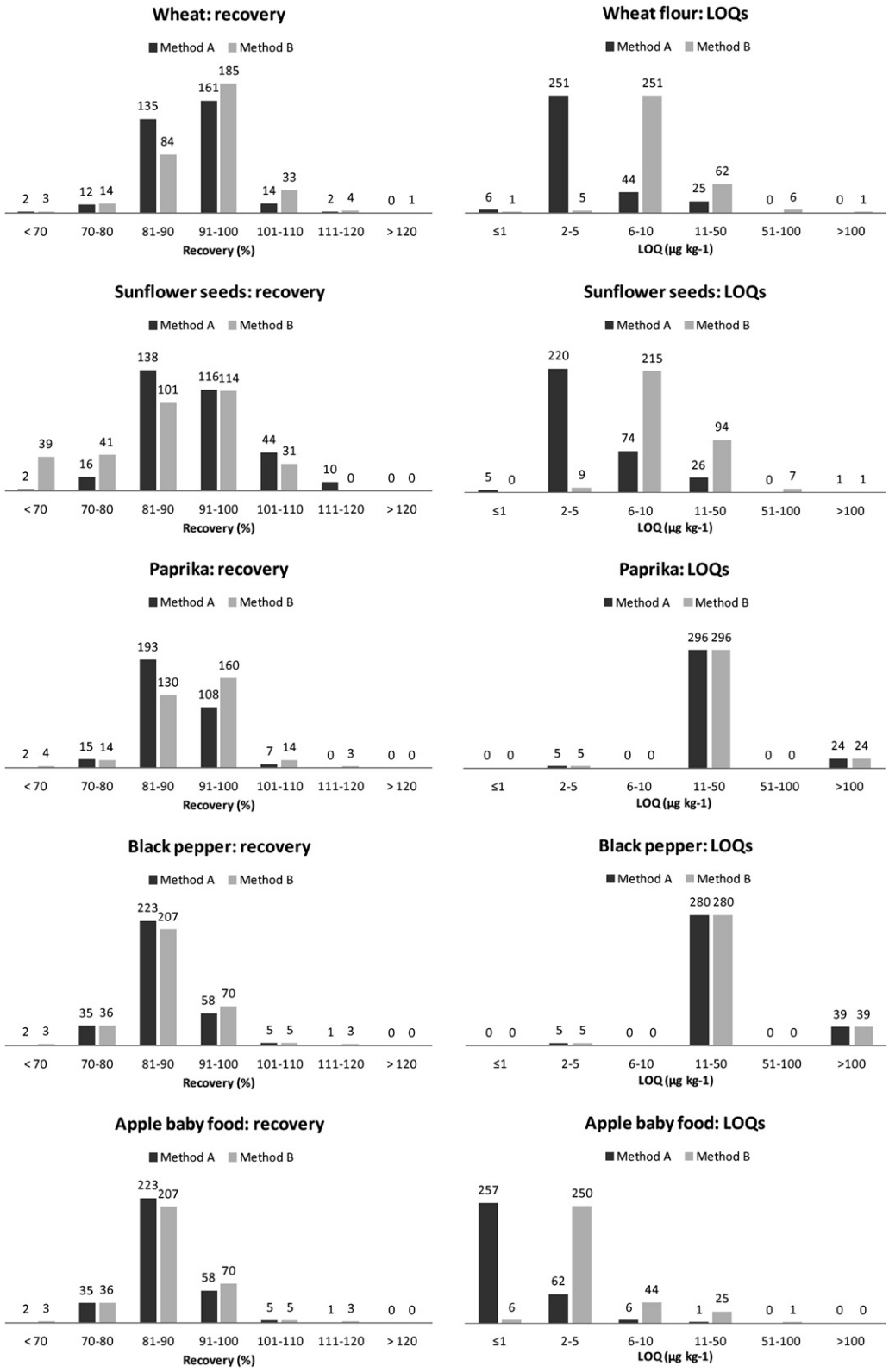

Fig. 1. Histograms of distribution of recoveries and LOQs achieved for the methods A and B for all matrices tested during the validation study. Source data are listed in Table S2.

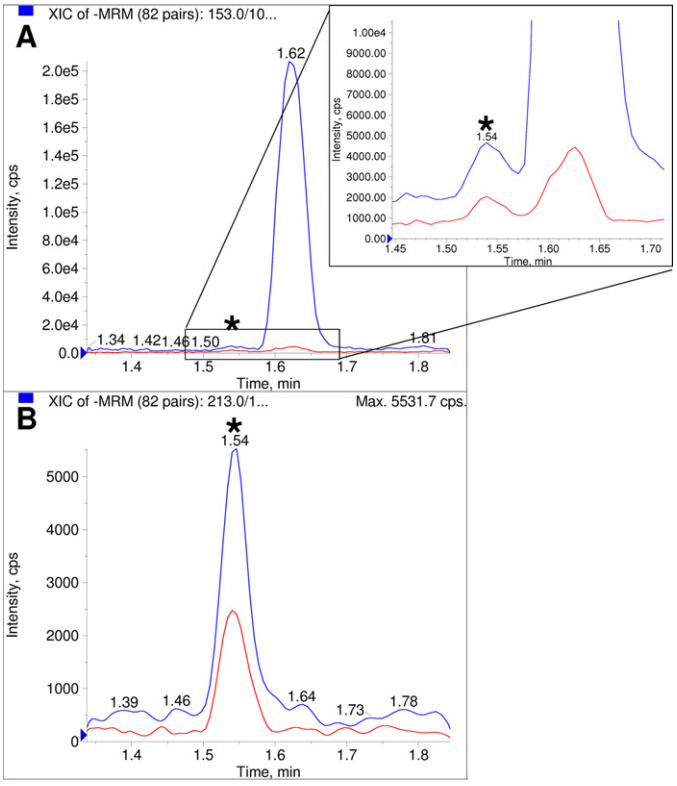

Fig. 2. UHPLC–ESI(−)-MS/MS chromatogram of patulin (*) in apple baby food matrix-matched standard at 10 μg kg^{-1} prepared by the method A (QuEChERS). (A) Detection of an abundant matrix interference in the extract at MRMs of patulin (*m*/*z* 153 > 108.9; *m*/*z* 153 > 81) and (B) improved selectivity when acetate adduct (*m*/*z* 213 > 152.9; *m*/*z* 213 > 109) is detected.

method A procedure, a bulk of lipids were co-extracted, thus dSPE with the C_{18} sorbent was used for extract clean-up.

Due to the higher polarity of a water:MeCN mixture used in the method B, no signals corresponding to TAGs were detected in the extract, but low recoveries (30–70%) of less polar analytes especially pyrethroids, were obtained (Fig. 1). On the contrary, no significant decrease of recoveries was observed during the method A extraction.

3.6.4. Spices

Spices (paprika and black pepper) are notoriously known as difficult matrices, since they contain a bulk of extractable compounds (essential oils, pigments, *etc.*) causing significant matrix effects during the LC–MS/MS analysis. An extensive clean-up usually limits a scope of target analytes, thus, it is not feasible in the multi-class multi-analyte analysis. Under these circumstances, a sample dilution is the only viable way to decrease matrix effects and preserve all target compounds in the extract. Worth to notice, a precipitation of the matrix components should be avoided; otherwise adsorption of analytes on coagulated matrix may occur. The method A extracts (QuEChERS) were diluted with pure MeCN and the extraction mixture (MeCN:water:FA, 75:24:1, v/v/v) was employed for dilution of the extracts prepared by the method B. Bearing in mind the established maximum (residue) limits for the control purposes, a dilution factor could not be as high as needed to avoid extensive matrix effects. In this respect, the final dilution factor was 24 for both methods, which still allowed the control of aflatoxins at the EU limit for spices (5 μg kg^{-1}). Matrix effects in diluted paprika extracts decreased significantly and signals only rarely dropped below 70%. However, extensive signal suppression (30–70%) of approximately one half of all analytes occurred in the diluted black pepper extracts prepared by both A and B methods.

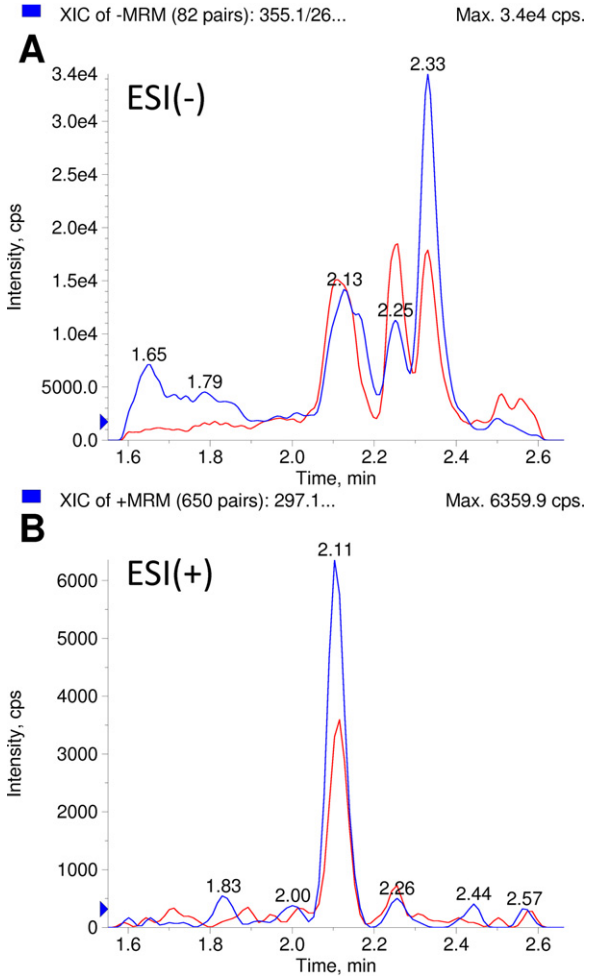

Fig. 3. UHPLC–MS/MS chromatogram of DON in paprika matrix-matched standard (480 μg kg^{-1}) prepared by the method B. (A) Matrix interferences were observed at both DON's MRMs in ESI(−) (*m*/*z* 355.1 > 295.1; *m*/*z* 355.1 > 265.1). (B) Switching to ESI(+) lead to significant improvement of selectivity (*m*/*z* 297.1 > 249; *m*/*z* 297.1 > 203.1).

In addition to the extensive matrix effects, a number of interferences in LC–MS/MS were detected in black pepper and paprika extracts. Since also in our study a common approach of two MRM transitions per analyte and their ratio was used to meet identification criteria [10], interference at one transition (18 analytes in black pepper and 8 analytes paprika) made the identification impossible. Moreover, for some analytes (*e.g.* diniconazole and hexaconazole) mass interferences on both transitions were observed, so strategies to overcome them were investigated in follow-up experiments described below.

3.7. Alternative approaches to overcome interferences in multi-analyte methods

Due to the interferences observed especially for the black pepper extracts and in lower extent also for other matrices, additional analyte identification was required. Chromatographic system with orthogonal selectivity could be used to effectively separate matrix interferences; however, it is difficult to use such approach for the methods involving hundreds of target analytes with a wide range of physico-chemical properties. Therefore, we focused on the improvement of the analyte detection. Two approaches are already suggested in the literature [11–14] and also mentioned in the Document SANCO/12495/2011 [10]: (*i*) the acquisition of

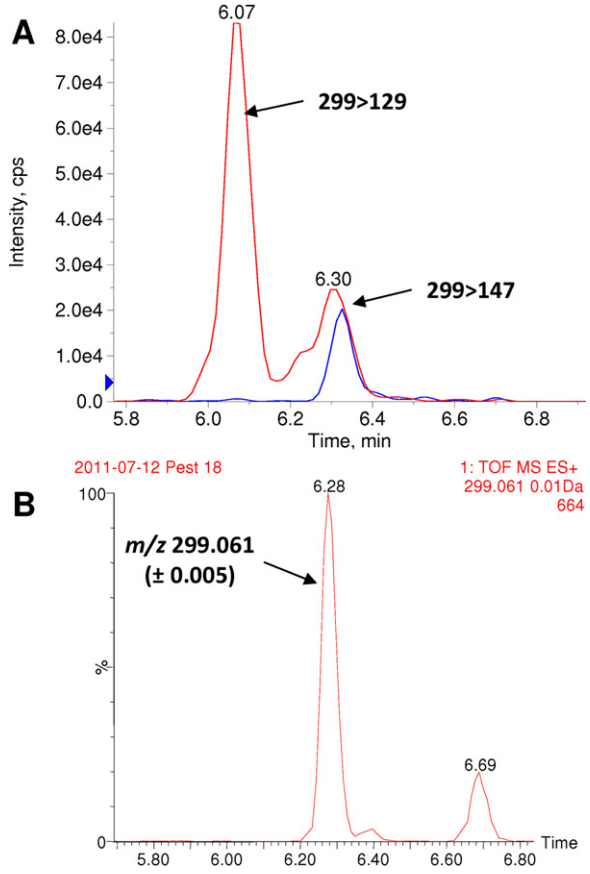

Fig. 4. Confirmation of quinalphos in black pepper at 48 μg kg^{-1} provided by UHPLC–ESI(+)-TOFMS. (A) UHPLC–ESI(+)-MS/MS analysis of quinalphos with an interference at transition *m*/*z* 299 > 129 (transition *m*/*z* 299 > 147 not influenced) and (B) confirmation of the presence of quinalphos by means of UHPLC–ESI(+)-TOFMS (exact mass *m*/*z* 299.061, mass window 0.01 Da).

some additional MRM transitions, and (*ii*) the utilisation of HRMS. Although modern UHPLC–MS/MS instruments are very fast and are capable to detect a high number of MRM transitions, acquisition of three or even more transitions was not applicable for all target analytes from following reasons: (i) not all compounds provide more than two fragments with sufficient sensitivity (*e.g.* aldicarb, formetanate, iprovalicarb, phorate and pyrifenox), and (ii) the number of MRM transitions would increase significantly leading to the shorter dwell times, thus, S/N ratio would be lower. During the course of our experiments, the shortest dwell time of ≈3 ms (92 transitions acquired simultaneously) was used. If the third MRM transition would be considered for all analytes, the dwell time would be less than 1 ms, which is below to the instrument's limit. As a consequence, fewer data points per chromatographic peak would be acquired. Bearing this in mind, we added more MRM transitions only for those analytes for which we observed the interferences during the analysis of some matrices to prevent this scenario in the future. For this purpose, different fragments, molecular adduct ions or the opposite ESI polarity can be selected. For instance, abundant mass interference at MRM transition of patulin (*m*/*z* 153 > 109) was eluted close to the analyte peak in the apple baby food extracts (Fig. 2). Since the neutral loss of 44 Da relates to decarboxylation, it is not specific enough. However, patulin is a somewhat small molecule, thus only two fragments were available. Employing of patulin's acetate adduct allowed us to identify as well as quantify this mycotoxin even at the EU limit for baby food (10 μg kg^{-1}). Similarly, ^{37}Cl isotopes of diniconazole, hexaconazole and propiconazole were used instead of molecular ions (^{35}Cl isotopes), in which case the mass interferences at both MRMs were observed. Switching to ESI(+) was used to overcome interferences at all DON's MRMs in the paprika extracts acquired in ESI(−) mode (Fig. 3).

As mentioned above, not all analytes provide more MRM transitions with sufficient LOQs, thus LC–HRTOFMS was also used as an alternative way for additional analyte identification. In general, HRMS allows detection of the same scope of analytes as LC–MS/MS, but with different selectivity. Since HRMS has no limitation in terms of the maximum number of detected analytes, this instrumental approach can be used for additional confirmation of analytes [12,13]. In our case, the analyte identification was based on the exact mass measurement of molecular ions and in-source fragments, which was successfully used in our previous works [25,28]. The mass differences of analyte molecular ions and interferences in the paprika and black pepper extracts were high enough, thus practically all problematic analytes were identified by HRMS even when operated at a mass resolving power of only 10,000 FWHM (Fig. 4). The only exceptions were formetanate in paprika and jasmolin I and II in black pepper, in which case the mass resolving power of the used HRTOFMS instrument was not sufficient to effectively resolve the matrix interference from the target analyte ions. Since interferences at both MRMs of these analytes were also observed in MS/MS, none of these two techniques enabled their identification.

4. Conclusions

Simultaneous determination of mycotoxins and pesticide residues in various food matrices may significantly increase sample throughput and reduce the analysis cost. On this account, the experience obtained within the optimisation of LC–MS/MS determination and the critical assessment of three simple and rapid extraction strategies has been addressed. Three different sample preparation approaches were tested within this study: method A – aqueous acetonitrile extraction followed by partition (QuEChERS-like method), method B – aqueous acetonitrile extraction, and method C – pure acetonitrile extraction. The conclusions are summarised in following paragraphs:

(i) As documented on the analysis of CRMs and samples from the proficiency tests, acceptable results (*z-score* <|2|) were achieved only by the methods A and B. The extraction of incurred analytes with pure acetonitrile (method C) was not efficient enough.

(ii) Due to the higher matrix equivalent injected, the method A achieved lower LOQs in apple baby food, wheat and sunflower seeds compared to the method B. Thanks to the low LOQs, the method A enabled control of EU baby food limits (10 μg kg^{-1}) for all pesticide residues and patulin.

(iii) Repeatabilities of both A and B methods expressed as RSDs were <20% and recoveries were in the acceptable range (70–120%), for most of analyte/matrix combinations. The exceptions were rather poor recoveries of non-polar analytes isolated from fatty matrices by the method B. For that reason, the method A was assessed as a better choice for these samples despite of a necessity of a simple additional extract purification.

(iv) The method A showed lower recoveries for polar mycotoxins (DON-3-Glc, NIV, T-2 tetraol) and strong polar bases (pymetrozine), which were expectable due to the acidic conditions. The method A provided more consistent results for all matrices tested and the extracts in MeCN were also more stable as compared to the method B.

(v) Contrary to the method A, the method B gave better recoveries for all polar analytes due to the absence of the partition step. The only exception was the low recoveries of the most polar acidic compounds from basic matrices.

(vi) Thanks to the lower LOQs, more consistent and predictable results of the method A, we would assess it as a better choice. However, it should be noted, that results of such method comparison depends largely on the list of target analytes. When more polar compounds and/or strong bases would be included, the result would be opposite.

(vii) Since matrix interferences were detected during the UHPLC–MS/MS analysis of the sample extracts (especially in black pepper), an additional analyte identification suitable for extensive multi-analyte methods was investigated. To achieve analyte identification, different molecular ion or opposite ionisation polarity were used; however, this approach was not applicable for all target compounds. The utilisation of detection system with different selectivity such as HRMS represented by HRTOFMS was more general approach and this technique was found to be useful when mass interferences were detected in tandem MS with unit mass resolution.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2012.08.097.

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SUPPLEMENTARY DATA :

Critical assessment of extraction methods for the simultaneous determination of pesticide residues and mycotoxins in fruits, cereals, spices and oil seeds employing ultra-high performance liquid chromatography–tandem mass spectrometry

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Determination of the pH of tested matrices

Determination of the pH of tested matrices was done by measuring the pH value of their water extracts. An amount of 1 g of the sample was weighted into a 50-mL PP tube and 10 mL of MilliQ water added. The content of the tube was mixed and the matrix was left to soak for 30 min. Then, pH of water extracts as well as deionized water was measured by a calibrated pH meter HI 991001 (Hanna Instruments Inc.; Woonsocket, RI, USA).

Monitoring of lipids in the sample extracts by ambient mass spectrometry

For rapid monitoring of triacylglycerols (TAGs) in sunflower extracts, ambient mass spectrometry employing a direct analysis in real time ion source (DART-100; IonSense, MA, USA) coupled to an AccuTOF LP TOF, time-of-flight mass spectrometer (JEOL; Paris, France), equipped with an HTC PAL autosampler AutoDART-96 (Leap Technologies; Carrboro, NC, USA) was used. Settings of the DART–TOFMS system were as follows: helium flow: 3.0 L min^{-1}; gas temperature: 350°C; discharge needle voltage: –3000 V; perforated electrode: +150 V; grid electrode: +250 V; ion guide voltage: 1100 V. Mass spectra were recorded in the range *m*/*z* 100– 1200 at an acquisition rate of 2 spectra s^{-1}. Samples were automatically transferred in front of the DART gun exit on the glass rod of the Dip-it sampler (IonSense, MA, USA) and thermodesorbed from its surface in hot helium gas for 30 s. Three repeated measurements were carried out for each sample. To support the ionization of TAGs, ammonia vapours were used as a dopant. For this purpose, a 2 mL autosampler vial containing aqueous ammonia was placed beneath the ion source exit. At the end of each analysis, mass spectra of PEG 600 (dissolved in methanol, 200 µg mL^{-1}) were acquired to enable mass drift compensation and, thus, accurate mass measurements.

Table S1-A: Parameters of UHPLCï ESI(+)-MS/MS detection method.

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
TPP (IS)	6.58	327	77	156	67	12					
Acephate	1.65	184	143	66	13	16	184	49	66	27	6
Acetamiprid	2.6	223.1	126	81	31	16	223.1	72.9	81	77	10
Acetochlor	5.94	270.1	224.1	56	13	14	270.1	148.1	56	27	16
Acrinathrin	9.12	559.1	208.1	66	19	12	559.1	181.1	66	49	16
Alachlor	5.94	270.1	238.1	76	15	14	270.1	162.1	76	27	14
Aldicarb	3.11	208.1	116	31	11	14	208.1	89	31	23	10
Aldicarb sulfone	1.94	240.1	86	46	27	36	240.1	148.1	46	19	18
Aldicarb sulfoxide	1.84	224.1	132.1	31	15	14	224.1	69	31	27	10
Ametryn	4.36	228.1	186.1	76	27	10	228.1	68	76	55	10
Atrazine	4.33	216.1	174	66	25	10	216.1	104	66	39	12
Avermectine B1a	9.67	890.5	305.2	101	33	24	890.5	567.2	101	19	28
Avermectine B1b	9.27	876.5	291.1	86	35	30	876.5	145.1	86	53	14
Azadirachtin	4.09	703.3	685.1	171	17	40	703.3	567.1	171	21	34
Azinphos-ethyl	5.75	346	77	81	55	10	346	132	81	23	16
Azinphos-methyl	4.69	318	132	101	21	14	318	77	101	47	10
Azoxystrobin	4.93	404.1	372.1	71	21	20	404.1	329	71	43	24
Benalaxyl	6.59	326.2	148.1	86	29	10	326.2	91	86	61	10
Bendiocarb	3.53	224.1	109	76	25	14	224.1	167.1	76	13	20
Beta-cyfluthrin	8.6	451.1	191	61	21	16	453.1	193	61	21	16
Bifenthrin	9.95	440.2	181.1	56	19	10	440.2	165.1	56	93	10
Bitertanol	6.74	338.2	99.1	51	21	12	338.2	70	51	51	8
Boscalid	5.19	343	307	121	29	36	343	140	121	27	16
Bupirimate	5.71	317.2	166.1	111	33	10	317.2	108	111	35	12
Buprofezin	7.66	306.2	201.1	56	17	12	306.2	106	56	39	12
Cadusafos	7.1	271.1	159	51	19	16	271.1	96.9	51	49	14
Carbaryl	3.76	202.1	145	86	15	14	202.1	127	86	39	14
Carbendazim	2.17	192.1	160	71	25	18	192.1	132	71	41	16
Carbofuran	3.59	222	123.1	66	31	16	222	165.1	66	17	20
Carbofuran-3-hydroxy	2.59	255.1	163.1	41	25	18	255.1	220.1	41	15	30
Carbophenothion	8.31	343	157	56	19	18	345	159	56	21	18
Chlorfenvinphos	6.58	359	155.1	111	17	18	361	155.1	111	19	18
Chloroxuron	5.5	291.1	72	76	25	10	291.1	46	76	51	12
Chlorpropham	4.5	214	172	86	13	10	214	154	86	25	16
Chlorpyrifos	8.05	351.9	199.9	51	29	18	349.9	197.9	51	29	16
Chlorpyrifos-methyl	6.94	321.9	125	86	29	14	323.9	125	86	27	14
Cinerin I	8.49	317.2	107.1	81	27	12	317.2	149.1	81	15	16
Cinerin II	7.12	361.2	107	81	29	12	361.2	149.1	81	15	16
Clofentezine	6.74	303	138	61	21	16	303	101.9	61	55	14
Clomazone	4.77	240.1	125	66	31	12	240.1	89	66	65	12
Clothianidin	2.46	250	169.1	66	19	10	250	132	66	25	14
Cyanazine	3.34	241.1	214.1	96	25	26	241.1	104	96	41	14
Cyazofamid	5.9	325	108	56	19	16	327	108	56	19	16

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Cycloxidim	7.4	326.2	280.1	91	19	14	326.2	180.1	91	27	12
Cymoxanil	2.81	199.1	128	66	13	14	199.1	111	66	25	14
Cypermethrin	8.8	433.1	191	56	19	24	435.1	193	56	19	16
Cyproconazole	5.5	292	70	86	23	8	292	125.1	86	45	8
Cyprodinyl	5.86	226.1	93	91	47	10	226.1	77	91	61	10
Deltametrin	8.91	521	278.9	56	21	22	523	280.9	56	21	22
Demeton-S-methyl	3.66	231	89	56	25	38	231	61	56	43	10
Demeton-S-methyl sulfone	2.15	263	169	66	21	20	263	109	66	37	12
Desmedipham	4.55	318.1	182.1	76	19	22	318.1	136	76	39	16
Desmetryn	3.68	214.1	172	81	25	10	214.1	82	81	41	10
Diazinon	6.57	305.1	169.1	81	29	16	305.1	96.9	81	47	12
Dichlofluanid	5.68	350	123	46	41	14	350	223.9	46	21	26
Dichlorvos	3.48	221	109	106	25	14	221	127	106	23	14
Diclofop-methyl	7.63	358.1	281	41	21	30	358.1	120	41	39	14
Dicrotophos	2.33	238.1	72.1	66	43	10	238.1	112.1	66	17	16
Diethofencarb	4.98	268.1	226.1	61	13	16	268.1	124	61	41	14
Difenoconazole	7	406.1	251	111	37	14	408.1	253	111	37	14
Diflubenzuron	6	311	158	76	21	16	311	141	76	45	14
Diflufenican	7.12	395.1	266	91	35	16	395.1	245.9	91	51	14
Dimethenamid-P	5.19	276.1	244	66	21	28	276.1	168.1	66	33	20
Dimethoate	2.63	230	125	66	29	16	230	198.9	66	13	22
Dimethomorph	5.18	388.1	301	86	29	16	388.1	165	86	43	14
Dimoxystrobin	6.2	327.1	205.1	66	15	14	327.1	116	66	29	12
Diniconazole	6.9	326.1	70	106	77	10	326.1	159	106	50	10
Diniconazole 37Cl	6.9	328.1	70	106	77	10	328.1	161	106	50	10
Disulfoton	6.9	275	89	21	21	10	275	61	21	47	10
Disulfotone sulfone	4.16	307	96.9	96	45	12	307	125	96	23	14
Disulfotone sulfoxid	4.08	291	96.9	71	51	12	291	185	71	19	20
Diuron	4.45	233	72	96	39	10	235	72	96	39	10
DMSA	3.09	201.1	92	71	27	12	201.1	65	71	47	10
DMST	3.63	215.1	106	71	21	12	215.1	77	71	57	10
Dodine	6.24	228.2	57.1	146	31	8	228.2	60	146	31	10
EPN	7.04	324	296	86	19	14	324	157	86	31	16
Epoxiconazole	5.88	330.1	121.1	71	27	14	330.1	101	71	69	12
Ethiofencarb	3.96	226.1	107	76	23	12	226.1	164.1	76	11	18
Ethion	7.95	385	96.9	51	65	12	385	143	51	33	18
Ethofumesate	4.95	304.1	121.1	41	29	16	304.1	161.1	41	33	20
Ethoprophos	5.86	243.1	96.9	61	45	12	243.1	130.9	61	29	14
Etofenprox	9.78	394.2	107	61	61	12	394.2	177.1	61	21	16
Etrimfos	6.37	293.1	125	66	35	14	293.1	264.9	66	23	30
Fenamiphos	6.07	304.1	217	96	31	12	304.1	202	96	47	18
Fenamiphos sulfon	3.67	336.1	266	131	27	18	336.1	188	131	37	10
Fenamiphos sulfoxid	3.57	320.1	108.1	111	57	12	320.1	233	111	35	22
Fenarimol	5.71	331	268	96	33	28	331	189	96	69	14

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Fenazaquin	8.97	307.2	161.1	81	23	18	307.2	57.1	81	39	16
Fenbuconazole	5.93	337.1	125	101	45	16	337.1	70	101	25	10
Fenchlorphos	6.2	320.9	125.1	106	27	16	320.9	78.9	106	53	12
Fenhexamid	5.72	302.1	97.1	116	31	12	302.1	55	116	55	8
Fenoxaprop	6.2	334	288.1	121	25	32	334	244	121	29	28
Fenoxycarb	6.05	302.1	88	86	27	10	302.1	116.1	86	15	12
Fenpropathrin	8.53	367.2	125.1	51	21	14	367.2	350.1	51	11	12
Fenpropidin	4.36	274.3	117	86	73	14	274.3	147.1	86	39	18
Fenpropimorph	4.6	304.3	117	91	79	12	304.3	147.1	91	41	18
Fenpyroximate	8.69	422.2	366.1	121	23	12	422.2	135	121	43	16
Fensulfothion	4.33	309	157	106	33	18	309	173	106	33	20
Fensulfothion-PO sulfon	4.45	325	269	91	23	20	325	94	91	59	12
Fenthion	6.35	279	169	86	25	20	279	247	86	19	28
Fipronil	6.12	436.9	367.8	106	25	36	438.9	369.8	106	25	36
Flonicamid	2.19	230.1	203	81	25	24	230.1	98	81	53	12
Fluazifop	5.15	328.1	282	111	25	8	328.1	91	111	37	12
Fluazifop-P-butyl	7.64	384.1	282	141	29	28	384.1	91	141	45	12
Flufenacet	5.79	364.1	152	66	27	14	364.1	194.1	66	15	12
Flufenoxuron	8.41	489	158	131	25	10	489	141	131	67	12
Fluoxastrobin	5.69	459.1	427	101	25	22	459.1	188	101	47	12
Fluquinconazole	5.67	376	307	86	35	20	376	108	86	61	12
Fluroxypyr	3.35	255	209	76	23	24	255	181	76	31	20
Flusilazole	6.05	316.1	165.1	86	39	18	316.1	247.1	86	25	28
Fomesafen	5.16	456	344	61	21	40	456	223	61	45	30
Fonofos	6.45	247.1	109	51	27	8	247.1	137	51	15	16
Formetanate	1.6	222.1	165.1	91	21	20	222.1	120	91	37	14
Formothion	3.2	258	198.9	71	17	18	258	125	71	25	10
Haloxyfop	6.31	362.1	316	121	25	24	362.1	91	121	39	12
Haloxyfop-ethoxyethyl	7.59	434.1	316	126	27	12	434.1	91	126	45	12
Haloxyfop-methyl	7.08	376	316	121	25	12	376	91	121	39	12
Heptenophos	4.45	251	127	71	19	12	251	124.9	71	23	14
Hexaconazole	6.6	314.1	70	81	51	10	314.1	159	81	49	16
Hexaconazole 37Cl	6.6	316.1	70	81	51	10	316.1	161	81	49	16
Hexazinon	3.63	253.2	171.1	81	23	10	253.2	71	81	41	8
Hexythiazox	8.12	353.1	228	61	21	16	353.1	168	61	35	14
Imazalil	3.85	297.1	159	106	33	16	299.1	161	106	33	16
Imazapyr	2.51	262.1	217.1	71	27	24	262.1	149	71	35	20
Imazaquin	3.65	312.1	128	91	71	14	312.1	153.1	91	65	10
Imazethapyr	3.33	290.1	245.1	106	29	14	290.1	177	106	37	10
Imazosulfuron	5.27	413	153	46	17	12	413	156	46	25	18
Imidacloprid	2.42	256	175.1	71	27	10	256	209	71	23	12
Indoxacarb	7.1	528.1	203	126	59	14	528.1	56	126	79	14
Iodosulfuron-methyl	4.73	508	167	61	25	18	508	83	61	69	10
Iprodion	6.02	330	244.8	66	21	24	332	246.9	66	21	22

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Iprovalicarb	5.72	321.2	119.1	51	28	14	321.2	91	51	68	12
Isofenphos	6.88	346.1	244.9	46	17	20	346.1	216.9	46	31	16
Isofenphos-methyl	6.36	332.1	231	46	21	26	332.1	121	46	45	14
Isoproturon	4.36	207.1	72.1	71	27	12	207.1	165.1	71	19	18
Jasmolin I (4%)	9	331.2	163.1	91	13	18	331.2	77	91	79	10
Jasmolin II (2%)	7.7	375.2	163.1	96	13	18	375.2	77	96	91	10
Kresoxim-methyl	6.24	331.2	116	46	25	16	331.2	206	41	13	26
Lambda-cyhalothrin	8.68	467.1	225	61	23	26	469.1	227	61	23	26
Lenacil	4.38	235.1	153.1	61	23	14	235.1	136	61	45	8
Linuron	4.96	249	160	76	25	14	249	182	76	23	22
Lufenuron	8.05	511	141	86	72	18	511	158	86	27	18
Malaoxon	3.61	315.1	99	111	31	12	315.1	127	111	17	12
Malathion	5.34	331	127	76	17	14	331	99	76	33	14
Mecarbam	5.8	330.1	227	56	13	26	330.1	96.9	56	57	12
Mefenpyr-diethyl	6.65	373.1	327	116	21	22	373.1	160	116	43	10
Mepanipyrim	5.64	224.1	106	101	35	46	224.1	104	101	37	14
Mepronil	5.4	270.1	119	41	33	20	270.1	91	41	59	12
Metalaxyl	4.45	280.1	220.1	86	17	12	280.1	192.1	86	25	12
Metamitron	2.64	203.1	175.1	96	23	10	203.1	104	96	31	12
Metamitron-desamino	2.64	188.1	160.1	111	25	18	188.1	77	111	43	12
Metazachlor	4.35	278.1	134.1	41	31	14	278.1	210.1	41	15	22
Metconazole	6.69	320.1	70	86	63	8	320.1	125	86	61	12
Methacrifos	4.58	258	209	11	17	12	258	125	11	33	14
Methamidophos	1.5	142	94	66	21	12	142	125	66	19	16
Methidathion	4.6	320	145	41	17	8	320	85	41	33	10
Methiocarb	5.03	226.1	121.1	71	27	14	226.1	169.1	71	15	20
Methiocarb sulfone	2.65	275.1	122.1	51	31	14	275.1	107	51	59	12
Methiocarb sulfoxide	2.49	242.1	185.1	56	19	12	242.1	122.1	56	41	14
Methomyl	2.15	163	88	46	13	10	163	106	46	15	12
Methoxyfenozide	5.46	369.2	149.1	61	25	16	369.2	313.1	61	11	30
Metobromuron	4.17	261	148.1	71	21	18	259	148.1	71	21	18
Metolachlor	6.03	284.1	252	51	21	14	284.1	176.1	51	35	12
Metolcarb	3.28	166.1	109	56	15	12	166.1	94	56	43	10
Metosulam	3.61	418	175	86	37	16	418	140	86	73	14
Metoxuron	3.1	229.1	72	91	23	10	229.1	46	91	37	12
Metribuzin	3.63	215.1	187.1	76	25	18	215.1	84	76	29	12
Metsulfuron-methyl	3.53	382.1	167.1	61	23	20	382.1	199	61	33	22
Mevinphos	2.8	242.1	127	36	27	12	242.1	192.9	36	15	12
Monocrotophos	2.23	224.1	127.1	96	21	16	224.1	193	96	11	22
Monolinuron	3.94	215	126	71	25	16	215	148	71	21	16
Monuron	3.45	199.1	72.1	81	24	12	199.1	126	81	35	14
Myclobutanil	5.41	289.1	70	86	23	8	289.1	125	86	47	18
Naled	4.5	380.8	127	101	19	16	380.8	108.9	101	57	16
Napropamid	5.85	272.2	129.1	81	23	14	272.2	171.1	81	27	18

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Neburon	6.2	275.1	88.2	76	23	14	275.1	114.1	76	21	14
Norflurazone	4.48	304	284	106	33	18	306	286	106	33	18
Omethoat	1.75	214	125	71	29	6	214	182.9	71	15	14
Oxadixyl	3.17	279.1	219.1	56	15	22	279.1	132.1	56	45	14
Oxamyl	1.98	237.1	72	51	33	32	237.1	90.1	51	11	12
Oxamyl-oxime	1.8	163	72.1	71	17	10	163	90	71	25	14
Oxydemeton-methyl	2.07	247	169	61	19	10	247	109	61	39	12
Oxyfluorfen	7.6	362	316	96	21	24	362	237	96	35	14
Paclobutrazol	5.28	294.1	70	76	61	10	294.1	125	76	57	14
Penconazole	6.3	284.1	70	76	21	10	284.1	158.9	76	45	18
Pencycuron	6.93	329.1	125	101	37	14	331.1	127	101	37	14
Pendimethalin	8.14	282.1	212	61	15	14	282.1	194.1	61	25	16
Permethrin	9.5	408.1	183.1	51	32	20	410.1	183.1	51	32	24
Phenmedipham	4.66	318.1	136.1	56	35	16	318.1	168.1	56	19	18
Phenothrin	9.56	351.2	183	81	31	20	351.2	248.9	81	25	28
Phenthoate	6.2	321	107.1	66	39	14	321	135	66	27	16
Phorate	6.71	261	75	46	23	18	261	96.9	46	45	18
Phorate sulfon	4.2	310	96.9	61	57	14	310	171	61	21	20
Phorate sulfoxid	4.1	277	96.9	76	47	12	277	199	76	13	20
Phosalone	6.78	385	182	61	27	20	385	110.9	61	63	14
Phosmet	4.75	318	160	111	25	18	318	133	111	51	16
Phosmet-oxon	3.2	302	160	56	21	18	302	77	56	73	10
Phosphamidon	3.25	300.1	174	96	19	16	300.1	127	96	29	16
Picloram	2.33	240.9	222.9	61	21	14	240.9	194.8	61	31	16
Picoxystrobin	6.1	368.1	145	71	29	14	368.1	205.1	71	13	12
Piperonyl Butoxide	7.93	356.2	177.1	61	21	22	356.2	119	61	49	14
Pirimicarb	3.28	239.1	72	61	35	12	239.1	182.1	61	23	10
Pirimicarb-desmethyl	2.36	225.1	72.1	86	35	10	225.1	168.1	81	19	22
Pirimiphos-ethyl	7.76	334.1	198	71	31	22	334.1	182.1	71	31	18
Pirimiphos-methyl	6.7	306.1	108	101	41	12	306.1	164.1	101	31	10
Prochloraz	6.53	376	308	61	17	10	378	310	66	17	10
Profenofos	7.49	372.9	302.8	101	27	32	374.9	304.8	101	27	32
Prometon	3.88	226.1	142	126	31	10	226.1	184.1	126	27	20
Prometryn	5.11	242.1	200.1	106	27	22	242.1	158.1	106	33	18
Propachlor	4.39	212.1	170	91	21	10	212.1	94	91	37	14
Propamocarb	1.79	189.2	102.1	86	23	12	189.2	144.1	86	17	18
Propaquizafop	7.78	444.1	100.1	86	23	12	444.1	56	86	67	8
Propargite	8.4	368.2	175.1	66	23	22	368.2	231.1	66	13	28
Propham	4.2	180.1	138.1	61	13	16	180.1	120.1	61	23	14
Propiconazole	6.52	342.1	159	81	41	10	342.1	69	81	25	8
Propiconazole 37Cl	6.52	344.1	161	81	41	10	344.1	69	81	25	8
Propoxur	3.55	210.1	111.1	61	21	14	210.1	168	61	11	18
Propyzamide	5.37	256	190	66	19	12	256	172.9	66	31	14
Proquinazid	8.72	373	331	66	21	38	373	288.9	66	33	30

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Prosulfocarb	7.34	252.1	91.1	66	39	12	252.1	128.1	66	17	16
Pymetrozine	1.6	218.1	105.1	81	29	12	218.1	78	81	59	10
Pyraclostrobin	6.68	388.1	194	66	17	18	388.1	163	66	35	12
Pyrazophos	6.87	374.1	222	76	31	12	374.1	194	76	45	18
Pyrethrin I	8.54	329.2	161.1	116	15	16	329.2	77	116	85	10
Pyrethrin II	7.22	373.2	161.1	101	15	18	373.2	77	101	93	10
Pyridaben	9.06	365.1	147.1	61	35	14	365.1	309	61	17	20
Pyridate	9.52	379.1	207	96	25	26	379.1	68	96	97	10
Pyrifenox	5.25	295	93.1	86	45	12	297	93.1	86	45	12
Pyrimethanil	4.66	200.1	107	106	33	12	200.1	82	106	35	10
Pyriproxyfen	7.88	322.1	96.1	66	21	14	322.1	185	66	31	22
Quinalphos	6.22	299	147	81	31	18	299	129	81	53	16
Quinmerac	2.81	222	204	61	25	12	222	141	61	45	14
Quinoxyfen	7.97	308	162	81	61	10	308	196.9	81	45	20
Quizalofop	6.2	345	299.1	81	27	22	345	163	81	55	18
Quizalofop-P-ethyl	7.52	373.1	299.1	116	27	26	373.1	91.1	116	37	12
Resmethrin	9.26	339.2	171.1	106	21	12	339.2	128.1	106	65	12
Rimsulfuron	3.83	432	182	111	33	20	432	139	111	65	14
Simazine	3.64	202.1	132.1	71	27	14	202.1	124.1	71	25	14
Simetryn	3.65	214.1	124.1	81	27	14	214.1	96.1	81	33	12
Spinosyn A	6.52	732.5	142.1	101	35	12	732.5	98.1	101	97	12
Spinosyn D	6.9	746.5	142.1	96	37	8	746.5	98.1	96	95	12
Spiroxamin	4.75	298.3	144.1	126	27	14	298.3	100.1	126	43	12
Sulfotep	6.32	323	96.9	81	57	12	323	115	81	41	14
Tau-Fluvalinate	9.36	503.1	208	121	17	12	503.1	181.1	121	43	10
Tebuconazole	6.38	308.1	70	61	57	10	308.1	125	61	53	14
Tebufenozide	6.15	353.2	133	66	27	16	353.2	297	66	11	16
Tebufenpyrad	7.68	334.2	117	121	73	14	334.2	145.1	121	35	18
Teflubenzuron	7.76	381	158.1	51	23	10	381	141	51	57	16
Tepraloxydim	5.71	342.1	250.1	71	19	14	342.1	166.1	71	29	10
Terbufos	7.66	289	103	56	13	12	289	57	56	33	8
Terbufos sulfon	4.93	321	96.9	96	61	12	321	115	96	37	14
Terbufos sulfoxide	4.95	305	96.9	61	57	12	305	187	61	15	20
Terbuthylazine	5.19	230.1	174	71	23	10	230.1	68	71	53	8
Terbutryn	5.19	242.1	186.1	76	27	22	242.1	96.1	76	39	12
Tetraconazole	5.74	372	159	66	45	18	372	70	66	67	10
Thiabendazole	2.38	202	175	136	37	20	202	131.1	136	45	16
Thiacloprid	2.79	253	126	81	29	16	253	90	81	55	12
Thiamethoxam	2.17	292	211.1	81	19	24	292	132	81	33	14
Thifensulfuron-methyl	3.4	388	167.1	56	23	20	388	204.9	56	37	22
Thiodicarb	3.96	355	88	81	33	12	355	108	81	21	14
Thiometon	4.19	247	89.1	51	19	10	247	61	51	45	16
Thiophanate-methyl	3.5	343	151.1	86	29	18	343	93	86	71	12
Tolclofos-methyl	6.72	300.9	125	101	25	16	300.9	268.9	101	23	12

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Tolylfluanid	6.32	364	137	46	39	18	364	238	46	19	28
Triadimefon	5.43	294.1	69.1	61	27	10	294.1	197.1	61	21	20
Triadimenol	5.58	296.1	70	51	39	10	296.1	227	51	17	26
Triazamate	5.8	315.1	72	56	53	10	315.1	226.1	56	17	26
Triazophos	5.54	314.1	162.1	71	27	18	314.1	119.1	71	49	14
Trichlorfon	2.65	256.9	109	86	25	12	258.9	109	86	25	12
Trifloxystrobin	7.17	409.1	186.1	66	29	18	409.1	206.1	66	19	24
Triflumuron	6.7	359	156	81	23	20	359	139	81	49	16
Triforine	4.7	434.9	389.9	56	17	46	436.9	391.9	56	17	38
Vamidothion	2.56	288	146.1	56	17	18	288	118	56	31	14
Vamidothion sulfon	1.82	320	178.1	116	21	20	320	57.9	116	59	16
Vamidothion sulfoxid	1.73	304	169	66	23	18	304	108.9	66	47	12
15-ADON	*2.74*	*356.1*	*321*	*46*	*17*	*32*	*356.1*	*137.1*	*46*	*21*	*18*
3-ADON_octan	*2.74*	*339.1*	*203.1*	*116*	*21*	*22*	*339.1*	*231*	*116*	*17*	*30*
Aflatoxin B1	*3.46*	*313*	*285*	*136*	*33*	*20*	*313*	*241*	*136*	*51*	*20*
Aflatoxin B2	*3.29*	*315*	*287.1*	*141*	*37*	*20*	*315*	*259*	*141*	*41*	*24*
Aflatoxin G1	*3.05*	*329*	*243*	*146*	*37*	*18*	*329*	*200*	*146*	*57*	*12*
Aflatoxin G2	*2.9*	*331.1*	*313*	*136*	*35*	*18*	*331.1*	*189*	*136*	*57*	*12*
Altenuene	*4.38*	*259*	*185.1*	*161*	*43*	*30*	*259*	*128*	*161*	*65*	*24*
Alternariol	*5.86*	*273*	*128*	*176*	*63*	*16*	*273*	*115*	*176*	*71*	*14*
Alternariol methylether	*3.34*	*293.1*	*257*	*76*	*21*	*14*	*293.1*	*275.1*	*76*	*13*	*14*
aZOL	*5.29*	*321.1*	*285.3*	*116*	*15*	*16*	*321.1*	*303.1*	*116*	*11*	*34*
bZOL	*4.72*	*321.2*	*285.3*	*116*	*15*	*16*	*321.2*	*303.1*	*116*	*11*	*34*
Citrinin	*3.72*	*251.1*	*233.1*	*96*	*23*	*24*	*251.1*	*205.1*	*96*	*37*	*24*
deepoxyDON	*2.42*	*281.1*	*233.2*	*96*	*17*	*24*	*281.1*	*109.1*	*96*	*33*	*14*
Diacetoxyscirpenol	*3.54*	*384*	*307.2*	*66*	*15*	*16*	*384*	*105*	*66*	*63*	*12*
DON	*2.08*	*297.1*	*249*	*116*	*15*	*28*	*297.1*	*203.1*	*116*	*23*	*20*
DON-3-Glc	*1.98*	*476.2*	*297.1*	*61*	*17*	*36*	*476.2*	*249.1*	*61*	*31*	*26*
Ergocornine	*3.26*	*562.1*	*544.3*	*86*	*21*	*32*	*562.1*	*223.2*	*86*	*51*	*22*
Ergocorninine	*3.85*	*562.2*	*544.3*	*86*	*21*	*32*	*562.2*	*223.2*	*86*	*51*	*22*
Ergocristine	*3.7*	*610.4*	*592.2*	*86*	*21*	*36*	*610.4*	*223.1*	*86*	*51*	*20*
Ergocristinine	*4.32*	*610*	*592.2*	*86*	*21*	*36*	*610*	*223.1*	*86*	*51*	*20*
Ergocryptine	*3.65*	*576.4*	*223.1*	*86*	*49*	*12*	*576.4*	*208.1*	*86*	*67*	*12*
Ergocryptinine	*4.2*	*576*	*223.1*	*86*	*49*	*12*	*576*	*208.1*	*86*	*67*	*12*
Ergosine/inine	*3.05*	*548.4*	*530.3*	*86*	*23*	*30*	*548.4*	*223.1*	*86*	*45*	*12*
Fumonisin B1	*4.38*	*722.4*	*334.3*	*165*	*55*	*20*	*722.4*	*352.3*	*165*	*49*	*26*
Fumonisin B2	*5.64*	*706.3*	*336.2*	*165*	*53*	*16*	*706.3*	*318.3*	*165*	*53*	*18*
Fumonisin B3	*5.08*	*706.4*	*336.2*	*165*	*53*	*16*	*706.4*	*318.3*	*165*	*53*	*18*
Fus X	*2.33*	*372.1*	*247*	*51*	*17*	*30*	*372.1*	*175.1*	*51*	*33*	*18*
HT-2 toxin	*4.3*	*442.2*	*263*	*61*	*17*	*30*	*442.2*	*215.1*	*61*	*19*	*28*
Neosolaniol	*2.38*	*400*	*185.1*	*66*	*29*	*18*	*400*	*305.1*	*66*	*17*	*36*
NIV	*1.54*	*312.9*	*115*	*130*	*83*	*14*	*312.9*	*177.1*	*130*	*21*	*18*
Ochratoxin A	*5.55*	*403.9*	*102*	*91*	*97*	*12*	*403.9*	*239*	*91*	*35*	*22*
Sterigmatocystin	*5.8*	*325*	*281*	*106*	*51*	*18*	*325*	*310*	*106*	*35*	*20*

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
T-2 tetraol	*1.52*	*316*	*215.1*	*46*	*13*	*12*	*316*	*233*	*46*	*9*	*22*
T-2 toxin	*4.96*	*484.2*	*305.2*	*76*	*19*	*20*	*484.2*	*215.1*	*76*	*25*	*26*
T-2 triol	*2.37*	*400*	*215.1*	*46*	*17*	*12*	*400*	*233.1*	*46*	*11*	*22*
ZON	*5.5*	*319.1*	*283*	*136*	*17*	*36*	*319.1*	*301.1*	*136*	*13*	*34*

*) Mycotoxins are in italic.

Table S1-B: Parameters of UHPLC–ESI(-)–MS/MS detection method.

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Nicarbazim (IS)	5.59	301	136.9	-40	-18	-11	301	106.9	-40	-48	-7
2,4,5-T	3.84	252.9	194.9	-75	-18	-11	254.9	196.9	-75	-18	-11
2,4-D	3.14	219	160.9	-55	-20	-9	221	162.9	-55	-18	-9
2,4-DB	4.22	247	160.9	-30	-18	-9	249	162.9	-30	-18	-9
2-naphthoxyacetic acid	2.85	201	143.1	-55	-20	-11	201	115.1	-55	-52	-13
4-CPA	2.56	185	127	-50	-18	-7	187	129	-45	-18	-7
Bentazone	2.3	239	132.1	-55	-34	-9	239	197	-55	-28	-11
Bromoxynil	2.71	273.8	78.9	-75	-64	-9	275.8	80.9	-75	-60	-9
Clopyralid	1.55	189.9	145.9	-30	-12	-13	191.9	147.9	-30	-12	-13
Dicamba	2.35	219	175	-20	-10	-15	221	177	-20	-8	-11
Dichlorprop	3.62	233	160.9	-55	-18	-9	235	162.9	-55	-18	-9
Fenoprop	4.36	266.9	194.9	-50	-16	-11	268.9	196.9	-50	-18	-11
Fipronil	6.15	434.9	329.9	-65	-24	-15	436.9	331.9	-65	-24	-17
Fluazinam	7.45	462.9	415.9	-60	-30	-23	464.9	417.9	-60	-28	-21
Fludioxonil	5.11	247	126	-90	-40	-11	247	180	-90	-40	-9
Fluroxypyr	2.33	252.9	194.8	-45	-18	-11	252.9	233	-45	-10	-21
Fomesafen	4.52	437	195	-105	-50	-11	437	222	-105	-44	-11
Ioxynil	3.17	369.8	126.9	-105	-42	-13	369.8	215	-105	-42	-11
Lufenuron	8.07	509	339	-65	-16	-13	509	175	-65	-50	-11
MCPA	3.13	199	141	-75	-20	-13	201	143	-75	-18	-9
MCPB	4.26	227	141	-50	-16	-9	229	143	-50	-16	-9
Mecoprop	3.57	213	141	-45	-20	-9	215	143	-65	-20	-9
Quizalofop	4.4	343	271	-60	-20	-15	345	273	-60	-20	-15
3-ADON	*2.77*	*397.1*	*306.9*	*-55*	*-20*	*-7*	*397.1*	*336.9*	*-55*	*-12*	*-17*
Altenuene	*3.36*	*291.1*	*202.9*	*-150*	*-44*	*-11*	*291.1*	*247.9*	*-150*	*-34*	*-15*
Alternariol	*4.34*	*256.9*	*213*	*-130*	*-32*	*-11*	*256.9*	*214.9*	*-130*	*-34*	*-13*
Alternariol methylether	*5.89*	*271*	*255.9*	*-120*	*-30*	*-13*	*271*	*228*	*-120*	*-40*	*-13*
aZOL	*5.3*	*319*	*174*	*-110*	*-36*	*-9*	*319*	*275*	*-110*	*-30*	*-5*
bZOL	*4.73*	*319.1*	*174*	*-110*	*-36*	*-9*	*319.1*	*275*	*-110*	*-30*	*-5*
deepoxyDON	*2.49*	*339.1*	*248.9*	*-30*	*-16*	*-7*	*339.1*	*59*	*-30*	*-42*	*-11*
DON	*2.1*	*355.1*	*295.1*	*-45*	*-14*	*-7*	*355.1*	*265.1*	*-45*	*-20*	*-15*
DON-3-Glc	*2*	*517.1*	*456.9*	*-60*	*-20*	*-23*	*517.1*	*426.9*	*-60*	*-28*	*-21*
FUS X	*2.35*	*413.1*	*353*	*-50*	*-14*	*-7*	*413.1*	*263*	*-50*	*-20*	*-17*
NIV	*1.74*	*371.1*	*311.1*	*-50*	*-14*	*-7*	*371.1*	*281*	*-50*	*-20*	*-17*

Analyte	Retention time (min)	Quantitative transition					Qualitative transition				
		Q1	Q2	DP (V)	CE (V)	CXP (V)	Q1	Q2	DP (V)	CE (V)	CXP (V)
Ochratoxin A	*4.1*	*402*	*166.8*	*-60*	*-48*	*-9*	*402*	*358.1*	*-60*	*-28*	*-19*
Ochratoxin alfa	*2.74*	*255*	*166.9*	*-60*	*-34*	*-11*	*255*	*211*	*-60*	*-22*	*-11*
Patulin [M+CH3COO]	*1.72*	*213*	*152.9*	*-30*	*-8*	*-7*	*213*	*109*	*-30*	*-16*	*-9*
Patulin [M-H]	*1.72*	*153*	*108.9*	*-55*	*-12*	*-11*	*153*	*81*	*-55*	*-16*	*-5*
ZON	*5.53*	*317.1*	*131.1*	*-85*	*-38*	*-9*	*317.1*	*175*	*-85*	*-32*	*-11*

*) Mycotoxins are in italic.

Table S2-A: Validation data obtained on spiked wheat and sunflower seeds samples for the methods A and B.

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
2,4,5-T	ESI-	101	3	4	108	3	8	86	4	4	79	3	8
2,4-D	ESI-	106	4	4	105	2	8	89	3	4	82	3	8
2,4-DB	ESI-	93	8	4	103	3	8	89	5	4	95	3	8
2-naphthoxyacetic acid	ESI-	100	4	4	99	3	8	91	4	4	86	3	8
4-CPA	ESI-	105	4	4	100	3	8	90	4	4	84	3	8
Abamectin:													
Avermectine B1a (98%)	ESI+	85	6	4	108	6	8	89	6	4	92	10	8
Avermectine B1b (2%)	ESI+	88	13	4	130	22	8	85	8	4	86	10	8
Acephate	ESI+	80	3	4	101	1	8	93	3	4	100	12	8
Acetamiprid	ESI+	88	3	4	102	2	8	102	7	4	103	2	8
Acetochlor	ESI+	93	7	8	98	4	16	97	10	8	95	6	16
Acrinathrin	ESI+	81	6	4	99	5	8	86	7	4	80	13	8
Alachlor	ESI+	94	3	8	93	4	16	83	8	8	97	7	16
Aldicarb	ESI+	91	4	4	107	1	8	98	12	4	97	4	8
Aldicarb sulfone	ESI+	89	2	4	104	1	8	108	5	4	107	9	8
Aldicarb sulfoxide	ESI+	85	3	8	103	1	16	96	12	8	93	11	16
Ametryn	ESI+	91	4	4	97	2	8	83	7	4	93	6	8
Atrazine	ESI+	86	3	4	96	2	8	92	16	4	100	3	8
Azadirachtin ESI	**+**	**84**	**8**	**40**	**94**	**15 80**		**111**	**13 20**		**89**	**35 80**	
Azinphos-ethyl	ESI+	89	5	4	98	3	8	97	7	4	95	7	8
Azinphos-methyl	ESI+	87	6	4	89	1	8	87	4	4	97	3	8
Azoxystrobin	ESI+	87	4	4	107	1	8	102	13	4	105	6	8
Benalaxyl	ESI+	90	2	4	102	3	8	102	14	4	103	4	8
Bendiocarb	ESI+	93	2	4	106	2	8	102	17	4	95	8	8
Bentazone	ESI-	108	3	4	118	7	8	92	4	4	95	3	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Beta-cyfluthrin ESI+		**86**	**12**	**40**	**79 5**		**160**	**84 5**		**40**	**61**	**4**	**80**
Bifenthrin	ESI+	83	5	4	106	2	8	71	6	4	28	7	8
Bitertanol	ESI+	90	2	4	100	3	8	91	9	4	111	13	8
Boscalid	ESI+	90	3	4	98	4	8	78	14	4	98	11	8
Bromoxynil	ESI-	99	3	4	104	2	8	88	3	4	89	3	8
Bupirimate	ESI+	98	4	4	100	3	8	75	10	4	111	6	8
Buprofezin	ESI+	93	3	4	101	2	8	79	9	4	71	8	8
Cadusafos	ESI+	93	3	4	104	3	8	81	15	4	100	3	8
Carbaryl	ESI+	91	2	4	102	3	8	114	10	4	93	7	8
Carbendazim	ESI+	93	2	4	114	1	8	107	9	4	97	4	8
Carbofuran	ESI+	95	3	4	103	2	8	96	7	4	90	8	8
Carbofuran-3-hydroxy	ESI+	94	2	4	101	2	8	110	6	8	96	5	16
Carbophenothion	ESI+	91	8	8	92	8	16	71	5	8	41	5	16
Chlorfenvinphos	ESI+	89	3	4	100	2	8	97	6	8	95	3	16
Chloroxuron	ESI+	90	4	4	97	2	8	86	11	8	103	5	16
Chlorpropham	ESI+	95	5	20	**106 5**		**40**	**83 10**		**8**	**100**	**3**	**16**
Chlorpyrifos	ESI+	91	5	4	109	2	8	80	5	8	58	8	16
Chlorpyrifos-methyl	ESI+	96	6	8	100	8	16	93	11	8	73	7	16
Clofentezine	ESI+	93	5	4	99	5	8	88	7	4	76	10	8
Clomazone	ESI+	93	2	4	105	2	8	90	9	4	104	5	8
Clopyralid	**ESI-**	**93**	**5**	**40 65**		**12**	**80 74**		**10**	**40 52**		**5**	**80**
Clothianidin	ESI+	93	1	8	96	2	16	114	12	8	102	2	16
Cyanazine	ESI+	91	3	4	99	3	8	88	5	4	96	3	8
Cyazofamid	ESI+	111	4	4	101	1	8	98	13	4	116	6	8
Cycloxidim	ESI+	77	3	4	94	3	8	84	8	4	83	19	8
Cymoxanil	ESI+	99	1	8	105	2	16	100	6	8	95	7	16

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Cypermethrin	ESI+	83	7	8	107	6	16	79	7	8	53	8	16
Cyproconazole	ESI+	87	4	4	100	4	8	84	5	4	97	6	8
Cyprodinyl	ESI+	83	4	4	102	2	8	78	8	4	79	6	8
Deltametrin	ESI+	77	7	4	108	8	8	81	6	4	59	8	8
Demeton-S-methyl	ESI+	95	2	4	108	4	8	113	6	4	102	5	8
Demeton-S-methyl sulfon	ESI+	92	2	4	104	1	8	91	8	4	105	6	8
Desmedipham	ESI+	91	4	4	93	4	8	108	11	4	101	6	8
Desmetryn	ESI+	92	2	4	101	2	8	95	9	4	102	5	8
Diazinon	ESI+	98	4	4	94	5	8	79	8	4	97	5	8
Dicamba	**ESI-**	**104**	**2**	**40 77**		**14**	**80 92**		**3**	**40 56**		**8**	**80**
Dichlofluanid	ESI+	87	7	4	95	4	8	83	8	4	79	6	8
Dichlorprop	ESI-	101	4	4	101	3	8	89	4	8	88	3	16
Dichlorvos	ESI+	95	1	4	108	5	8	116	5	4	103	7	8
Diclofop-methyl	ESI+	93	4	8	93	3	16	79	7	4	82	7	8
Dicrotophos	ESI+	92	2	4	108	2	8	109	12	4	104	8	8
Diethofencarb	ESI+	92	4	4	103	2	8	92	14	4	103	6	8
Difenoconazole	ESI+	87	5	4	104	3	8	85	8	4	97	9	8
Diflubenzuron	ESI+	93	4	4	92	3	8	89	17	4	100	6	8
Diflufenican	ESI+	91	2	4	104	3	8	87	9	4	85	5	8
Dimethenamid-P	ESI+	92	3	4	103	1	8	94	10	4	97	4	8
Dimethoate	ESI+	97	3	4	106	3	8	103	10	4	106	6	8
Dimethomorph	ESI+	88	3	4	101	1	8	93	8	4	97	7	8
Dimoxystrobin	ESI+	90	4	4	94	1	8	95	9	4	103	6	8
Diniconazole	ESI+	90	4	4	102	5	8	74	7	4	99	7	8
Disulfoton	ESI+	86	6	8	105	12	16	90	4	8	85	4	16
Disulfotone sulfone	ESI+	93	3	4	103	2	8	102	12	4	111	6	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Disulfotone sulfoxid	ESI+	96	2	4	101	2	8	101	11	4	99	6	8
Diuron	ESI+	91	3	4	98	1	8	93	7	4	103	4	8
DMSA	ESI+	98	3	4	110	3	8	112	9	4	100	7	8
DMST	ESI+	94	3	4	109	3	8	110	12	4	114	5	8
Dodine	ESI+	82	7	4	96	2	8	76	6	4	98	3	8
EPN	ESI+	81	10	8	92	13	16	85	9	20	72	6	40
Epoxiconazole	ESI+	88	3	4	95	3	8	86	6	8	95	11	16
Ethiofencarb	ESI+	92	3	4	109	1	8	86	6	8	103	5	16
Ethion	ESI+	85	4	4	107	2	8	83	7	8	69	4	16
Ethofumesate	ESI+	94	7	4	104	1	8	92	13	8	104	7	16
Ethoprophos	ESI+	93	3	4	96	2	8	81	8	4	111	7	8
Etofenprox	ESI+	87	3	4	107	3	8	68	5	8	31	3	16
Etrimfos	ESI+	95	3	4	97	4	8	83	9	4	90	7	8
Fenamiphos	ESI+	91	2	4	99	1	8	94	8	4	106	5	8
Fenamiphos sulfon	ESI+	90	1	4	104	2	8	96	15	4	99	5	8
Fenamiphos sulfoxid	ESI+	94	1	4	104	3	8	96	8	4	92	4	8
Fenarimol	ESI+	88	5	4	92	2	8	86	10	4	113	7	8
Fenazaquin	ESI+	77	2	4	100	2	8	70	6	4	53	6	8
Fenbuconazole	ESI+	87	6	4	95	2	8	101	8	4	109	5	8
Fenchlorphos	ESI+	94	5	4	96	3	8	94	11	4	90	5	8
Fenhexamid	ESI+	85	6	4	94	7	8	111	8	4	106	4	8
Fenoprop	ESI-	98	3	4	102	4	8	88	2	4	84	3	8
Fenoxaprop	ESI+	90	6	8	83	7	16	84	10	20	105	11	80
Fenoxycarb	ESI+	86	5	4	91	3	8	108	19	4	100	4	8
Fenpropathrin	ESI+	89	2	4	103	4	8	77	10	4	96	4	8
Fenpropidin	ESI+	93	3	4	103	2	8	96	8	4	115	9	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Fenpropimorph	ESI+	93	2	4	108	1	8	97	8	4	96	5	8
Fenpyroximate	ESI+	75	4	4	100	3	8	76	9	4	116	7	8
Fensulfothion	ESI+	95	3	4	98	2	8	103	11	4	116	3	8
Fensulfothion-PO sulfon	ESI+	90	3	4	101	2	8	87	4	4	97	6	8
Fenthion	ESI+	84	4	8	97	7	16	82	9	8	90	7	16
Fipronil	ESI-	103	3	20(+)/4(-)	107	2	40(+)/8(-)	92	1	20(+)/4(-)	96	3	40(+)/8(-)
Flonicamid	ESI+	90	4	8	104	3	16	118	19	8	99	9	16
Fluazifop	ESI+	89	2	4	104	4	8	101	9	4	105	7	8
Fluazifop-P-butyl	ESI+	90	3	4	106	1	8	86	8	4	92	5	8
Fluazinam	ESI-	77	6	4	103	4	8	83	3	4	89	3	8
Fludioxonil	ESI-	99	2	4	106	1	8	91	2	4	95	3	8
Flufenacet	ESI+	90	2	4	91	5	8	101	16	4	108	10	8
Flufenoxuron	ESI+	85	4	4	106	2	8	87	3	4	78	3	8
Fluoxastrobin	ESI+	92	6	4	104	2	8	99	13	4	103	7	8
Fluquinconazole	ESI+	86	3	8	104	2	16	76	8	4	100	6	8
Fluroxypyr	ESI-	101	4	8(+)/4(-)	101	3	16(+)/8(-)	92	5	8(+)/4(-)	82	5	16(+)/8(-)
Flusilazole	ESI+	90	5	4	98	3	8	102	13	8	111	9	16
Fomesafen	ESI-	112	2	20(+)/4(-)	113	3	40(+)/8(-)	93	2	20(+)/4(-)	95	4	40(+)/8(-)
Fonofos	ESI+	92	4	8	106	7	16	76	9	20	85	9	16
Formetanate	ESI+	96	4	4	87	8	8	83	9	8	91	7	16
Formothion	ESI+	91	6	8	85	4	16	104	8	8	96	13	16
Haloxyfop	ESI+	92	5	4	92	4	8	103	15	8	106	11	16
Haloxyfop-ethoxyethyl	ESI+	87	4	4	108	2	8	92	7	8	99	3	16
Haloxyfop-methyl	ESI+	87	1	4	103	3	8	89	7	8	95	4	16
Heptenophos	ESI+	95	2	4	101	1	8	78	9	8	107	2	16
Hexaconazole	ESI+	90	1	4	100	2	8	84	13	8	102	5	16

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Hexazinon	ESI+	98	4	4	101	3	8	97	11	8	91	4	16
Hexythiazox	ESI+	88	4	4	103	2	8	75	8	8	49	7	16
Imazalil	ESI+	99	3	4	109	1	8	93	16	8	114	9	16
Imazapyr	ESI+	91	4	4	93	2	8	104	12	8	89	7	16
Imazaquin	ESI+	91	6	4	101	2	8	87	11	8	100	6	16
Imazethapyr	ESI+	90	2	4	96	2	8	91	9	8	93	2	16
Imazosulfuron	ESI+	60	2	4	70	5	8	96	19	8	96	15	16
Imidacloprid	ESI+	88	2	4	99	4	8	103	8	8	106	10	16
Indoxacarb	ESI+	86	3	4	107	2	8	102	10	8	105	3	16
Iodosulfuron-methyl	ESI+	73	4	8	91	17	16	101	18	8	82	5	16
Ioxynil	ESI-	95	3	4	101	4	8	84	3	4	85	3	8
Iprodion ESI	**+**	**104**	**7 40**		**84**	**6 80**		**94**	**18**	**200**	**73**	**16**	**800**
Iprovalicarb	ESI+	91	3	4	97	4	8	96	11	4	108	7	8
Isofenphos	ESI+	93	4	4	100	3	8	99	5	4	90	6	8
Isofenphos-methyl	ESI+	88	5	4	100	2	8	84	10	4	92	5	8
Isoproturon	ESI+	91	4	4	99	1	8	103	10	4	102	3	8
Kresoxim-methyl	ESI+	90	6	4	97	5	8	86	9	8	101	5	16
Lambda-cyhalothrin ESI	**+**	**86**	**5**	**20 91**		**8**	**40 85**		**10**	**20 60**		**7**	**40**
Lenacil	ESI+	88	4	4	96	1	8	88	13	8	100	5	16
Linuron	ESI+	88	4	4	103	4	8	95	6	4	104	6	8
Lufenuron	ESI+	86	6	4(+)/4(-)	103	6	8(+)/8(-)	90	2	4(+)/4(-)	71	3	8(+)/8(-)
Malaoxon	ESI+	98	2	4	106	1	8	99	13	4	96	4	8
Malathion	ESI+	94	4	4	101	3	8	97	15	4	106	6	8
MCPA	ESI-	101	4	4	101	2	8	90	2	4	87	3	8
MCPB	ESI-	98	3	4	104	3	8	89	3	4	94	4	8
Mecarbam	ESI+	92	2	4	91	4	8	98	10	4	100	6	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Mecoprop	ESI-	102	3	4	104	3	8	91	4	4	89	3	8
Mefenpyr-diethyl	ESI+	90	2	4	102	1	8	88	10	4	96	6	8
Mepanipyrim	ESI+	92	4	4	100	4	8	78	5	4	81	5	8
Mepronil	ESI+	88	2	4	92	3	8	90	8	4	101	6	8
Metalaxyl	ESI+	97	4	4	96	1	8	104	7	4	111	6	8
Metamitron	ESI+	87	3	8	95	6	16	95	13	8	90	7	16
Metamitron-desamino	ESI+	86	4	4	95	4	8	89	6	4	91	9	8
Metazachlor	ESI+	92	2	4	97	1	8	90	11	4	104	7	8
Metconazole	ESI+	88	2	4	100	1	8	82	12	4	101	5	8
Methacrifos	ESI+	89	9	8	101	5	16	94	10	8	104	7	16
Methamidophos	ESI+	73	1	4	97	1	8	94	8	4	91	12	8
Methidathion	ESI+	94	4	4	101	1	8	89	8	4	96	3	8
Methiocarb	ESI+	91	3	4	103	0	8	98	9	4	97	6	8
Methiocarb sulfon	ESI+	91	2	4	101	1	8	109	12	4	106	9	8
Methiocarb sulfoxid	ESI+	91	2	4	102	1	8	90	11	4	101	4	8
Methomyl	ESI+	97	2	4	106	2	8	110	8	4	88	3	8
Methoxyfenozide	ESI+	90	5	4	94	3	8	101	6	4	110	4	16
Metobromuron	ESI+	95	3	4	103	1	8	90	9	4	103	6	8
Metolachlor	ESI+	93	3	4	94	3	8	86	11	4	103	3	8
Metolcarb	ESI+	95	2	4	106	3	8	95	19	8	85	8	16
Metosulam	ESI+	88	4	4	109	0	8	113	6	4	91	5	8
Metoxuron	ESI+	91	3	4	104	2	8	95	9	4	98	5	8
Metribuzin	ESI+	87	4	8	96	4	16	113	17	8	98	26	16
Metsulfuron-methyl	ESI+	78	3	4	86	1	8	87	13	4	102	16	8
Mevinphos	ESI+	102	4	4	110	3	8	102	6	4	113	6	8
Monocrotophos	ESI+	91	2	4	106	2	8	106	15	4	103	9	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Monolinuron	ESI+	94	3	4	111	2	8	101	9	4	102	7	8
Monuron	ESI+	94	2	4	103	2	8	86	19	4	98	5	8
Myclobutanil	ESI+	91	2	4	103	3	8	93	9	8	109	6	16
Naled	ESI+	87	11	8	83	9	16	75	16	8	76	14	16
Napropamid	ESI+	93	2	4	87	5	8	81	18	4	112	3	8
Neburon	ESI+	93	3	4	96	2	8	73	13	4	89	6	8
Norflurazone	ESI+	95	2	4	98	3	8	107	17	4	103	8	8
Omethoat	ESI+	83	2	4	104	2	8	102	9	4	86	4	8
Oxadixyl	ESI+	91	4	4	101	4	8	102	8	4	99	2	8
Oxamyl	ESI+	89	3	4	103	2	8	97	8	4	101	7	8
Oxamyl-oxime	ESI+	92	2	8	101	1	16	94	6	8	106	4	16
Oxydemeton-methyl	ESI+	90	3	4	105	2	8	93	12	4	100	3	8
Oxyfluorfen ESI	**+**	**86**	**12**	**20 92**		**3**	**40 96**		**6**	**20 88**		**7**	**40**
Paclobutrazol	ESI+	89	9	4	93	3	8	96	7	4	109	6	8
Penconazole	ESI+	89	3	4	100	3	8	93	7	8	98	4	16
Pencycuron	ESI+	96	3	4	110	1	8	89	6	8	101	6	16
Pendimethalin	ESI+	87	4	8	98	3	16	75	7	8	57	9	16
Permethrin	ESI+	80	2	8	103	5	16	74	4	8	30	3	16
Phenmedipham	ESI+	84	4	4	100	4	8	95	19	4	102	9	8
Phenothrin	ESI+	83	4	4	102	2	8	73	6	4	34	10	8
Phenthoate	ESI+	94	5	4	101	5	8	98	12	4	95	10	8
Phorate	ESI+	95	5	8	115	4	16	84	14	8	79	7	16
Phorate sulfon	ESI+	93	3	4	107	2	8	88	5	4	107	6	8
Phorate sulfoxid	ESI+	95	2	4	101	2	8	96	8	4	110	6	8
Phosalone	ESI+	90	3	4	96	2	8	90	8	4	88	4	8
Phosmet	ESI+	89	3	4	99	3	8	89	8	4	101	7	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Phosmet-oxon	ESI+	94	2	8	105	2	16	103	11	8	100	4	16
Phosphamidon	ESI+	95	2	4	104	2	8	84	6	4	98	5	8
Picloram	ESI+	83	4	8	72	6	16	81	8	20	45	16	40
Picoxystrobin	ESI+	91	3	4	99	1	8	102	10	4	109	8	8
Piperonyl Butoxide	ESI+	86	3	4	106	2	8	87	5	4	86	4	8
Pirimicarb	ESI+	100	2	4	108	2	8	109	14	4	108	5	8
Pirimicarb-desmethyl	ESI+	95	3	4	105	1	8	98	11	4	104	3	8
Pirimiphos-ethyl	ESI+	91	2	4	104	1	8	79	10	4	81	5	8
Pirimiphos-methyl	ESI+	91	4	4	103	3	8	84	12	4	92	6	8
Prochloraz	ESI+	88	3	4	105	2	8	88	7	4	96	6	8
Profenofos	ESI+	86	2	4	103	2	8	74	13	4	79	5	8
Prometon	ESI+	95	3	4	100	2	8	94	11	4	105	5	8
Prometryn	ESI+	90	4	4	96	3	8	79	9	8	94	7	16
Propachlor	ESI+	93	2	4	104	1	8	85	17	4	107	6	8
Propamocarb	ESI+	91	3	4	120	1	8	93	8	4	115	5	8
Propaquizafop	ESI+	86	4	4	108	4	8	87	7	4	90	6	8
Propargite	ESI+	89	2	4	104	3	8	81	4	4	73	9	8
Propham ESI	**+**	**95 8**		**20**	**96 6**		**40**	**90 9**		**8**	**85**	**4**	**16**
Propiconazole	ESI+	89	2	4	103	1	8	93	12	4	98	10	8
Propoxur	ESI+	95	1	4	105	2	8	90	7	4	93	7	8
Propyzamide	ESI+	93	2	4	99	4	8	94	11	4	97	4	8
Proquinazid	ESI+	103	3	4	96	2	8	73	9	4	55	5	8
Prosulfocarb	ESI+	90	2	4	106	1	8	77	5	4	73	4	8
Pymetrozine	ESI+	10	7	4	88	2	8	28	12	4	84	5	8
Pyraclostrobin	ESI+	89	2	4	101	0	8	83	5	4	94	6	8
Pyrazophos	ESI+	90	3	4	103	2	8	98	8	4	97	10	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Pyrethrum:													
Cinerin I (6%)	**ESI+**	**94**	**7 4**		**92**	**4 8**		**81**	**6 4**		**63**	**9 8**	
Cinerin II (6%)	**ESI+**	**88**	**6 4**		**100**	**5 8**		**89**	**8 4**		**78**	**13**	**8**
Jasmolin I (4%)	**ESI+**	**86 8**		**4**	**109**	**10**	**8**	**76 9**		**4**	**61**	**12**	**8**
Jasmolin II (2%)	**ESI+**	**98**	**7 4**		**102**	**8 8**		**80**	**11**	**4**	**75**	**9 8**	
Pyrethrin I (50%)	**ESI+**	**87**	**4 4**		**97**	**3 8**		**77**	**5 4**		**68**	**7 8**	
Pyrethrin II (30%)	**ESI+**	**87**	**5**	**4 98**		**4**	**8 86**		**10**	**4 80**		**9**	**8**
Pyridaben	ESI+	84	3	4	108	2	8	72	3	4	51	8	8
Pyridate	ESI+	87	5	4	93	5	8	72	4	4	36	4	8
Pyrifenox	ESI+	93	5	4	101	2	8	95	10	4	102	4	8
Pyrimethanil	ESI+	91	4	4	101	1	8	74	8	4	91	12	8
Pyriproxyfen	ESI+	90	4	4	101	2	8	71	5	4	50	7	8
Quinalphos	ESI+	95	3	4	99	2	8	78	8	4	92	8	8
Quinmerac	ESI+	84	3	4	91	1	8	87	5	4	82	5	8
Quinoxyfen	ESI+	91	4	4	100	6	8	71	7	4	46	9	8
Quizalofop	ESI-	96	2	20(+)/4(-)	108	2	40(+)/8(-)	91	6	20(+)/4(-)	109	6	40(+)/8(-)
Quizalofop-P-ethyl	ESI+	85	3	4	101	2	8	79	9	4	82	4	8
Resmethrin	ESI+	99	3	4	119	3	8	75	5	4	47	8	8
Rimsulfuron	ESI+	95	11	8	93	12	16	99	13	8	101	17	16
Simazine	ESI+	88	2	8	94	3	16	92	14	8	84	12	16
Simetryn	ESI+	89	3	4	100	4	8	88	14	4	98	6	8
Spinosad:													
Spinosyn A (70%)	ESI+	93	5	4	111	1	8	97	12	4	100	3	8
Spinosyn D (30%)	ESI+	91	4	4	114	3	8	89	6	4	85	5	8
Spiroxamin	ESI+	93	3	4	102	1	8	96	9	4	102	8	8
Sulfotep	ESI+	92	3	4	104	2	8	84	9	4	105	5	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Tau-Fluvalinate	ESI+	89	5	8	96	1	16	83	5	8	35	9	16
Tebuconazole	ESI+	88	3	4	98	1	8	87	14	4	107	7	8
Tebufenozide	ESI+	93	5	4	96	1	8	92	8	4	97	30	8
Tebufenpyrad	ESI+	89	3	4	105	1	8	81	7	4	86	5	8
Teflubenzuron	ESI+	86	9	4	100	6	8	82	9	4	65	7	8
Tepraloxydim	ESI+	87	8	8	92	9	16	92	8	8	98	7	16
Terbufos	ESI+	91	7	4	95	1	8	76	8	8	81	5	16
Terbufos sulfon	ESI+	93	3	4	107	1	8	90	9	4	105	6	8
Terbufos sulfoxide	ESI+	95	3	4	101	2	8	101	10	4	111	7	8
Terbuthylazine	ESI+	88	3	4	96	2	8	85	9	4	94	6	8
Terbutryn	ESI+	93	4	4	101	3	8	82	6	4	93	6	8
Tetraconazole	ESI+	89	2	4	97	3	8	95	5	4	110	5	8
Thiabendazole	ESI+	81	2	4	94	2	8	84	8	4	78	7	8
Thiacloprid	ESI+	89	4	4	103	1	8	105	11	4	90	7	8
Thiamethoxam	ESI+	92	3	4	104	3	8	102	6	4	97	4	8
Thifensulfuron-methyl	ESI+	82	4	4	94	1	8	92	9	4	91	13	8
Thiodicarb	ESI+	84	2	4	88	1	8	86	16	4	85	7	8
Thiometon ESI	**+**	**88**	**7 20**		**104**	**3 40**		**79**	**12**	**20**	**99**	**12**	**40**
Thiophanate-methyl	ESI+	87	4	4	87	8	8	76	19	4	73	5	8
Tolclofos-methyl	ESI+	100	8	8	98	5	16	85	12	8	86	15	16
Tolylfluanid	ESI+	88	6	4	94	3	8	80	8	4	86	3	8
Triadimefon	ESI+	91	3	4	98	1	8	99	8	4	106	6	8
Triadimenol	ESI+	95	3	8	97	4	16	91	11	8	105	6	16
Triazamate	ESI+	94	4	4	103	4	8	91	5	4	99	6	8
Triazophos	ESI+	92	3	4	100	2	8	100	13	4	104	7	8
Trichlorfon	ESI+	96	3	4	105	3	8	101	14	4	106	7	8

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Trifloxystrobin	ESI+	90	3	4	102	2	8	98	16	4	98	6	8
Triflumuron	ESI+	91	5	4	100	3	8	80	20	4	92	6	8
Triforine	ESI+	87	4	8	99	7	16	106	9	8	103	11	16
Vamidothion	ESI+	96	1	4	100	1	8	93	14	4	102	5	8
Vamidothion sulfon	ESI+	92	3	8	102	4	16	96	4	8	91	5	16
Vamidothion sulfoxid1	ESI+	86	11	20	106	5	40	89	8	20	96	5	40
15-ADON	*ESI+*	*96*	*6*	*20*	*96*	*6*	*40*	*93*	*5*	*20*	*98*	*6*	*40*
3-ADON	*ESI-*	*91*	*3*	*40(+)/20(-)*	*97*	*3*	*80(+)/40(-)*	*95*	*3*	*40(+)/20(-)*	*96*	*8*	*80(+)/40(-)*
Aflatoxin B1	*ESI+*	*78*	*13*	*0.8*	*118*	*6*	*1.6*	*83*	*11*	*0.8*	*98*	*8*	*1.6*
Aflatoxin B2	*ESI+*	*95*	*10*	*0.8*	*101*	*6*	*1.6*	*97*	*6*	*0.8*	*96*	*9*	*1.6*
Aflatoxin G1	*ESI+*	*97*	*6*	*0.8*	*96*	*7*	*1.6*	*96*	*7*	*0.8*	*110*	*5*	*1.6*
Aflatoxin G2	*ESI+*	*91*	*10*	*0.8*	*95*	*7*	*1.6*	*93*	*6*	*0.8*	*98*	*9*	*1.6*
Altenuene	*ESI-*	*91*	*2*	*20(+)/4(-)*	*107*	*3*	*40(+)/8(-)*	*88*	*4*	*20(+)/4(-)*	*111*	*6*	*40(+)/8(-)*
Alternariol	*ESI-*	*90*	*3*	*80(+)/4(-)*	*105*	*2*	*160(+)/8(-)*	*91*	*6*	*80(+)/4(-)*	*110*	*3*	*80(+)/4(-)*
Alternariol methylether	*ESI-*	*96*	*2*	*80(+)/4(-)*	*117*	*2*	*160(+)/8(-)*	*97*	*3*	*80(+)/4(-)*	*107*	*5*	*80(+)/4(-)*
aZOL	*ESI-*	*91*	*1*	*80(+)/4(-)*	*112*	*1*	*160(+)/8(-)*	*96*	*3*	*80(+)/4(-)*	*98*	*3*	*80(+)/4(-)*
bZOL	*ESI-*	*90*	*3*	*80(+)/4(-)*	*103*	*1*	*160(+)/8(-)*	*93*	*3*	*80(+)/4(-)*	*106*	*3*	*80(+)/4(-)*
Citrinin	*ESI+*	*86*	*5*	*20*	*91*	*5*	*40*	*83*	*6*	*20*	*94*	*5*	*40*
deepoxyDON	*ESI-*	*81*	*6*	*80(+)/20(-)*	*100*	*4*	*160(+)/40(-)*	*86*	*4*	*80(+)/20(-)*	*106*	*5*	*160(+)/40(-)*
Diacetoxyscirpenol	*ESI+*	*87*	*3*	*4*	*98*	*4*	*8*	*93*	*4*	*4*	*98*	*3*	*8*
DON	*ESI-*	*79*	*12*	*80(+)/20(-)*	*86*	*4*	*160(+)/40(-)*	*88*	*6*	*80(+)/20(-)*	*93*	*7*	*160(+)/40(-)*
DON-3-Glc	*ESI-*	*30*	*8*	*80(+)/20(-)*	*87*	*5*	*160(+)/40(-)*	*34*	*11*	*80(+)/20(-)*	*84*	*7*	*160(+)/40(-)*
Ergocornine	*ESI+*	*86*	*6*	*8*	*84*	*11*	*16*	*83*	*5*	*8*	*91*	*6*	*16*
Ergocorninine	*ESI+*	*92*	*5*	*8*	*113*	*7*	*16*	*89*	*4*	*8*	*105*	*4*	*16*
Ergocristine	*ESI+*	*89*	*6*	*8*	*94*	*9*	*16*	*93*	*5*	*8*	*89*	*3*	*16*
Ergocristinine	*ESI+*	*94*	*4*	*8*	*108*	*6*	*16*	*90*	*6*	*8*	*109*	*5*	*16*

Analyte		Wheat, Spike 20 µg kg^{-1} (n=6)						Sunflower seeds, Spike 20 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Ergocryptine	*ESI+*	*88*	*5*	*8*	*86*	*7*	*16*	*84*	*6*	*8*	*96*	*3*	*16*
Ergocryptinine	*ESI+*	*101*	*8*	*8*	*110*	*9*	*16*	*92*	*4*	*8*	*102*	*5*	*16*
Ergosine/inine	*ESI+*	*98*	*3*	*8*	*100*	*6*	*16*	*84*	*5*	*8*	*103*	*4*	*16*
Fumonisin B1	*ESI+*	*76*	*6*	*20*	*105*	*2*	*40*	*73*	*9*	*20*	*103*	*4*	*40*
Fumonisin B2	*ESI+*	*78*	*4*	*20*	*106*	*5*	*40*	*76*	*5*	*20*	*108*	*3*	*40*
Fumonisin B3	*ESI+*	*76*	*13*	*20*	*94*	*9*	*40*	*73*	*14*	*20*	*97*	*8*	*40*
FUS X	*ESI-*	*94*	*4*	*80(+)/20(-)*	*103*	*2*	*160(+)/40(-)*	*88*	*5*	*80(+)/20(-)*	*96*	*6*	*160(+)/40(-)*
HT-2 toxin	*ESI+*	*91*	*6*	*20*	*94*	*1*	*40*	*90*	*4*	*20*	*94*	*4*	*40*
Neosolaniol	*ESI+*	*98*	*4*	*4*	*95*	*4*	*8*	*91*	*3*	*4*	*96*	*6*	*8*
NIV	*ESI-*	*73*	*4*	*400(+)/40(-)*	*91*	*1*	*800(+)/80(-)*	*71*	*10*	*400(+)/40(-)*	*94*	*7*	*800(+)/80(-)*
Ochratoxin A	*ESI+*	*91*	*6*	*4(+)/0.8(-)*	*95*	*2*	*8(+)/1.6(-)*	*96*	*8*	*4(+)/0.8(-)*	*93*	*9*	*8(+)/1.6(-)*
Ochratoxin alfa	*ESI-*	*87*	*9*	*8*	*96*	*9*	*16*	*93*	*8*	*8*	*97*	*8*	*16*
Patulin	*ESI-*	*85*	*3*	*40*	*98*	*5*	*80*	*88*	*5*	*40*	*96*	*4*	*80*
Sterigmatocystin	*ESI+*	*92*	*2*	*4*	*96*	*2*	*8*	*98*	*2*	*4*	*95*	*2*	*8*
T-2 tetraol	*ESI+*	*73*	*12*	*20*	*92*	*11*	*40*	*74*	*11*	*20*	*98*	*8*	*40*
T-2 toxin	*ESI+*	*91*	*6*	*4*	*102*	*5*	*8*	*95*	*6*	*4*	*108*	*5*	*8*
T-2 triol	*ESI+*	*84*	*5*	*4*	*102*	*5*	*8*	*89*	*5*	*4*	*94*	*4*	*8*
ZON	*ESI-*	*92*	*2*	*80(+)/4(-)*	*110*	*2*	*160(+)/8(-)*	*93*	*3*	*80(+)/4(-)*	*106*	*1*	*80(+)/4(-)*

*) Mycotoxins are in italic. In bold are less sensitive analytes, which validation data are based on 10× higher spiked concentrations.

Table S2-B: Validation data obtained on spiked paprika and black pepper samples for the methods A and B.

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
2,4,5-T	ESI-	88	2	24	92	2	24	88	5	24	85	3	24
2,4-D	ESI-	85	3	24	89	4	24	86	3	24	84	3	24
2,4-DB	ESI-	89	4	24	95	4	24	96	7	24	93	3	24
2-naphthoxyacetic acid	ESI-	86	4	24	90	3	24	81	4	24	84	2	24
4-CPA	ESI-	88	2	24	92	3	24	85	4	24	85	3	24
Abamectin:													
Avermectine B1a (98%)	ESI+	100	4	24	107	5	24	82	5	24	80	5	24
Avermectine B1b (2%)	ESI+	92	9	24	126	14	24	85	11	24	112	9	24
Acephate	ESI+	84	2	24	87	1	24	82	2	24	79	3	24
Acetamiprid	ESI+	91	3	24	99	2	24	86	2	24	89	5	24
Acetochlor	ESI+	96	3	48	94	1	48	83	7	120	74	9	120
Acrinathrin	ESI+	84	4	24	97	3	24	81	8	24	79	5	24
Alachlor	ESI+	89	3	24	98	2	24	84	3	48	82	3	48
Aldicarb	ESI+	91	3	24	100	3	24	82	1	24	83	6	24
Aldicarb sulfone	ESI+	91^{+}	3^{+}	24^{+}	97^{+}	2^{+}	24^{+}	84	4	24	87	3	24
Aldicarb sulfoxide	ESI+	97	4	48	91	4	48	82	3	48	84	7	48
Ametryn	ESI+	91	3	24	93	2	24	91	3	24	84	2	24
Atrazine	ESI+	94	5	24	97	2	24	93	2	24	88	4	24
Azadirachtin	**ESI+**	**108**	**14**	**240**	**106**	**16**	**240 87 7**			**480**	**101**	**6**	**480**
Azinphos-ethyl	ESI+	87	3	24	103	4	24	88	5	24	83	4	24
Azinphos-methyl	ESI+	91	3	24	102	5	24	80	4	24	82	4	24
Azoxystrobin	ESI+	92	2	24	100	1	24	87	3	24	82	4	24
Benalaxyl	ESI+	97	3	24	99	3	24	91	4	24	85	7	24
Bendiocarb	ESI+	91	3	24	97	2	24	81	4	24	85	4	24
Bentazone	ESI-	95	1	24	101	2	24	91	4	24	92	2	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Beta-cyfluthrin	**ESI+**	**96**	**2**	**240**	**97**	**11**	**240 111**		**10**	**480**	**95 10**		**480**
Bifenthrin	ESI+	96	5	24	100	4	24	94	2	24	82	3	24
Bitertanol	ESI+	86	8	24	97	4	24	92	6	48	97	11	48
Boscalid	ESI+	85	1	24	95	2	24	81	3	24	86	7	24
Bromoxynil	ESI-	87	1	24	92	3	24	87	3	24	89	1	24
Bupirimate	ESI+	95	4	24	98	3	24	95	5	24	94	11	24
Buprofezin	ESI+	82	3	24	96	2	24	84	1	24	87	4	24
Cadusafos	ESI+	91	1	24	97	1	24	86	2	24	87	6	24
Carbaryl	ESI+	93	2	24	98	2	24	88	2	24	84	5	24
Carbendazim	ESI+	91	1	24	96	2	24	87	3	24	77	5	24
Carbofuran	ESI+	93	2	24	102	3	24	92	2	24	88	4	24
Carbofuran-3-hydroxy	ESI+	92	1	24	99	1	24	90	3	48	88	3	48
Carbophenothion	ESI+	97	8	24	88	6	24	93	3	48	86	10	48
Chlorfenvinphos	ESI+	91	2	24	100	4	24	93	6	24	84	6	24
Chloroxuron	ESI+	86	2	24	99	5	24	87	2	24	88	5	24
Chlorpropham	**ESI+**	**96**	**3**	**120**	**99**	**3**	**120 99**		**10**	**120**	**86 5**		**120**
Chlorpyrifos	ESI+	91	6	24	90	2	24	93	7	24	86	7	24
Chlorpyrifos-methyl	ESI+	96	3	24	109	12	24	94	6	48	82	7	48
Clofentezine	ESI+	90	2	24	101	7	24	93	4	24	97	12	24
Clomazone	ESI+	92	5	24	96	3	24	85	1	24	87	3	24
Clopyralid	**ESI-**	**83**	**10**	**240**	**92**	**10**	**240 85 8**			**240**	**54**	**15**	**240**
Clothianidin	ESI+	89	3	48	99	7	48	91	5	48	92	3	48
Cyanazine	ESI+	89	2	24	103	5	24	87	2	24	91	4	24
Cyazofamid	ESI+	92	6	24	111	8	24	86	4	48	84	5	48
Cycloxidim	ESI+	84	1	24	102	6	24	85	2	24	81	5	24
Cymoxanil	ESI+	91	4	48	111	5	48	93	3	24	88	5	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Cypermethrin	ESI+	88	9	48	94	7	48	90	11	48	82	3	48
Cyproconazole	ESI+	84	3	24	101	3	24	84	3	24	82	5	24
Cyprodinyl	ESI+	93	3	24	91	5	24	91	5	48	81	4	48
Deltametrin	ESI+	87	4	24	95	6	24	85	7	24	85	5	24
Demeton-S-methyl	ESI+	94	3	24	100	3	24	83	4	24	89	4	24
Demeton-S-methyl sulfon	ESI+	90	1	24	99	2	24	88	1	24	82	2	24
Desmedipham	ESI+	88	2	24	98	2	24	87	3	24	90	5	24
Desmetryn	ESI+	89	2	24	101	3	24	90	2	24	81	4	24
Diazinon	ESI+	96	6	24	103	5	24	91	3	24	85	4	24
Dicamba	**ESI-**	**87**	**6**	**240**	**85**	**9**	**240**	**80 12**		**240**	**67 16**		**240**
Dichlofluanid	ESI+	87	4	24	90	12	24	102	9	48	85	12	48
Dichlorprop	ESI-	86	3	24	95	2	24	91	3	24	88	4	24
Dichlorvos	ESI+	92	6	24	98	8	24	94	4	48	92	3	48
Diclofop-methyl	ESI+	96	3	48	92	6	48	83	6	48	84	11	48
Dicrotophos	ESI+	90	2	24	96	2	24	83	6	24	86	3	24
Diethofencarb	ESI+	88	2	24	105	4	24	83	2	24	88	2	24
Difenoconazole	ESI+	87	1	24	97	1	24	91	2	24	75	7	24
Diflubenzuron	ESI+	81	2	24	96	2	24	86	3	24	79	7	24
Diflufenican	ESI+	93	1	24	102	2	24	81	2	24	91	6	24
Dimethenamid-P	ESI+	87	2	24	108	4	24	84	4	24	87	2	24
Dimethoate	ESI+	92	1	24	110	3	24	85	3	24	91	4	24
Dimethomorph	ESI+	87	3	24	109	2	24	81^{+}	4^{+}	24^{+}	86^{+}	9^{+}	24^{+}
Dimoxystrobin	ESI+	93	1	24	106	2	24	90	5	24	93	3	24
Diniconazole	ESI+	91	3	24	95	6	24	94	8	48	84	8	48
Disulfoton	ESI+	87	7	48	116	11	48	**85 9**		**120**	**87 9**		**120**
Disulfotone sulfone	ESI+	90	2	24	102	6	24	86	1	24	91	4	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Disulfotone sulfoxid	ESI+	91	2	24	105	3	24	84	3	24	88	3	24
Diuron	ESI+	86	1	24	100	6	24	82	3	24	87	5	24
DMSA	ESI+	90	2	24	112	4	24	94	3	24	88	2	24
DMST	ESI+	94	5	24	109	1	24	93	2	24	100	3	24
Dodine	ESI+	86	6	24	87	4	24	83	8	24	72	12	24
EPN	ESI+	91	9	48	94	7	48	**80^{+}**	**6^{+} 120**	**$^{+}$ 87**	**$^{+}$**	**9^{+} 120**	**$^{+}$**
Epoxiconazole	ESI+	86	2	24	100	3	24	81	5	24	84	2	24
Ethiofencarb	ESI+	88	1	24	98	4	24	83	2	24	87	2	24
Ethion	ESI+	87	1	24	100	6	24	88	1	24	90	4	24
Ethofumesate	ESI+	90	8	24	104	3	24	85	5	48	84	8	48
Ethoprophos	ESI+	86	2	24	97	2	24	90	5	24	79	3	24
Etofenprox	ESI+	85	5	24	91	2	24	80	3	24	78	3	24
Etrimfos	ESI+	91	3	24	96	2	24	85	1	24	79	1	24
Fenamiphos	ESI+	87	3	24	98	2	24	80	4	24	88	4	24
Fenamiphos sulfon	ESI+	94	3	24	106	4	24	91	3	24	88	6	24
Fenamiphos sulfoxid	ESI+	91	3	24	99	3	24	80	2	24	90	5	24
Fenarimol	ESI+	93	6	48	100	4	48	98	7	48	97	11	48
Fenazaquin	ESI+	76	4	24	89	4	24	88	5	24	85	3	24
Fenbuconazole	ESI+	88	2	24	106	4	24	84	6	24	84	6	24
Fenchlorphos	ESI+	89	5	24	106	13	24	86	5	24	91	4	24
Fenhexamid	ESI+	85	2	24	102	6	24	83^{+}	3^{+}	120^{+}	83^{+}	8^{+}	120^{+}
Fenoprop	ESI-	87	3	24	95	3	24	87	3	24	86	1	24
Fenoxaprop	ESI+	100	4	48	94	5	48	80	3	120	87	8	120
Fenoxycarb	ESI+	86	3	24	99	3	24	77	2	24	85	4	24
Fenpropathrin	ESI+	92	6	24	101	5	24	88	4	24	83	3	24
Fenpropidin	ESI+	84	2	24	98	1	24	85	3	24	84	4	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Fenpropimorph	ESI+	88	2	24	100	2	24	84	3	24	84	4	24
Fenpyroximate	ESI+	84	1	24	94	2	24	86	4	24	88	5	24
Fensulfothion	ESI+	92	1	24	101	3	24	84	2	24	88	5	24
Fensulfothion-PO sulfon	ESI+	93	2	24	107	6	24	85	3	24	86	4	24
Fenthion	ESI+	96	5	48	99	15	48	81	2	48	89	8	48
Fipronil	ESI-	95	2	120(+)/24(-)	100	2	120(+)/24(-)	92	2	240(+)/24(-)	97	2	240(+)/24(-)
Flonicamid	ESI+	90	2	48	108	5	48	80	3	24	87	5	24
Fluazifop	ESI+	87	3	24	98	5	24	84	6	24	81	6	24
Fluazifop-P-butyl	ESI+	90	2	24	97	1	24	79	3	24	83	7	24
Fluazinam	ESI-	85	2	24	93	2	24	87	3	24	93	2	24
Fludioxonil	ESI-	90	2	24	98	2	24	92	3	24	95	2	24
Flufenacet	ESI+	90	2	24	102	1	24	76	3	24	85	3	24
Flufenoxuron	ESI+	82	6	24	96	2	24	81	5	24	86	3	24
Fluoxastrobin	ESI+	94	5	24	91	5	24	85	8	48	83	8	48
Fluquinconazole	ESI+	91	11	48	94	5	48	102	1	48	94	7	48
Fluroxypyr	ESI-	89	4	48(+)/24(-)	98	6	48(+)/24(-)	86	5	48(+)/24(-)	93	5	48(+)/24(-)
Flusilazole	ESI+	91	6	24	99	2	24	76^{+}	4^{+}	48^{+}	85^{+}	3^{+}	48^{+}
Fomesafen	ESI-	103	7	120(+)/24(-)	97	8	120(+)/24(-)	94	3	120(+)/24(-)	94	12	120(+)/24(-)
Fonofos	ESI+	103	6	48	95	4	48	87	6	48	81	4	48
Formetanate	ESI+	Interference	Interference	Interference	Interfernce	Interfernce	Interference	82^{+}	3^{+}	24^{+}	76^{+}	12^{+}	24^{+}
Formothion	ESI+	96	2	48	79	12	48	91	7	48	96	10	48
Haloxyfop	ESI+	91	6	24	102	8	24	105	9	24	88	9	24
Haloxyfop-ethoxyethyl	ESI+	90	1	24	99	2	24	84	4	24	85	4	24
Haloxyfop-methyl	ESI+	89	2	24	100	1	24	86	1	24	87	5	24
Heptenophos	ESI+	89	2	24	100	2	24	83	3	24	86	2	24
Hexaconazole	ESI+	90	6	24	102	7	24	87	6	48	96	6	48

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Hexazinon	ESI+	90	4	24	100	3	24	86	2	24	88	4	24
Hexythiazox	ESI+	80	3	24	90	2	24	83	4	24	87	3	24
Imazalil	ESI+	89	2	24	96	3	24	83	1	24	79	3	24
Imazapyr	ESI+	93	3	24	90	2	24	84	5	24	78	4	24
Imazaquin	ESI+	87	5	24	96	2	24	87	2	48	93	3	48
Imazethapyr	ESI+	89	2	24	99	3	24	81	4	24	86	5	24
Imazosulfuron	ESI+	97	2	24	102	3	24	89	6	24	82	5	24
Imidacloprid	ESI+	91	2	24	98	3	24	82	3	24	90	4	24
Indoxacarb	ESI+	93	9	24	102	4	24	82	5	48	80	9	48
Iodosulfuron-methyl	ESI+	85^{+}	2^{+}	48^{+}	96^{+}	5^{+}	48^{+}	86	6	48	76	7	48
Ioxynil	ESI-	86	2	24	90	3	24	88	3	24	91	2	24
Iprodion	**ESI+**	**81**	**12**	**240**	**93**	**11**	**240**	**83 17**		**480**	**91 22**		**480**
Iprovalicarb	ESI+	88	1	24	106	3	24	86^{+}	3^{+}	24^{+}	88^{+}	6^{+}	24^{+}
Isofenphos	ESI+	88	1	24	97	2	24	85	3	24	84	3	24
Isofenphos-methyl	ESI+	95	3	24	100	7	24	81	2	24	85	7	24
Isoproturon	ESI+	90	2	24	100	3	24	81	1	24	85	2	24
Kresoxim-methyl	ESI+	91	2	24	97	3	24	77	2	48	88	4	48
Lambda-cyhalothrin	**ESI+**	**76**	**5**	**120**	**101**	**13**	**120 97 8**			**120**	**79**	**12**	**120**
Lenacil	ESI+	86	3	48	100	5	48	83	5	48	82	4	48
Linuron	ESI+	85	1	24	107	6	24	88	3	24	89	4	24
Lufenuron	ESI+	93	6	24(+)/24(-)	100	5	24(+)/24(-)	87	4	24(+)/24(-)	93	6	24(+)/24(-)
Malaoxon	ESI+	92	2	24	102	2	24	86	3	24	93	1	24
Malathion	ESI+	84	2	24	100	3	24	83	2	24	86	3	24
MCPA	ESI-	86	1	24	92	3	24	84	2	24	87	1	24
MCPB	ESI-	88	4	24	94	3	24	91	4	24	94	4	24
Mecarbam	ESI+	85	1	24	99	1	24	77	3	24	87	5	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Mecoprop	ESI-	87	2	24	95	2	24	87	3	24	90	1	24
Mefenpyr-diethyl	ESI+	85	2	24	100	2	24	94	5	24	99	7	24
Mepanipyrim	ESI+	82	3	24	90	6	24	93	6	48	80	12	48
Mepronil	ESI+	91	1	24	102	3	24	84	3	24	91	3	24
Metalaxyl	ESI+	89	2	24	101	2	24	85	3	24	87	7	24
Metamitron	ESI+	84	2	24	97	9	24	83	4	120	91	12	120
Metamitron-desamino	ESI+	78	3	24	99	6	24	78	3	24	84	4	24
Metazachlor	ESI+	88	2	24	99	2	24	83	2	24	88	5	24
Metconazole	ESI+	83	3	24	97	1	24	96	5	24	95	4	24
Methacrifos	ESI+	98	12	48	70	17	48	79	6	48	87	3	48
Methamidophos	ESI+	79	3	24	86	3	24	85	3	24	80	2	24
Methidathion	ESI+	90	3	24	99	2	24	82	1	24	86	3	24
Methiocarb	ESI+	88	2	24	97	2	24	79	4	24	86	6	24
Methiocarb sulfon	ESI+	91	2	24	100	4	24	90	2	24	94	4	24
Methiocarb sulfoxid	ESI+	91	1	24	100	2	24	83	2	24	88	3	24
Methomyl	ESI+	92	3	24	94	3	24	83	4	24	86	5	24
Methoxyfenozide	ESI+	90	9	24	100	8	24	79^{+}	4^{+}	48^{+}	103^{+}	6^{+}	48^{+}
Metobromuron	ESI+	87	2	24	101	3	24	82	1	24	90	3	24
Metolachlor	ESI+	90	3	24	108	5	24	79	3	24	89	4	24
Metolcarb	ESI+	89	3	48	112	4	48	83	5	48	89	7	48
Metosulam	ESI+	92	4	24	105	3	24	79	2	24	92	4	24
Metoxuron	ESI+	91	2	24	98	2	24	82	2	24	83	1	24
Metribuzin	ESI+	91	6	24	107	7	24	87	4	24	93	4	24
Metsulfuron-methyl	ESI+	88	6	24	93	5	24	82	10	24	88	6	24
Mevinphos	ESI+	92	2	24	97	2	24	84	1	24	89	2	24
Monocrotophos	ESI+	90	2	24	95	2	24	82	4	24	87	4	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Monolinuron	ESI+	88	2	24	99	3	24	82	3	24	87	4	24
Monuron	ESI+	93	5	24	98	3	24	82	5	24	84	5	24
Myclobutanil	ESI+	86	3	24	108	11	24	85^{+}	3^{+}	48^{+}	90^{+}	6^{+}	48^{+}
Naled	ESI+	85	9	24	93	7	24	86	9	48	96	3	48
Napropamid	ESI+	86	2	24	98	2	24	81	5	24	92	5	24
Neburon	ESI+	88	3	24	97	3	24	82	4	24	88	6	24
Norflurazone	ESI+	88	2	24	100	2	24	87	3	24	87	4	24
Omethoat	ESI+	87	1	24	92	1	24	80	2	24	80	2	24
Oxadixyl	ESI+	90	6	24	102	5	24	83	2	48	89	5	48
Oxamyl	ESI+	92	4	24	96	4	24	83	4	24	83	3	24
Oxamyl-oxime	ESI+	92	2	48	94	1	48	83	2	48	83	3	48
Oxydemeton-methyl	ESI+	87	2	24	96	2	24	82	1	24	84	3	24
Oxyfluorfen	**ESI+**	**93**	**13**	**120**	**98**	**19**	**120 74 7**			**120**	**85 5**		**120**
Paclobutrazol	ESI+	86	1	24	100	3	24	84	6	24	85	2	24
Penconazole	ESI+	84	3	24	95	2	24	86	1	48	86	6	48
Pencycuron	ESI+	88	3	24	99	1	24	78^{+}	3^{+}	48^{+}	83^{+}	8^{+}	48^{+}
Pendimethalin	ESI+	84	4	24	89	2	24	82	3	48	84	4	48
Permethrin	ESI+	77	10	48	81	1	48	88	5	24	80	7	24
Phenmedipham	ESI+	86	2	24	98	2	24	82	3	24	87	4	24
Phenothrin	ESI+	81	9	24	98	3	24	90	8	48	85	8	48
Phenthoate	ESI+	96	10	24	101	1	24	84	4	24	88	7	24
Phorate	ESI+	80	11	48	101	10	48	89	7	120	78	10	120
Phorate sulfon	ESI+	91	5	24	102	3	24	84	2	24	91	6	24
Phorate sulfoxid	ESI+	91	1	24	102	2	24	86	3	24	89	4	24
Phosalone	ESI+	96	8	24	96	2	24	84	3	24	95	6	24
Phosmet	ESI+	88	4	24	99	7	24	83	2	24	88	2	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Phosmet-oxon	ESI+	86	4	48	104	9	48	81	4	120	86	5	120
Phosphamidon	ESI+	91	3	24	99	3	24	83	3	24	87	5	24
Picloram	ESI+	88	10	48	78	13	48	93	6	48	61	14	48
Picoxystrobin	ESI+	88	4	24	99	1	24	75	3	24	86	3	24
Piperonyl Butoxide	ESI+	83	1	24	102	1	24	83	3	24	90	7	24
Pirimicarb	ESI+	92	1	24	99	2	24	82	2	24	85	2	24
Pirimicarb-desmethyl	ESI+	87	3	24	96	3	24	81	3	24	82	4	24
Pirimiphos-ethyl	ESI+	89	2	24	96	1	24	84	3	24	87	4	24
Pirimiphos-methyl	ESI+	88	1	24	96	1	24	91	5	24	94	2	24
Prochloraz	ESI+	87	3	24	97	1	24	89	7	24	91	11	24
Profenofos	ESI+	87	3	24	94	1	24	82	1	24	82	6	24
Prometon	ESI+	88	1	24	101	2	24	80	1	24	83	4	24
Prometryn	ESI+	87	3	24	100	2	24	84^{+}	2^{+}	48^{+}	86^{+}	2^{+}	48^{+}
Propachlor	ESI+	88	2	24	101	3	24	84	2	24	85	4	24
Propamocarb	ESI+	87	1	24	93	2	24	81	2	24	77	2	24
Propaquizafop	ESI+	88	5	24	96	2	24	81	3	24	79	9	24
Propargite	ESI+	85	2	24	95	1	24	92^{+}	8^{+}	48^{+}	86^{+}	5^{+}	48^{+}
Propham	**ESI+**	**88**	**4**	**120**	**74**	**10**	**120**	**103**	**7**		**240**	**83**	**7**	**240**
Propiconazole	ESI+	84	4	24	97	4	24	86	6	48	97	7	48
Propoxur	ESI+	95	3	24	102	3	24	82	3	24	85	6	24
Propyzamide	ESI+	86	4	24	100	7	24	82	4	24	86	4	24
Proquinazid	ESI+	102	1	24	77	2	24	88	6	24	84	5	24
Prosulfocarb	ESI+	87	3	24	93	1	24	85	3	24	84	5	24
Pymetrozine	ESI+	31	3	24	77	3	24	37	3	48	77	5	48
Pyraclostrobin	ESI+	88	3	24	96	2	24	82	2	24	94	4	24
Pyrazophos	ESI+	88	2	24	102	1	24	84	4	24	91	4	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Pyrethrum:													
Cinerin I (6%)	**ESI+**	**89**	**4**	**24**	**108**	**7**	**24**	**96**	**9**	**24**	**91**	**11**	**24**
Cinerin II (6%)	**ESI+**	**92**	**7**	**24**	**121**	**10**	**24**	**99 6**		**24**	**97 4**		**24**
Jasmolin I (4%)	**ESI+**	**84**	**5**	**24**	**94**	**6**	**24**	**Interference**	**Interference**	**Interference I**	**nterference**	**Interference**	**Interference**
Jasmolin II (2%)	**ESI+**	**78**	**6**	**24**	**90**	**13**	**24**	**Interference**	**Interference**	**Interference I**	**nterference**	**Interference**	**Interference**
Pyrethrin I (50%)	**ESI+**	**85**	**7**	**24**	**99**	**5**	**24**	**89**	**3**	**24**	**92**	**8**	**24**
Pyrethrin II (30%)	**ESI+**	**90**	**7**	**24**	**97**	**7**	**24**	**85**	**4**	**24**	**84**	**11**	**24**
Pyridaben	ESI+	85	1	24	90	2	24	87	8	24	84	6	24
Pyridate	ESI+	83	8	24	86	5	24	92	9	1200	76	13	1200
Pyrifenox	ESI+	84^{+}	2^{+}	24^{+}	93^{+}	3^{+}	24^{+}	82	1	24	91	4	24
Pyrimethanil	ESI+	85	1	24	87	3	24	86	3	24	79	3	24
Pyriproxyfen	ESI+	86	3	24	91	1	24	83	2	24	86	8	24
Quinalphos	ESI+	90	2	24	97	3	24	80^{+}	4^{+}	48^{+}	83^{+}	2^{+}	48^{+}
Quinmerac	ESI+	89	6	24	85	3	24	91	3	24	80	4	24
Quinoxyfen	ESI+	84	5	24	81	2	24	83	3	24	83	4	24
Quizalofop	ESI-	86	2	120(+)/24(-)	100	8	120(+)/24(-)	90	3	120(+)/24(-)	98	5	120(+)/24(-)
Quizalofop-P-ethyl	ESI+	92	1	24	97	4	24	82	2	24	83	5	24
Resmethrin	ESI+	98	5	24	87	1	24	83	7	24	83	6	24
Rimsulfuron	ESI+	89	10	48	80	14	48	81	12	48	82	10	48
Simazine	ESI+	90	1	24	98	2	24	81	3	48	91	5	48
Simetryn	ESI+	88	1	24	93	2	24	82	2	24	84	2	24
Spinosad:													
Spinosyn A (70%)	ESI+	88	3	24	96	2	24	89	4	24	92	8	24
Spinosyn D (30%)	ESI+	93	4	24	96	4	24	91	5	120	89	5	120
Spiroxamin	ESI+	89	1	24	101	4	24	85	3	24	85	4	24
Sulfotep	ESI+	89	2	24	100	2	24	91	3	24	84	3	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Tau-Fluvalinate	ESI+	86	2	48	93	2	48	80	6	48	78	8	48
Tebuconazole	ESI+	84	2	48	104	4	48	83	5	24	84	7	24
Tebufenozide	ESI+	91	2	24	106	6	24	89	4	24	87	3	24
Tebufenpyrad	ESI+	85	3	24	95	3	24	81	5	24	84	5	24
Teflubenzuron	ESI+	79	12	24	104	9	24	85	8	24	85	5	24
Tepraloxydim	ESI+	88	4	48	102	8	48	98	8	120	87	7	120
Terbufos	ESI+	98	9	48	98	15	48	89	8	120	87	5	120
Terbufos sulfon	ESI+	89	4	24	103	2	24	85	5	24	84	6	24
Terbufos sulfoxide	ESI+	88	1	24	100	3	24	84	3	24	86	3	24
Terbuthylazine	ESI+	84	2	24	95	3	24	81	3	24	87	3	24
Terbutryn	ESI+	91	2	24	97	1	24	83	2	24	87	4	24
Tetraconazole	ESI+	89	4	24	98	3	24	94	2	48	93	3	48
Thiabendazole	ESI+	81	1	24	93	6	24	81	3	24	74	3	24
Thiacloprid	ESI+	90	1	24	99	3	24	83	1	24	83	2	24
Thiamethoxam	ESI+	93	3	24	95	4	24	87	4	48	79	3	48
Thifensulfuron-methyl	ESI+	91	6	24	101	6	24	82	5	24	89	8	24
Thiodicarb	ESI+	84	3	24	100	1	24	80	4	24	84	4	24
Thiometon	**ESI+**	**89**	**9**	**120**	**103**	**9**	**120 89 8**			**120**	**87 8**		**120**
Thiophanate-methyl	ESI+	91	4	24	88	7	24	92	3	24	97	7	24
Tolclofos-methyl	ESI+	89	10	48	106	9	48	89	10	120	103	8	120
Tolylfluanid	ESI+	90	3	24	101	9	24	91	3	24	82	6	24
Triadimefon	ESI+	85	4	24	101	1	24	86	4	24	90	4	24
Triadimenol	ESI+	78	5	48	96	6	48	83	6	120	82	3	120
Triazamate	ESI+	89	2	24	95	2	24	89	6	24	88	10	24
Triazophos	ESI+	91	1	24	102	2	24	82	4	24	83	4	24
Trichlorfon	ESI+	92	3	24	98	5	24	86	2	24	92	4	24

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Trifloxystrobin	ESI+	87	2	24	96	3	24	83	2	24	85	5	24
Triflumuron	ESI+	87	5	24	105	5	24	93	6	24	86	5	24
Triforine	ESI+	88	6	48	102	9	48	86	4	48	79	7	48
Vamidothion	ESI+	90	2	24	95	2	24	86	3	24	89	3	24
Vamidothion sulfon	ESI+	90	2	48	102	3	48	80	3	48	99	4	48
Vamidothion sulfoxid	**ESI+**	**92**	**5**	**120**	**85**	**10**	**120 84 7**			**120**	**87 8**		**120**
15-ADON	*ESI+*	*92*	*9*	*120*	*101*	*4*	*120*	*90*	*7*	*120*	*95*	*6*	*120*
3-ADON	*ESI-*	*90*	*4*	*240(+)/120(-)*	*103*	*4*	*240(+)/120(-)*	*87*	*6*	*240(+)/120(-)*	*95*	*6*	*240(+)/120(-)*
Aflatoxin B1	*ESI+*	*88*	*5*	*4.8*	*91*	*5*	*4.8*	*86*	*2*	*4.8*	*85*	*7*	*4.8*
Aflatoxin B2	*ESI+*	*91*	*5*	*4.8*	*99*	*2*	*4.8*	*83*	*2*	*4.8*	*83*	*4*	*4.8*
Aflatoxin G1	*ESI+*	*88*	*4*	*4.8*	*93*	*4*	*4.8*	*92*	*7*	*4.8*	*87*	*4*	*4.8*
Aflatoxin G2	*ESI+*	*92*	*4*	*4.8*	*100*	*4*	*4.8*	*81*	*7*	*4.8*	*85*	*9*	*4.8*
Altenuene	*ESI-*	*88*	*1*	*120(+)/24(-)*	*97*	*3*	*120(+)/24(-)*	*88*	*3*	*120(+)/24(-)*	*92*	*2*	*120(+)/24(-)*
Alternariol	*ESI-*	*85*	*2*	*480(+)/24(-)*	*97*	*4*	*480(+)/24(-)*	*92*	*9*	*480(+)/24(-)*	*78*	*7*	*480(+)/24(-)*
Alternariol methylether	*ESI-*	*87*	*1*	*480(+)/24(-)*	*97*	*4*	*480(+)/24(-)*	*87*	*2*	*480(+)/24(-)*	*94*	*2*	*480(+)/24(-)*
aZOL	*ESI-*	*85*	*3*	*480(+)/24(-)*	*95*	*3*	*480(+)/24(-)*	*90*	*3*	*480(+)/24(-)*	*95*	*6*	*480(+)/24(-)*
bZOL	*ESI-*	*85*	*1*	*480(+)/24(-)*	*97*	*4*	*480(+)/24(-)*	*87*	*3*	*480(+)/24(-)*	*92*	*4*	*480(+)/24(-)*
Citrinin	*ESI+*	*89*	*6*	*120*	*81*	*7*	*120*	*107*	*12*	*120*	*87*	*8*	*120*
deepoxyDON	*ESI-*	*102*	*37*	*480(+)/120(-)*	*123*	*11*	*480(+)/120(-)*	*83*	*9*	*480(+)/120(-)*	*< LOQ*	*< LOQ*	*480(+)/120(-)*
Diacetoxyscirpenol	*ESI+*	*90*	*5*	*24*	*99*	*3*	*24*	*82*	*8*	*24*	*84*	*3*	*24*
DON	*ESI-*	*109*	*13*	*480(+)*	*99*	*10*	*480(+)*	*79*	*7*	*480(+)/120(-)*	*82*	*9*	*480(+)/120(-)*
DON-3-Glc	*ESI-*	*39*	*1*	*480(+)/120(-)*	*83*	*3*	*480(+)/120(-)*	*46*	*7*	*480(+)/120(-)*	*84*	*7*	*480(+)/120(-)*
Ergocornine	*ESI+*	*82*	*6*	*48*	*90*	*7*	*48*	*84*	*4*	*48*	*75*	*2*	*48*
Ergocorninine	*ESI+*	*87*	*4*	*48*	*106*	*6*	*48*	*89*	*6*	*48*	*116*	*5*	*48*
Ergocristine	*ESI+*	*86*	*8*	*48*	*99*	*6*	*48*	*93*	*5*	*48*	*86*	*3*	*48*
Ergocristinine	*ESI+*	*89*	*4*	*48*	*106*	*8*	*48*	*91*	*6*	*48*	*112*	*4*	*48*

Analyte		Paprika, Spike 50 µg kg^{-1} (n=6)						Black Pepper, Spike 50 µg kg^{-1} (n=6)					
		Method A			Method B			Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Ergocryptine	*ESI+*	*91*	*6*	*48*	*96*	*9*	*48*	*92*	*6*	*48*	*89*	*1*	*48*
Ergocryptinine	*ESI+*	*94*	*3*	*48*	*101*	*7*	*48*	*96*	*4*	*48*	*108*	*3*	*48*
Ergosine/inine	*ESI+*	*84*	*3*	*48*	*98*	*4*	*48*	*86*	*3*	*48*	*105*	*4*	*48*
Fumonisin B1	*ESI+*	*77*	*8*	*120*	*105*	*2*	*120*	*73*	*17*	*120*	*80*	*11*	*120*
Fumonisin B2	*ESI+*	*75*	*5*	*120*	*106*	*5*	*120*	*77*	*12*	*120*	*91*	*13*	*120*
Fumonisin B3	*ESI+*	*73*	*12*	*120*	*94*	*9*	*120*	*76*	*15*	*120*	*87*	*9*	*120*
FUS X	*ESI-*	*101*	*4*	*480(+)/120(-)*	*100*	*7*	*480(+)/120(-)*	*83*	*4*	*480(+)/120(-)*	*86*	*11*	*480(+)/120(-)*
HT-2 toxin	*ESI+*	*98*	*6*	*48*	*102*	*6*	*48*	*85*	*3*	*120*	*72*	*5*	*120*
Neosolaniol	*ESI+*	*90*	*5*	*24*	*94*	*5*	*24*	*83*	*5*	*24*	*88*	*5*	*24*
NIV	*ESI-*	*77*	*3*	*2400(+)/240(-)*	*89*	*7*	*2400(+)/240(-)*	*76*	*10*	*2400(+)/240(-)*	*82*	*7*	*2400(+)/240(-)*
Ochratoxin A	*ESI+*	*91*	*3*	*24(+)/4.8(-)*	*89*	*9*	*24(+)/4.8(-)*	*95*	*9*	*24(+)/4.8(-)*	*91*	*8*	*24(+)/4.8(-)*
Ochratoxin alfa	*ESI-*	*98*	*7*	*48*	*93*	*8*	*48*	*88*	*7*	*48*	*93*	*6*	*48*
Patulin	*ESI-*	*87*	*6*	*240*	*78*	*6*	*240*	*90*	*9*	*240*	*98*	*4*	*240*
Sterigmatocystin	*ESI+*	*91*	*4*	*24*	*92*	*3*	*24*	*89*	*2*	*24*	*90*	*6*	*24*
T-2 tetraol	*ESI+*	*73*	*11*	*120*	*92*	*11*	*120*	*74*	*12*	*120*	*96*	*16*	*120*
T-2 toxin	*ESI+*	*86*	*5*	*24*	*99*	*5*	*24*	*88*	*6*	*24*	*88*	*11*	*24*
T-2 triol	*ESI+*	*93*	*4*	*24*	*95*	*4*	*24*	*82*	*3*	*24*	*87*	*7*	*24*
ZON	*ESI-*	*87*	*2*	*480(+)/24(-)*	*96*	*2*	*480(+)/24(-)*	*97*	*4*	*480(+)/24(-)*	*96*	*2*	*480(+)/24(-)*

*) Mycotoxins are in italic. In bold are less sensitive analytes, which validation data are based on 10× higher spiked concentrations.

$^{+}$) Analytes for which identification employing UHPLC–TOFMS had to be used.

Table S2-C: Validation data obtained on spiked apple baby food samples for the methods A and B.

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
2,4,5-T	ESI-	97	1	1	96	6	4
2,4-D	ESI-	99	2	1	97	5	4
2,4-DB	ESI-	103	2	1	99	6	4
2-naphthoxyacetic acid	ESI-	98	2	1	88	7	4
4-CPA	ESI-	105	3	1	102	5	4
Abamectin:							
Avermectine B1a (98%)	ESI+	99	10	1	90	10	4
Avermectine B1b (2%)	ESI+	105	14	1	104	12	4
Acephate	ESI+	89	3	1	106	4	4
Acetamiprid	ESI+	94	3	1	104	3	4
Acetochlor	ESI+	94	4	2	102	9	8
Acrinathrin	ESI+	86	9	1	90	9	4
Alachlor	ESI+	94	7	2	102	6	8
Aldicarb	ESI+	93	2	1	104	5	4
Aldicarb sulfone	ESI+	90	2	1	101	3	4
Aldicarb sulfoxide	ESI+	89	2	2	104	2	8
Ametryn	ESI+	95	2	1	106	1	4
Atrazine	ESI+	96	3	1	109	3	4
Azadirachtin	**ESI+**	**83 19**		**10**	**75 13**		**40**
Azinphos-ethyl	ESI+	92	10	1	101	12	4
Azinphos-methyl	ESI+	88	4	1	92	6	4
Azoxystrobin	ESI+	95	3	1	102	7	4
Benalaxyl	ESI+	96	3	1	101	3	4
Bendiocarb	ESI+	99	5	1	108	6	4
Bentazone	ESI-	93	2	1	100	8	4
Beta-cyfluthrin	**ESI+**	**108**	**15 20**		**84**	**92 80**	
Bifenthrin	ESI+	95	2	1	95	8	4
Bitertanol	ESI+	91	6	1	105	7	4
Boscalid	ESI+	86	5	1	97	6	4
Bromoxynil	ESI-	84	4	1	100	5	4
Bupirimate	ESI+	101	2	1	114	4	4
Buprofezin	ESI+	99	3	1	104	4	4
Cadusafos	ESI+	94	1	1	111	3	4
Carbaryl	ESI+	88	3	1	104	3	4
Carbendazim	ESI+	100	3	1	113	2	4
Carbofuran	ESI+	93	2	1	108	4	4
Carbofuran-3-hydroxy	ESI+	91	2	1	107	6	4
Carbophenothion	ESI+	94	8	2	99	16	8
Chlorfenvinphos	ESI+	91	3	1	100	4	4
Chloroxuron	ESI+	86	2	1	99	9	4
Chlorpropham	**ESI+**	**106 10**		**5**	**110 12**		**20**
Chlorpyrifos	ESI+	97	4	1	106	5	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Chlorpyrifos-methyl	ESI+	102	9	2	73	12	8
Clofentezine	ESI+	97	9	1	95	9	4
Clomazone	ESI+	97	2	1	108	5	4
Clopyralid ESI	**-**	**96**	**8**	**10**	**109**	**17**	**40**
Clothianidin	ESI+	93	5	2	106	8	8
Cyanazine	ESI+	96	8	1	100	4	4
Cyazofamid	ESI+	98	6	1	114	3	4
Cycloxidim	ESI+	87	5	1	90	4	4
Cymoxanil	ESI+	91	2	2	95	7	8
Cypermethrin	ESI+	103	6	2	94	12	8
Cyproconazole	ESI+	86	4	1	95	10	4
Cyprodinyl	ESI+	93	4	1	99	10	4
Deltametrin	ESI+	104	7	1	110	10	4
Demeton-S-methyl	ESI+	101	3	1	106	4	4
Demeton-S-methyl sulfon	ESI+	95	0	1	104	3	4
Desmedipham	ESI+	89	3	1	99	3	4
Desmetryn	ESI+	91	1	1	102	2	4
Diazinon	ESI+	91	6	1	98	7	4
Dicamba ESI	**-**	**99**	**8**	**10**	**98**	**14**	**40**
Dichlofluanid	ESI+	89	4	1	98	6	4
Dichlorprop	ESI-	82	1	1	99	3	4
Dichlorvos	ESI+	90	5	1	95	5	4
Diclofop-methyl	ESI+	80	11	2	102	13	8
Dicrotophos	ESI+	94	1	1	107	3	4
Diethofencarb	ESI+	88	4	1	103	7	4
Difenoconazole	ESI+	96	2	1	108	3	4
Diflubenzuron	ESI+	90	7	1	102	5	4
Diflufenican	ESI+	97	5	1	101	7	4
Dimethenamid-P	ESI+	93	1	1	105	3	4
Dimethoate	ESI+	97	2	1	104	5	4
Dimethomorph	ESI+	89	2	1	81	37	4
Dimoxystrobin	ESI+	88	2	1	103	4	4
Diniconazole	ESI+	92	6	1	102	9	4
Disulfoton	ESI+	102	11	2	90	9	8
Disulfotone sulfone	ESI+	92	4	1	102	2	4
Disulfotone sulfoxid	ESI+	93	2	1	109	4	4
Diuron	ESI+	90	4	1	97	6	4
DMSA	ESI+	97	3	1	109	5	4
DMST	ESI+	93	2	1	105	6	4
Dodine	ESI+	90	4	1	108	6	4
EPN	ESI+	88	13	2	98	18	8
Epoxiconazole	ESI+	89	5	1	109	9	4
Ethiofencarb	ESI+	94	3	1	104	5	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Ethion	ESI+	93	3	1	101	4	4
Ethofumesate	ESI+	94	6	1	107	4	4
Ethoprophos	ESI+	99	2	1	117	2	4
Etofenprox	ESI+	97	1	1	100	3	4
Etrimfos	ESI+	93	2	1	102	8	4
Fenamiphos	ESI+	89	4	1	99	3	4
Fenamiphos sulfon	ESI+	91	1	1	103	2	4
Fenamiphos sulfoxid	ESI+	90	2	1	106	4	4
Fenarimol	ESI+	92	6	1	94	11	4
Fenazaquin	ESI+	98	1	1	100	2	4
Fenbuconazole	ESI+	92	7	1	96	4	4
Fenchlorphos	ESI+	91	3	1	100	7	4
Fenhexamid	ESI+	91	4	1	91	10	4
Fenoprop	ESI-	91	2	1	96	7	4
Fenoxaprop	ESI+	86	8	2	99	15	8
Fenoxycarb	ESI+	93	3	1	101	3	4
Fenpropathrin	ESI+	99	5	1	105	6	4
Fenpropidin	ESI+	92	3	1	105	4	4
Fenpropimorph	ESI+	94	4	1	101	3	4
Fenpyroximate	ESI+	93	3	1	98	4	4
Fensulfothion	ESI+	91	3	1	99	6	4
Fensulfothion-PO sulfon	ESI+	91	2	1	102	4	4
Fenthion	ESI+	90	12	2	104	10	8
Fipronil	ESI-	83	3	5(+)/1(-)	97	5	20(+)/4(-)
Flonicamid	ESI+	95	4	2	108	6	8
Fluazifop	ESI+	94	6	1	98	6	4
Fluazifop-P-butyl	ESI+	96	3	1	104	3	4
Fluazinam	ESI-	99	19	1	101	2	4
Fludioxonil	ESI-	82	2	1	96	6	4
Flufenacet	ESI+	94	3	1	106	5	4
Flufenoxuron	ESI+	93	4	1	96	2	4
Fluoxastrobin	ESI+	98	7	1	105	3	4
Fluquinconazole	ESI+	89	12	2	92	9	8
Fluroxypyr	ESI-	87	6	2(+)/1(-)	102	4	48(+)/24(-)
Flusilazole	ESI+	91	8	1	87	8	4
Fomesafen	ESI-	81	2	5(+)/1(-)	94	7	20(+)/4(-)
Fonofos	ESI+	97	6	2	99	12	8
Formetanate	ESI+	88	3	1	91	6	4
Formothion	ESI+	94	4	2	66	15	8
Haloxyfop	ESI+	94	5	1	98	7	4
Haloxyfop-ethoxyethyl	ESI+	96	2	1	101	3	4
Haloxyfop-methyl	ESI+	97	3	1	101	2	4
Heptenophos	ESI+	95	2	1	111	2	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Hexaconazole	ESI+	88	4	1	110	5	4
Hexazinon	ESI+	95	2	1	103	5	4
Hexythiazox	ESI+	94	3	1	97	3	4
Imazalil	ESI+	89	1	1	107	10	4
Imazapyr	ESI+	93	5	1	105	4	4
Imazaquin	ESI+	98	8	1	105	9	4
Imazethapyr	ESI+	88	3	1	101	5	4
Imazosulfuron	ESI+	84	10	1	63	15	4
Imidacloprid	ESI+	94	4	1	103	3	4
Indoxacarb	ESI+	85	4	1	98	9	4
Iodosulfuron-methyl	ESI+	85	5	2	75	7	8
Ioxynil	ESI-	97	3	1	102	4	4
Iprodion	**ESI+**	**106**	**10 10**		**36**	**43 40**	
Iprovalicarb	ESI+	91	2	1	101	3	4
Isofenphos	ESI+	102	2	1	101	6	4
Isofenphos-methyl	ESI+	81	5	1	90	7	4
Isoproturon	ESI+	93	2	1	105	2	4
Kresoxim-methyl	ESI+	90	6	1	97	4	4
Lambda-cyhalothrin ESI	**+**	**107**	**13**	**5**	**91**	**11**	**20**
Lenacil	ESI+	86	5	1	100	8	4
Linuron	ESI+	94	3	1	103	8	4
Lufenuron	ESI+	89	3	1(+)/1(-)	95	7	4(+)/4(-)
Malaoxon	ESI+	94	3	1	107	3	4
Malathion	ESI+	89	3	1	107	4	4
MCPA	ESI-	103	3	1	98	5	4
MCPB	ESI-	99	3	1	96	6	4
Mecarbam	ESI+	96	2	1	107	4	4
Mecoprop	ESI-	97	2	1	98	5	4
Mefenpyr-diethyl	ESI+	94	2	1	100	4	4
Mepanipyrim	ESI+	94	2	1	106	3	4
Mepronil	ESI+	86	2	1	103	5	4
Metalaxyl	ESI+	93	3	1	106	3	4
Metamitron	ESI+	88	4	2	108	6	8
Metamitron-desamino	ESI+	92	4	1	102	5	4
Metazachlor	ESI+	89	3	1	106	3	4
Metconazole	ESI+	89	3	1	102	3	4
Methacrifos	ESI+	104	12	2	98	11	8
Methamidophos	ESI+	80	2	1	109	2	4
Methidathion	ESI+	89	2	1	107	3	4
Methiocarb	ESI+	90	2	1	100	7	4
Methiocarb sulfon	ESI+	92	5	1	101	7	4
Methiocarb sulfoxid	ESI+	88	2	1	101	5	4
Methomyl	ESI+	97	3	1	113	4	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Methoxyfenozide	ESI+	89	2	1	103	3	4
Metobromuron	ESI+	92	3	1	104	8	4
Metolachlor	ESI+	91	3	1	106	6	4
Metolcarb	ESI+	95	2	1	100	6	4
Metosulam	ESI+	94	5	1	98	2	4
Metoxuron	ESI+	90	3	1	101	4	4
Metribuzin	ESI+	85	8	2	64	25	8
Metsulfuron-methyl	ESI+	81	3	1	85	6	4
Mevinphos	ESI+	99	3	1	109	1	4
Monocrotophos	ESI+	90	2	1	105	3	4
Monolinuron	ESI+	96	3	1	101	3	4
Monuron	ESI+	95	1	1	101	3	4
Myclobutanil	ESI+	85	5	1	100	4	4
Naled	ESI+	86	13	2	80	10	8
Napropamid	ESI+	91	3	1	105	4	4
Neburon	ESI+	87	5	1	96	4	4
Norflurazone	ESI+	88	2	1	94	5	4
Omethoat	ESI+	92	3	1	107	4	4
Oxadixyl	ESI+	100	5	1	96	11	4
Oxamyl	ESI+	90	3	1	101	3	4
Oxamyl-oxime	ESI+	91	2	2	103	9	8
Oxydemeton-methyl	ESI+	95	4	1	108	3	4
Oxyfluorfen ESI	**+**	**85**	**18**	**5**	**100**	**10**	**20**
Paclobutrazol	ESI+	90	6	1	102	2	4
Penconazole	ESI+	87	3	1	104	4	4
Pencycuron	ESI+	98	2	1	110	4	4
Pendimethalin	ESI+	90	3	2	107	7	8
Permethrin	ESI+	92	5	2	96	13	8
Phenmedipham	ESI+	90	3	1	97	4	4
Phenothrin	ESI+	93	5	1	94	15	4
Phenthoate	ESI+	91	4	1	108	8	4
Phorate	ESI+	100	8	2	105	22	8
Phorate sulfon	ESI+	91	3	1	104	3	4
Phorate sulfoxid	ESI+	92	4	1	109	3	4
Phosalone	ESI+	91	4	1	98	7	4
Phosmet	ESI+	90	2	1	94	8	4
Phosmet-oxon	ESI+	90	4	2	101	5	8
Phosphamidon	ESI+	92	2	1	105	3	4
Picloram	ESI+	95	7	2	100	9	8
Picoxystrobin	ESI+	92	1	1	105	4	4
Piperonyl Butoxide	ESI+	92	2	1	95	7	4
Pirimicarb	ESI+	98	1	1	115	2	4
Pirimicarb-desmethyl	ESI+	102	1	1	109	4	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Pirimiphos-ethyl	ESI+	97	3	1	107	3	4
Pirimiphos-methyl	ESI+	98	4	1	106	3	4
Prochloraz	ESI+	91	3	1	102	6	4
Profenofos	ESI+	92	2	1	101	2	4
Prometon	ESI+	94	2	1	105	6	4
Prometryn	ESI+	92	1	1	105	5	4
Propachlor	ESI+	98	2	1	109	6	4
Propamocarb	ESI+	96	2	1	122	3	4
Propaquizafop	ESI+	95	3	1	97	4	4
Propargite	ESI+	91	1	1	101	2	4
Propham	**ESI+**	**82 10**		**5**	**109 8**		**20**
Propiconazole	ESI+	88	2	1	96	3	4
Propoxur	ESI+	95	2	1	107	3	4
Propyzamide	ESI+	92	4	1	106	3	4
Proquinazid	ESI+	97	3	1	90	4	4
Prosulfocarb	ESI+	94	2	1	107	3	4
Pymetrozine	ESI+	27	10	1	99	3	4
Pyraclostrobin	ESI+	90	3	1	104	2	4
Pyrazophos	ESI+	95	1	1	99	4	4
Pyrethrum:							
Cinerin I (6%)	**ESI+**	**91**	**9**	**1**	**99**	**10**	**4**
Cinerin II (6%)	**ESI+**	**88**	**7 1**		**119**	**1 4**	
Jasmolin I (4%)	**ESI+**	**95 7**		**1**	**97 8**		**4**
Jasmolin II (2%)	**ESI+**	**83**	**10**	**1**	**105**	**17**	**4**
Pyrethrin I (50%)	**ESI+**	**94**	**4**	**1**	**104**	**5**	**4**
Pyrethrin II (30%)	**ESI+**	**90 3**		**1**	**97 5**		**4**
Pyridaben	ESI+	100	2	1	109	4	4
Pyridate	ESI+	83	6	1	76	9	4
Pyrifenox	ESI+	91	3	1	113	1	4
Pyrimethanil	ESI+	97	4	1	107	11	4
Pyriproxyfen	ESI+	92	2	1	103	3	4
Quinalphos	ESI+	93	5	1	101	9	4
Quinmerac	ESI+	90	5	1	105	8	4
Quinoxyfen	ESI+	90	2	1	109	3	4
Quizalofop	ESI-	95	6	5(+)/1(-)	98	5	20(+)/4(-)
Quizalofop-P-ethyl	ESI+	83	3	1	84	8	4
Resmethrin	ESI+	90	5	1	85	6	4
Rimsulfuron	ESI+	96	9	2	87	11	8
Simazine	ESI+	93	5	2	96	10	8
Simetryn	ESI+	92	2	1	107	4	4
Spinosad:							
Spinosyn A (70%)	ESI+	102	3	1	104	4	4
Spinosyn D (30%)	ESI+	108	4	1	99	3	4

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
Spiroxamin	ESI+	94	3	1	108	3	4
Sulfotep	ESI+	94	3	1	110	9	4
Tau-Fluvalinate	ESI+	89	7	2	91	11	8
Tebuconazole	ESI+	89	3	1	99	5	4
Tebufenozide	ESI+	91	3	1	100	7	4
Tebufenpyrad	ESI+	95	3	1	100	2	4
Teflubenzuron	ESI+	89	6	1	90	21	4
Tepraloxydim	ESI+	91	8	2	103	9	8
Terbufos	ESI+	80	10	1	115	5	4
Terbufos sulfon	ESI+	97	2	1	107	7	4
Terbufos sulfoxide	ESI+	94	2	1	108	3	4
Terbuthylazine	ESI+	96	1	1	104	3	4
Terbutryn	ESI+	95	3	1	115	4	4
Tetraconazole	ESI+	96	6	1	100	7	4
Thiabendazole	ESI+	90	3	1	104	5	4
Thiacloprid	ESI+	96	5	1	103	5	4
Thiamethoxam	ESI+	97	5	1	105	5	4
Thifensulfuron-methyl	ESI+	86	2	1	88	5	4
Thiodicarb	ESI+	95	5	1	84	5	4
Thiometon	**ESI+**	**91 12**		**5**	**108 5**		**20**
Thiophanate-methyl	ESI+	93	9	1	84	10	4
Tolclofos-methyl	ESI+	94	10	2	121	14	8
Tolylfluanid	ESI+	93	3	1	101	11	4
Triadimefon	ESI+	89	5	1	102	4	4
Triadimenol	ESI+	88	6	2	108	12	8
Triazamate	ESI+	95	3	1	108	2	4
Triazophos	ESI+	93	2	1	106	4	4
Trichlorfon	ESI+	96	2	1	105	7	4
Trifloxystrobin	ESI+	91	3	1	101	5	4
Triflumuron	ESI+	89	2	1	99	6	4
Triforine	ESI+	96	7	2	101	6	8
Vamidothion	ESI+	92	4	1	106	4	4
Vamidothion sulfon	ESI+	92	6	2	105	12	8
Vamidothion sulfoxid	**ESI+**	**84 10**		**5**	**118 6**		**20**
15-ADON	*ESI+*	*92*	*9*	*5*	*93*	*6*	*20*
3-ADON	*ESI-*	*90*	*2*	*10(+)/5(-)*	*100*	*2*	*40(+)/20(-)*
Aflatoxin B1	*ESI+*	*91*	*6*	*0.2*	*83*	*12*	*0.8*
Aflatoxin B2	*ESI+*	*88*	*2*	*0.2*	*103*	*6*	*0.8*
Aflatoxin G1	*ESI+*	*83*	*12*	*0.2*	*81*	*13*	*0.8*
Aflatoxin G2	*ESI+*	*80*	*7*	*0.2*	*102*	*6*	*0.8*
Altenuene	*ESI-*	*90*	*3*	*5(+)/1(-)*	*99*	*1*	*20(+)/4(-)*
Alternariol	*ESI-*	*88*	*1*	*20(+)/1(-)*	*103*	*2*	*80(+)/4(-)*
Alternariol methylether	*ESI-*	*89*	*3*	*20(+)/1(-)*	*104*	*2*	*80(+)/4(-)*

Analyte		Apple baby food, Spike 10 µg kg^{-1} (n=6)					
		Method A			Method B		
		Recovery (%)	RSD (%)	LOQ (µg kg^{-1})	Recovery (%)	RSD (%)	LOQ (µg kg^{-1})
aZOL	*ESI-*	*90*	*2*	*20(+)/1(-)*	*104*	*3*	*80(+)/4(-)*
bZOL	*ESI-*	*90*	*2*	*20(+)/1(-)*	*102*	*4*	*80(+)/4(-)*
Citrinin	*ESI+*	*89*	*4*	*5*	*96*	*5*	*20*
deepoxyDON	*ESI-*	*99*	*11*	*20(+)/5(-)*	*91*	*16*	*80(+)/20(-)*
Diacetoxyscirpenol	*ESI+*	*92*	*3*	*1*	*97*	*5*	*4*
DON	*ESI-*	*78*	*9*	*20(+)/5(-)*	*102*	*4*	*80(+)/20(-)*
DON-3-Glc	*ESI-*	*30*	*6*	*20(+)/5(-)*	*100*	*4*	*80(+)/20(-)*
Ergocornine	*ESI+*	*81*	*8*	*2*	*81*	*8*	*8*
Ergocorninine	*ESI+*	*87*	*6*	*2*	*110*	*9*	*8*
Ergocristine	*ESI+*	*86*	*6*	*2*	*84*	*11*	*8*
Ergocristinine	*ESI+*	*91*	*5*	*2*	*115*	*10*	*8*
Ergocryptine	*ESI+*	*84*	*7*	*2*	*87*	*11*	*8*
Ergocryptinine	*ESI+*	*98*	*6*	*2*	*106*	*9*	*8*
Ergosine/inine	*ESI+*	*96*	*3*	*2*	*92*	*8*	*8*
Fumonisin B1	*ESI+*	*74*	*9*	*5*	*94*	*7*	*20*
Fumonisin B2	*ESI+*	*77*	*5*	*5*	*96*	*5*	*20*
Fumonisin B3	*ESI+*	*73*	*12*	*5*	*91*	*13*	*20*
FUS X	*ESI-*	*99*	*3*	*20(+)/5(-)*	*102*	*6*	*80(+)/20(-)*
HT-2 toxin	*ESI+*	*93*	*3*	*5*	*97*	*8*	*20*
Neosolaniol	*ESI+*	*106*	*5*	*1*	*95*	*4*	*4*
NIV	*ESI-*	*73*	*9*	*100(+)/10(-)*	*100*	*3*	*400(+)/40(-)*
Ochratoxin A	*ESI+*	*109*	*5*	*1(+)/0.2(-)*	*87*	*7*	*4(+)/0.8(-)*
Ochratoxin alfa	*ESI-*	*91*	*11*	*2*	*97*	*7*	*8*
Patulin	*ESI-*	*87*	*4*	*10*	*93*	*3*	*40*
Sterigmatocystin	*ESI+*	*95*	*2*	*1*	*98*	*3*	*4*
T-2 tetraol	*ESI+*	*74*	*13*	*5*	*112*	*4*	*20*
T-2 toxin	*ESI+*	*95*	*2*	*1*	*100*	*3*	*4*
T-2 triol	*ESI+*	*100*	*5*	*1*	*102*	*12*	*4*
ZON	*ESI-*	*90*	*5*	*20(+)/1(-)*	*102*	*1*	*80(+)/4(-)*

*) Mycotoxins are in italic. In bold are less sensitive analytes, which validation data are based on 10× higher spiked concentrations.