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Comprehensive assessment of clean-up strategies for optimizing an analytical multi-method to determine pesticides and mycotoxins in Brazilian medicinal herbs using QuEChERS-LC-TQ-MS/MS

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The use of medicinal herbs has increased significantly. However, the presence of pesticide residues and mycotoxins in medicinal herbs has generated constant discussion and concern among regulatory agencies. Developing and validating an analytical method for determining pesticides and mycotoxins in medicinal plants is challenging due to the naturally occurring substances in these plants. The purpose of this work was to develop and to optimize a sensitive, accurate, precise, effective QuEChERS method for simultaneous determination of over 160 pesticide and mycotoxin residues in complex medicinal plant matrices using LC-TQ-MS/MS. A comprehensive comparison of clean-up procedures and other parameters was conducted to achieve this goal. The validation procedure was performed according to SANTE 11312/2021. More polar analytes, such as acephate, methamidophos and omethoate, presented a higher negative matrix effect in both *Melissa officinalis* L. and *Malva sylvestris* L. However, other molecules, such as spirodiclofen, showed a 24% signal enhancement in *M. officinalis* and a 46% signal suppression in *M. sylvestris*, indicating that a representative matrix-matched calibration would lead to inaccurate quantification of the analyte. Accuracy and precision were satisfactory according to SANTE 11312/2021 for 157 pesticide residues and mycotoxins in *M. officinalis* and for 152 molecules in *M. sylvestris*. LOQs at 10 μg kg^{-1} were achieved for 117 pesticides in *M. officinalis* and 99 pesticides in *M. sylvestris*. Among the mycotoxins, all four aflatoxins (B1, B2, G1 and G2) presented LOQs of 5 μg kg^{-1}, and ochratoxin A had an LOQ of 10 μg kg^{-1} in *M. officinalis*. The same LOQ values were shown for these mycotoxins in *M. sylvestris*, except for aflatoxin B2 and ochratoxin A, which had LOQs of 20 μg kg^{-1}. Moreover, in Southern Brazil, there has been no previous study on mycotoxin and pesticide contamination in medicinal herbs. Therefore, the application of this method was assessed through the analysis of forty-two real samples. Imidacloprid was found in *M. officinalis*, and methyl pirimiphos was found in *M. sylvestris*. The proposed method not only serves as a helpful tool for routine monitoring but also offers a basis for further research on risk assessment and control in food safety.

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Introduction

Brazil is one of the most biodiverse countries in the world, with plant species which have been widely used by the population for medicinal purposes as well as providing material for research into the search for new drugs against different diseases.[1] During recent years, the consumption of natural resources has gained notoriety for its increase along with national policies related to traditional and complementary medicine. Medicinal plants have been an essential part of ancient healthcare practices and have become a valuable resource in the treatment of illnesses and pathologies.[2]

Melissa officinalis L., popularly known as lemon balm, is an edible and medicinal plant belonging to the Lamiaceae. It has been traditionally used as a sedative, analgesic, and hypnotic,[3] and with its antioxidant effects being beneficial to the brain, as a treatment for memory disorders and Alzheimers.[4,5]

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Another plant that presents therapeutic properties is *Malva sylvestris* L., known as high mallow, which is another important medicinal plant and has been considered a good candidate for drug discovery.[6] Currently distributed worldwide, *M. sylvestris* presents anti-inflammatory properties mainly due to the presence of some flavonoids and mucilage. *M. sylvestris* has been used to treat many diseases, such as gingivitis, toothache, abdominal pain, gastrointestinal disorders, and diarrhea. In addition, its flowers are recommended for acne, the treatment of eczema, and inflammatory diseases.[7]

The growing demand for medicinal plants requires an increase in production and thus, it is necessary to protect them from pests, increase their production and shelf life whilst reducing post-harvest and storage losses. Therefore, like other plants, medicinal herbs can not only be exposed to pesticides during agricultural practices but also contaminated by mycotoxins during processing and storage.[8,9]

According to Sedova,[10] mycotoxins, pesticide residues, and toxic heavy metals are the most common chemical pollutants found in tea and medicinal herbs during production, storage, and consumption. Through eating polluted foods, chemical pollutants may cause significant health issues, such as carcinogenesis, immunosuppression, teratogenicity, as well as hepatotoxic, genotoxic, and nephrotoxic effects[11,12] and result in huge commercial losses. For these reasons, the quality and safety of medicinal plants are of big concern[13] and specific legislation for these matrices need to be created in order to control contamination by pesticide residues and mycotoxins. Since 2018, Brazilian legislation recommends the determination of pesticides according to RDC n° 105/2016 (ref. 14) and mycotoxins on herbal products, in all registration requests and post-registration petitions.

Several analytical methods can be used to identify and quantify this large variety of chemical compounds.[15] In an effort to reduce the number of methods needed to perform a complete chemical analysis, recent trends have focused on the development of multi-residue[16,17] and multi-class methods.[18–20] Development of improved methods for multi-mycotoxin and multi-pesticide analysis, including sample preparation and extraction and detection parameters, has become an increasingly large research field due to co-occurrence processes while still responding to the wide range of physicochemical properties and low residue levels found in different matrices.[21] These analyses are difficult since the analytes have varied properties and polarity. As a result, selecting the best extraction process can be difficult.[13,22]

Different methods for multi-compound analysis have been proposed for the analysis of mycotoxins and pesticides, in which ultra-performance liquid chromatography (UHPLC) coupled with tandem mass spectrometry (MS/MS) has become the technique of choice for the analysis of a wide range of contaminants in food. It allows the simultaneous determination and accurate quantification of several analytes at very low concentrations in complex matrices in a short chromatographic run time.[23,24] It is important to have effective and reliable analytical methods for the determination of mycotoxins and pesticides at the legislated levels in representative samples, not only to perform accurate risk assessments, but also to enforce the regulatory limits established worldwide.[21]

A QuEChERS (quick, easy, cheap, effective, rugged and safe) method originally used just for pesticide residue analysis in vegetables and fruits[16,17,25] has been further modified for pesticide determination in several matrices. Currently, this method is quickly becoming one of the most popular dispersive solid-phase extraction (d-SPE) methods in food safety.[26] Parameters such as time, solvent consumption, simplicity, selectivity, and sensitivity are crucial when considering an appropriate extraction/clean-up strategy.[21] According to recent investigations, different types of adsorbents, such as primary secondary amines (PSA), octadecyl (C18), and graphitized carbon black (GCB) have been used based on their physical and chemical properties.[27,28]

However, while many analytical methods have been reported for the determination of pesticides and mycotoxins in different foodstuffs,[29,30] there is a lack of a simple and generic method for the simultaneous determination of such residues in medicinal plants due to matrices complexity as well as the diversity of species. Due to low water content, natural pigments, essential oils, and a high number of undesired components such as sugars, phenolics, and flavonoids, medicinal plants present more complicated interference when compared with other matrices, like fruits and vegetables.[31] In addition, different species and parts of plants can affect analyte responses, making the development of analytical procedures a challenging task. Thus, it is necessary to develop a general multiclass-residue method to monitor different kinds of residues in medicinal plants, such as *M. officinalis* and *M. sylvestris*.

So far, there are no representative matrices for different medicinal parts and families, indicating that it is necessary to validate each medicinal plant separately. Additionally, even employing LC-MS/MS techniques for quantification, the present work is very significant considering that it is necessary to apply sample preparation for two distinct complex matrices whilst being able to minimize interference effects in addition to extracting with acceptable accuracy and precision the distinct classes of compounds (pesticides and mycotoxins).

The purpose of this work was to develop and optimize a sensitive, precise, effective QuEChERS method for the analysis of over 160 compounds in medicinal plant matrices by LC-MS/MS. As far as we know, the present study is the first method for simultaneous analysis of pesticides and mycotoxins in complex matrices such as *M. sylvestris* (flowers) and *M. officinalis* (leaves). In this matter, a comprehensive comparison of clean-up procedure efficiencies and other parameters were evaluated to achieve this goal. To ensure the adequate analysis of the selected mycotoxins and pesticides in medicinal plant samples, a validation process was ultimately performed for the most efficient extraction procedure. Moreover, in South Brazil, there has been no study on mycotoxin and pesticide contamination in medicinal herbs and an application of the method was assessed through the analysis of forty-two real samples. The proposed method not only works as a helpful tool for routine and surveillance monitoring but also offers a basis for further research on risk assessment and control in food safety.

Experimental

Chemicals and reagents

All reagents used were of at least analytical grade purity. Acetonitrile and acetone were obtained from Merck (Darmstadt, Germany), while methanol and toluene were purchased from Honeywell Chromasolv (Seelze, Germany). Anhydrous magnesium sulfate and sodium chloride were obtained from Êxodo Científica (São Paulo, Brazil), and formic acid from JT Baker (Deventer, Netherlands). Ultrapure water (resistivity of 18.2 MΩ cm) was obtained using a Milli-Q purification system (Millipore, Bedford, MA, USA).

Two dispersive SPE (d-SPE) kits (Agilent Technologies, Santa Clara, CA, USA) were used for clean-up purposes. These kits contained 25 mg of primary-secondary amine (PSA), 2.5 mg of graphitized carbon (GCB) and 150 mg of $MgSO_4$ (pigmented fruits and vegetables) (tests B and C – Table 1), or 25 mg of PSA, 7.5 mg of GCB and 150 mg of $MgSO_4$ (highly pigmented fruits and vegetables) (tests D and E – Table 1).

Reference standards

Reference standards of pesticides (purity > 97%) were obtained from Dr Ehrenstorfer (Augsburg, Germany), while the mycotoxin standards (purity > 98%) were obtained from Fermentek Biotechnology (Jerusalem, Israel) and Sigma-Aldrich (St. Louis, USA).

Individual stock solutions of pesticides (1000 mg L^{-1}) were prepared by dissolving the reference standards in toluene, methanol, or acetone, depending on their solubility. Similarly, individual stock solutions of mycotoxins (500 or 1000 mg L^{-1}) were prepared in acetonitrile or methanol. A standard mixture solution of 150 pesticides (1 mg L^{-1}) was prepared by diluting 100 μL of each stock solution in 100 mL of 0.1% formic acid in methanol (v/v). The 11 mycotoxins were divided into two groups based on their sensitivity in the liquid chromatographer-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) system. Group M1 included aflatoxins B1, B2, G1, G2, and ochratoxin A, while Group M2 included diacetoxyscirpenol (DAS), deoxynivalenol (DON), fumonisins B1 and B2, T2-toxin, zearalenone (ZEN). A solution containing 0.5 mg L^{-1} of standard mixture M1 and 25 mg L^{-1} of M2 was prepared by appropriately diluting the stock solutions with acetonitrile.

Analytical work solutions of pesticides and mycotoxins were prepared by suitably diluting the mixture solutions with acetonitrile. All solutions were stored at −18 °C in amber glass.

LC-MS/MS

Chromatographic analysis was performed using an Agilent 1260 prime II Liquid chromatography system coupled to a triple quadrupole mass spectrometer (LC-TQ-MS/MS) (ULTIVO, Agilent technologies, USA) with an Agilent Jet Stream Technology ion source (AJS), operating in dynamic multiple reaction monitoring (dMRM) mode. Chromatographic separations were carried out on an Infinity Lab Poroshell 120 EC1-C18 (2.1 mm i.d. O 100 mm O2.7 μm) reverse phase analytical column coupled to a pre-column (UHPLC GUARD Infinity Lab Poroshell) of the same stationary phase. Water (A) and acetonitrile (B), both acidified with 0.1% (v/v) formic acid, were used as the mobile phase at a constant flow rate of 0.3 mL min^{-1}. The gradient elution program ranged from 20 to 90% B from 0 to 5 min. This condition was maintained for 4 min, then changed to 95% B from 9 to 9.25 min and maintained for 2 min. Finally, the mobile phase was changed to the initial composition from 11.25 to 14 min. The chromatographic column was maintained at 45 °C (±0.5 °C) and the injection volume was 2 μL.

All mass spectrometer parameters were optimized using the Optimizer software version 1.1 (Agilent, USA).

Sample preparation

According to the Brazilian pharmacopeia,[32] the pharmacologically active parts of *M. officinalis* are the dried leaves, while for *M. sylvestris*, they are the entire or fragmented dried flowers. Therefore, all samples used as blank samples (free of pesticides and mycotoxins) were in accordance with Brazilian pharmacopeia criteria.

Commercially available organic samples identified by sellers as *M. officinalis* and *M. sylvestris* were purchased from local pharmacies in Santa Maria city, Brazil. These samples were checked for the absence of pesticides and mycotoxins before being used as blank samples for method optimization and validation.

Samples were obtained individually or in groups of packages with the same lot number, containing a minimum amount of 200 g, as recommended by sampling methods.[33] The dried

Table 1 Extraction protocols tested prior to validation

Extraction protocol	A B	C	D E
Slurry portion	10 g of *M. officinalis* (1 : 4 ratio) or 14 g of *M. sylvestris* (1 : 6 ratio)		
Extraction solvent	10 mL of acetonitrile		10 mL of acetonitrile + 1% formic acid
Partitioning salts	4 g $MgSO_4$ + 1 g NaCl		
Clean-up	— 1 mL upper layer to 25 mg of PSA, 2.5 mg of GCB and 150 mg of $MgSO_4$	1 mL upper layer to 50 mg of PSA, 5 mg of GCB and 300 mg of $MgSO_4$	1 mL upper layer to 25 mg of PSA, 7.5 mg of GCB and 150 mg of $MgSO_4$
Dilution	1 : 1		
Analysis	LC-MS/MS		

leaves and flowers were ground separately in a multiprocessor and sieved (granulometry 1 μm). Before the extraction procedure, the samples were hydrated for 30 min with ultrapure water 1 : 4 and 1 : 6 (w/w) for *M. officinalis* and *M. sylvestris*, respectively, at 8 °C, forming a slurry.

Extraction procedure

The extraction procedure employed was a modification of the QuEChERS method using the highly pigmented fruits and vegetables clean-up kit from Agilent Technologies. A slurry of 10 g (1 : 4 ratio) of *M. officinalis* leaves or 14 g (1 : 6 ratio) of *M. sylvestris* flowers was weighed in a 50 mL PTFE centrifuge tube. Subsequently, 10 mL of acetonitrile acidified with 1% formic acid was added, along with 40 μL of propoxur, which served as the internal standard solution. It should be noted that the concentration of propoxur in this study was 20 ng mL^{-1}. The tubes were shaken using an automatic mechanical shaker (Orbital Shaker 3016, Gesellschaft für Labortechnik mbH, Germany) for 1 minute. Following this, 4 g of magnesium sulfate and 1 g of sodium chloride were added, and the samples were vortexed for an additional 1 minute. The extracts were then centrifuged at 4000 rpm for 4 minutes, and 1 mL of the supernatant was transferred to a dispersive clean-up kit. After homogenizing the tubes in a vortex for 1 minute, they were centrifuged again (4000 rpm, 4 minutes), and 0.5 mL of the extract was transferred to a vial and diluted with 0.5 mL of acetonitrile/water (1 : 1, v/v) containing the injection internal standard solution of PCB-153 at a concentration of 100 ng mL^{-1}.

To develop a fast extraction protocol that causes less damage to the chromatographic system, which is robust and reliable, and still presents acceptable recovery rates, five preliminary studies were conducted to evaluate the accuracy, precision and matrix effects. For all tests, the slurries of *M. officinalis* and *M. sylvestris* samples were spiked ($n = 3$) at two different levels with pesticides (10 and 70 μg kg^{-1}) and mycotoxins (group 1 : 2 and 20 μg kg^{-1}; group 2 : 100 and 1000 μg kg^{-1}), simultaneously.

Solvent extraction evaluation

Since the proposed method aims to extract a variety of target analytes with different polarities, pK_a, and other chemical properties, two approaches were tested to evaluate the recovery rate of analytes. The first approach used pure acetonitrile according to the original QuEChERS method. The second approach employed acetonitrile acidified with 1% (v/v) formic acid to improve recovery, especially for mycotoxins.

Sorbent evaluation for clean-up

The absence of and different proportions of dispersive solid-phase extraction (d-SPE) sorbents (Table 1) were tested for selectivity, sensitivity, reliability, acceptable accuracy and precision, and to achieve less damage to the chromatographic system. Mixtures of primary secondary amine (PSA) and graphitized carbon black (GCB) were tested to remove pigments (mostly chlorophyll), sugars, lipids, flavonoids, acids, and carotenoids.[34]

Method performance

Analyte identification and confirmation were conducted according to SANTE document 11312/2021,[35] including retention time standard (±0.1 min), and at least two product ions with fully overlapping peaks and ion ratio within ± 30%.

Method validation

A validation protocol in accordance with SANTE document 11312/2021 (ref. 35) was conducted for the simultaneous determination of pesticides and mycotoxins in *M. officinalis* and *M. sylvestris*. The analytical method validation assessed the following parameters: sensitivity, selectivity, linearity of the analytical curves, matrix effects, trueness (expressed as recovery percentage), precision as repeatability RSDr and reproducibility (RSD_{WR}), limit of detection (LOD), and limit of quantification (LOQ).

For linearity, sensitivity, and matrix effect evaluation, seven different solutions for each concentration were prepared. For pesticides and mycotoxins of group 1, the concentrations of the solutions were 0.1, 0.5, 1, 5, 10, 25, 50 and 100 ng mL^{-1}. For mycotoxins of group 2 the concentrations of analytical solutions prepared in neat organic solvent (acetonitrile) and in blank *M. officinalis* and *M. sylvestris* extracts were 5, 25, 50, 250, 500, 1250, 2500 and 5000 ng mL^{-1}. Each solution was injected seven times.

The LOD was considered the lowest concentration level, injected repeatedly, obtained from 7 injections of an analytical solution prepared in blank matrix extract with a signal-to-noise ratio (S/N) ≥ 3. The LOQ was considered the lowest concentration level spiked with acceptable accuracy (70–120%) and precision (RSD ≤ 20%) obtained by the proposed analytical method.

Spiking/recovery experiments were performed by two different analysts on two different days to evaluate method reproducibility (RSD_{WR}). Matrix effects were calculated as described by Dias *et al.*[36] For accuracy (trueness and precision), recovery experiments were conducted by spiking blank *M. officinalis* and *M. sylvestris* at concentration levels of 10, 20, 50, and 70 μg kg^{-1} for pesticides; 2, 5, 10, and 20 μg kg^{-1} for mycotoxins of group 1; and 100, 250, 500, and 1000 μg kg^{-1} for mycotoxins of group 2. Seven replicates for each spiked level ($n = 7$) were performed by each analyst on two different days, totaling fourteen replicates ($n = 14$). All samples were extracted as mentioned in the section 'Extraction Procedure'.

Repeatability (RSDr) was calculated for each analyst from recovery experiments performed using the same extraction protocol, quantification method, system, and blank sample on the same day. Reproducibility (RSD_{WR}) was obtained *via* intermediate precision assessment by executing the same recovery experiments with different analysts, with a one-week interval between recovery experiments.

Sampling

The medicinal herb samples were obtained from the Public Market in Porto Alegre city, Rio Grande do Sul State, Brazil, due to the commercialization, consumer turnover, and location.

The samples were collected from 10 commercial stores between May 2021 and July 2022. Each sample consisted of at least 200 g of medicinal herbs, comprising 23 samples of *M. officinalis* leaves and 19 samples of *M. sylvestris* flowers, totaling 42 samples over the course of the study.

Results and discussion

Over the years, with the rise in food inspection and the escalating demand for quality control analyses, coupled with the need for promptly delivering results, multianalyte methods have garnered attention for their ability to analyze a diverse range of substances in a single operation. Methods enabling the simultaneous detection of pesticides and mycotoxins are available for various matrices, including fruits,[37] cereals,[38–40] wine,[41] eggs,[42] feed,[15,43,44] raw coffee,[45] and even some teas,[18,46] spices, medicinal herbs,[47] and infant milk formulae.[48]

While there are methods available for analyzing teas and spices, these primarily focus on green and black teas. Additionally, there is currently no validated method for the simultaneous analysis of mycotoxins and pesticides in medicinal herbs, specifically comparing the dried flowers of *M. sylvestris* and the dried leaves of *M. officinalis*.

Clean-up optimization

Each matrix submitted to an extraction protocol for the analysis of residues and contaminants must undergo an optimization process. This optimization improves the selectivity of the analytes, reduces the matrix effect, and achieves quantification limits at low concentration levels while maintaining the accuracy and precision required in an analytical method.

Medicinal herbs are particularly challenging matrices containing various extractable compounds such as pigments, essential oils, and flavonoids that may cause notable matrix effects in chromatographic analysis. The concern is not only about signal suppression caused by the co-extracts but also the potential damage caused to the systems, reducing the overall lifespan of the consumables. In addition, in long injection sequences, dirt can accumulate in the ionization source, decreasing the detectability along the sequence. Thus, a sample injected at the beginning and at the end of the sequence can present significant deviations in results, decreasing the accuracy and precision of the method.[34]

To improve method performance, different sorbent quantities were compared *via* recovery experiments, applying the following spike levels for mycotoxins groups: group 1: 2 and 20 μg kg^{-1}; group 2: 100 and 1000 μg kg^{-1}; and for pesticides: 10 and 70 μg kg^{-1}, $n = 3$.

No clean-up step and two d-SPE kits (25 mg PSA + 2.5 mg GCB + 150 mg $MgSO_4$ (tests B and C), and 25 mg PSA, 7.5 mg GCB + 150 mg of $MgSO_4$ (tests D and E)) were tested (Table 1). The results are shown in Fig. 1 and 2, respectively, for the mycotoxins and pesticides. The concentration levels 1 and 2 were, respectively, 10 and 50 μg kg^{-1} for the pesticides; 2 and 10 μg kg^{-1} for the mycotoxins of group 1; and 100 and 500 μg kg^{-1} for the mycotoxins of group 2.

When no clean-up step was conducted, a highly pigmented extract was obtained for both matrices, causing the extensive deposition of co-extractives in the ion source, decreasing precision and causing a significant loss in detectability within the same injection sequence.

To efficiently remove pigment interferences from the extracts, graphitized carbon black (GCB) is a worthy option. However, it might also retain specific analytes, such as aromatic compounds and/or planar pesticides, due to π–π interactions.[49] To mitigate this problem, small quantities of GCB were tested (2.5, 5 and 7.5 mg), with the latter being able to remove enough pigment while maintaining acceptable method accuracy and precision.

In this study, the final combination of PSA (25 mg) and GCB (7.5 mg) plus 150 mg of $MgSO_4$ was the most effective for removing matrix co-extracts while maintaining acceptable recoveries and avoiding significant damage to the LC-TQ-MS/MS system. For instance, cyprodinil presented recoveries ranging from 71% to 83% and proper precision (RSD < 18%) despite the use of GCB. These results were also verified by Ly *et al.*[50] who used GCB in green tea extraction and obtained

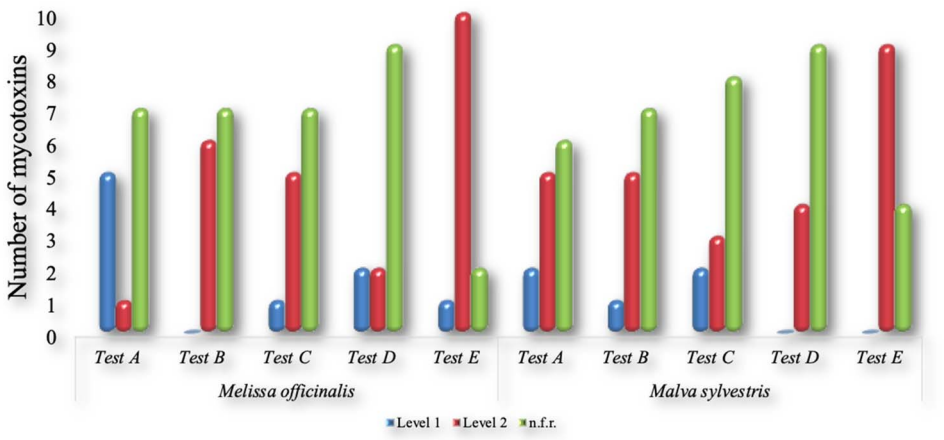

Fig. 1 Number of mycotoxins presenting recoveries within the range of 70–120% in assays A, B, C, D and E, for *M. officinalis* and *M. sylvestris*.

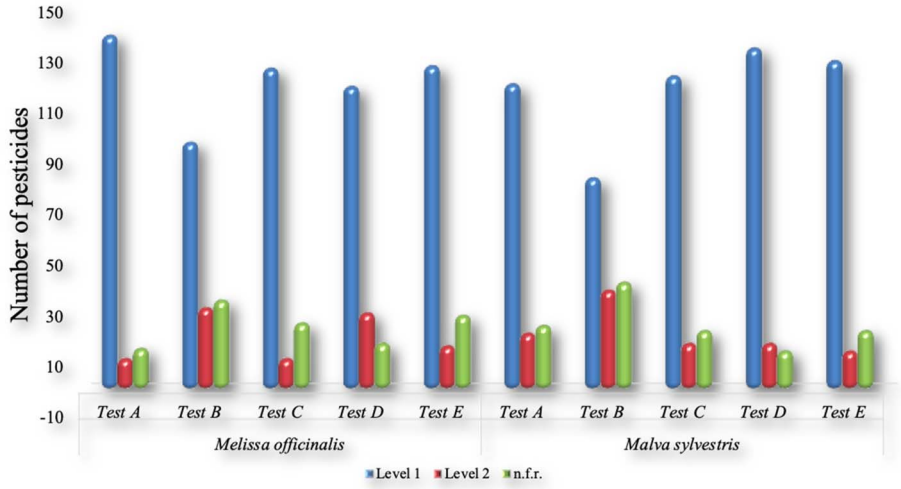

Fig. 2 Number of pesticides presenting recoveries within the range of 70–120% in assays A, B, C, D and E, for *M. officinalis* and *M. sylvestris*.

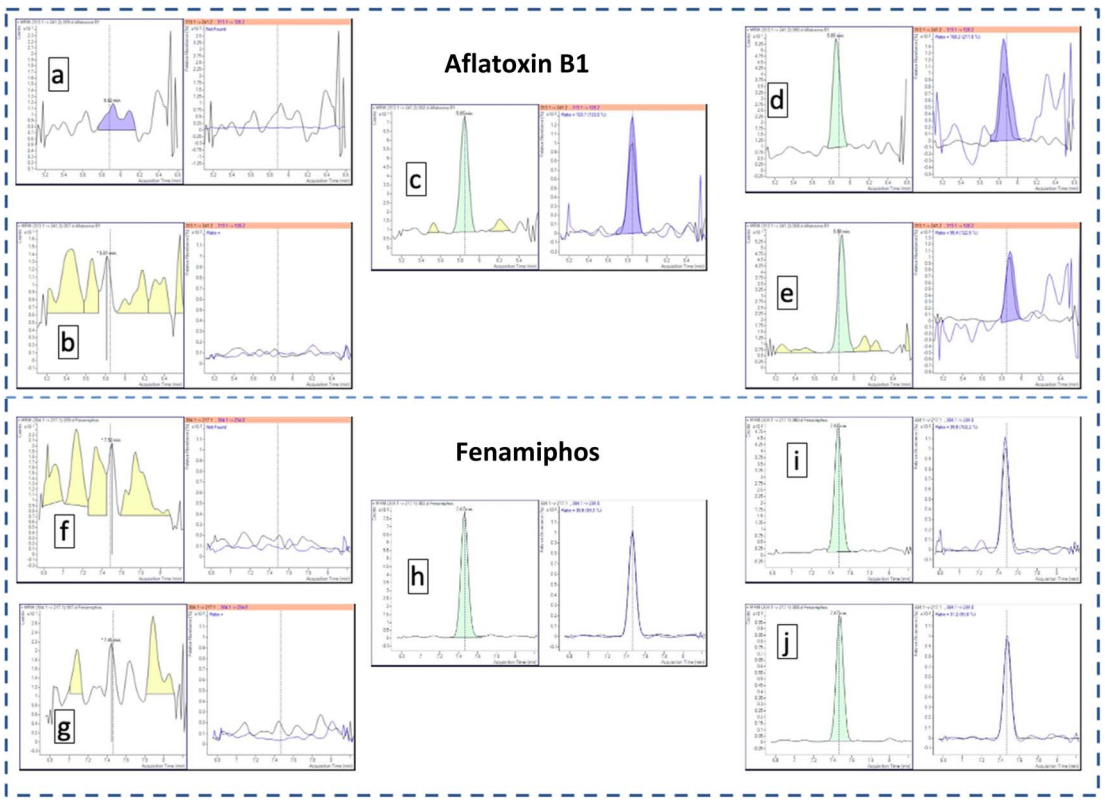

Fig. 3 Mycotoxin Aflatoxin B1 and pesticide Fenamiphos chromatograms obtained by analysis of: (a)(f) *M. sylvestris* blank extract, (b)(g) melissa blank extract, (c)(h) 1 ng mL^{-1} analytical solution in organic solvent, (d)(i) 1 ng mL^{-1} analytical solution in malva blank extract, (e)(j) 1 ng mL^{-1} analytical solution in *M. officinalis* blank extract.

satisfactory results for this pesticide. Fig. 3 represents a total ion chromatogram of two injections of the same vial, at the beginning and the end of a work list of over 100 injections and 16 h difference between those two injections, of fenamiphos and aflatoxin B1. No significant loss in precision was verified when comparing those two injections of both analytes.

Sample preparation optimization

Furthermore, the wide range of polarities, acidities and solubilities of pesticides and mycotoxins makes it challenging to develop and validate an appropriate analytical method for simultaneous determination. Additionally, representative food matrices belonging to the same food group (SANTE 11312/2021)

Table 2 Linear range, matrix effect (ME), LOD and LOQ for all analytes in *M. officinalis* and *M. sylvestris*

	Melissa officinalis				*Malva sylvestris*			
Pesticide/Mycotoxin	Linear range (μg kg^{-1})	ME (%)	LOD (μgkg^{-1})	LOQ (μg kg^{-1})	Linear range (μg kg^{-1})	ME (%)	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
Acephate	5–1000	−74	5	10	5–1000	−80	1	20
Acetamiprid	5–1000	−10	5	10	1–1000	50	1	10
Acetochlor	10–1000	−5	5	20	10–1000	−16	5	10
Aflatoxin B1[a]	**5–500**	−70	**1**	**5**	**5–500**	**−20**	**1**	**5**
Aflatoxin B2[a]	**5–500**	−71	**3**	**5**	**10–500**	**−17**	**1**	**20**
Aflatoxin G1[a]	**5–500**	−53	**3**	**5**	**5–1000**	**31**	**4**	**5**
Aflatoxin G2[a]	**5–500**	−12	**3**	**5**	**5–1000**	**9**	**1**	**5**
Aldicarb sulfone	1–500	−24	5	10	5–1000	−29	1	10
Aldicarb sulfoxide	5–500	−77	1	10	5–500	−76	5	10
Atrazine	5–1000	−17	1	10	5–500	−10	1	10
Azamethiphos	5–500	0	1	10	5–1000	−4	1	10
Azinphos-methyl	10–500	23	5	10	50–1000	−15	1	50
Azoxystrobin	5–500	55	1	10	10–500	29	1	10
Bifenazate	10–500	11	1	10	10–500	11	1	n.f.r.[b]
Bitertanol	5–1000	20	1	10	5–1000	−12	1	20
Boscalid	10–500	−8	1	10	5–500	−10	1	10
Bupirimate	5–500	−26	1	10	5–500	−21	1	10
Buprofezin	5–500	−32	1	10	5–500	−37	1	10
Cadusafos	10–500	8	1	10	5–1000	47	1	10
Carbaryl	5–500	−22	1	10	5–1000	−18	1	10
Carbendazin	5–500	−67	1	10	10–1000	−75	1	70
Carbofuran	5–500	−11	1	10	10–500	7	1	10
Carpropamid	5–500	−13	5	10	5–500	−28	1	20
Chlorantraniliprol	5–500	−5	5	20	5–1000	6	5	20
Chlorfenvinphos	10–500	13	1	10	5–500	3	5	10
Chlorpyrifos	5–500	−3	5	10	5–1000	−19	5	10
Clofentezine	10–1000	−25	8	10	10–1000	−7	8	10
Clomazone	10–500	−14	1	10	5–1000	−13	1	10
Clothianidin	10–1000	−14	8	10	5–1000	−2	5	10
Cyazofamid	50–500	−29	5	10	10–500	−36	5	20
Cyproconazol	10–500	7	5	10	5–1000	−14	5	10
Cyprodinil	5–500	−48	5	10	10–500	−48	5	10
Demeton-*S*-methyl sulfone	5–1000	9	5	10	5–1000	21	1	10
Demeton-*S*-methyl sulfoxide	10–1000	−72	5	10	5–1000	−71	1	20
Deoxynivalenol[a]	**250–5000**	−67	**50**	**250**	**250–5000**	**−65**	**250**	**500**
Diacetoxyscirpenol[a]	**250–5000**	−15	**25**	**250**	**500–2500**	**21**	**250**	**500**
Diazinon	10–500	−12	1	10	5–1000	2	1	10
Diethofencarb	10–500	17	1	10	50–1000	n.f.r.[b]	1	n.f.r.[b]
Difenoconazole	5–1000	−15	1	10	10–1000	−7	1	10
Diflubenzuron	50–1000	−18	10	n.f.r.[b]	50–1000	15	10	70
Dimethoate	1–1000	−23	1	10	1–1000	−3	1	10
Dimethomorph	10–500	42	1	10	50–500	50	1	10
Diniconazol	5–500	−8	5	10	5–1000	−10	1	10
Diphenylamine	5–1000	−17	1	10	5–500	−34	5	10
Diuron	10–500	−42	5	10	5–1000	−8	1	10
DMST	10–1000	−7	10	50	10–1000	5	10	50
Epoxiconazol	10–1000	−4	1	10	10–1000	15	1	10
Ethion	10–500	58	1	10	10–500	−5	1	10
Ethiprole	10–500	−15	1	10	10–500	−7	5	10
Ethoprophos	10–500	10	1	10	5–500	−7	5	10
Etofenprox	10–500	−10	1	10	5–1000	−6	1	10
Etoxazol	10–1000	−19	1	10	5–1000	−44	1	10
Fenamidone	5–500	3	1	10	5–500	5	1	10
Fenamiphos	10–500	78	1	10	5–1000	29	1	20
Fenarimol	5–1000	−17	5	20	5–500	15	1	50
Fenazaquin	5–500	30	1	10	5–1000	−29	1	10
Fenbuconazol	5–500	−2	1	10	5–500	7	5	20
Fenhexamid	10–500	−37	1	10	10–500	9	1	20
Fenobucarb	10–500	−19	1	10	10–500	−32	1	10
Fenoxycarb	10–500	−31	5	20	10–1000	−40	1	20

Table 2 (*Contd.*)

	Melissa officinalis				*Malva sylvestris*			
Pesticide/Mycotoxin	Linear range (μg kg^{-1})	ME (%)	LOD (μgkg^{-1})	LOQ (μg kg^{-1})	Linear range (μg kg^{-1})	ME (%)	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
Fenpropimorph	5–1000	−13	1	10	5–1000	−14	1	10
Fenpyroximate	5–500	−4	1	10	5–1000	−16	1	10
Fensulfothion	50–1000	39	5	50	50–1000	23	10	50
Fluazifop-butyl	10–500	−5	1	10	5–1000	7	1	10
Fludioxonil	5–1000	−17	5	10	10–500	−20	1	10
Flufenoxuron	10–500	−42	1	10	50–1000	−24	20	50
Fluquinconazol	10–1000	−25	10	20	5–500	−25	1	20
Flusilazol	5–500	−8	1	10	5–500	−26	1	10
Flutolanil	50–1000	−2	1	50	5–1000	−10	1	20
Flutriafol	10–1000	−9	8	10	5–500	2	1	10
Fosthiazate	10–1000	7	1	10	5–1000	−6	1	10
Fumonisin B1[a]	**250–5000**	51	**250**	**500**	**250–5000**	**−1**	**250**	**n.f.r.**[b]
Fumonisin B2[a]	**250–5000**	−16	**250**	**500**	**250–5000**	**−31**	**500**	**n.f.r.**[b]
Furalaxyl	10–500	18	1	10	5–500	20	1	20
Furathiocarb	5–1000	8	1	10	5–1000	4	1	10
Halofenozide	50–1000	−23	10	50	10–1000	−33	10	n.f.r.[b]
Haloxyfop-2-ethoxyethyl	5–1000	−8	1	10	5–1000	−41	1	n.f.r.[b]
Hexaconazol	5–1000	−16	5	10	5–1000	−31	5	10
Hexytiazox	5–1000	−6	1	10	1–1000	−42	1	10
Imazalil	10–1000	−26	10	20	10–1000	−22	5	10
Imazapic	5–500	−32	5	10	10–500	5	5	10
Imazetapyr	5–1000	3	1	10	5–1000	35	5	10
Imidacloprid	5–1000	31	1	10	10–1000	98	8	10
Indoxacarb	5–1000	34	1	20	5–1000	97	5	10
Iprovalicarb	5–1000	20	1	10	5–1000	−6	1	10
Isoxaflutole	5–1000	−30	5	50	50–1000	−20	10	50
Kresoxim-methyl	5–1000	−16	1	10	5–1000	−16	5	20
Linuron	50–1000	−40	10	50	50–1000	−32	20	50
Lufenuron	10–500	−58	8	10	5–500	−84	5	10
Malathion	5–1000	14	1	10	5–1000	11	5	20
Mecarbam	5–1000	5	5	10	5–1000	4	1	10
Mepanipyrim	5–500	−44	1	20	10–1000	−17	10	50
Metalaxyl	5–1000	23	1	20	10–1000	33	1	10
Metconazole	5–1000	−75	5	20	5–1000	−29	5	20
Methamidophos	50–1000	−77	10	50	10–1000	−76	5	70
Methidathion	10–1000	−5	10	20	50–1000	−31	5	n.f.r.[b]
Methiocarb	5–1000	−33	5	20	5–1000	−30	5	20
Methomyl	5–1000	−10	1	10	5–500	−21	1	10
Methoxyfenozide	5–1000	31	1	10	5–500	15	1	20
Monocrotophos	1–1000	−62	1	10	10–1000	−57	1	20
Myclobutanil	5–1000	−45	1	10	5–1000	−1	1	10
Nitenpyram	10–1000	−76	5	50	50–1000	−82	1	70
Ochratoxin A[a]	**10–1000**	20	**8**	**10**	**10–1000**	**6**	**10**	**20**
Ofurace	10–500	46	1	10	5–1000	59	1	10
Omethoate	5–1000	−76	1	10	n.f.r.[b]	−76	n.f.r.[b]	n.f.r.[b]
Oxadixyl	10–500	5	5	10	5–1000	−10	1	10
Oxamyl	5–1000	−20	1	10	5–1000	−35	1	10
Paclobutrazol	10–1000	2	10	20	5–500	−4	1	10
Penconazole	5–500	−22	1	10	10–1000	−29	1	10
Pencycuron	5–1000	6	1	10	5–1000	64	1	10
Pendimethalin	5–500	−4	5	10	5–1000	−21	1	10
Phenothrin	50–1000	−19	20	50	50–1000	2	20	50
Phenthoate	5–500	−28	5	10	5–500	−21	1	10
Phosalone	50–1000	−4	10	50	50–1000	2	20	50
Phosmet	50–1000	−8	5	50	5–1000	−21	5	20
Picoxystrobin	5–500	−18	1	10	10–1000	−22	1	10
Piperonyl butoxide	5–1000	−25	1	10	5–1000	−27	1	10
Pirimicarb	5–1000	−21	1	10	5–1000	−17	1	10
Pirimiphos-ethyl	1–1000	−15	1	10	5–1000	−25	1	10
Pirimiphos-methyl	5–1000	−20	1	10	5–1000	−15	1	10

Table 2 (*Contd.*)

Pesticide/Mycotoxin	Melissa officinalis				*Malva sylvestris*			
	Linear range (μg kg^{-1})	ME (%)	LOD (μgkg^{-1})	LOQ (μg kg^{-1})	Linear range (μg kg^{-1})	ME (%)	LOD (μg kg^{-1})	LOQ (μg kg^{-1})
Prochloraz	1–1000	11	1	10	5–1000	6	1	10
Profenofos	5–500	−29	1	10	5–1000	−45	1	20
Prometryn	5–1000	−22	1	10	5–1000	−20	1	10
Propamocarb	10–500	−36	1	n.f.r.[b]	10–500	−61	1	70
Propanil	1–1000	−26	10	50	5–1000	−21	5	50
Prophan	10–1000	−33	8	10	50–1000	−8	20	50
Propiconazol	5–500	−13	1	10	5–500	5	1	10
Propyzamide	10–1000	−19	8	10	5–1000	22	5	10
Pyraclostrobin	5–1000	−27	1	10	5–1000	−25	1	10
Pyrazophos	10–500	35	5	10	5–1000	50	1	10
Pyridaben	5–1000	−9	1	10	5–1000	−58	1	10
Pyrimethanil	5–500	−38	1	10	5–1000	−31	1	10
Pyriproxyfen	5–500	−24	1	10	5–1000	−30	1	10
Quinalphos	1–1000	−42	1	10	5–500	−18	5	10
Quinoxyfen	1–1000	−16	1	10	5–1000	−15	1	10
Simazine	5–500	−35	1	10	10–1000	−23	5	10
Spinosyn A	5–1000	−39	1	10	5–1000	−25	1	20
Spinosyn D	5–1000	−35	5	10	5–1000	−35	5	10
Spirodiclofen	5–500	24	5	50	5–500	−46	5	10
Spiromesifen	5–500	19	5	20	10–1000	−58	10	20
Spiroxamine	1–1000	−11	1	10	1–1000	−11	1	10
Tau-fluvalinate	50–1000	19	50	70	50–1000	−55	10	50
Tebuconazol	5–500	8	5	10	5–500	14	1	10
Tebufenozide	5–1000	−12	1	20	5–500	−14	1	10
Tebufenpyrad	5–500	−15	5	10	5–1000	−35	1	10
Terbutryn	5–1000	−37	1	10	5–1000	−20	1	10
Tetrachlorvinphos	10–1000	−13	10	50	50–1000	−58	10	50
Tetraconazole	5–500	0	5	10	10–1000	−4	5	10
Tetramethrin	10–1000	−4	8	10	10–500	−13	5	10
Thiacloprid	1–500	−8	1	10	5–500	2	1	10
Thiamethoxam	5–1000	−7	5	70	5–500	17	1	10
Thiodicarb	5–500	−2	5	10	10–1000	55	1	n.f.r.[b]
Toxin T2[a]	**50–2500**	−12	**25**	**500**	**250–50 000**	**3**	**5**	**1000**
Triadimefon	10–1000	9	8	10	10–1000	49	1	10
Triadimenol	10–1000	21	8	n.f.r.[b]	1–500	23	1	70
Triazophos	5–500	20	1	10	10–1000	−22	1	20
Trifloxystrobin	5–500	−8	1	10	5–1000	−45	1	10
Triflumizol	5–1000	−40	1	10	10–1000	−40	1	10
Triticonazol	1–1000	4	1	10	5–500	−6	1	10
Zearalenone[a]	**25–2500**	−31	**25**	**250**	**250–25 000**	**−35**	**25**	**500**
Zoxamide	5–500	−19	5	10	5–500	−21	5	10

[a] Mycotoxins. [b] n.f.r.: not fulfill requirements of SANTE document.

are often used for optimization of time, reagents, and other parameters. However, in the case of dry medicinal plants, which contain a larger number of secondary metabolites (such as flavonoids, saponins and alkaloids), using a single representative matrix may present weaknesses in quantification due to differences in analytical signal suppression and enhancement in the LC-TQ-MS/MS system.

For matrices with low water content, it is recommended to add water to increase the extraction efficiency. Therefore, a slurry was prepared with cold water (8 °C) for matrix rehydration (≈30 minutes) to facilitate the extraction of the analytes and prevent matrix components from being extracted and interfering with the instrumental analysis.

Analytical method validation

The validation data summarized in Table 2 show the linear range, matrix effect, LOQ, and LOD. Tables 3 and 4 demonstrate recoveries, precision (RSDr) and intermediate precision (RSD_{WR}) for *M. officinalis* and *M. sylvestris* obtained from the method validation procedure for all spike levels studied.

For all pesticides and mycotoxins, the criterion for linearity was $r^2 \geq 0.99$ and the deviation of back-calculated

Table 3 Average recoveries, precision (RSDr) and intermediate precision (RSD_{WR}) obtained for *M. officinalis* from the method validation procedure

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Acephate	82 (16)	76 (15)	79 (15)	0.214	82 (8)	74 (11)	78 (11)	0.156	81 (5)	80 (20)	81 (14)	0.949	91 (8)	85 (10)	88 (9)	0.109
Acetamiprid	99 (15)	85 (7)	92 (14)	0.071	87 (14)	76 (6)	81 (13)	0.075	95 (16)	83 (11)	89 (16)	0.102	83 (16)	79 (5)	81 (12)	0.496
Acetochlor	90 (27)	81 (12)	86 (22)	0.424	91 (14)	78 (12)	84 (15)	0.139	88 (14)	87 (16)	88 (15)	0.926	87 (9)	82 (15)	84 (12)	0.526
Aflatoxin B1[a]	**60 (60)**	**114 (26)**	**87 (48)**	**0.000**	**99 (18)**	**95 (19)**	**97 (17)**	**0.785**	**88 (16)**	**104 (13)**	**96 (17)**	**0.112**	**84 (17)**	**97 (8)**	**91 (14)**	**0.138**
Aflatoxin B2[a]	**77 (19)**	**31 (0)**	**54 (47)**	**0.000**	**83 (12)**	**95 (15)**	**89 (15)**	**0.196**	**87 (18)**	**92 (8)**	**90 (13)**	**0.406**	**83 (7)**	**89 (8)**	**86 (8)**	**0.056**
Aflatoxin G1[a]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**86 (19)**	**83 (18)**	**84 (18)**	**0.543**	**85 (9)**	**88 (6)**	**87 (8)**	**0.418**	**91 (14)**	**99 (5)**	**95 (11)**	**0.083**
Aflatoxin G2[a]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**102 (19)**	**79 (6)**	**90 (20)**	**0.035**	**97 (15)**	**81 (11)**	**89 (16)**	**0.093**	**80 (12)**	**73 (6)**	**77 (11)**	**0.060**
Aldicarb sulfone	98 (15)	91 (14)	95 (15)	0.302	98 (8)	91 (11)	95 (10)	0.064	106 (5)	113 (16)	110 (12)	0.361	103 (14)	106 (11)	105 (12)	0.547
Aldicarb sulfoxide	94 (19)	81 (15)	87 (18)	0.212	83 (13)	75 (16)	79 (14)	0.334	80 (14)	75 (5)	77 (11)	0.224	81 (4)	82 (8)	81 (6)	0.762
Atrazine	100 (10)	89 (12)	95 (12)	0.163	91 (8)	83 (11)	87 (10)	0.083	88 (4)	78 (12)	83 (10)	0.019	83 (9)	76 (9)	79 (10)	0.052
Azamethiphos	85 (15)	75 (3)	80 (13)	0.114	87 (11)	75 (7)	81 (12)	0.060	86 (12)	78 (22)	82 (17)	0.217	96 (7)	84 (15)	90 (13)	0.155
Azinphos-methyl	88 (16)	81 (16)	85 (16)	0.431	92 (18)	102 (6)	97 (13)	0.196	80 (8)	74 (4)	77 (7)	0.141	96 (14)	105 (4)	101 (11)	0.087
Azoxystrobin	95 (13)	99 (6)	97 (10)	0.493	91 (9)	81 (8)	86 (10)	0.060	85 (10)	78 (18)	81 (14)	0.236	83 (18)	71 (5)	77 (16)	0.091
Bifenazate	78 (9)	86 (9)	82 (10)	0.081	84 (16)	91 (1)	88 (11)	0.283	72 (3)	69 (8)	71 (6)	0.260	86 (15)	99 (8)	93 (13)	0.072
Bitertanol	85 (13)	81 (16)	83 (14)	0.505	85 (13)	77 (15)	81 (14)	0.076	91 (7)	87 (20)	89 (14)	0.490	90 (8)	96 (20)	93 (15)	0.480
Boscalid	96 (12)	107 (12)	101 (13)	0.119	94 (7)	99 (5)	96 (6)	0.256	87 (3)	80 (11)	84 (9)	0.108	83 (8)	80 (20)	81 (14)	0.764
Bupirimate	98 (9)	91 (11)	94 (10)	0.094	89 (7)	84 (15)	86 (12)	0.303	85 (3)	80 (18)	82 (13)	0.409	80 (8)	74 (10)	77 (10)	0.117
Buprofezin	90 (11)	79 (19)	85 (16)	0.165	86 (5)	76 (19)	81 (14)	0.153	83 (2)	75 (18)	79 (13)	0.177	74 (15)	86 (16)	80 (17)	0.196
Cadusafos	96 (10)	98 (8)	97 (9)	0.735	91 (6)	101 (14)	96 (12)	0.053	87 (5)	77 (16)	82 (13)	0.141	87 (9)	83 (16)	85 (13)	0.496
Carbaryl	93 (11)	78 (18)	85 (16)	0.089	89 (11)	83 (7)	86 (10)	0.197	85 (10)	77 (11)	81 (12)	0.061	78 (18)	87 (2)	83 (13)	0.159
Carbendazim	79 (9)	72 (14)	75 (12)	0.258	74 (11)	77 (19)	76 (15)	0.517	72 (15)	80 (11)	76 (14)	0.137	71 (6)	74 (6)	72 (6)	0.35
Carbofuran	111 (9)	100 (13)	106 (12)	0.082	111 (11)	99 (8)	105 (11)	0.073	118 (8)	108 (16)	113 (13)	0.080	113 (11)	103 (5)	108 (9)	0.083
Carpropamid	84 (18)	94 (17)	89 (18)	0.306	82 (14)	95 (19)	88 (18)	0.161	83 (12)	96 (12)	89 (14)	0.115	97 (13)	103 (12)	100 (12)	0.387
Chlorantraniliprole	56 (41)	39 (37)	48 (43)	0.247	82 (18)	86 (19)	84 (18)	0.579	96 (15)	85 (19)	90 (17)	0.240	92 (9)	77 (17)	85 (15)	0.074
Chlorfenvinphos	92 (18)	108 (10)	100 (16)	0.134	94 (13)	101 (4)	97 (10)	0.156	80 (9)	79 (5)	80 (7)	0.749	85 (16)	85 (5)	85 (12)	0.931
Chlorpyrifos	101 (15)	92 (19)	96 (17)	0.339	97 (20)	106 (19)	102 (19)	0.335	76 (10)	72 (8)	74 (9)	0.336	84 (12)	79 (8)	82 (11)	0.272
Clofentezine	83 (17)	99 (7)	91 (15)	0.065	100 (9)	110 (14)	105 (13)	0.170	78 (14)	73 (10)	75 (13)	0.370	91 (15)	79 (10)	85 (15)	0.054
Clomazone	88 (15)	80 (6)	84 (12)	0.193	90 (8)	83 (7)	87 (9)	0.060	85 (5)	77 (16)	81 (12)	0.216	83 (16)	75 (15)	79 (16)	0.388
Clothianidin	89 (18)	77 (8)	83 (16)	0.076	98 (7)	85 (22)	91 (16)	0.145	99 (11)	87 (14)	93 (14)	0.07	90 (11)	79 (9)	84 (12)	0.134
Cyazofamid	103 (16)	100 (14)	101 (15)	0.765	83 (13)	76 (10)	79 (12)	0.132	88 (9)	76 (19)	82 (15)	0.172	95 (8)	82 (19)	88 (15)	0.095
Cyproconazole	102 (10)	105 (10)	103 (10)	0.641	82 (12)	81 (10)	81 (10)	0.808	87 (4)	80 (13)	84 (10)	0.159	83 (13)	72 (5)	78 (12)	0.057
Cyprodinil	83 (10)	79 (4)	81 (8)	0.475	77 (6)	72 (13)	75 (10)	0.407	71 (6)	75 (10)	73 (9)	0.476	73 (4)	79 (8)	76 (8)	0.063
Demeton-*S*-methyl sulfone	103 (17)	95 (3)	99 (13)	0.254	96 (8)	89 (12)	93 (11)	0.176	94 (4)	83 (18)	89 (13)	0.095	96 (20)	80 (9)	88 (19)	0.075
Demeton-*S*-methyl sulfoxide	86 (9)	97 (17)	91 (15)	0.163	90 (18)	78 (4)	84 (16)	0.083	79 (12)	75 (20)	77 (16)	0.455	79 (12)	73 (11)	76 (12)	0.359
Deoxynivalenol[a]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**n.f.r.**[b]	**89 (9)**	**101 (16)**	**95 (15)**	**0.092**	**86 (14)**	**97 (5)**	**91 (12)**	**0.077**	**84 (9)**	**78 (2)**	**81 (8)**	**0.054**
Diacetoxyscirpenol[a]	**67 (17)**	**128 (161)**	**98 (148)**	**0.000**	**85 (15)**	**90 (1)**	**88 (11)**	**0.353**	**81 (11)**	**76 (1)**	**79 (8)**	**0.144**	**97 (10)**	**99 (9)**	**98 (9)**	**0.697**
Diazinon	95 (10)	101 (8)	98 (10)	0.266	94 (5)	99 (10)	97 (8)	0.322	92 (4)	84 (6)	88 (7)	0.052	87 (8)	84 (6)	86 (7)	0.467

Table 3 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	
	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value
Diethofencarb	91 (14)	79 (9)	85 (14)	0.124	89 (10)	80 (7)	85 (10)	0.127	87 (7)	88 (7)	88 (7)	0.648	81 (15)	88 (7)	84 (12)	0.175
Difenoconazole	94 (16)	81 (13)	87 (16)	0.073	91 (10)	83 (3)	87 (9)	0.051	81 (6)	72 (15)	76 (12)	0.094	80 (12)	73 (1)	76 (9)	0.095
Diflubenzuron	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.	n.f.r.
Dimethoate	103 (16)	87 (10)	95 (16)	0.073	100 (11)	91 (9)	95 (11)	0.180	98 (9)	85 (13)	91 (13)	0.091	89 (17)	88 (3)	88 (12)	0.799
Dimethomorph	96 (20)	81 (15)	89 (19)	0.059	101 (9)	94 (12)	98 (11)	0.185	87 (15)	77 (12)	82 (15)	0.110	91 (17)	81 (17)	86 (17)	0.278
Diniconazole	89 (19)	78 (9)	83 (16)	0.159	88 (10)	83 (13)	86 (11)	0.141	86 (8)	76 (11)	81 (11)	0.071	83 (14)	72 (8)	78 (13)	0.097
Diphenylamine	86 (19)	83 (1)	84 (13)	0.590	88 (17)	78 (16)	83 (17)	0.196	90 (16)	78 (15)	84 (17)	0.112	82 (11)	76 (14)	79 (13)	0.183
Diuron	83 (19)	81 (10)	82 (15)	0.687	81 (13)	72 (12)	76 (13)	0.220	78 (12)	74 (15)	76 (13)	0.567	82 (12)	70 (11)	76 (14)	0.095
DMST	64 (57)	90 (21)	77 (40)	0.188	88 (34)	62 (27)	75 (36)	0.072	97 (16)	83 (14)	90 (17)	0.149	107 (13)	93 (15)	100 (15)	0.099
Epoxiconazole	113 (19)	93 (7)	103 (17)	0.058	94 (20)	82 (4)	88 (16)	0.148	86 (9)	74 (19)	80 (16)	0.116	89 (8)	81 (13)	85 (11)	0.161
Ethion	84 (16)	79 (15)	81 (15)	0.502	83 (20)	95 (8)	89 (15)	0.130	77 (11)	78 (0)	77 (8)	0.831	84 (16)	78 (0)	81 (12)	0.300
Ethiprole	95 (14)	97 (6)	96 (11)	0.689	90 (19)	103 (17)	97 (18)	0.238	90 (17)	93 (7)	92 (13)	0.632	91 (10)	82 (19)	86 (15)	0.113
Ethoprophos	101 (13)	86 (7)	94 (13)	0.060	96 (9)	84 (12)	90 (12)	0.080	89 (6)	81 (14)	85 (11)	0.106	88 (12)	80 (14)	84 (13)	0.175
Etofenprox	93 (8)	86 (11)	89 (10)	0.124	89 (6)	86 (5)	87 (6)	0.215	75 (8)	83 (6)	79 (9)	0.072	82 (11)	82 (6)	82 (9)	0.990
Etoxazole	89 (10)	75 (16)	82 (15)	0.101	84 (4)	79 (11)	81 (8)	0.112	81 (4)	75 (15)	78 (11)	0.302	80 (11)	75 (15)	78 (13)	0.306
Fenamidone	94 (14)	101 (19)	97 (17)	0.573	88 (7)	97 (11)	92 (10)	0.069	91 (15)	93 (7)	92 (11)	0.638	86 (12)	95 (7)	90 (11)	0.130
Fenamiphos	91 (14)	94 (1)	93 (10)	0.560	88 (8)	84 (11)	86 (9)	0.381	83 (8)	81 (10)	82 (9)	0.581	82 (15)	73 (17)	78 (16)	0.113
Fenarimol	98 (47)	89 (1)	94 (34)	0.610	88 (13)	101 (16)	94 (16)	0.077	92 (13)	86 (19)	89 (16)	0.188	85 (8)	81 (4)	83 (7)	0.076
Fenazaquin	89 (11)	94 (6)	91 (9)	0.427	85 (8)	100 (16)	93 (15)	0.056	81 (9)	77 (14)	79 (12)	0.443	85 (11)	76 (14)	81 (14)	0.098
Fenbuconazole	115 (15)	104 (5)	110 (13)	0.199	95 (15)	109 (19)	102 (18)	0.280	89 (7)	86 (10)	88 (9)	0.419	91 (20)	86 (10)	88 (16)	0.509
Fenhexamid	107 (19)	108 (15)	107 (16)	0.892	99 (11)	85 (20)	92 (16)	0.071	87 (9)	74 (15)	80 (14)	0.072	87 (10)	78 (9)	83 (11)	0.062
Fenobucarb	86 (17)	75 (18)	81 (18)	0.070	93 (4)	86 (12)	89 (9)	0.136	92 (5)	89 (17)	90 (12)	0.696	81 (17)	73 (16)	77 (17)	0.334
Fenoxycarb	74 (43)	11 (444)	42 (121)	0.002	94 (15)	87 (18)	91 (16)	0.498	83 (18)	73 (11)	78 (16)	0.140	80 (18)	71 (11)	76 (16)	0.132
Fenpropimorph	84 (15)	76 (6)	80 (13)	0.112	77 (5)	74 (5)	76 (5)	0.213	77 (3)	73 (8)	75 (7)	0.093	77 (5)	75 (9)	76 (7)	0.316
Fenpyroximate	88 (12)	92 (4)	90 (9)	0.406	87 (16)	103 (12)	95 (16)	0.079	78 (15)	74 (11)	76 (13)	0.543	83 (20)	73 (11)	78 (17)	0.287
Fensulfothion	−41 (0)	941 (3)	450 (113)	0.000	−20 (0)	493 (2)	236 (113)	0.000	97 (15)	105 (8)	101 (12)	0.234	92 (16)	108 (8)	100 (14)	0.071
Fluazifop-butyl	92 (13)	95 (8)	94 (10)	0.652	101 (11)	109 (13)	105 (12)	0.318	87 (8)	74 (14)	80 (13)	0.064	89 (15)	74 (14)	81 (17)	0.071
Fludioxonil	85 (16)	92 (17)	88 (17)	0.349	100 (18)	100 (13)	100 (15)	0.983	84 (19)	89 (13)	86 (16)	0.372	79 (18)	89 (13)	84 (16)	0.130
Flufenoxuron	105 (9)	89 (18)	97 (16)	0.072	96 (14)	87 (7)	91 (12)	0.151	95 (12)	85 (12)	90 (13)	0.058	81 (14)	72 (8)	77 (13)	0.125
Fluquinconazole	82 (13)	78 (17)	80 (15)	0.592	102 (15)	103 (6)	102 (11)	0.757	90 (14)	79 (12)	84 (14)	0.103	77 (11)	68 (12)	73 (13)	0.120
Flusilazole	96 (12)	112 (12)	104 (14)	0.107	90 (7)	85 (15)	88 (12)	0.320	87 (3)	84 (4)	86 (4)	0.258	83 (8)	72 (19)	77 (15)	0.081
Flutolanil	98 (15)	108 (7)	103 (12)	0.124	90 (7)	89 (15)	90 (11)	0.857	88 (8)	80 (13)	84 (11)	0.135	86 (14)	80 (13)	83 (13)	0.191
Flutriafol	98 (17)	107 (10)	103 (14)	0.303	87 (17)	100 (16)	94 (17)	0.226	87 (9)	88 (10)	87 (9)	0.889	82 (9)	90 (10)	86 (10)	0.088
Fosthiazate	92 (12)	81 (8)	87 (12)	0.067	91 (12)	81 (17)	86 (15)	0.146	87 (11)	76 (8)	81 (12)	0.014	92 (17)	77 (10)	84 (17)	0.066
Fumonisin B1[a]	**378 (2)**	**378 (2)**	**378 (1)**	**n.f.r.**[b]	**152 (3)**	**152 (3)**	**152 (3)**	**n.f.r.**[b]	**77 (4)**	**78 (3)**	**78 (3)**	**0.083**	**94 (5)**	**93 (5)**	**94 (5)**	**0.724**
Fumonisin B2[a]	**351 (1)**	**351 (1)**	**351 (1)**	**0.819**	**147 (3)**	**149 (3)**	**148 (3)**	**0.085**	**77 (5)**	**78 (3)**	**78 (4)**	**0.356**	**75 (3)**	**83 (11)**	**79 (10)**	**0.107**
Furalaxyl	93 (9)	79 (19)	86 (16)	0.055	91 (5)	85 (13)	88 (10)	0.266	88 (6)	77 (13)	82 (12)	0.081	88 (11)	75 (10)	81 (13)	0.054
Furathiocarb	93 (12)	98 (7)	96 (10)	0.437	88 (11)	85 (17)	87 (14)	0.668	84 (8)	75 (16)	80 (13)	0.100	88 (17)	75 (16)	82 (18)	0.08
Halofenozide	143 (23)	441 (60)	292 (81)	0.000	151 (27)	161 (81)	156 (59)	1.000	91 (10)	93 (18)	92 (14)	0.697	106 (9)	115 (15)	110 (13)	0.096

Table 3 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	
	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value
Haloxyfop-2-ethoxyethyl	93 (19)	102 (11)	98 (15)	0.188	83 (11)	93 (12)	88 (13)	0.051	80 (10)	79 (15)	79 (12)	0.913	79 (18)	79 (15)	79 (16)	0.939
Hexaconazole	92 (16)	77 (14)	84 (17)	0.12	84 (11)	73 (13)	78 (13)	0.069	83 (6)	77 (10)	80 (9)	0.140	78 (8)	74 (17)	76 (13)	0.565
Hexytiazox	87 (15)	95 (11)	91 (13)	0.368	81 (13)	87 (19)	84 (17)	0.516	81 (10)	73 (15)	77 (13)	0.064	76 (15)	73 (15)	75 (15)	0.451
Imazalil	90 (42)	−268 (−3)	−89 (−211)	0.000	84 (16)	95 (12)	90 (15)	0.086	70 (9)	69 (9)	70 (9)	0.809	80 (12)	90 (7)	85 (11)	0.127
Imazapic	88 (13)	97 (8)	93 (11)	0.141	83 (6)	97 (19)	90 (17)	0.154	81 (6)	75 (11)	78 (9)	0.197	81 (3)	75 (11)	78 (9)	0.127
Imazetapyr	83 (13)	78 (19)	81 (16)	0.318	81 (4)	78 (8)	79 (6)	0.103	77 (4)	72 (17)	75 (12)	0.288	74 (14)	79 (2)	77 (10)	0.203
Imidacloprid	95 (12)	83 (12)	89 (14)	0.099	114 (16)	119 (12)	117 (14)	0.441	100 (12)	105 (8)	102 (10)	0.518	97 (8)	107 (10)	102 (10)	0.069
Indoxacarb	106 (9)	92 (20)	99 (16)	0.078	88 (19)	98 (18)	93 (19)	0.067	81 (14)	75 (16)	78 (15)	0.291	84 (18)	76 (16)	80 (17)	0.183
Iprovalicarb	95 (13)	101 (18)	98 (16)	0.519	92 (15)	109 (17)	100 (18)	0.060	87 (10)	95 (8)	91 (10)	0.078	92 (16)	95 (8)	94 (12)	0.666
Isoxaflutole	−30 (0)	903 (59)	437 (139)	0.000	95 (41)	105 (143)	100 (106)	1.000	84 (16)	85 (21)	85 (18)	0.896	98 (16)	93 (9)	96 (13)	0.548
Kresoxim-methyl	74 (18)	72 (20)	73 (18)	0.716	90 (13)	97 (10)	94 (12)	0.121	78 (14)	77 (12)	77 (13)	0.811	82 (21)	77 (12)	79 (17)	0.577
Linuron	111 (76)	20 (216)	66 (121)	0.000	80 (26)	78 (40)	79 (33)	0.884	73 (19)	75 (19)	74 (18)	0.816	84 (13)	85 (18)	84 (15)	0.862
Lufenuron	94 (15)	96 (9)	95 (12)	0.730	88 (16)	94 (3)	91 (11)	0.381	82 (6)	79 (12)	81 (9)	0.369	83 (20)	79 (12)	81 (16)	0.608
Malathion	91 (15)	97 (9)	94 (13)	0.380	85 (9)	95 (8)	90 (10)	0.051	85 (11)	77 (7)	81 (10)	0.111	84 (15)	79 (7)	81 (12)	0.44
Mecarbam	79 (12)	92 (13)	85 (14)	0.098	84 (4)	88 (4)	86 (5)	0.078	81 (11)	88 (8)	85 (10)	0.289	82 (19)	89 (8)	86 (14)	0.424
Mepanipyrim	86 (18)	92 (11)	89 (14)	0.189	85 (18)	100 (13)	92 (17)	0.062	77 (15)	78 (8)	78 (12)	0.622	86 (18)	80 (8)	83 (14)	0.374
Metalaxyl	116 (8)	117 (18)	117 (14)	0.905	114 (16)	110 (15)	112 (15)	0.252	96 (8)	92 (14)	94 (11)	0.249	94 (11)	84 (17)	89 (15)	0.188
Metconazole	320 (136)	123 (17)	222 (141)	0.000	97 (13)	86 (14)	91 (14)	0.078	85 (9)	77 (13)	81 (12)	0.264	80 (6)	72 (15)	76 (12)	0.186
Methamidophos	84 (17)	73 (15)	79 (17)	0.191	83 (12)	90 (17)	86 (15)	0.294	72 (8)	79 (12)	76 (11)	0.064	81 (12)	93 (10)	87 (13)	0.102
Methidathion	17 (422)	17 (422)	17 (406)	n.f.r.[b]	88 (16)	76 (5)	82 (14)	0.057	84 (4)	84 (6)	84 (5)	0.811	75 (15)	76 (15)	76 (14)	0.853
Methiocarb	87 (20)	85 (3)	86 (14)	0.751	88 (14)	99 (19)	93 (17)	0.152	81 (8)	88 (9)	84 (9)	0.098	80 (12)	88 (9)	84 (11)	0.113
Methomyl	90 (11)	81 (7)	85 (11)	0.136	89 (9)	81 (8)	85 (10)	0.066	88 (4)	80 (12)	84 (10)	0.071	85 (13)	74 (5)	80 (13)	0.066
Methoxyfenozide	99 (15)	103 (7)	101 (11)	0.601	91 (9)	109 (18)	100 (17)	0.060	89 (8)	79 (12)	84 (12)	0.140	90 (14)	78 (12)	84 (15)	0.109
Monocrotophos	85 (12)	73 (18)	79 (16)	0.159	90 (9)	77 (15)	84 (14)	0.090	87 (4)	81 (15)	84 (11)	0.263	91 (19)	81 (8)	86 (16)	0.181
Myclobutanil	96 (18)	81 (11)	88 (17)	0.129	92 (7)	81 (12)	86 (12)	0.077	88 (2)	82 (18)	85 (12)	0.350	84 (9)	74 (14)	79 (13)	0.111
Nitenpyram	−267 (0)	−78 (−35)	−173 (−58)	0.000	−134 (0)	−20 (−145)	−77 (−81)	0.000	100 (19)	99 (7)	100 (14)	0.933	92 (19)	98 (9)	95 (15)	0.200
Ochratoxin A[a]	**53 (0)**	**53 (0)**	**53 (0)**	**n.f.r.**[b]	**39 (15)**	**40 (4)**	**39 (10)**	**0.772**	**106 (19)**	**109 (8)**	**107 (14)**	**0.686**	**81 (18)**	**89 (5)**	**85 (13)**	**0.220**
Ofurace	99 (13)	93 (17)	96 (15)	0.244	90 (12)	76 (11)	83 (14)	0.067	89 (8)	82 (17)	85 (13)	0.300	99 (9)	88 (18)	93 (15)	0.171
Omethoate	102 (7)	98 (19)	100 (14)	0.629	84 (4)	80 (20)	82 (14)	0.466	79 (8)	76 (12)	78 (10)	0.194	84 (13)	73 (8)	78 (13)	0.057
Oxadixyl	93 (16)	81 (9)	87 (15)	0.109	91 (13)	80 (13)	86 (14)	0.115	87 (7)	80 (10)	83 (9)	0.055	88 (8)	84 (11)	86 (10)	0.266
Oxamyl	96 (12)	82 (12)	89 (14)	0.098	94 (8)	89 (14)	92 (11)	0.328	89 (3)	83 (11)	86 (8)	0.120	93 (6)	89 (11)	91 (9)	0.389
Paclobutrazol	109 (15)	100 (19)	105 (17)	0.354	99 (12)	92 (14)	96 (13)	0.429	89 (5)	83 (13)	86 (10)	0.102	83 (5)	75 (13)	79 (11)	0.053
Penconazole	94 (14)	77 (19)	86 (18)	0.071	85 (9)	79 (11)	82 (10)	0.127	85 (8)	74 (17)	80 (14)	0.080	79 (12)	70 (6)	75 (11)	0.086
Pencycuron	83 (14)	87 (8)	85 (11)	0.511	89 (15)	102 (13)	95 (15)	0.075	87 (14)	94 (4)	90 (10)	0.192	88 (13)	93 (4)	91 (9)	0.352
Pendimethalin	83 (19)	79 (5)	81 (14)	0.588	72 (11)	71 (3)	72 (8)	0.630	82 (17)	78 (15)	80 (15)	0.544	88 (6)	79 (15)	83 (12)	0.165
Phenothrin	n.f.r.[b]	49 (72)	n.f.r.[b]	n.f.r.[b]	87 (12)	88 (6)	87 (9)	0.774	81 (18)	97 (16)	89 (18)	0.133	91 (6)	98 (16)	95 (12)	0.315
Phenthoate	91 (15)	95 (15)	93 (15)	0.520	85 (9)	91 (16)	88 (13)	0.195	85 (11)	81 (11)	83 (11)	0.412	84 (15)	83 (11)	83 (13)	0.862
Phosalone	43 (113)	15 (215)	29 (146)	0.000	115 (12)	105 (18)	110 (15)	0.390	93 (8)	85 (14)	89 (12)	0.219	81 (20)	88 (13)	85 (17)	0.433

Table 3 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	
	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value
Phosmet	84 (17)	102 (14)	93 (18)	0.080	92 (10)	99 (13)	96 (12)	0.293	80 (19)	83 (12)	81 (15)	0.655	84 (15)	84 (12)	84 (13)	0.968
Picoxystrobin	103 (11)	110 (13)	106 (12)	0.201	87 (8)	89 (7)	88 (7)	0.617	84 (10)	82 (4)	83 (7)	0.311	86 (17)	81 (4)	84 (13)	0.403
Piperonyl butoxide	94 (11)	103 (11)	98 (12)	0.129	88 (8)	96 (9)	92 (9)	0.067	84 (7)	76 (9)	80 (9)	0.063	83 (14)	76 (9)	79 (12)	0.202
Pirimicarb	94 (11)	87 (9)	90 (11)	0.067	93 (7)	82 (9)	88 (10)	0.06	89 (3)	82 (11)	86 (8)	0.090	85 (3)	82 (14)	83 (10)	0.458
Pirimiphos-ethyl	94 (12)	84 (10)	89 (12)	0.128	89 (4)	81 (9)	85 (8)	0.077	87 (1)	77 (15)	82 (12)	0.057	83 (9)	77 (16)	80 (13)	0.269
Pirimiphos-methyl	95 (13)	96 (19)	96 (16)	0.926	92 (4)	80 (19)	86 (14)	0.091	87 (3)	77 (13)	82 (11)	0.051	84 (10)	73 (11)	79 (12)	0.070
Prochloraz	78 (11)	93 (14)	86 (15)	0.053	79 (9)	90 (13)	85 (13)	0.103	76 (9)	81 (4)	78 (7)	0.211	72 (13)	80 (4)	76 (11)	0.103
Profenofos	93 (11)	83 (8)	88 (11)	0.096	83 (14)	105 (17)	94 (19)	0.058	77 (19)	71 (7)	74 (15)	0.273	77 (16)	72 (7)	75 (12)	0.299
Prometryn	89 (13)	80 (4)	85 (11)	0.082	89 (5)	83 (11)	86 (9)	0.079	85 (2)	80 (12)	82 (9)	0.284	82 (6)	78 (13)	80 (10)	0.274
Propamocarb	262 (7)	218 (4)	240 (11)	0.000	212 (4)	171 (5)	191 (12)	0.000	181 (2)	157 (16)	169 (13)	0.059	176 (9)	147 (6)	162 (12)	0.002
Propanil	50 (193)	28 (252)	39 (210)	1.000	104 (41)	75 (81)	89 (59)	0.368	102 (13)	97 (13)	99 (13)	0.597	85 (17)	102 (13)	93 (17)	0.059
Propham	96 (11)	102 (11)	99 (11)	0.340	102 (12)	105 (5)	104 (9)	0.567	93 (17)	94 (8)	94 (13)	0.963	94 (12)	95 (8)	95 (10)	0.840
Propiconazole	89 (10)	76 (19)	82 (16)	0.152	84 (14)	65 (14)	74 (19)	0.025	79 (8)	70 (17)	74 (13)	0.150	83 (10)	75 (17)	79 (14)	0.136
Propyzamide	88 (17)	82 (19)	85 (18)	0.597	90 (10)	82 (16)	86 (14)	0.342	88 (18)	76 (16)	82 (18)	0.247	82 (15)	75 (15)	78 (15)	0.104
Pyraclostrobin	98 (13)	109 (9)	104 (12)	0.062	95 (13)	102 (2)	98 (9)	0.201	76 (11)	82 (7)	79 (9)	0.069	84 (6)	83 (7)	84 (6)	0.643
Pyrazophos	103 (12)	112 (8)	107 (11)	0.097	92 (15)	101 (2)	96 (11)	0.151	82 (14)	78 (5)	80 (11)	0.384	83 (18)	78 (5)	81 (14)	0.410
Pyridaben	91 (16)	79 (19)	85 (18)	0.223	78 (12)	86 (11)	82 (12)	0.101	73 (15)	71 (5)	72 (11)	0.711	78 (17)	71 (5)	74 (13)	0.190
Pyrimethanil	84 (13)	77 (10)	81 (12)	0.293	80 (6)	73 (11)	77 (9)	0.099	77 (3)	71 (13)	74 (10)	0.071	73 (11)	70 (18)	71 (14)	0.622
Pyriproxyfen	87 (12)	96 (7)	91 (10)	0.137	82 (8)	83 (11)	82 (9)	0.862	79 (8)	78 (13)	79 (10)	0.869	82 (4)	78 (13)	80 (9)	0.371
Quinalphos	86 (20)	76 (15)	81 (18)	0.241	83 (20)	75 (9)	79 (16)	0.341	81 (9)	87 (9)	84 (9)	0.223	90 (7)	87 (9)	89 (8)	0.452
Quinoxyfen	97 (15)	108 (4)	102 (12)	0.100	87 (11)	97 (11)	92 (12)	0.146	83 (15)	70 (4)	77 (14)	0.055	73 (6)	69 (4)	71 (6)	0.198
Simazine	88 (18)	77 (12)	82 (16)	0.289	89 (10)	75 (16)	82 (15)	0.076	90 (7)	81 (15)	86 (12)	0.157	87 (2)	81 (8)	84 (7)	0.082
Spinosyn A	79 (16)	74 (13)	77 (14)	0.408	72 (8)	72 (4)	72 (6)	0.748	71 (6)	73 (2)	72 (5)	0.221	74 (6)	72 (14)	73 (10)	0.646
Spinosyn D	70 (16)	74 (19)	72 (17)	0.502	78 (18)	84 (6)	81 (13)	0.348	70 (9)	74 (10)	72 (10)	0.394	72 (6)	74 (10)	73 (8)	0.442
Spirodiclofen	77 (53)	66 (23)	71 (42)	0.517	72 (36)	81 (17)	77 (27)	0.395	79 (18)	78 (16)	78 (17)	0.896	84 (7)	79 (16)	81 (12)	0.270
Spiromesifen	98 (7)	97 (19)	97 (14)	0.877	101 (17)	99 (16)	100 (16)	0.798	85 (11)	96 (19)	90 (16)	0.213	107 (17)	96 (19)	102 (18)	0.248
Spiroxamine	89 (11)	81 (10)	85 (11)	0.212	83 (4)	78 (8)	81 (7)	0.087	82 (2)	77 (11)	80 (8)	0.123	81 (2)	77 (19)	79 (13)	0.588
Tau-fluvalinate	64 (114)	334 (52)	199 (95)	0.000	112 (63)	247 (33)	180 (56)	0.000	76 (30)	123 (17)	100 (33)	0.010	85 (15)	85 (12)	85 (13)	0.999
Tebuconazole	97 (12)	85 (13)	91 (14)	0.068	79 (13)	89 (4)	84 (11)	0.089	85 (3)	81 (1)	83 (3)	0.017	83 (7)	76 (19)	79 (14)	0.324
Tebufenozide	115 (29)	143 (3)	129 (21)	0.056	111 (5)	107 (2)	109 (4)	0.276	101 (5)	93 (16)	97 (12)	0.251	95 (9)	83 (11)	89 (12)	0.051
Tebufenpyrad	94 (18)	106 (7)	100 (14)	0.133	87 (12)	92 (1)	89 (9)	0.320	83 (13)	71 (7)	77 (13)	0.074	80 (16)	71 (7)	75 (14)	0.081
Terbutryn	91 (11)	81 (13)	86 (13)	0.142	88 (4)	81 (10)	85 (8)	0.069	85 (2)	80 (12)	83 (8)	0.167	82 (6)	77 (9)	80 (8)	0.157
Tetrachlorvinphos	94 (9)	90 (18)	92 (14)	0.473	91 (32)	57 (31)	74 (39)	0.039	86 (12)	89 (13)	88 (12)	0.472	98 (16)	89 (13)	94 (15)	0.302
Tetraconazole	97 (14)	81 (14)	89 (17)	0.067	85 (10)	73 (14)	79 (14)	0.078	93 (11)	91 (13)	92 (12)	0.61	84 (10)	81 (14)	82 (12)	0.354
Tetramethrin	98 (12)	90 (20)	94 (16)	0.309	84 (13)	95 (8)	90 (12)	0.113	86 (4)	81 (13)	83 (10)	0.312	84 (15)	80 (13)	82 (14)	0.548
Thiabendazole	45 (16)	39 (8)	42 (15)	0.070	38 (4)	36 (8)	37 (7)	0.144	37 (4)	39 (17)	38 (12)	0.348	38 (8)	38 (12)	38 (10)	0.952
Thiacloprid	88 (16)	76 (8)	82 (15)	0.085	81 (14)	70 (12)	76 (15)	0.059	78 (14)	74 (26)	76 (20)	0.526	82 (15)	71 (13)	76 (15)	0.222
Thiamethoxam	139 (24)	42 (35)	90 (63)	0.000	118 (42)	71 (24)	94 (46)	0.091	104 (28)	96 (33)	100 (30)	0.155	100 (7)	89 (17)	95 (13)	0.177
Thiodicarb	97 (13)	81 (13)	89 (16)	0.103	89 (11)	82 (19)	85 (15)	0.381	84 (8)	74 (16)	79 (13)	0.101	86 (7)	77 (19)	81 (14)	0.176

Table 3 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)		Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	
	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value	Analyst 1	Analyst 2		*P* value
Toxin T2[a]	**n.f.r.**[b]	**486 (52)**	**n.f.r.**[b]	**n.f.r.**[b]	**946 (27)**	**729 (30)**	**838 (31)**	**0.000**	**82 (14)**	**73 (8)**	**78 (12)**	**0.101**	**98 (7)**	**88 (17)**	**93 (13)**	**0.135**
Triadimefon	102 (17)	86 (2)	94 (16)	0.067	90 (8)	82 (16)	86 (13)	0.236	85 (12)	75 (12)	80 (13)	0.170	85 (5)	79 (20)	82 (14)	0.364
Triadimenol	142 (186)	−604 (−4)	−231 (−185)	0.000	66 (106)	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	−89 (−15)	n.f.r.[b]	n.f.r.[b]	41 (62)	−53 (−18)	−6 (−829)	0.000
Triazophos	91 (12)	98 (20)	94 (16)	0.215	88 (8)	85 (7)	87 (7)	0.429	86 (9)	87 (9)	86 (9)	0.747	91 (6)	86 (9)	89 (8)	0.365
Trifloxystrobin	86 (11)	86 (8)	86 (9)	0.954	84 (17)	83 (16)	84 (16)	0.859	77 (11)	73 (6)	75 (9)	0.270	87 (9)	83 (9)	85 (9)	0.080
Triflumizole	91 (12)	78 (14)	84 (15)	0.074	83 (5)	73 (18)	78 (14)	0.119	83 (4)	85 (15)	84 (10)	0.606	81 (5)	77 (20)	79 (14)	0.517
Triticonazole	92 (16)	96 (11)	94 (13)	0.532	94 (9)	106 (9)	100 (10)	0.056	85 (7)	90 (4)	88 (7)	0.055	91 (13)	90 (4)	91 (9)	0.936
Zearalenone[a]	**−5131 (0)**	**−5131 (0)**	**−5131 (0)**	**n.f.r.**[b]	**105 (11)**	**86 (44)**	**96 (30)**	**0.225**	**107 (8)**	**112 (19)**	**109 (14)**	**0.554**	**93 (19)**	**88 (19)**	**91 (18)**	**0.636**
Zoxamide	86 (16)	93 (15)	90 (15)	0.388	84 (14)	71 (19)	77 (18)	0.174	81 (16)	77 (8)	79 (13)	0.440	87 (10)	80 (11)	84 (11)	0.237

[a] Mycotoxins. [b] n.f.r.: not fulfill requirements of SANTE document.

concentration to be within ± 20% of the assigned concentration. If this value was not achieved, the *t*-test was applied to r^2 to prove linearity. If the value of t_r for analytical curve regression was greater than or equal to the critical (tabulated) bilateral *t*-value, for a confidence level of 95% and (Nx – 2) degrees of freedom, the range was considered linear, rejecting the null hypothesis H_0: $r = 0$ (there is no correlation between *x* and *y*).

Although most pesticides presented a linear range of 5–1000 or 5–500 μg kg^{-1}, 63% of analytes presented different linear ranges for *M. officinalis* and *M. sylvestris*, especially at the first analytical curve concentration. Mycotoxins of Group 1 presented a linear range of 5–500 μg kg^{-1} for all aflatoxins and 10–1000 μg kg^{-1} for ochratoxin A, while mycotoxins of Group 2 presented 250–5000 μg kg^{-1} for both fumonisins, deoxynivalenol, and diacetoxyscirpenol, 50–2500 μg kg^{-1} for toxin T2, and 25–500 μg kg^{-1} for zearalenone.

Method selectivity was evaluated in two different ways, in terms of the matrix effect calculated from the slope of the analytical curves obtained from solutions in a blank matrix extract and in organic solvent (at 1 ng mL^{-1} for pesticides and mycotoxins of group 1, and 50 ng mL^{-1} for mycotoxins of group 2). Afterwards, by comparing the selected chromatograms from the blank matrix extract and from solutions in organic solvent.

This evaluation verified the absence of analytes in the matrix by comparing the peak shape, ion ratio, and resolution in the solvent and matrix extract. These calculations and observations were performed automatically using the Mass Hunter Workstation Quantitative Analysis software, version 10.0. Fig. 3 presents an example of the selectivity obtained from the extracted chromatograms of aflatoxin B1 and fenamiphos.

Matrix effects can be described as an increase or decrease in the analytical signal due to co-extractives from the matrix when compared with the detection response for the analytes in organic solvent.[51] Table 1 presents the matrix effects for all analytes in *M. officinalis* and *M. sylvestris*.

Analytes with more polar characteristics presented a higher negative matrix effect. For instance, acephate presented a matrix effect of −74% and −80%, methamidophos −77% and −76%, and omethoate −76% and −76% for *M. officinalis* and *M. sylvestris*, respectively. Wu X and Ding Z[52] demonstrated that early and late eluting pesticides were observed with strong signal suppression. The suppression effects of the initially eluting pesticides can be explained by the co-elution of polar coexisting compounds in the reversed-phase column, which can affect the ionization efficiency of the target analyte. Additionally, in the initial part of the chromatographic run, the low organic content may affect ESI ionization, leading to high signal suppression.[53]

Although more polar pesticides presented a similar matrix effect in both matrices, other compounds presented very different matrix effects in each medicinal plant. Fig. 4 shows the analytes with the highest dissimilar matrix effects. Log K_{ow} of the analytes ranges from 0.5 to 7.02, indicating that both more polar and nonpolar analytes may experience different matrix effects in the two plants studied. For example, spirodiclofen showed a 24% signal enhancement in *M. officinalis* while it showed a 46% signal suppression in *M. sylvestris*, indicating

Table 4 Average recoveries, precision (RSDr) and intermediate precision (RSD_{WR}) obtained for *M. sylvestris* from the method validation procedure

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	*P* value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Acephate	76 (20)	84 (9)	80 (15)	0.164	84 (13)	101 (12)	93 (15)	0.061	86 (16)	90 (13)	88 (14)	0.619	94 (17)	108 (10)	101 (15)	0.063
Acetamiprid	107 (9)	102 (5)	105 (7)	0.273	94 (6)	89 (11)	92 (9)	0.396	86 (17)	78 (5)	82 (14)	0.295	95 (11)	98 (2)	97 (8)	0.367
Acetochlor	106 (17)	95 (11)	100 (15)	0.127	99 (8)	98 (16)	99 (12)	0.811	87 (6)	83 (9)	85 (8)	0.371	99 (5)	97 (10)	98 (8)	0.446
Aflatoxin B1[a]	**51 (21)**	**84 (15)**	**67 (31)**	**0.001**	**76 (8)**	**71 (19)**	**73 (14)**	**0.353**	**88 (18)**	**76 (14)**	**82 (18)**	**0.237**	**95 (10)**	**91 (12)**	**93 (11)**	**0.403**
Aflatoxin B2[a]	**−111 (-11)**	**−120 (-20)**	**−115 (-17)**	**0.438**	**9 (220)**	**8 (195)**	**8 (203)**	**0.883**	**57 (18)**	**62 (10)**	**59 (15)**	**0.167**	**75 (18)**	**75 (6)**	**75 (13)**	**0.985**
Aflatoxin G1[a]	**66 (58)**	**83 (38)**	**75 (47)**	**0.191**	**78 (13)**	**84 (16)**	**81 (15)**	**0.223**	**96 (14)**	**85 (14)**	**90 (15)**	**0.143**	**84 (15)**	**85 (11)**	**85 (12)**	**0.832**
Aflatoxin G2[a]	**n.f.r.**	**39 (228)**	**n.f.r.**[b]	**n.f.r.**[b]	**90 (20)**	**85 (11)**	**88 (16)**	**0.434**	**89 (19)**	**88 (7)**	**89 (14)**	**0.801**	**85 (11)**	**96 (11)**	**90 (12)**	**0.119**
Aldicarb sulfone	90 (16)	93 (18)	91 (16)	0.726	90 (13)	84 (13)	87 (13)	0.416	99 (4)	98 (9)	98 (7)	0.728	103 (6)	111 (5)	107 (7)	0.063
Aldicarb sulfoxide	101 (17)	86 (20)	94 (20)	0.180	90 (13)	106 (13)	98 (15)	0.087	86 (16)	91 (19)	89 (17)	0.616	83 (5)	94 (13)	89 (12)	0.106
Atrazine	104 (13)	114 (8)	109 (11)	0.184	107 (12)	116 (3)	111 (9)	0.155	90 (10)	83 (2)	87 (8)	0.118	87 (10)	82 (2)	84 (7)	0.224
Azamethiphos	80 (16)	89 (14)	85 (16)	0.298	89 (20)	102 (6)	95 (15)	0.135	87 (19)	96 (3)	91 (14)	0.214	87 (12)	98 (3)	93 (10)	0.054
Azinphos-methyl	75 (49)	123 (57)	99 (60)	0.059	81 (51)	168 (19)	124 (46)	0.008	82 (17)	93 (18)	88 (18)	0.294	92 (14)	79 (19)	85 (18)	0.120
Azoxystrobin	95 (19)	110 (4)	103 (14)	0.089	93 (11)	102 (6)	98 (9)	0.063	90 (9)	98 (4)	94 (8)	0.054	93 (12)	96 (1)	94 (8)	0.509
Bifenazate	23 (48)	−10 (−52)	6 (301)	0.000	42 (12)	11 (97)	26 (68)	0.000	56 (15)	16 (56)	36 (63)	0.000	56 (16)	19 (27)	38 (53)	0.000
Bitertanol	83 (18)	79 (11)	81 (15)	0.518	89 (19)	81 (12)	85 (17)	0.281	95 (16)	85 (9)	90 (14)	0.195	94 (16)	92 (5)	93 (11)	0.712
Boscalid	87 (10)	110 (24)	98 (23)	0.052	83 (11)	75 (14)	79 (13)	0.219	88 (8)	82 (13)	85 (11)	0.282	91 (15)	80 (6)	85 (13)	0.061
Bupirimate	102 (10)	96 (7)	99 (9)	0.224	98 (12)	89 (5)	93 (10)	0.119	93 (9)	93 (5)	93 (7)	0.907	93 (8)	88 (3)	91 (7)	0.143
Buprofezin	101 (15)	114 (5)	108 (12)	0.091	111 (15)	111 (5)	111 (11)	0.968	86 (9)	103 (24)	94 (20)	0.172	106 (16)	110 (3)	108 (11)	0.528
Cadusafos	100 (17)	112 (7)	106 (13)	0.133	96 (13)	107 (12)	102 (13)	0.254	103 (13)	113 (8)	108 (11)	0.081	103 (19)	116 (2)	109 (14)	0.136
Carbaryl	99 (18)	104 (6)	102 (13)	0.592	96 (11)	108 (7)	102 (10)	0.087	106 (15)	113 (3)	109 (10)	0.318	99 (11)	110 (5)	105 (10)	0.071
Carbendazim	65 (54)	48 (11)	57 (45)	0.263	53 (40)	75 (11)	64 (30)	0.067	62 (11)	90 (4)	76 (20)	0.000	82 (11)	91 (3)	86 (9)	0.060
Carbofuran	118 (11)	115 (5)	116 (8)	0.632	115 (5)	107 (10)	111 (8)	0.139	113 (10)	104 (5)	108 (9)	0.093	116 (13)	104 (2)	110 (11)	0.117
Carpropamid	−40 (0)	34 (24)	−3 (−1288)	0.000	108 (10)	92 (19)	100 (16)	0.050	88 (9)	75 (17)	81 (15)	0.133	100 (8)	97 (5)	98 (7)	0.211
Chlorantraniliprole	78 (52)	56 (26)	67 (47)	0.199	78 (20)	87 (19)	82 (19)	0.488	84 (10)	91 (13)	87 (12)	0.172	97 (12)	93 (9)	95 (10)	0.390
Chlorfenvinphos	97 (19)	102 (9)	100 (14)	0.599	92 (8)	100 (9)	96 (9)	0.066	89 (11)	80 (19)	84 (16)	0.340	93 (16)	108 (4)	101 (13)	0.074
Chlorpyrifos	112 (5)	101 (18)	107 (13)	0.174	102 (14)	103 (16)	102 (15)	0.915	83 (7)	90 (13)	87 (11)	0.116	81 (16)	81 (6)	81 (11)	0.995
Clofentezine	90 (20)	79 (16)	84 (19)	0.096	76 (12)	76 (18)	76 (15)	0.998	75 (11)	93 (18)	84 (19)	0.066	89 (19)	79 (19)	84 (19)	0.289
Clomazone	83 (20)	73 (13)	78 (18)	0.271	92 (6)	98 (8)	95 (7)	0.192	93 (10)	105 (14)	99 (13)	0.209	105 (9)	111 (12)	108 (11)	0.352
Clothianidin	109 (8)	95 (12)	102 (12)	0.051	101 (11)	88 (13)	94 (14)	0.055	92 (19)	78 (6)	85 (17)	0.049	89 (17)	84 (5)	87 (13)	0.419
Cyazofamid	76 (47)	41 (54)	59 (58)	0.136	91 (17)	93 (19)	92 (17)	0.746	96 (10)	105 (7)	101 (10)	0.091	99 (11)	107 (10)	103 (11)	0.277
Cyproconazole	92 (19)	94 (7)	93 (14)	0.866	94 (9)	103 (9)	99 (10)	0.101	90 (9)	90 (6)	90 (8)	0.946	94 (10)	88 (12)	91 (11)	0.310
Cyprodinil	75 (17)	71 (10)	73 (14)	0.469	71 (5)	73 (7)	72 (6)	0.401	70 (9)	72 (8)	71 (8)	0.678	71 (18)	78 (5)	75 (13)	0.142
Demeton-*S*-methyl sulfone	94 (17)	93 (6)	94 (13)	0.836	93 (9)	99 (4)	96 (7)	0.146	101 (10)	107 (5)	104 (8)	0.147	104 (8)	103 (4)	104 (6)	0.780
Demeton-*S*-methyl sulfoxide	77 (60)	79 (16)	78 (42)	0.913	87 (10)	102 (15)	95 (15)	0.128	89 (16)	105 (20)	97 (20)	0.118	96 (11)	107 (3)	102 (9)	0.074
Deoxynivalenol[a]	**202 (358)**	**1010 (67)**	**606 (131)**	**0.147**	**657 (68)**	**109 (283)**	**383 (122)**	**0.015**	**25 (11)**	**32 (14)**	**28 (18)**	**0.038**	**26 (8)**	**25 (9)**	**26 (9)**	**0.155**

Table 4 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Diacetoxyscirpenol[a]	**2 (291)**	**−4 (-167)**	**−1 (-728)**	**0.036**	**16 (60)**	**17 (20)**	**16 (41)**	**0.699**	**23 (7)**	**23 (8)**	**23 (7)**	**0.547**	**22 (12)**	**25 (4)**	**24 (11)**	**0.038**
Diazinon	98 (12)	108 (15)	103 (14)	0.330	99 (6)	107 (15)	103 (12)	0.226	108 (19)	113 (9)	111 (14)	0.509	93 (9)	108 (15)	100 (15)	0.106
Diethofencarb	82 (37)	39 (27)	61 (51)	0.013	109 (20)	98 (18)	104 (19)	0.140	89 (14)	95 (6)	92 (11)	0.357	100 (13)	94 (5)	97 (10)	0.155
Difenoconazol	91 (17)	81 (6)	86 (14)	0.109	94 (10)	96 (7)	95 (8)	0.594	89 (10)	100 (5)	94 (10)	0.063	105 (17)	101 (4)	103 (12)	0.641
Diflubenzuron	49 (168)	14 (560)	32 (253)	0.347	91 (44)	54 (92)	73 (66)	0.147	89 (11)	101 (13)	95 (13)	0.170	95 (14)	115 (19)	105 (19)	0.092
Dimethoate	101 (11)	100 (9)	101 (9)	0.831	93 (7)	98 (6)	95 (7)	0.161	88 (18)	92 (3)	90 (12)	0.464	89 (18)	91 (2)	90 (12)	0.816
Dimethomorph	93 (12)	106 (8)	100 (12)	0.125	102 (12)	110 (6)	106 (10)	0.197	91 (12)	87 (4)	89 (9)	0.398	94 (13)	86 (3)	90 (10)	0.189
Diniconazole	91 (13)	83 (14)	87 (14)	0.129	91 (16)	80 (7)	85 (14)	0.061	85 (8)	79 (9)	82 (9)	0.189	89 (10)	82 (11)	85 (11)	0.275
Diphenylamine	115 (13)	96 (15)	106 (16)	0.114	98 (11)	87 (10)	92 (12)	0.071	89 (11)	84 (8)	86 (10)	0.388	86 (10)	86 (8)	86 (9)	0.944
Diuron	86 (17)	74 (7)	80 (16)	0.096	90 (8)	93 (7)	91 (7)	0.248	92 (9)	102 (5)	97 (8)	0.055	90 (9)	89 (20)	90 (15)	0.850
DMST	86 (16)	100 (18)	93 (19)	0.110	105 (20)	97 (13)	101 (17)	0.532	97 (9)	98 (16)	97 (13)	0.963	94 (13)	82 (10)	88 (13)	0.088
Epoxiconazol	89 (5)	102 (17)	96 (14)	0.088	96 (10)	111 (14)	104 (14)	0.061	97 (6)	100 (15)	98 (12)	0.587	89 (15)	103 (9)	96 (14)	0.059
Ethion	87 (14)	108 (17)	98 (19)	0.051	92 (8)	104 (14)	98 (13)	0.063	89 (9)	96 (5)	93 (8)	0.155	88 (13)	94 (6)	91 (10)	0.170
Ethiprole	86 (14)	79 (19)	82 (16)	0.393	102 (12)	86 (17)	94 (16)	0.093	95 (6)	97 (17)	96 (13)	0.735	102 (14)	103 (5)	103 (10)	0.827
Ethoprophos	98 (16)	112 (9)	105 (14)	0.213	87 (13)	86 (8)	87 (10)	0.952	88 (9)	81 (20)	84 (15)	0.427	98 (10)	106 (10)	102 (11)	0.200
Etofenprox	95 (19)	87 (20)	91 (19)	0.478	107 (18)	98 (20)	103 (19)	0.452	86 (9)	80 (15)	83 (13)	0.366	85 (15)	87 (6)	86 (11)	0.821
Etoxazole	92 (16)	88 (3)	90 (11)	0.464	89 (9)	86 (5)	87 (7)	0.177	86 (11)	88 (2)	87 (8)	0.572	87 (6)	87 (3)	87 (4)	0.817
Fenamidone	97 (12)	108 (8)	102 (11)	0.111	100 (7)	97 (20)	98 (14)	0.761	93 (11)	92 (13)	93 (12)	0.689	91 (11)	86 (4)	88 (9)	0.164
Fenamiphos	105 (12)	98 (11)	102 (11)	0.352	91 (13)	91 (5)	91 (9)	0.948	87 (10)	91 (3)	89 (8)	0.475	90 (14)	92 (2)	91 (9)	0.654
Fenarimol	76 (35)	48 (24)	62 (39)	0.097	89 (11)	102 (15)	96 (15)	0.118	76 (19)	74 (10)	75 (15)	0.739	89 (16)	80 (10)	85 (15)	0.117
Fenazaquin	89 (18)	84 (7)	86 (14)	0.499	89 (16)	94 (7)	91 (12)	0.384	84 (14)	93 (3)	88 (11)	0.062	83 (15)	91 (2)	87 (11)	0.161
Fenbuconazol	65 (27)	40 (47)	53 (42)	0.025	90 (19)	110 (16)	100 (20)	0.158	98 (19)	106 (11)	102 (15)	0.403	98 (6)	99 (21)	98 (15)	0.908
Fenhexamid	81 (34)	78 (20)	79 (27)	0.854	95 (15)	94 (19)	94 (16)	0.910	93 (10)	103 (13)	98 (13)	0.099	99 (14)	104 (15)	102 (15)	0.684
Fenobucarb	89 (20)	103 (7)	96 (16)	0.116	99 (13)	111 (9)	105 (12)	0.107	91 (10)	106 (16)	98 (15)	0.084	101 (7)	113 (13)	107 (12)	0.074
Fenoxycarb	72 (55)	52 (0)	62 (47)	0.231	81 (19)	73 (14)	77 (17)	0.191	86 (15)	79 (18)	82 (16)	0.457	94 (13)	84 (19)	89 (17)	0.259
Fenpropimorph	100 (13)	107 (7)	103 (11)	0.341	96 (6)	105 (12)	100 (11)	0.139	93 (5)	96 (4)	94 (5)	0.401	86 (11)	95 (2)	90 (9)	0.068
Fenpyroximate	85 (17)	93 (4)	89 (12)	0.252	83 (11)	94 (8)	88 (11)	0.058	85 (15)	95 (5)	90 (12)	0.151	85 (7)	91 (9)	88 (9)	0.174
Fensulfothion	104 (13)	101 (19)	103 (16)	0.752	100 (14)	99 (9)	100 (12)	0.871	113 (14)	101 (11)	107 (14)	0.079	119 (5)	111 (6)	115 (7)	0.068
Fluazifop-butyl	89 (13)	99 (10)	94 (12)	0.117	87 (9)	99 (9)	93 (11)	0.066	88 (10)	93 (18)	90 (14)	0.361	87 (12)	98 (14)	93 (14)	0.195
Fludioxonil	108 (14)	92 (15)	100 (16)	0.085	90 (18)	89 (15)	89 (16)	0.817	97 (11)	98 (12)	97 (11)	0.853	95 (9)	95 (8)	95 (8)	0.992
Flufenoxuron	−22 (0)	57 (34)	18 (245)	0.000	105 (17)	101 (12)	103 (15)	0.522	78 (11)	79 (12)	78 (11)	0.911	96 (14)	98 (19)	97 (16)	0.833
Fluquinconazol	89 (53)	65 (40)	77 (51)	0.308	94 (15)	94 (20)	94 (17)	0.968	93 (17)	89 (17)	91 (16)	0.715	94 (14)	86 (12)	90 (14)	0.125
Flusilazol	84 (19)	104 (15)	94 (20)	0.055	94 (18)	104 (10)	99 (15)	0.172	88 (8)	78 (10)	83 (11)	0.057	96 (10)	85 (14)	91 (13)	0.157
Flutolanil	56 (39)	25 (22)	41 (54)	0.016	81 (19)	99 (18)	90 (20)	0.106	85 (13)	80 (17)	82 (15)	0.502	97 (18)	84 (16)	91 (19)	0.066
Flutriafol	99 (16)	87 (9)	93 (15)	0.118	93 (9)	84 (12)	89 (11)	0.122	87 (11)	90 (5)	88 (8)	0.509	91 (15)	82 (7)	87 (13)	0.223
Fosthiazate	105 (15)	95 (7)	100 (12)	0.172	98 (6)	94 (10)	96 (8)	0.269	89 (13)	90 (4)	89 (9)	0.788	91 (13)	89 (4)	90 (9)	0.722
Fumonisin B1[a]	**156 (2)**	**163 (14)**	**159 (10)**	**0.490**	**72 (17)**	**61 (0)**	**67 (15)**	**0.047**	**49 (39)**	**30 (1)**	**40 (41)**	**0.044**	**23 (31)**	**15 (1)**	**19 (32)**	**0.030**
Fumonisin B2[a]	**186 (4)**	**186 (1)**	**186 (3)**	**0.996**	**86 (8)**	**72 (1)**	**79 (11)**	**0.002**	**51 (8)**	**36 (0)**	**44 (19)**	**0.000**	**26 (28)**	**18 (1)**	**22 (29)**	**0.032**
Furalaxyl	81 (33)	124 (5)	102 (28)	0.003	79 (14)	131 (4)	105 (27)	0.000	83 (10)	89 (2)	86 (8)	0.146	95 (11)	89 (2)	92 (9)	0.154
Furathiocarb	92 (19)	108 (6)	100 (15)	0.118	92 (9)	103 (10)	97 (11)	0.151	88 (9)	100 (13)	94 (13)	0.072	87 (12)	98 (11)	93 (12)	0.086

Table 4 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Halofenozide	−177 (0)	−177 (0)	−177 (0)	n.f.r.[b]	−88 (0)	127 (34)	19 (603)	0.000	91 (20)	103 (20)	97 (20)	0.161	103 (15)	97 (20)	100 (17)	0.544
Haloxyfop-2-ethoxyethyl	87 (18)	92 (12)	89 (15)	0.464	87 (10)	91 (9)	89 (9)	0.312	86 (7)	98 (11)	92 (11)	0.072	93 (8)	102 (8)	97 (9)	0.151
Hexaconazol	97 (15)	95 (12)	96 (13)	0.677	97 (6)	93 (13)	95 (10)	0.464	90 (12)	85 (6)	88 (9)	0.393	86 (10)	84 (8)	85 (9)	0.670
Hexytiazox	100 (18)	81 (17)	91 (20)	0.059	90 (15)	87 (19)	88 (16)	0.712	86 (8)	83 (9)	85 (8)	0.507	86 (14)	92 (9)	89 (12)	0.327
Imazalil	96 (18)	83 (5)	89 (16)	0.101	83 (9)	88 (8)	85 (9)	0.337	85 (9)	93 (5)	89 (9)	0.087	86 (9)	89 (4)	87 (7)	0.530
Imazapic	111 (7)	75 (10)	93 (22)	0.000	91 (8)	82 (16)	87 (13)	0.083	86 (20)	71 (10)	78 (19)	0.114	81 (18)	74 (6)	77 (14)	0.239
Imazetapyr	94 (14)	86 (12)	90 (13)	0.118	84 (5)	89 (8)	86 (7)	0.119	72 (17)	79 (4)	76 (12)	0.220	78 (16)	79 (3)	78 (11)	0.844
Imidacloprid	100 (13)	92 (15)	96 (14)	0.428	101 (18)	88 (12)	95 (17)	0.058	99 (8)	89 (14)	94 (12)	0.062	89 (19)	92 (21)	91 (19)	0.807
Indoxacarb	82 (17)	102 (18)	92 (21)	0.091	87 (12)	90 (14)	89 (12)	0.543	93 (14)	107 (18)	100 (17)	0.054	101 (8)	109 (8)	105 (9)	0.124
Iprovalicarb	72 (13)	76 (14)	74 (13)	0.381	79 (15)	92 (10)	86 (14)	0.050	81 (11)	97 (10)	89 (13)	0.055	94 (15)	101 (1)	98 (11)	0.223
Isoxaflutole	281 (110)	203 (94)	242 (103)	0.324	168 (35)	225 (85)	196 (71)	0.474	96 (18)	106 (21)	101 (19)	0.076	100 (15)	92 (10)	96 (13)	0.392
Kresoxim-methyl	86 (17)	93 (19)	89 (18)	0.468	92 (13)	95 (17)	94 (15)	0.646	100 (19)	117 (6)	108 (15)	0.067	96 (11)	109 (7)	103 (11)	0.069
Linuron	−14 (0)	55 (29)	21 (183)	0.000	93 (13)	101 (16)	97 (15)	0.187	118 (12)	119 (7)	119 (9)	0.803	113 (10)	116 (10)	114 (10)	0.636
Lufenuron	86 (20)	97 (11)	91 (17)	0.169	93 (15)	84 (17)	89 (16)	0.130	81 (14)	81 (9)	81 (11)	0.931	92 (11)	84 (6)	88 (10)	0.124
Malathion	103 (15)	104 (12)	104 (13)	0.962	81 (13)	91 (14)	86 (14)	0.200	84 (6)	79 (17)	82 (12)	0.378	106 (8)	114 (5)	110 (8)	0.148
Mecarban	91 (19)	89 (14)	90 (16)	0.732	98 (11)	87 (14)	92 (14)	0.103	93 (12)	101 (11)	97 (12)	0.096	99 (7)	100 (9)	100 (7)	0.741
Mepanipyrin	56 (44)	186 (31)	121 (66)	0.002	59 (31)	78 (40)	69 (39)	0.147	77 (13)	77 (14)	77 (13)	0.919	91 (7)	101 (10)	96 (10)	0.101
Metalaxyl	109 (11)	100 (4)	105 (9)	0.111	96 (5)	94 (6)	95 (5)	0.438	89 (15)	88 (2)	88 (11)	0.850	88 (13)	87 (2)	88 (9)	0.857
Metconazol	92 (20)	110 (8)	101 (16)	0.102	90 (15)	103 (5)	96 (13)	0.060	86 (18)	96 (6)	91 (14)	0.134	88 (14)	97 (5)	92 (11)	0.131
Methamidophos	51 (107)	166 (79)	109 (104)	0.063	104 (15)	101 (20)	102 (17)	0.711	44 (18)	64 (11)	54 (24)	0.003	78 (17)	93 (14)	86 (17)	0.071
Methidathion	−73 (−89)	65 (65)	−4 (−2073)	0.005	92 (18)	97 (17)	94 (17)	0.616	89 (18)	84 (15)	86 (16)	0.309	104 (13)	113 (10)	109 (12)	0.212
Methiocarb	56 (43)	17 (62)	37 (74)	0.005	112 (17)	113 (13)	112 (15)	0.957	86 (9)	78 (8)	82 (10)	0.073	98 (13)	103 (16)	100 (14)	0.563
Methomyl	103 (13)	113 (7)	108 (11)	0.146	100 (14)	104 (13)	102 (13)	0.679	97 (19)	107 (18)	102 (19)	0.119	102 (10)	105 (19)	103 (15)	0.841
Methoxyfenozide	89 (31)	164 (8)	127 (35)	0.001	89 (17)	105 (18)	97 (19)	0.089	85 (13)	86 (19)	85 (16)	0.748	98 (9)	107 (14)	103 (13)	0.274
Monocrotophos	94 (13)	104 (11)	99 (13)	0.241	75 (14)	87 (17)	81 (17)	0.077	91 (13)	99 (8)	95 (11)	0.133	89 (10)	96 (7)	93 (9)	0.143
Myclobutanil	99 (17)	82 (10)	91 (17)	0.060	103 (6)	92 (15)	98 (12)	0.130	96 (15)	112 (8)	104 (14)	0.075	91 (12)	91 (4)	91 (9)	0.895
Nitenpyran	290 (41)	871 (28)	580 (61)	0.002	141 (92)	666 (37)	404 (82)	0.002	93 (47)	244 (46)	169 (67)	0.011	109 (14)	187 (70)	148 (66)	0.183
Ochratoxin A[a]	**101 (8)**	**109 (4)**	**105 (7)**	**0.106**	**70 (11)**	**69 (15)**	**70 (13)**	**0.760**	**81 (14)**	**73 (8)**	**77 (12)**	**0.137**	**70 (5)**	**71 (10)**	**70 (7)**	**0.648**
Ofurace	97 (19)	95 (13)	96 (16)	0.783	92 (9)	85 (3)	88 (8)	0.059	91 (17)	77 (5)	84 (15)	0.079	90 (12)	81 (5)	85 (11)	0.127
Omethoate	980 (72)	697 (58)	839 (68)	0.377	210 (83)	739 (16)	475 (65)	0.001	96 (20)	107 (19)	102 (20)	0.228	89 (4)	84 (18)	86 (13)	0.447
Oxadixyl	90 (17)	83 (5)	86 (13)	0.318	88 (7)	88 (8)	88 (7)	0.945	90 (17)	93 (1)	92 (12)	0.639	94 (11)	92 (3)	93 (8)	0.666
Oxamyl	91 (16)	80 (6)	85 (14)	0.086	82 (14)	88 (9)	85 (12)	0.337	84 (5)	90 (12)	87 (9)	0.331	85 (10)	89 (4)	87 (7)	0.241
Paclobutrazol	105 (15)	119 (12)	112 (15)	0.163	98 (11)	111 (9)	105 (12)	0.054	96 (6)	107 (9)	102 (9)	0.063	93 (10)	108 (14)	100 (14)	0.063
Penconazol	92 (17)	102 (11)	97 (14)	0.086	90 (9)	92 (6)	91 (7)	0.715	92 (9)	96 (6)	94 (8)	0.303	88 (9)	98 (3)	93 (8)	0.073
Pencycuron	94 (17)	106 (11)	100 (15)	0.103	91 (10)	107 (13)	99 (14)	0.063	95 (11)	108 (12)	101 (13)	0.113	99 (7)	106 (4)	103 (6)	0.052
Pendimethalin	85 (18)	80 (18)	83 (17)	0.689	88 (11)	92 (11)	90 (11)	0.517	86 (9)	94 (6)	90 (9)	0.081	81 (7)	88 (13)	84 (11)	0.080
Phenothrin	113 (18)	107 (14)	110 (16)	0.548	97 (13)	113 (13)	105 (15)	0.082	83 (12)	90 (9)	86 (11)	0.154	88 (15)	82 (7)	85 (13)	0.339

Table 4 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Phenthoate	416 (266)	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]	516 (207)	4543 (67)	2530 (120)	0.027	141 (216)	n.f.r.[b]	n.f.r.[b]	n.f.r.[b]
Phosalone	86 (46)	−67 (−205)	9 (1328)	0.029	100 (17)	106 (13)	103 (15)	0.510	86 (10)	98 (15)	92 (14)	0.057	93 (9)	105 (9)	99 (11)	0.052
Phosmet	−79 (0)	31 (71)	−24 (−247)	0.000	85 (17)	93 (16)	89 (16)	0.241	94 (15)	87 (4)	91 (12)	0.157	106 (13)	90 (15)	98 (16)	0.072
Picoxystrobin	101 (17)	115 (2)	108 (13)	0.068	90 (11)	102 (15)	96 (15)	0.176	95 (15)	104 (18)	99 (17)	0.419	107 (15)	112 (4)	109 (11)	0.467
Piperonyl butoxide	92 (16)	103 (6)	97 (13)	0.173	91 (8)	97 (9)	94 (9)	0.140	86 (8)	95 (11)	91 (10)	0.189	89 (10)	96 (12)	93 (11)	0.137
Pirimicarb	101 (12)	97 (5)	99 (9)	0.420	92 (5)	97 (8)	95 (7)	0.356	85 (15)	96 (4)	91 (12)	0.071	86 (11)	91 (8)	88 (10)	0.171
Pirimiphos-ethyl	98 (13)	104 (6)	101 (10)	0.405	97 (3)	99 (4)	98 (3)	0.245	92 (7)	99 (12)	95 (10)	0.070	104 (18)	101 (2)	103 (12)	0.650
Pirimiphos-methyl	102 (13)	104 (9)	103 (11)	0.761	97 (4)	105 (7)	101 (7)	0.011	99 (13)	110 (6)	104 (11)	0.135	91 (10)	105 (14)	98 (14)	0.097
Prochloraz	86 (19)	105 (9)	95 (17)	0.074	85 (8)	87 (7)	86 (7)	0.728	85 (10)	92 (4)	89 (8)	0.128	90 (10)	89 (5)	90 (8)	0.907
Profenofos	100 (19)	88 (12)	94 (17)	0.193	91 (17)	91 (18)	91 (17)	0.956	92 (6)	102 (9)	97 (9)	0.074	88 (14)	103 (11)	96 (14)	0.094
Prometryn	97 (12)	101 (4)	99 (9)	0.445	94 (7)	96 (3)	95 (5)	0.477	88 (8)	95 (2)	91 (7)	0.105	88 (10)	92 (2)	90 (7)	0.305
Propamocarb	44 (73)	−4 (−707)	20 (197)	0.030	52 (39)	5 (74)	29 (99)	0.002	59 (16)	18 (8)	38 (58)	0.000	86 (19)	107 (15)	97 (20)	0.063
Propanil	71 (59)	−80 (0)	−5 (−1818)	0.000	67 (70)	73 (45)	70 (56)	0.811	105 (17)	95 (19)	100 (18)	0.306	86 (18)	80 (16)	83 (17)	0.491
Propham	77 (18)	88 (20)	82 (20)	0.269	84 (16)	90 (16)	87 (16)	0.475	96 (18)	89 (8)	92 (14)	0.188	103 (8)	89 (19)	96 (15)	0.157
Propiconazol	82 (15)	88 (13)	85 (14)	0.258	84 (11)	96 (17)	90 (16)	0.229	84 (10)	76 (5)	80 (10)	0.082	90 (7)	98 (14)	94 (12)	0.100
Propyzamide	93 (20)	102 (12)	98 (16)	0.361	84 (20)	102 (20)	93 (22)	0.196	92 (16)	79 (9)	85 (15)	0.055	100 (9)	110 (5)	105 (8)	0.056
Pyraclostrobin	88 (16)	71 (13)	79 (18)	0.056	88 (10)	93 (10)	91 (10)	0.375	83 (8)	94 (11)	89 (11)	0.132	93 (7)	97 (3)	95 (5)	0.127
Pyrazophos	275 (11)	296 (7)	286 (10)	0.097	236 (14)	257 (2)	246 (10)	0.151	205 (14)	195 (4)	200 (10)	0.384	205 (18)	193 (5)	199 (13)	0.410
Pyridaben	88 (18)	84 (10)	86 (14)	0.649	87 (5)	89 (5)	88 (5)	0.146	82 (7)	89 (8)	85 (9)	0.058	82 (9)	89 (8)	85 (10)	0.097
Pyrimethanil	85 (16)	73 (4)	79 (14)	0.064	78 (5)	77 (5)	78 (5)	0.367	77 (8)	73 (3)	75 (7)	0.161	78 (13)	74 (2)	76 (9)	0.475
Pyriproxyfen	96 (16)	88 (6)	92 (13)	0.331	90 (8)	91 (7)	90 (7)	0.569	82 (8)	91 (10)	87 (10)	0.114	85 (8)	92 (3)	88 (7)	0.089
Quinalphos	95 (19)	101 (16)	98 (17)	0.457	90 (12)	97 (17)	94 (15)	0.171	99 (17)	105 (8)	102 (13)	0.443	95 (8)	102 (7)	98 (8)	0.100
Quinoxyfen	95 (16)	89 (11)	92 (14)	0.483	81 (13)	93 (11)	87 (13)	0.087	83 (9)	88 (5)	85 (8)	0.147	80 (8)	84 (5)	82 (7)	0.252
Simazine	98 (15)	96 (10)	97 (12)	0.714	92 (9)	89 (9)	90 (9)	0.480	87 (14)	89 (3)	88 (10)	0.586	89 (13)	88 (3)	89 (9)	0.863
Spinosyn A	92 (16)	79 (14)	86 (16)	0.142	89 (8)	84 (7)	86 (8)	0.097	92 (10)	85 (3)	89 (8)	0.069	93 (9)	91 (5)	92 (7)	0.727
Spinosyn D	100 (17)	84 (16)	92 (19)	0.139	94 (10)	93 (13)	93 (11)	0.789	88 (6)	86 (5)	87 (6)	0.443	92 (11)	89 (5)	90 (9)	0.412
Spirodiclofen	78 (17)	86 (17)	82 (17)	0.324	80 (15)	99 (12)	90 (17)	0.055	91 (11)	99 (8)	95 (10)	0.206	93 (9)	98 (5)	95 (7)	0.169
Spiromesifen	74 (33)	83 (23)	79 (28)	0.359	78 (6)	91 (17)	85 (15)	0.127	80 (15)	77 (9)	78 (12)	0.675	88 (13)	78 (10)	83 (13)	0.152
Spiroxamine	104 (12)	97 (5)	101 (10)	0.208	97 (4)	100 (3)	98 (4)	0.067	91 (8)	96 (2)	93 (6)	0.153	89 (12)	96 (2)	92 (9)	0.179
Tau-fluvalinate	161 (41)	80 (119)	121 (74)	0.091	102 (10)	103 (5)	102 (8)	0.720	93 (17)	91 (16)	92 (16)	0.754	79 (20)	98 (16)	89 (20)	0.103
Tebuconazol	97 (17)	110 (6)	104 (13)	0.110	92 (23)	112 (7)	102 (18)	0.069	86 (7)	86 (20)	86 (15)	0.904	97 (8)	108 (19)	102 (15)	0.282
Tebufenozide	98 (12)	95 (9)	97 (10)	0.444	104 (5)	107 (17)	105 (12)	0.667	93 (8)	102 (7)	97 (8)	0.108	101 (5)	107 (4)	104 (5)	0.081
Tebufenpyrad	95 (18)	95 (12)	95 (15)	0.974	90 (15)	101 (11)	95 (14)	0.236	97 (15)	107 (6)	102 (12)	0.156	88 (10)	101 (7)	95 (11)	0.067
Terbutryn	100 (12)	101 (3)	100 (9)	0.746	94 (4)	95 (4)	95 (4)	0.465	88 (8)	94 (3)	91 (7)	0.090	86 (11)	92 (2)	89 (8)	0.202
Tetrachlorvinphos	77 (99)	72 (110)	74 (100)	0.858	68 (44)	64 (25)	66 (35)	0.759	82 (17)	83 (16)	83 (16)	0.912	82 (14)	78 (9)	80 (11)	0.384
Tetraconazol	100 (18)	115 (9)	108 (15)	0.106	100 (10)	112 (11)	106 (12)	0.158	97 (10)	110 (10)	103 (12)	0.104	91 (17)	83 (2)	87 (13)	0.223

Table 4 (*Contd.*)

	Concentration 1				Concentration 2				Concentration 3				Concentration 4			
	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value	Average recovery (%) (RSDr (%)) ($n = 7$)		Average recovery (%) (RSD_{WR} (%)) ($n = 14$)	P value
	Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2			Analyst 1	Analyst 2		
Tetramethrin	97 (14)	97 (16)	97 (14)	0.969	90 (14)	104 (12)	97 (15)	0.124	83 (9)	92 (9)	88 (10)	0.091	88 (12)	100 (10)	94 (12)	0.068
Thiabendazol	26 (82)	37 (7)	31 (50)	0.226	33 (49)	58 (12)	45 (39)	0.009	43 (14)	65 (9)	54 (24)	0.001	57 (14)	68 (6)	62 (14)	0.012
Thiacloprid	96 (13)	88 (11)	92 (12)	0.157	89 (9)	90 (8)	90 (8)	0.762	84 (10)	92 (1)	88 (8)	0.059	96 (11)	90 (4)	93 (9)	0.135
Thiamethoxan	96 (21)	113 (4)	104 (16)	0.076	86 (13)	93 (17)	90 (15)	0.437	91 (6)	97 (10)	94 (9)	0.229	93 (9)	99 (10)	96 (10)	0.093
Thiodicarb	86 (14)	77 (6)	82 (12)	0.141	78 (9)	74 (5)	76 (8)	0.183	70 (9)	70 (5)	70 (7)	0.970	65 (13)	74 (20)	70 (18)	0.202
Thiophanate-methyl	40 (28)	23 (55)	32 (45)	0.044	54 (12)	37 (15)	46 (23)	0.002	72 (18)	85 (18)	78 (19)	0.097	73 (6)	72 (18)	72 (13)	0.935
Toxin T2[a]	**15 (40)**	**17 (47)**	**16 (43)**	**0.623**	**24 (25)**	**22 (19)**	**23 (22)**	**0.585**	**109 (4)**	**109 (6)**	**109 (5)**	**0.896**	**87 (3)**	**84 (3)**	**86 (3)**	**0.157**
Triadimefon	97 (17)	83 (10)	90 (16)	0.129	97 (5)	104 (14)	100 (11)	0.325	90 (9)	91 (14)	91 (11)	0.945	92 (11)	105 (4)	99 (10)	0.052
Triadimenol	193 (92)	−32 (−66)	80 (210)	0.018	96 (19)	73 (19)	84 (23)	0.071	93 (19)	98 (13)	95 (16)	0.587	96 (20)	77 (11)	86 (20)	0.075
Triazophos	90 (16)	103 (7)	97 (13)	0.094	82 (17)	77 (7)	80 (13)	0.449	90 (14)	88 (18)	89 (15)	0.832	108 (13)	97 (5)	102 (11)	0.065
Trifloxystrobin	89 (19)	84 (10)	86 (15)	0.497	98 (10)	89 (16)	94 (14)	0.104	88 (7)	98 (15)	93 (13)	0.081	94 (7)	95 (12)	94 (10)	0.818
Triflumizole	97 (18)	92 (4)	95 (13)	0.554	94 (9)	92 (7)	93 (8)	0.527	86 (7)	93 (5)	89 (7)	0.122	89 (7)	96 (4)	92 (7)	0.097
Triticonazole	90 (20)	104 (16)	97 (19)	0.113	89 (11)	82 (6)	85 (10)	0.121	83 (9)	83 (7)	83 (8)	0.987	91 (12)	84 (5)	87 (10)	0.138
Zearalenone[a]	**45 (109)**	**−180 (-45)**	**−67 (-198)**	**0.001**	**23 (123)**	**−17 (-50)**	**3 (975)**	**0.011**	**29 (8)**	**1 (577)**	**15 (101)**	**0.000**	**22 (12)**	**8 (22)**	**15 (49)**	**0.000**
Zoxamide	86 (17)	96 (11)	91 (15)	0.092	92 (9)	95 (8)	93 (8)	0.584	89 (13)	95 (12)	92 (13)	0.129	94 (7)	96 (5)	95 (6)	0.475

[a] Mycotoxins. [b] n.f.r.: not fulfill requirements of SANTE document.

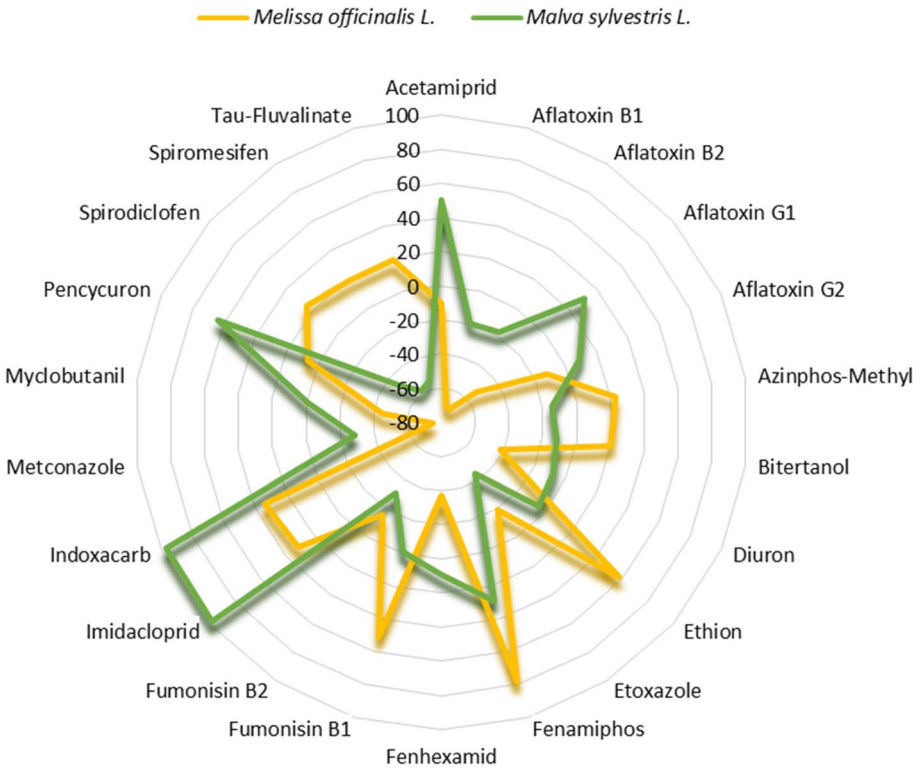

Fig. 4 Percentage of analytes presenting a matrix effect in the ranges of ± 20%, between ± 20% and ± 50% and higher than ± 50%.

that a representative matrix-matched calibration would lead to inaccurate quantification of the analyte. No analyte had a matrix effect within the ± 20% range nor was the same matrix effect observed for an analyte in both matrices. Therefore, individual analytical curves for each matrix were used. Table 2 presents a summary of the analytes' matrix effect for *M. officinalis* and *M. sylvestris*.

Method accuracy was determined by assessing trueness (as recovery) and precision (as repeatability and as reproducibility – RSDr and RSD_{WR}, respectively). *M. officinalis* and *M. sylvestris* were spiked at 12, 20, 50, and 75 μg kg^{-1} for pesticides, 2, 5, 10 and 20 μg kg^{-1} for mycotoxins of group 1, and 100, 250, 500 and 1000 μg kg^{-1} for mycotoxins of group 2, with sevens replicates at each level. As shown in Tables 3 and 4, the recovery percentages obtained (70–120%) and the standard deviations associated with the replicates showed RSD < 20%, which are acceptable according to the SANTE document 11312/2021 (ref. 35) for the 157 pesticide residues and mycotoxins in *M. officinalis* and the 152 in *M. sylvestris*.

The LOD and LOQ were established as the lowest tested solution with a S/N > 3 and the lowest spiked concentration with acceptable accuracy and precision (RSDr and RSD_{WR}), respectively, fulfilling the requirements of SANTE document 11312/2021 (ref. 35) for a quantitative method. When the data were analyzed, 117 pesticides presented an LOQ at 10 μg kg^{-1}, and 15, 14 and 2 pesticides presented an LOQ at 20, 50, and 70 μg kg^{-1}, respectively, for *M. officinalis*. For *M. sylvestris*, 99 pesticides presented an LOQ at 10 μg kg^{-1}, and 20, 14 and 6 pesticides presented an LOQ at 20, 50, and 70 μg kg^{-1}, respectively, showing that most pesticides met the accuracy and precision requirements at the lowest spiked level.

In some cases, such as diflubenzuron, propamocarb, and triadimenol, an LOQ (70 μg kg^{-1}) was achieved in *M. sylvestris* that did not fulfill validation requirements (n.f.r.) for *M. officinalis*. Conversely, analytes validated in *M. officinalis* but not in *M. sylvestris* included bifenazate, diethofencarb, fumonisin B1 and B2, halofenozide, haloxyfop-2-ethoxyethyl, methidathion, omethoate and thiodicarb. Most of these analytes had recovery fluctuations between all 14 replicates, leading to a low precision, indicating the method was not repeatable nor reproducible for these analytes in this specific matrix. For mycotoxins, all four aflatoxins presented an LOQ at 5 μg kg^{-1} and ochratoxin A at 10 μg kg^{-1}.

In this study, two different medicinal herbs, from distinct families and genera, with different pharmacological parts were used for method validation. When comparing the two matrices for all compounds, it is evident that significant deviation in results can occur due to the unique matrix effect caused by each matrix on each analyte. The matrix-matched calibration for both matrices presented similar matrix effects for 111 analytes. Most mycotoxins presented a difference higher than 20% in matrix effect between the two matrices. Fenazaquin, fenhexamid, imazapic, and propyzamid showed signal suppression in *M. officinalis* while in *M. sylvestris*, an enhancement in the analytical signal was observed. More polar compounds, such as acephate, methamidophos, and omethoate, presented the same matrix effect in both matrices, indicating that

a representative matrix could be used without compromising the results.

Commercial sample

Imidacloprid residues (13 μg kg^{-1}) were found in a *M. officinalis* sample. However, there is no MRL for this pesticide, meaning there should be no residues in medicinal herbs sold in the country. Only one sample of *M. sylvestris* showed residues of methyl pirimiphos, at a concentration of 11.6 μg kg^{-1}, which is within the MRL (4000 μg kg^{-1}) set by Brazilian legislation.[32]

Sample comparisons were carried out with herbarium reference material (SMDB) and *via* anatomical analysis of samples that showed pesticide residues. These evaluations were carried out in the herbarium of the Botanical Garden (SMDB) and in the Laboratory of Plant Taxonomy (Biology Department/UFSM). The sample sold as *M. officinalis* was not confirmed to be this species but was compatible with species of Lamiaceae and Verbenaceae. Thus, the consumer used a species other than *M. officinalis*, and in addition to not having its pharmacological properties, they were also exposed to pesticide residue. The *Malva sylvestris* sample was identified as partially compatible with *Malva* sp., mostly mixed with other Malvaceae species.

Despite the limited sampling, the results obtained suggest the non-application of pesticides or the conscious use of pesticides on the medicinal herbs analyzed. In China, in green tea samples analyzed by Y. Huang *et al.*,[54] 67% of the samples contained some pesticide residue, and the majority contained more than five pesticides.

Regarding the presence of mycotoxins, none of those studied were detected in the analyzed samples, indicating correct drying and storage. In the study by N. Pallarés *et al.*,[55] 224 samples of herbal medicines and their infusions were analyzed. The results revealed that aflatoxins B2, G1, and G2 as well as zearalenone, were detected in infusions with incidences ≤ 6% and at concentrations below the limit of quantification up to 82.2 μg L^{-1}. Even though in this study the majority of samples were not positive for the target compounds, investigations need to continue so that more data can be collected to guide national public policies.

Conclusion

This study presents the first reported method for the determination of over 160 mycotoxins/pesticides in medicinal herbs. The developed approach involves a rapid, simple, and effective extraction applying QuEChERS coupled with dSPE clean-up and LC-TQ-MS/MS quantification, which proved to be sufficiently sensitive to meet the diverse analytical requirements for multi-mycotoxin and multi-pesticide analysis. Through a comprehensive clean-up study, it was determined that a combination of GCB, PSA, and $MgSO_4$ provided the optimal conditions for the simultaneous determination of mycotoxins and pesticides. Validation of the method was conducted using two complex matrices, *M. officinalis* and *M. sylvestris*, demonstrating that the majority of analytes met the criteria outlined in the EU SANTE/11312/2021 method validation guidelines. The method demonstrates reliable recoveries, as well as excellent accuracy and precision. Additionally, quality controls were implemented for both the extraction process and equipment injection to identify any potential method deviations during the analysis of commercial samples. Analysis of forty-two commercial samples from Southern Brazil revealed the presence of imidacloprid in *M. officinalis* and methyl pirimiphos in *M. sylvestris* underscoring the efficacy of the method for routine analysis of medicinal plants.

Importantly, this method addresses a significant gap in the literature, as specific analytical methods for mycotoxins and pesticides in *M. officinalis* and *M. sylvestris* are currently limited. Consequently, this method represents a valuable tool for monitoring programs aimed at generating data on residue and contaminants in medicinal plants, thereby aiding in the establishment of maximum residue levels (MRLs) and facilitating risk assessment procedures.

Data availability

At this moment, the raw data generated from this study are only available from computers located at the Center of Research and Analysis of Residues and Contaminants (CEPARC) – Chemistry Department – Federal University of Santa Maria, Santa Maria, Brazil. However, the great majority of secondary data obtained are already present in the tables, figures and text submitted here.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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