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Development and method validation for determination of 128 pesticides in bananas by modified QuEChERS and UHPLC–MS/MS analysis

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ABSTRACT

A multiresidue method for the quantification of 128 pesticides in banana is described. It involves the application of a modified QuEChERS procedure followed by UHPLC–MS/MS (Ultra High Performance Liquid Chromatography coupled to Tandem Mass Spectrometry) analysis. The method was validated according to the European Union SANCO/12495/2011 guidelines and Brazilian Manual of Analytical Quality Assurance. The validation levels were 10.0; 25.0; 50.0 and 100 μg kg^{-1}. Acceptable values were obtained for the following parameters: linearity, limit of detection – LOD (5.00 μg kg^{-1}) and limit of quantification – LOQ (10.0 μg kg^{-1}), except for fenamiphos and mevinphos (LOD = 7.5 μg kg^{-1} and LOQ = 25 μg kg^{-1}), trueness (for the levels: 10.0, 25.0, 50.0 and 100 μg kg^{-1} the recovery assays values were between 70 and 120%) except for methamidophos at 10 μg kg^{-1} level (67.5%), intermediate precision (<20.0%) and measurement uncertainty tests (<50.0%). These results demonstrate the applicability of this method in the routine practice by the laboratories of Ministry of Agriculture, Livestock and Food Supply of Brazil that attend the

1. Introduction

Bananas are one of the most important fruits produced and consumed around the world, having a high nutritional and energetic value as they contain many essential nutrients and have between 90 and 100 kcal per 100 g of edible fruit (Curbelo, Borges, Pérez, & Delgado, 2011). The contribution to the intake of sugars, fibers, vitamins, and minerals from the consumption of bananas is high, with a very low contribution to the intake of fat (Veneziano, Vacca, Arana, De Simone, & Rastrelli, 2004). Bananas are among the most important crops in tropical and subtropical regions of the world. They are grown in an area of about 4.8 million hectares, with an average yield of 19 tonnes/hectare/year and total production of 95.6 million tons. According to the United Nations Food and Agriculture Organization (FAO), approximately 84% of bananas produced are intended for consumption by people of the countries where they are produced. Only 16% of the total production is for export, and contribute to the accounting for revenues of approximately 8.5 billion U.S. dollars annually, benefiting many developing countries (Neto & Guimarães, 2011).

Pesticides are part of a large group of organic compounds that present extremely diverse physico-chemical properties and are widely used in the control or prevention of weeds or banana crop diseases (Štěpán, Tichá, Hajšlová, Kovalczuk, & Kocourek, 2005). Organophosphorus pesticides (OPPs), for example, are one of the most frequently employed worldwide. They are normally sprayed over banana trees and, as a result of their large production and high stability, they constitute a hazard to the environment and also to human health (OPPs are toxic when absorbed by human organisms because of acetyl-cholinesterase deactivation) (Borges, Cabrera, Delgado, Suárez, & Saúco, 2009; Tock, Lai, Lee, Tan, & Bhatia, 2010; Tsoukali & Tsoungas, 1996). Even when applied in accordance with Good Agricultural Practices (GAP), pesticides can leave residues, which can be detrimental to food safety. These compounds are widely used not only during cultivation but also in post-harvest storage. However, the widespread use of pesticides can cause serious health problems in humans such as cancer; neurological diseases and adverse reproductive effects are associated

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with eating and/or exposure to pesticides. Furthermore, the presence of several of the pesticides used in banana production has been identified in surface waters receiving runoff from banana plantations. The most frequently encountered compounds are the fungicides thiabendazole, propiconazole and imazalil; the nematicides terbufos and cadusafos; and the insecticide chlorpyrifos (Castillo et al., 2006). Acute and chronic risk ratios based on observed exposure levels and toxicity values from the literature indicate that some of these pesticides analyzed, including most of the insecticides and nematicides, represent a toxic risk to aquatic organisms (Castillo et al., 2006).

To minimize such problems various organizations have set stringent regulatory controls on pesticide use in order to minimize exposure of the population to pesticide residues in food (Kmellár, Pareja, Ferrer, Fodor, & Alba, 2011). For most of these compounds, regulatory guidelines set maximum residue levels (MRLs) in drinking water and food to help protecting people against contamination and potential negative health effects. Then, the MRLs list for a wide variety of commodities and pesticides is updated from time to time and is part of the EU Plant Protection Products Directive (2005/396/EEC) (European Commission, 2005) and (2009/1107/EEC) (European Commission, 2009), which is the update of the former directive (91/414/EEC) (European Commission, 1991). In Brazil, the Ministry of Agriculture has as one of its duties to further the development of programs that promote improvement of the quality of food for domestic consumption and also for export, ensuring the food safety. Thus, the Ministry of Agriculture published the Normative Instruction n ° 42 of 31 December 2008 (Brasil, 2008) establishing the National Control Plan for Residues and Contaminants (PNCRC) for products of vegetal origin. Thus, to meet the current Brazilian legislation's requirements, it is necessary the development of specific and sensitive methods for the determination of pesticides in food.

In this sense, gas chromatography (GC) and liquid chromatography (LC) have been utilized for pesticides analysis. Unlike GC, laborious and costly derivatisation steps can be avoided in LC especially for the analysis of polar compounds. LC has been coupled to conventional detectors such as photo diode array and fluorescence detectors (Fang, Lau, Law, & Li, 2012; Tadeo, Brunete, Albero, & Valcárcel, 2010). However, mass spectrometry (MS) is preferred as it provides confirmatory evidence of the identity of the compound (Fang et al., 2012). Thus liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods based on triple quadrupole (QqQ) analyzers are frequently used in environmental and food analysis because of the high sensitivity achieved using Selected Reaction Monitoring (SRM) acquisition mode. As a compromise between sensitivity, acceptable chromatographic peak shape, and confirmation purposes established by 2002/657/EC directive (European Commission 2002), two SRM transitions are currently monitored (Núñez, Ayala, Ferrer, Moyano, & Galceran, 2012). Recently, mass spectrometry (MS/MS) has been coupled with certain advances in chromatographic technology such as Ultra Fast Liquid Chromatography (UHPLC). These techniques have made possible the development of multiresidue methodologies covering many trace contaminants. Moreover, UHPLC can reduce the analyses time and increase sensitivity. Thus, high selectivity can be achieved with minimal time. Some papers described the use of this technique for the analysis of pesticides in food (González, Frenich, & Vidal, 2008; López, Reyes, Alba, & Díaz, 2010).

Despite the use of selective detection techniques such as MS, sample preparation is a major challenge in any analytical procedure for the determination of chemical residues in food. Solid–liquid extraction (SLE) (Salces et al., 2005), solid phase extraction (SPE) (Karazafiris, Menkissoglu-Spiroudi, & Thrasyvoulou, 2008), matrix solid-phase dispersion (MSPD) (Viana, Moltó, & Font, 1996), solid-phase microextraction (SPME) (Sagratini, Mañes, Giardiná, Damiani, & Picó, 2007) pressurized liquid extraction (PLE) (Blasco, Font, & Picó, 2005) and stir bar sorptive extraction (SBSE) (Ochiai et al., 2011) are techniques applied in pesticide residue analysis. However, many of them fail in performance in multiresidue applications or are complicated, tedious or time-consuming. Rapid, simple, and robust extraction methods are consequently requested in routine analysis laboratories. In this sense, QuEChERS (quick, easy, cheap, effective, rugged and safe) method is employed frequently as a sample preparation methodology for multiresidue pesticide analysis, and has been modified and validated for the detection of a broad range of pesticides in food, including acidic and basic ones (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003; Lehotay, Mastovská, & Lightfield, 2005; Madureira et al., 2012; Oliveira et al., 2012). The original QuEChERS method consists of initial extraction with acetonitrile, followed by partitioning after the addition of adequately mixed salts (anhydrous magnesium sulfate and sodium chloride) and subsequently submitted to a clean up step. However, many modifications have been introduced, such as buffering the extraction medium with an acetate (Lehotay et al., 2005) or citrate buffer (Lehotay et al., 2010), or changes in the extraction solutions (Lopes, Freitas et al., 2012; Lopes, Reyes, González, Vidal, & Frenich, 2012), among others.

A few methods are reported in the literature for multiresidue analysis of pesticides in bananas. Paranthaman and coworkers (Paranthaman, Sudha, & Kumaravel, 2012) developed a method to investigate the occurrence of endosulfan, carbendazim and chlorpyriphos (belonging to organochlorine, benzimidazole and organophosphate pesticides classes, respectively) for the analysis of 10 different kinds of bananas in southern area of Tamilnadu, India. The analysis was carried out using LC-UV (liquid chromatography coupled to ultraviolet detector) and results were confirmed by GC–MS. However, the method is very laborious and involves the addition of large amounts of solvent. Another study was conducted by Borges et al. (2009) for analysis of 10 organophosphate pesticides (ethoprofos, dimethoate, diazinon, malaoxon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos, fenamiphos, and phosmet) and buprofezin (pesticide not classified) in 57 banana samples taken from the local markets of the Canary Islands (Spain). The analysis method was based on QuEChERS procedure, however this method was applied to a very small number of analytes and, in addition, a cleaning step is included. The analysis was carried out using GC with nitrogen–phosphorus detection (NPD).

In this paper, we present the development, optimization and validation of a method for analysis of 128 pesticide residues (belonging to 46 pesticides classes: aryloxyalkanoic acid/ester, aryloxyphenoxypropionate, pyridinecarboxylic acid/ester, acylalanine, anilinopyrimidine, avermectin, benzamide, benzimidazole, benzofuran, benzothiazinone, carbamate, carbamate oxime, carboxamide, cyanoacetamide oxime, cyanoimidazole, chloroacetamide, diacylhydrazine, dicarboximide, dinitroaniline, sulfite ester, strobilurin, phenylamide, phenylpyrazole, phenylpyridazin, phosphorothiolate, hidroxianilide, imidazole, isoxazole, methylcarbamate, morpholine, neonicotinoid, organophosphate, oxadiazine, piperazine, pyrazole, pyrethroid, pyridazinone, pyridine, pyridinecarboxamide, pyrimidine, sulphamide, sulfonylurea, thiocarbamate, triazinilsulfonilureia, triazole and urea) in bananas aiming to meet the demand of PNCRC monitoring program in Brazil. Banana samples were submitted to a modified QuEChERS extraction without clean-up procedure and sequentially submitted to a selective and sensitive UHPLC–MS/MS analysis. Validation of the method was made based on the European Union SANCO/12495/2011 guidelines (European Union, 2011).

2. Experimental

2.1. Materials and reagents

All reagents were of analytical grade. HPLC-grade acetonitrile and glacial acetic acid were supplied by Merck (Darmstadt, Germany). Methanol was obtained from Baker (Xalostoc, México). Anhydrous magnesium sulfate (purity ≥ 97%) was purchased from Sigma–Aldrich while anhydrous sodium acetate PA and ammonium acetate (purity ≥ 98%) were purchased from Vetec (Rio de Janeiro, RJ) respectively. Formic acid was purchased from Tedia (Ohio, USA). Ultrapure water was generated by a Millipore Milli-Q system (Milford, MA, USA). All the standards were of high purity grade (>98.0%) and were purchased from Riedel-de Haën degree PESTANAL (Seelze, Germany) or Sigma–Aldrich (Saint Louis, USA). Individual stock solutions were prepared at 1000 μg L^{-1} in acetonitrile or methanol and stored at −20 ± 2 °C in a freezer. The working solutions were prepared as appropriate dilutions of the stock solutions.

2.2. Instrumentation

2.2.1. Chromatographic conditions

Chromatographic analyses were performed using an UHPLC system (Shimadzu LC20ADXR) equipped with a binary pump (Shimadzu LC20ADXR), an auto sampler (Shimadzu SIL20ACXR) and a column oven (Shimadzu CTO20AC). The separations were achieved using a Shim-pack XR-ODSII column (2.0 × 100 mm, 2.2 μm particle size). Chromatographic separation was carried out with a mobile phase consisting of ammonium acetate (10 mmol L^{-1}) acidified with 0.01% formic acid (phase A) and methanol (phase B) at a flow rate of 0.5 mL min^{-1}. The gradient elution program was as follows: A (50%)–B (50%) (1 min), A (20%)–B (80%) (6 min), A (10%)–B (90%) (4 min), A (50%)–B (50%) (0.5 min), and A (50%)–B (50%) (1.5 min). The total chromatographic run time was 13 min. Injection volume was 5 μL and the column temperature was set at 60 °C. The chromatographic method was previously developed by Madureira et al. (2012) and was adapted for the UHPLC system.

2.2.2. Mass spectrometric conditions

Mass spectrometry analysis was carried out using a 5500 Triple Quadrupole mass spectrometer (Applied Biosystems, MDS SCIEX, Ontario, Canada). The instrument was operated using electrospray ionization (ESI) in positive and negative ion modes. Instrument settings, data acquisitions and processing were controlled by the software Analyst (Version 1.5.1, Applied Biosystems). Source parameters were optimized as follows: ion spray voltage, 5.5 kV for ESI (+) and 4.5 kV for ESI (−); curtain gas, 20 psi; collision gas, 8 psi; nebulizer gas and auxiliary gas, 30 and 30 psi, respectively; ion source temperature, 500 °C. Optimal declustering potential (DP), collision energy potentials (CE) and collision exit potentials (CXP) are shown in Table 1

2.3. Sample preparation

The blank banana samples were acquired from a crop grown with no use of pesticides, located in Minas Gerais (Brazil). Pesticide-free samples were used as blanks for validation experiments. A representative portion of sample was processed using a homogenizer, transferred to plastic bags and stored at −20 °C prior to analysis. The homogenized sample (10.0 g) was weighed into a polypropylene centrifuge tube (50 mL) and spiked with proper amounts of working standard solutions of pesticides. Next, 10 mL of acetonitrile with 1% acetic acid (v/v) were added and the mixture was shaken vigorously (at 3000 rpm) for 1 min. Then, anhydrous magnesium sulfate (4.0 g) and sodium acetate (1.0 g) were added and the mixture was immediately shaken (at 3000 rpm) for further 1 min. The system was centrifuged at 4000 rpm (1900 *g*) for 9 min. After centrifugation, the supernatant was transferred to another tube (50 mL) containing 1.5 g of magnesium sulfate. The system was stirred for 1 min (at 3000 rpm − 1400 *g*) and posteriorly centrifuged for 9 min (at 4000 rpm 1900 *g*). Finally, an aliquot of supernatant was transferred to vial followed by injection at the UHPLC–MS/MS system.

2.4. Method validation

2.4.1. Selectivity and calibration curves

The selectivity of the method was evaluated by injecting extracted blank samples. The absence of signal above a signal-to-noise ratio of 3 at the retention times of the target compounds showed that the method is free of interferences. Matrix-matched calibration (MMC) was used in order to minimize the matrix effect because matrix constituents may increase or decrease the analytical signal. For the preparation of analytical MMC curves, blank banana extracts were spiked with proper amounts of standard solutions at the final concentrations of 5.00; 7.50; 10.0; 25.0; 50.0; 75.0; 100 μg kg^{-1} (where this sequence was randomly injected ($n = 6$)). All solutions were prepared independently. For simultaneous quantification and identification purposes, two SRM transitions for each analyte (Table 1) were used in order to avoid false negatives at trace pesticide levels. The data were treated by using Analyst software (Version 1.5.1, Applied Biosystems). The best type of fit regression curve was decided for each compound by applying the homoscedasticity test. The Ordinary Least Squares method (OLS) was used for the homoscedastic data, while Weighted Least Squares method (WLS) was used for heteroscedastic data. The fit quality and significance of the regression model employed were evaluated using the Lack of Fit test. The significance level used in all tests was 95%.

2.4.2. Trueness and precision

The trueness was determined from the recovery assay results of samples spiked with all the analytes at four distinct levels: 10.0; 25.0; 50.0 and 100 μg kg^{-1} ($n = 6$ replicates per level) on three different days by two analysts. Recoveries were calculated by comparing the concentrations of the extracted compounds with those from the MMC calibration curves. These data were also used to determine the intermediate precision of the method and quantifying the measurement uncertainty (MU). Repeatability, expressed as relative standard deviation (RSD), was evaluated through the data from replicates samples ($n = 6$) analyzed at same day for each level. The intermediate precision, expressed as relative standard deviation (RSD), was evaluated through the replicates data ($n = 18$) of the three different days for each level.

2.4.3. Limit of detection, limit of quantification and measurement uncertainty

The limit of detection (LOD) was experimentally determined by spiked blank banana extracts with all the analytes. The LOD was defined as the lowest concentration of analyte that could be differentiated of the matrix signal with a signal-to-noise ratio (*S/N*) greater than 6. The LOQ was based on the trueness and precision data, obtained via the recovery determinations and was defined as the lowest validated spike level meeting the requirements of a recovery within the range 70–120% and an RSD ≤ 20%. Measurement uncertainty (MU) was accessed according to ISO/TS 21748:2004 (International Organization for Standardization, 2004) and EURACHEM guide (EURACHEM, 2000).

Table 1
Retention time windows (RTWs) and MS/MS conditions for each compound.

Compound	RTWs, min	Precursor ion	Quantification transition (CE[a], V; CXP[b], V)	Confirmation transition (CE[a], V; CXP[b], V)	Declustering Potential (V)
2,4,5-T	1.97–2.08	$[M-H]^-$	252.7 > 195.0 (−18, −1)	252.7 > 158.9 (−40, −15)	−15
2,4-D	1.17–1.24	$[M-H]^-$	218.9 > 160.9 (−20, −5)	218.9 > 125.0 (−40, −11)	−55
2,4-DB	2.97–3.13	$[M-H]^-$	246.8 > 161.0 (−22, −17)	246.8 > 125.0 (−36, −13)	−65
3-hydroxy carbofuran	0.76–0.80	$[M+H]^+$	238.1 > 163.1 (21, 4)	238.1 > 181.2 (15, 2)	82
Acetamipride	0.74–0.78	$[M+H]^+$	223.1 > 126.0 (29, 12)	223.1 > 73.0 (71, 8)	51
Aldicarb	1.18–1.25	$[M+NH_4]^+$	208.1 > 116.0 (11, 3)	208.1 > 88.9 (20, 3)	51
Aldicarb sulfone	0.50–0.53	$[M+H]^+$	223.1 > 86.1 (21, 8)	223.1 > 76.1 (11, 8)	101
Aldicarb sulfoxide	0.47–0.50	$[M+H]^+$	207.1 > 132.0 (9, 12)	207.1 > 89.0 (21, 8)	86
Allethrin	7.99–8.41	$[M+H]^+$	303.1 > 135.1 (17, 12)	303.1 > 91.1 (55, 8)	106
Avermectin B1a	10.08–10.60	$[M+NH_4]^+$	890.5 > 305.2 (33, 28)	890.5 > 145.1 (53, 28)	91
Azinphos ethyl	5.07–5.33	$[M+H]^+$	346.0 > 132.2 (23, 12)	346.0 > 160.2 (15, 12)	76
Azinphos methyl	3.34–3.52	$[M+H]^+$	318.1 > 132.1 (23, 12)	318.1 > 261.1 (9, 24)	106
Azoxystrobin	3.99–4.20	$[M+H]^+$	404.1 > 371.9 (21, 34)	404.1 > 343.9 (29, 34)	101
Barban	4.41–4.64	$[M+H]^+$	258.1 > 178.0 (13, 16)	258.1 > 143.1 (27, 14)	81
Benalaxyl	6.21–6.52	$[M+H]^+$	326.0 > 148.0 (31, 12)	326.0 > 294.0 (15, 28)	81
Benfuracarb	7.57–7.96	$[M+H]^+$	411.1 > 190.1 (17, 18)	411.1 > 102.1 (43, 8)	86
Bentazone	0.59–0.63	$[M-H]^-$	238.9 > 132.0 (−38, −13)	238.9 > 197.0 (−28, −19)	−95
Bifenthrin	10.94–11.51	$[M+NH_4]^+$	440.1 > 181.2 (19, 16)	440.1 > 166.2 (55, 16)	66
Boscalid	4.36–4.92	$[M+H]^+$	343.0 > 307.0 (27, 28)	343.0 > 139.9 (27, 28)	126
Carbaryl	1.95–2.05	$[M+H]^+$	202.2 > 145.1 (15, 14)	202.2 > 127.1 (39, 12)	66
Carbendazin	0.95–1.00	$[M+H]^+$	192.0 > 160.1 (25, 14)	192.0 > 132.1 (41, 12)	56
Carbofuran	1.75–1.84	$[M+H]^+$	222.1 > 165.2 (17, 2)	222.1 > 123.0 (29, 2)	70
Chlorfenvinphos	6.53–6.86	$[M+H]^+$	359.9 > 155.0 (17, 14)	359.9 > 99.2 (43, 14)	111
Cloroxuron	4.68–4.92	$[M+H]^+$	291.2 > 72.0 (53, 8)	291.2 > 218.0 (33, 20)	96
Cyazofamid	5.25–5.52	$[M+H]^+$	324.9 > 108.0 (19, 10)	324.9 > 261.0 (13, 24)	66
Cymoxanil	0.91–0.96	$[M+H]^+$	199.1 > 128.0 (13, 12)	199.1 > 110.9 (25, 12)	96
Cyproconazole	4.74–5.00	$[M+H]^+$	292.1 > 70.1 (23, 6)	292.1 > 125.0 (37, 12)	81
Cyprodinil	5.98–6.28	$[M+H]^+$	226.1 > 92.9 (45, 34)	226.1 > 76.9 (63, 34)	71
Deltamethrin	9.33–9.80	$[M+NH_4]^+$	522.9 > 280.7 (23, 26)	522.9 > 181.3 (51, 26)	61
Diallate	7.27–7.64	$[M+H]^+$	271.0 > 86.1 (21, 8)	271.0 > 87.1 (21, 8)	71
Diazinon	6.32–6.65	$[M+H]^+$	305.1 > 97.0 (49, 10)	305.1 > 169.1 (31, 16)	71
Dichlofluanid	5.10–5.37	$[M+NH_4]^+$	349.9 > 223.9 (21, 20)	349.9 > 123.1 (39, 12)	56
Dichlorprop	1.67–1.76	$[M-H]^-$	233.0 > 161.0 (−22, −13)	233.0 > 125.0 (−38, −11)	−95
Difenoconazole	6.63–6.97	$[M+H]^+$	406.1 > 250.9 (35, 24)	406.1 > 337.2 (23, 24)	96
Dimethoate	0.78–0.82	$[M+H]^+$	230.0 > 125.0 (31, 12)	230.0 > 198.8 (13, 12)	71
Disulfoton sulfone	2.57–2.71	$[M+H]^+$	307.0 > 153.0 (17, 14)	307.0 > 171.0 (17, 14)	91
Disulfoton sulfoxide	2.45–2.58	$[M+NH_4]^+$	291.0 > 185.0 (21, 18)	291.0 > 157.0 (31, 18)	61
Ethion	7.93–8.34	$[M+H]^+$	385.0 > 199.1 (15, 18)	385.0 > 171.0 (23, 18)	91
Ethofumesate	3.93–4.14	$[M+NH_4]^+$	304.1 > 121.1 (29, 12)	304.1 > 161.2 (31, 12)	71
Ethoprophos	5.29–5.57	$[M+H]^+$	243.1 > 131.0 (27, 12)	243.1 > 96.9 (41, 10)	91
Ethoxysulfuron	1.60–1.69	$[M+H]^+$	399.0 > 261.0 (23, 24)	399.0 > 218.0 (35, 20)	81
Ethyl parathion	5.66–5.95	$[M+H]^+$	292.0 > 235.9 (21, 22)	292.0 > 97.0 (37, 10)	66
Etrinphos	5.98–6.29	$[M+H]^+$	293.1 > 125.0 (33, 12)	293.1 > 265.1 (21, 12)	66
Fenamidone	4.26–4.48	$[M+H]^+$	312.1 > 92.1 (35, 8)	312.1 > 236.1 (19, 22)	71
Fenamiphos	5.58–5.87	$[M+H]^+$	304.1 > 217.1 (29, 20)	304.1 > 202.0 (45, 20)	11
Fenamiphos sulfone	1.82–1.92	$[M+H]^+$	336.0 > 188.0 (39, 16)	336.0 > 266.0 (27, 24)	131
Fenarimol	5.07–5.34	$[M+H]^+$	330.9 > 268.0 (31, 24)	330.9 > 139.0 (47, 12)	101
Fenhexamid	5.13–5.40	$[M+H]^+$	302.1 > 97.2 (31, 10)	302.1 > 55.1 (55, 8)	116
Fenpropimorph	10.47–11.00	$[M+H]^+$	304.3 > 147.1 (37, 14)	304.3 > 117.1 (73, 10)	66
Fenthion	5.97–6.28	$[M+H]^+$	279.0 > 247.0 (19, 22)	279.0 > 169.0 (25, 14)	58
Fenthion sulfoxide	1.76–1.85	$[M+H]^+$	294.9 > 279.9 (25, 26)	294.9 > 109.0 (41, 10)	101
Fipronil	5.66–5.96	$[M+NH_4]^+$	453.9 > 368.1 (31, 34)	453.9 > 255.1 (51, 34)	56
Fluazifop p-butyl	7.75–8.15	$[M+H]^+$	384.1 > 282.0 (29, 26)	384.1 > 328.0 (23, 30)	116
Flumethrin	10.68–11.2	$[M+NH_4]^+$	527.0 > 267.0 (21, 24)	527.0 > 239.0 (31, 22)	46
Fluquinconazole	4.92–5.17	$[M+H]^+$	376.0 > 307.0 (33, 28)	376.0 > 349.0 (33, 28)	11
Fluroxypyr	1.96–2.07	$[M-H]^-$	252.9 > 194.9 (−22, −17)	252.9 > 158.9 (−32, −15)	−80
Flutriafol	2.70–2.83	$[M+H]^+$	302.1 > 122.9 (35, 12)	302.1 > 109.0 (43, 12)	85
Foramsulfuron	0.74–0.78	$[M+NH_4]^+$	453.1 > 182.1 (27, 16)	453.1 > 272.1 (19, 26)	86
Furathiocarb	7.64–8.04	$[M+H]^+$	383.2 > 195.2 (17, 3)	383.2252.2 (24, 3)	72
Hexaconazole	6.29–6.61	$[M+H]^+$	314.2 > 70.0 (53, 12)	314.2 > 159.2 (37, 12)	86
Hexythiazox	8.18–8.60	$[M+H]^+$	353.0 > 228.0 (21, 20)	353.0 > 168.1 (35, 16)	61
Imazalil	5.92–6.23	$[M+H]^+$	297.0 > 159.0 (29, 14)	297.0 > 200.9 (23, 14)	81
Imidacloprid	0.62–0.66	$[M+H]^+$	256.2 > 175.1 (27, 16)	256.2 > 209.1 (21, 20)	66
Indoxacarb	7.15–7.52	$[M+H]^+$	528.0 > 203.1 (59, 18)	528.0 > 150.1 (31, 14)	136
Iprodione	5.55–5.84	$[M+H]^+$	329.9 > 245.0 (21, 22)	329.9 > 246.9 (21, 22)	111
Iprovalicarb	5.14–5.41	$[M+H]^+$	321.2 > 203.2 (23, 3)	321.2 > 119.0 (12, 2)	61
Isoproturon	2.86–3.01	$[M+H]^+$	207.3 > 72.1 (23, 8)	207.3 > 165.1 (19, 14)	71
Isoxaflutole	2.95–3.11	$[M-H]^-$	357.8 > 79.0 (−20, −9)	357.8 > 63.9 (−80, −9)	−85
Kresoxim methyl	5.95–6.26	$[M+H]^+$	314.1 > 222.1 (21, 20)	314.1 > 116.0 (19, 10)	76
Linuron	3.71–3.90	$[M+H]^+$	249.1 > 159.2 (25, 4)	249.1 > 182.0 (21, 4)	76
Malathion	4.48–4.72	$[M+H]^+$	330.9 > 127.1 (17, 12)	330.9 > 285.1 (11, 26)	111
Metalaxyl	3.05–3.21	$[M+H]^+$	280.2 > 220.1 (19, 20)	280.2 > 192.2 (25, 18)	66
Metazachlor	2.89–3.04	$[M+H]^+$	278.1 > 134.1 (29, 12)	278.1 > 210.1 (15, 18)	51

Table 1 (*continued*)

Compound	RTWs, min	Precursor ion	Quantification transition (CE[a], V; CXP[b], V)	Confirmation transition (CE[a], V; CXP[b], V)	Declustering Potential (V)
Methamidophos	0.44–0.47	$[M + H]^+$	142.0 > 93.9 (19, 12)	142.0 > 124.9 (19, 12)	76
Methidathion	3.15–3.32	$[M + H]^+$	303.0 > 145.0 (13, 14)	303.0 > 85.1 (29, 8)	86
Methiocarb	3.90–4.10	$[M + H]^+$	226.1 > 169.1 (13, 14)	226.1 > 121.1 (25, 10)	76
Methiocarb sulfoxide	0.68–0.72	$[M + H]^+$	242.1 > 185.1 (19, 16)	242.1 > 122.1 (39, 12)	81
Methomyl	0.55–0.58	$[M + H]^+$	163.1 > 88.1 (13, 3)	163.1 > 106.1 (13, 3)	55
Metsulfuron methyl	0.57–0.60	$[M + H]^+$	383.0 > 167.1 (23, 16)	383.0 > 168.1 (21, 16)	51
Mevinphos	0.83–0.89	$[M + H]^+$	225.1 > 127.1 (21, 12)	225.1 > 193.0 (11, 16)	66
Monocrotophos	0.54–0.57	$[M + H]^+$	224.1 > 127.0 (23, 12)	224.1 > 98.0 (17, 12)	71
Monolinuron	2.16–2.28	$[M + H]^+$	215.1 > 125.9 (27, 12)	215.1 > 148.0 (19, 12)	91
Myclobutanil	4.64–4.88	$[M + H]^+$	289.1 > 70.1 (33, 10)	289.1 > 125.1 (39, 10)	91
Nuarimol	3.90–4.20	$[M + H]^+$	314.9 > 252.0 (31, 22)	314.9 > 81.1 (51, 8)	81
Omethoate	0.44–0.47	$[M + H]^+$	214.1 > 183.0 (15, 16)	214.1 > 125.0 (29, 12)	56
Oxadixyl	1.17–1.23	$[M + H]^+$	279.1 > 219.0 (15, 20)	279.1 > 132.1 (41, 12)	66
Oxamyl	0.50–0.53	$[M + NH_4]^+$	237.1 > 72.1 (25, 8)	237.1 > 90.0 (11, 10)	51
Oxasulfuron	0.70–0.74	$[M + H]^+$	407.1 > 150.1 (25, 14)	407.1 > 107.1 (63, 10)	111
Paclobutrazol	4.48–4.72	$[M + H]^+$	294.0 > 70.1 (55, 6)	294.0 > 125.0 (55, 12)	81
Penconazole	5.90–6.21	$[M + H]^+$	284.2 > 70.1 (21, 8)	284.2 > 159.0 (41, 14)	66
Pendimethalin	8.15–8.57	$[M + H]^+$	282.2 > 212.1 (15, 20)	282.2 > 91.0 (33, 8)	36
Phenthoate	5.80–6.10	$[M + H]^+$	321.0 > 79.1 (51, 16)	321.0 > 163.1 (17, 16)	96
Phorate	2.47–2.60	$[M + NH_4]^+$	278.1 > 97.0 (43, 10)	278.1 > 171.0 (25, 16)	21
Phorate sulfoxide	2.46–2.60	$[M + H]^+$	276.9 > 199.0 (13, 18)	276.9 > 142.9 (27, 12)	111
Phosalone	6.54–6.88	$[M + H]^+$	367.9 > 182.0 (21, 16)	367.9 > 111.0 (57, 10)	121
Phosmet	3.42–3.59	$[M + H]^+$	318.0 > 133.0 (51, 12)	318.0 > 160.0 (19, 12)	96
Pirimiphos methyl	6.63–6.97	$[M + H]^+$	306.1 > 164.1 (29, 14)	306.1 > 108.1 (39, 10)	51
Prochloraz	6.51–6.85	$[M + H]^+$	376.0 > 308.0 (17, 28)	376.0 > 265.9 (25, 28)	61
Propargite	8.56–9.00	$[M + NH_4]^+$	368.1 > 231.1 (15, 20)	368.1 > 175.1 (23, 16)	41
Propiconazole	6.24–6.57	$[M + H]^+$	342.1 > 159.1 (37, 14)	342.1 > 89.1 (99, 8)	76
Propoxur	1.68–1.77	$[M + H]^+$	210.1 > 111.0 (19, 3)	210.1 > 168.1 (11, 3)	61
Propyzamide	4.36–4.59	$[M + H]^+$	256.1 > 190.0 (19, 16)	256.1 > 173.0 (31, 16)	61
Prosulfuron	1.77–1.87	$[M + H]^+$	419.9 > 167.1 (25, 16)	419.9 > 109.1 (69, 10)	86
Pyraclostrobin	6.46–6.80	$[M + H]^+$	388.0 > 194.1 (17, 18)	388.0 > 163.1 (33, 14)	51
Pyrazophos	6.51–6.85	$[M + H]^+$	374.1 > 222.1 (29, 20)	374.1 > 194.1 (43, 20)	91
Pyridaben	9.43–9.95	$[M + H]^+$	365.1 > 309.1 (17, 30)	365.1 > 147.2 (31, 30)	41
Pyridate	10.08–10.60	$[M + H]^+$	379.1 > 207.1 (23, 18)	379.1 > 104.1 (55, 10)	61
Pyrifenox	7.99–8.40	$[M + H]^+$	294.2 > 93.1 (27, 8)	294.2 > 92.1 (83, 8)	86
Pyrimethanil	4.00–4.21	$[M + H]^+$	200.2 > 107.1 (33, 10)	200.2 > 80.0 (39, 8)	41
Quinalphos	5.73–6.03	$[M + H]^+$	299.1 > 163.1 (33, 14)	299.1 > 147.1 (31, 14)	61
Tebuconazole	5.98–6.29	$[M + H]^+$	308.1 > 70.1 (57, 8)	308.1 > 125.1 (53, 12)	71
Tebufempirade	7.80–8.20	$[M + H]^+$	334.1 > 145.1 (39, 4)	334.1 > 117.1 (67, 6)	111
Tebufenozide	5.73–6.03	$[M + H]^+$	353.1 > 133.1 (25, 12)	353.1 > 297.1 (11, 28)	56
TEPP	1.26–1.33	$[M + H]^+$	291.1 > 179.0 (29, 16)	291.1 > 99.0 (45, 10)	76
Thiacloprid	0.80–0.85	$[M + H]^+$	253.3 > 126.0 (29, 12)	253.3 > 186. 0 (21, 12)	101
Thiamethoxam	0.54–0.57	$[M + H]^+$	292.1 > 211.1 (17, 20)	292.1 > 181.1 (31, 16)	76
Thiodicarb	2.05–2.16	$[M + H]^+$	355.1 > 88.1 (27, 3)	355.1 > 108.0 (21, 3)	60
Tiabendazole	1.20–1.27	$[M + H]^+$	202.2 > 175.1 (35, 16)	202.2 > 131.1 (45, 12)	116
Tifensulfuron methyl	0.54–0.57	$[M + H]^+$	388.0 > 167.1 (21, 14)	388.0 > 205.0 (37, 18)	51
Tolylfluanid	6.02–6.33	$[M + NH_4]^+$	363.9 > 238.0 (19, 22)	363.9 > 137.1 (39, 12)	46
Triadimefon	4.67–4.91	$[M + H]^+$	294.0 > 197.0 (21, 18)	294.0 > 225.0 (17, 20)	66
Triadimenol	4.84–5.09	$[M + H]^+$	296.1 > 70.1 (31, 8)	296.1 > 70.0 (33, 8)	46
Triassulfuron	0.80–0.85	$[M + H]^+$	402.0 > 167.1 (23, 14)	402.0 > 141.1 (27, 12)	76
Triazophos	4.80–5.05	$[M + H]^+$	314.1 > 97.0 (45, 10)	314.1 > 65.1 (85, 10)	81
Trichlorfon	0.79–0.84	$[M + H]^+$	257.0 > 109.0 (23, 10)	257.0 > 221.0 (15, 20)	101
Tridemorph	11.3–12.0	$[M + H]^+$	298.3 > 130.1 (35, 12)	298.3 > 98.1 (37, 10)	121
Triflumizole	7.12–7.48	$[M + H]^+$	346.0 > 278.0 (15, 26)	346.0 > 73.1 (21, 8)	51
Triforin	3.51–3.69	$[M + H]^+$	434.9 > 389.8 (17, 36)	434.9 > 215.1 (37, 20)	56

[a] Collision energy.
[b] Collision cell exit potential.

3. Results and discussion

The total ion chromatograms (TIC) are shown in Fig. 1 (note the presence of chromatographic peaks related to each compound). To obtain these chromatograms, blank banana extracts were spiked with all the analytes at 10.0 μg L^{-1} while the more intense SRM transition (quantification transition) for each analyte was selected (Table 1). According to the European Commission Decision 2002/657/EC (European Commission, 2002), the identification of an analyte above the LOQ in the sample is done when the following interpretation criteria are fulfilled: a minimum of three identification points is required, i.e. when the two selected product ions are present. Moreover, according to European Union SANCO/12495/2011 guidelines (European Union, 2011) the precursor (parent) ion and the two SRM transitions (quantification and identification ion) should be present with a signal-to-noise (S/N) ratio greater than 3 (in the lowest calibration level this ratio should be greater than 6); and the ratio of the quantification/confirmation transitions in the sample and the previously injected standard should not differ by more than the percentage stipulated. Therefore, two transitions were selected for each compound (Table 1).

3.1. Extraction method

The original QuEChERS method consists of two steps, a salting-out extraction and a dispersive SPE (dSPE) clean up (Anastassiades

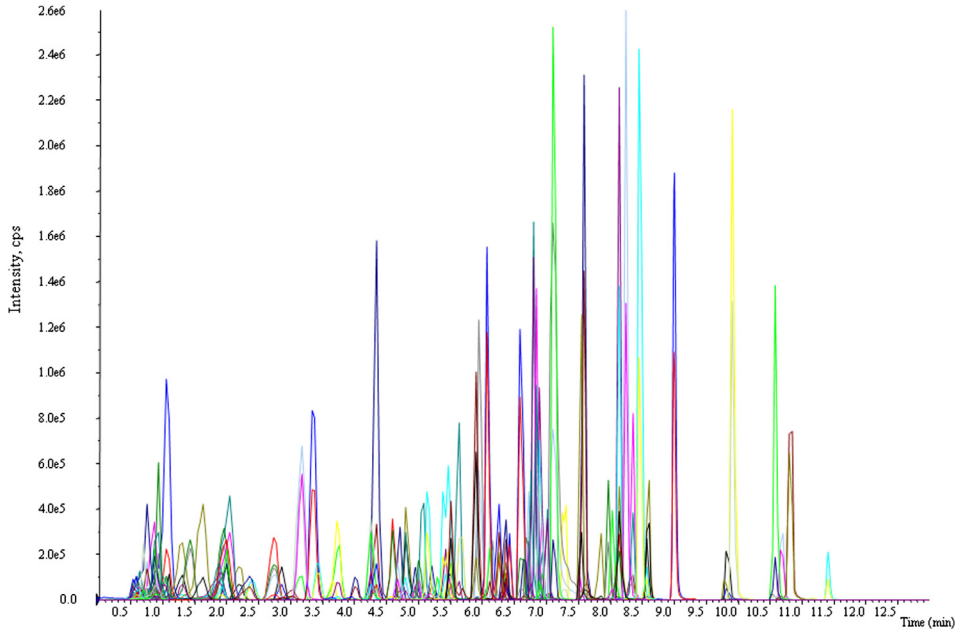

Fig. 1. Total ion chromatogram (TIC) obtained by LC–MS/MS (ESI positive mode) for blank banana extracts spiked with all the analytes at 10.0 μg L^{-1}.

et al., 2003). However, previous studies (not described here) with PSA (primary and secondary amine) and GCB (Graphitized Carbon Black) indicated that banana extracts dispensed later stages of clean up. Other studies in the literature support that QuEChERS procedure can be applied without clean up steps (Madureira et al., 2012). Furthermore, other tests involving the addition of different quantities of water indicated that there was no need for extra addition of water. Then QuEChERS procedure was used for the extraction of pesticides in bananas, but some modifications were made as shown in section 2.3, as for example besides the absence of additional cleaning steps, the adding of magnesium sulfate to the supernatant was performed to provide some clean up by removing residual water (and possibly other components via chelation) (Lehotay Maótovska, 2005b). The modified QuEChERS procedure was in-house validated to comply with the requirements of ISO/IEC 17025:2005 standard (International Organization for Standardization, 2005).

3.2. Method validation

Validation of the method was based on the European Union SANCO/12495/2011 guidelines (European Union, 2011) and Brazilian Manual of Analytical Quality Assurance (Brasil, 2011b). The selectivity of the method was evaluated by injecting blank sample extracts. The absence of signal above a signal-to-noise ratio of 3 at the retention times of the target compounds showed that the method is free of interferences. Identification was carried out by comparison of the ratio of the two chromatographic peak areas (from quantification and identification transitions) of the spiked samples with the calibration standards. The MMC curves for each compound were built using blank samples. For this, five concentrations levels were selected. The criteria adopted for the selection of the analytical curve levels were the signal to noise ratio and also the results of recovery studies. From this evaluation we selected the following concentration levels for the MMC curves: 10.0; 25.0; 50.0; 75.0 and 100 μg kg^{-1}. The concentration level 5.00 μg kg^{-1} was injected to confirm the LOD of the method. As described previously, OLS and WLS were used for homoscedastic or heteroscedastic data, respectively. Over the calibration ranges selected, all the calibration curves presented significant linearity according to the Lack of Fit test and *t*-test on determination coefficients (r^2). LOD and LOQ are shown in Table 2. It can be seen that LODs and LOQs were 5.0 and 10 μg kg^{-1}, respectively, except for fenamiphos and mevinphos (LOD = 7.5 μg kg^{-1} and LOQ = 25 μg kg^{-1}). For substances for which the MRL is above the working range, the applicability of the method should be implemented through recovery experiments with spiked samples above the MRL, and followed by appropriate dilution by a dilution factor so that the concentration is located in the working range. This dilution should be incorporated into the calculation of measurement uncertainty.

The trueness was assessed by recovery experiments of blank banana samples spiked at four levels, 10.0; 25.0; 50.0 and 100 μg kg^{-1} ($n = 6$ replicates per level) due to the lack of certified reference materials. Then the trueness (percentage recoveries) and precision (repeatability, in terms of % RSD) were estimated as can been seen in Table 2. As it is depicted in Fig. 2 and shown in Table 2, almost all results showed recoveries in the range considered acceptable (70–120%) except for methamidophos at 10 μg kg^{-1} level. However, the recovery (67.5%) is very close to the acceptable and others parameters as intermediation precision (6.5%) and measurement uncertainty (35.7%) are satisfactorily for this analyte. Furthermore, to ensure that the method is really reproducible, the methamidophos will monitored during routine assays. Moreover, in this same level, fenamiphos and mevinphos did not show acceptable parameters for the recovery assays. As it can be seen in Fig. 3, the vast majority of results showed coefficient of variation lower than 10% for all levels of fortification. Furthermore only three analytes had coefficients of variation between 15 and 20% in the LOQ.

The measurement uncertainty was based on a combination of "top-down" and "bottom-up" methodologies described in EURACHEM guide (EURACHEM, 2000). The main sources of uncertainty for the method were: (1) the mass measurements of the standards for the preparation of solutions; (2) dilution of the standard solutions; (3) the measurements of volume of the extraction solution;

Table 2
Validation parameters obtained for the optimized method: Average recovery (%), intermediate precision (%), measurement uncertainty, limit of detection (LOD), limit of quantification (LOQ), maximum residue levels (MRL) established by Brazilian law and MRL established by Community European.

Compound	Fit regression type	Average recovery, % (Intermediate precision, %)				Measurement uncertainty, %				LOD, (μg kg^{-1})	LOQ, (μg kg^{-1})	MRL* (μg kg^{-1})	MRL** (μg kg^{-1})
		10.0 (μg kg^{-1})	25.0 (μg kg^{-1})	50.0 (μg kg^{-1})	100 (μg kg^{-1})	10.0, (μg kg^{-1})	25.0 (μg kg^{-1})	50.0 (μg kg^{-1})	100 (μg kg^{-1})				
2,4,5-T	WLS	89.3 (9.0)	84.7 (12.0)	87.9 (12.0)	87.3 (12.9)	37.1	16.2	12.6	12.5	5.0	10.0	[a]	50
2,4-D	WLS	86.4 (9.8)	77.3 (11.5)	79.3 (12.6)	78.2 (13.9)	35.2	15.7	12.6	12.6	5.0	10.0	[b]	50
2,4-DB	WLS	102.0 (13.5)	96.5 (13.6)	101.6 (12.6)	101.4 (15.5)	32.1	15.2	12.5	12.7	5.0	10.0	[c]	50
3-Hydroxy carbofuran	WLS	95.6 (7.1)	105.5 (3.5)	99.1 (5.0)	99.9 (1.6)	26.6	13.5	11.6	11.4	5.0	10.0	100	20
Acetamipride	WLS	93.0 (8.3)	105.3 (4.2)	102.6 (6.6)	96.0 (2.8)	34.8	15.2	12.0	11.7	5.0	10.0	[b]	10
Aldicarb	WLS	80.3 (12.4)	94.7 (5.5)	93.2 (7.9)	86.2 (8.3)	21.3	12.5	11.6	11.6	5.0	10.0	[b]	20
Aldicarb sulfone	WLS	89.6 (10.7)	98.7 (7.2)	96.9 (5.4)	93.8 (2.9)	29.9	14.3	11.7	11.5	5.0	10.0	[b]	20
Aldicarb sulfoxide	WLS	102.2 (13.0)	100.0 (10.3)	96.5 (9.8)	99.4 (10.3)	29.2	14.3	12.0	12.0	5.0	10.0	[b]	20
Allethrin	WLS	101.1 (10.3)	105.7 (4.4)	99.7 (11.2)	100.6 (9.7)	20.5	12.4	11.9	11.7	5.0	10.0	[b]	–
Avermectin B1a	WLS	103.6 (7.4)	108.4 (12.7)	97.6 (11.2)	102.0 (10.0)	22.0	13.3	12.0	11.8	5.0	10.0	[a]	10
Azinphos ethyl	WLS	96.8 (6.6)	109.0 (5.4)	103.4 (4.8)	98.2 (3.9)	23.6	13.0	11.5	11.4	5.0	10.0	[c]	20
Azinphos methyl	OLS	100.3 (5.4)	107.0 (4.8)	100.8 (6.3)	100.5 (4.5)	13.4	11.4	11.4	11.3	5.0	10.0	[d]	50
Azoxystrobin	WLS	92.6 (5.2)	110.1 (4.3)	106.8 (3.3)	94.0 (2.8)	36.4	15.6	11.9	11.7	5.0	10.0	200	2000
Barban	WLS	98.4 (7.8)	110.2 (7.2)	109.1 (5.6)	97.9 (7.4)	24.7	13.3	11.6	11.6	5.0	10.0	[d]	50
Benalaxyl	WLS	91.9 (12.1)	110.9 (9.0)	109.7 (4.8)	94.2 (6.0)	48.4	18.7	12.6	12.3	5.0	10.0	[b]	50
Benfuracarb	WLS	74.5 (10.5)	87.6 (11.6)	87.6 (10.4)	87.8 (8.0)	28.8	14.4	12.1	11.8	5.0	10.0	[b]	50
Bentazone	WLS	101.0 (13.6)	96.4 (15.4)	104.6 (16.1)	111.5 (14.3)	39.1	16.9	13.2	12.8	5.0	10.0	[b]	100
Bifenthrin	WLS	95.5 (5.8)	98.4 (6.9)	94.4 (6.1)	97.6 (7.6)	17.0	12.0	11.4	11.5	5.0	10.0	20	100
Boscalid	WLS	100.1 (3.2)	105.5 (5.4)	103.9 (5.9)	97.8 (4.0)	14.7	11.6	11.4	11.3	5.0	10.0	[b]	600
Carbaryl	WLS	100.0 (4.1)	103.8 (4.9)	101.0 (4.4)	98.5 (3.5)	13.5	11.5	11.3	11.2	5.0	10.0	200	50
Carbendazin	WLS	102.9 (4.8)	112.4 (7.5)	109.4 (3.6)	98.4 (4.1)	34.1	15.2	11.8	11.7	5.0	10.0	[b]	100
Carbofuran	WLS	103.9 (3.7)	109.8 (4.2)	104.8 (4.7)	97.6 (2.1)	25.2	13.2	11.6	11.4	5.0	10.0	100	20
Chlorfenvinphos	WLS	98.8 (4.2)	109.7 (7.7)	104.4 (7.2)	101.3 (8.1)	16.8	12.1	11.5	11.5	5.0	10.0	[c]	20
Cloroxuron	WLS	94.3 (5.7)	108.7 (5.2)	105.3 (7.0)	96.1 (3.8)	24.9	13.2	11.7	11.4	5.0	10.0	[d]	50
Cyazofamid	WLS	97.3 (5.1)	110.5 (6.3)	107.9 (4.9)	95.0 (3.1)	23.8	13.1	11.5	11.4	5.0	10.0	[b]	10
Cymoxanil	WLS	102.9 (8.6)	115.1 (8.6)	105.1 (6.9)	98.0 (3.0)	30.1	14.4	11.8	11.6	5.0	10.0	[b]	50
Cyproconazole	WLS	100.7 (6.6)	106.7 (3.4)	102.5 (5.5)	97.4 (2.9)	15.1	11.6	11.3	11.2	5.0	10.0	[b]	50
Cyprodinil	WLS	99.7 (6.0)	105.0 (10.1)	99.3 (8.2)	97.2 (6.7)	23.4	13.3	11.7	11.6	5.0	10.0	[b]	50
Deltamethrin	WLS	104.6 (8.6)	108.6 (9.2)	97.8 (9.9)	101.3 (8.4)	27.3	13.9	12.0	11.8	5.0	10.0	[b]	50
Diallate	WLS	96.1 (19.4)	113.9 (14.9)	95.4 (14.5)	105.6 (10.8)	23.2	13.6	12.4	11.9	5.0	10.0	[a]	50
Diazinon	WLS	105.6 (5.8)	109.7 (8.1)	105.2 (6.4)	97.0 (4.5)	22.6	13.0	11.6	11.4	5.0	10.0	[b]	10
Dichlofluanid	WLS	104.7 (9.0)	106.5 (11.6)	101.1 (14.0)	108.6 (8.0)	25.0	13.7	12.4	11.7	5.0	10.0	[d]	–
Dichlorprop	WLS	87.4 (14.7)	85.1 (14.0)	91.7 (14.5)	90.8 (15.7)	32.3	15.3	12.7	12.7	5.0	10.0	[d]	50
Difenoconazole	WLS	99.4 (6.6)	103.2 (4.5)	100.7 (5.3)	96.5 (3.7)	27.5	13.7	11.7	11.5	5.0	10.0	500	100
Dimethoate	WLS	87.2 (14.4)	99.0 (10.8)	95.0 (8.7)	99.7 (6.8)	25.1	13.6	11.8	11.6	5.0	10.0	[b]	200
Disulfoton sulfone	WLS	101.1 (5.8)	108.4 (3.8)	102.9 (5.1)	100.2 (3.7)	17.3	11.9	11.4	11.3	5.0	10.0	[b]	200
Disulfoton sulfoxide	WLS	110.5 (4.2)	112.4 (5.7)	106.9 (6.4)	102.3 (6.6)	16.6	11.9	11.4	11.4	5.0	10.0	[b]	200
Ethion	WLS	100.9 (12.6)	108.9 (9.6)	100.6 (16.6)	102.6 (9.6)	28.4	14.1	12.8	11.9	5.0	10.0	[b]	100
Ethofumesate	WLS	103.1 (4.6)	111.5 (4.8)	106.3 (5.1)	98.2 (3.0)	21.6	12.6	11.5	11.3	5.0	10.0	[b]	50
Ethoprophos	WLS	102.2 (7.2)	106.3 (6.5)	100.5 (7.0)	101.2 (3.7)	14.6	11.7	11.4	11.2	5.0	10.0	[b]	20
Ethoxysulfuron	WLS	83.9 (8.2)	109.4 (6.5)	115.3 (5.1)	114.4 (6.4)	30.5	14.4	11.8	11.7	5.0	10.0	[b]	50
Ethyl parathion	WLS	94.4 (6.4)	100.5 (5.4)	100.6 (5.8)	96.1 (4.0)	31.2	14.5	11.8	11.6	5.0	10.0	[c]	–
Etrinphos	WLS	103.4 (7.4)	109.5 (10.8)	99.8 (10.1)	100.5 (4.6)	27.3	14.0	12.0	11.5	5.0	10.0	[c]	–
Fenamidone	WLS	100.2 (5.5)	107.8 (5.6)	101.9 (6.5)	98.2 (2.9)	18.0	12.1	11.5	11.3	5.0	10.0	[b]	20
Fenamiphos	WLS	–	95.6 (10.7)	93.0 (9.1)	82.1 (11.5)	–	18.3	12.7	12.7	5.0	25.0	100	20
Fenamiphos sulfone	WLS	97.8 (5.3)	107.0 (3.8)	102.1 (3.5)	96.2 (2.0)	21.4	12.6	11.4	11.3	5.0	10.0	100	20
Fenarimol	WLS	99.7 (6.2)	107.8 (6.7)	100.3 (7.0)	100.4 (5.8)	15.4	11.8	11.4	11.3	5.0	10.0	[b]	200
Fenhexamid	WLS	100.7 (7.2)	109.3 (5.3)	100.9 (7.4)	98.8 (5.5)	17.9	12.0	11.5	11.4	5.0	10.0	[d]	50
Fenpropimorph	WLS	95.0 (6.5)	107.7 (5.8)	101.3 (6.6)	97.9 (5.5)	20.5	12.5	11.5	11.4	5.0	10.0	[b]	2000
Fenthion	WLS	99.3 (9.2)	107.1 (10.7)	100.4 (13.3)	97.8 (10.5)	29.5	14.4	12.4	12.0	5.0	10.0	[b]	10
Fenthion sulfoxide	WLS	105.0 (6.2)	113.5 (5.0)	105.7 (5.0)	98.6 (4.2)	25.7	13.4	11.6	11.5	5.0	10.0	[d]	10
Fipronil	WLS	102.2 (8.1)	105.0 (7.2)	101.7 (5.8)	102.2 (4.6)	24.3	13.2	11.6	11.5	5.0	10.0	[b]	5
Fluazifop p-butyl	WLS	91.0 (17.7)	115.2 (11.5)	105.9 (10.8)	97.6 (8.4)	32.5	15.1	12.2	11.9	5.0	10.0	[b]	200
Flumethrin	WLS	86.4 (12.5)	84.5 (15.6)	98.2 (11.2)	102.2 (17.6)	37.1	16.5	12.5	13.2	5.0	10.0	[d]	–
Fluquinconazole	WLS	100.8 (3.2)	104.7 (6.5)	104.8 (5.3)	102.6 (6.0)	14.5	11.7	11.3	11.3	5.0	10.0	[b]	50
Fluroxypyr	WLS	89.9 (11.4)	82.8 (12.4)	89.2 (13.7)	86.8 (13.7)	31.7	15.0	12.5	12.4	5.0	10.0	[b]	50
Flutriafol	WLS	100.9 (5.1)	106.3 (3.8)	101.7 (4.4)	101.0 (3.4)	14.1	11.5	11.3	11.2	5.0	10.0	100	300
Foramsulfuron	WLS	92.4 (7.5)	103.5 (6.4)	99.3 (4.8)	98.9 (3.4)	18.0	12.1	11.4	11.3	5.0	10.0	[b]	10
Furathiocarb	WLS	104.3 (17.3)	100.8 (10.6)	104.1 (14.2)	93.3 (9.0)	15.6	12.0	12.2	11.6	5.0	10.0	[b]	50
Hexaconazole	WLS	98.3 (6.2)	107.0 (9.1)	105.7 (8.1)	99.1 (4.5)	22.9	13.1	11.7	11.4	5.0	10.0	[b]	10
Hexythiazox	WLS	97.9 (11.0)	103.8 (8.1)	97.9 (11.4)	96.5 (13.3)	32.9	14.9	12.3	12.4	5.0	10.0	[b]	500
Imazalil	WLS	88.9 (5.9)	101.6 (5.1)	101.2 (7.9)	91.1 (3.6)	18.2	12.1	11.6	11.3	5.0	10.0	1000	2000
Imidacloprid	WLS	87.9 (10.4)	103.6 (4.8)	102.8 (7.8)	97.2 (3.2)	39.8	16.4	12.3	11.9	5.0	10.0	100	50
Indoxacarb	WLS	103.3 (5.6)	109.1 (8.4)	103.2 (7.3)	102.9 (4.1)	19.9	12.6	11.6	11.3	5.0	10.0	[b]	200
Iprodione	WLS	92.5 (8.7)	103.3 (7.7)	95.6 (9.6)	96.0 (9.5)	33.0	15.0	12.2	12.0	5.0	10.0	[b]	20
Iprovalicarb	WLS	93.6 (5.1)	104.0 (3.8)	102.8 (3.9)	94.9 (1.7)	22.9	12.8	11.5	11.3	5.0	10.0	[b]	50
Isoproturon	WLS	93.0 (4.8)	103.6 (4.5)	102.4 (4.2)	94.9 (3.1)	22.6	12.8	11.5	11.4	5.0	10.0	[d]	50

(*continued on next page*)

Table 2 (*continued*)

Compound	Fit regression type	Average recovery, % (Intermediate precision, %)				Measurement uncertainty, %				LOD, (μg kg^{-1})	LOQ, (μg kg^{-1})	MRL* (μg kg^{-1})	MRL** (μg kg^{-1})
		10.0 (μg kg^{-1})	25.0 (μg kg^{-1})	50.0 (μg kg^{-1})	100 (μg kg^{-1})	10.0, (μg kg^{-1})	25.0 (μg kg^{-1})	50.0 (μg kg^{-1})	100 (μg kg^{-1})				
Isoxaflutole	WLS	109.3 (13.1)	108.8 (14.9)	115.6 (11.5)	108.8 (13.3)	24.9	14.0	12.1	12.2	5.0	10.0	[b]	50
Kresoxim methyl	WLS	99.9 (8.6)	108.9 (6.0)	107.4 (7.0)	99.8 (6.8)	18.4	12.2	11.5	11.5	5.0	10.0	[b]	50
Linuron	WLS	98.5 (2.5)	102.4 (4.3)	100.8 (4.8)	97.2 (2.2)	17.0	11.9	11.3	11.2	5.0	10.0	[b]	50
Malathion	WLS	95.1 (5.1)	104.4 (4.8)	104.2 (4.0)	97.8 (3.4)	19.4	12.3	11.4	11.3	5.0	10.0	[b]	20
Metalaxyl	WLS	**67.5** (6.5)	76.6 (9.1)	84.2 (4.7)	79.9 (3.5)	35.7	15.7	11.9	11.7	5.0	10.0	[b]	50
Metazachlor	WLS	93.5 (3.2)	106.3 (4.9)	104.5 (4.3)	95.8 (3.6)	24.8	13.2	11.5	11.4	5.0	10.0	[d]	50
Methamidophos	WLS	92.2 (3.2)	104.9 (3.2)	103.0 (4.7)	93.7 (3.0)	28.7	13.9	11.7	11.5	5.0	10.0	[b]	10
Methidathion	WLS	98.9 (3.1)	104.1 (3.3)	101.8 (5.4)	96.8 (2.7)	16.3	11.8	11.4	11.2	5.0	10.0	[b]	20
Methiocarb	WLS	99.5 (12.4)	105.3 (7.9)	99.0 (6.0)	95.3 (5.9)	48.4	18.7	12.6	12.3	5.0	10.0	[b]	100
Methiocarb sulfoxide	WLS	95.7 (5.5)	102.5 (4.7)	101.9 (5.7)	96.3 (2.8)	18.0	12.0	11.4	11.3	5.0	10.0	[b]	100
Methomyl	WLS	83.6 (10.1)	99.7 (5.5)	102.3 (9.4)	95.8 (4.3)	37.5	15.9	12.3	11.8	5.0	10.0	[b]	20
Metsulfuron methyl	WLS	91.1 (5.5)	102.4 (4.1)	100.4 (7.5)	97.2 (2.0)	32.2	14.6	12.0	11.6	5.0	10.0	[b]	50
Mevinphos	WLS	–	91.3 (16.7)	90.4 (11.1)	88.4 (5.3)	–	16.2	12.4	11.8	7.5	25.0	[b]	10
Monocrotophos	WLS	86.6 (7.3)	94.4 (5.0)	97.2 (8.6)	93.9 (3.0)	30.0	14.2	12.0	11.6	5.0	10.0	[c]	–
Monolinuron	WLS	97.7 (2.8)	101.3 (4.8)	100.7 (4.8)	99.1 (2.1)	16.0	11.8	11.3	11.2	5.0	10.0	[d]	50
Myclobutanil	WLS	99.0 (5.7)	109.3 (4.0)	103.7 (5.3)	96.0 (5.5)	26.1	13.4	11.6	11.6	5.0	10.0	[b]	2000
Nuarimol	WLS	96.1 (2.8)	104.5 (5.2)	100.1 (5.0)	95.6 (3.7)	17.4	12.0	11.4	11.3	5.0	10.0	[d]	–
Omethoate	WLS	77.2 (5.3)	87.2 (5.1)	88.1 (6.9)	84.9 (3.6)	35.6	15.4	12.1	11.7	5.0	10.0	[c]	20
Oxadixyl	WLS	98.2 (7.2)	103.9 (3.1)	101.8 (4.8)	96.5 (4.3)	17.2	11.9	11.3	11.3	5.0	10.0	[c]	10
Oxamyl	WLS	87.0 (5.7)	95.0 (5.1)	93.9 (8.4)	92.6 (5.1)	33.9	15.1	12.1	11.8	5.0	10.0	[c]	10
Oxasulfuron	WLS	87.9 (5.8)	105.3 (7.3)	100.9 (6.9)	94.1 (3.3)	26.8	13.7	11.7	11.5	5.0	10.0	[b]	50
Paclobutrazol	WLS	96.1 (5.0)	106.1 (7.2)	105.4 (5.4)	96.2 (5.4)	19.5	12.4	11.4	11.4	5.0	10.0	[b]	500
Penconazole	WLS	94.7 (8.2)	109.0 (6.3)	108.0 (8.0)	95.3 (5.6)	23.6	13.0	11.7	11.5	5.0	10.0	[d]	50
Pendimethalin	WLS	100.2 (4.2)	103.8 (5.9)	96.5 (9.9)	100.1 (11.0)	27.9	14.0	12.1	12.0	5.0	10.0	[b]	50
Phenthoate	WLS	102.6 (5.3)	106.9 (7.9)	105.0 (4.7)	98.4 (5.3)	16.2	12.0	11.3	11.3	5.0	10.0	[b]	–
Phorate	WLS	99.8 (4.7)	103.3 (5.1)	101.6 (4.4)	98.1 (3.7)	17.7	12.0	11.3	11.3	5.0	10.0	[a]	50
Phorate sulfoxide	WLS	100.5 (3.8)	104.5 (5.7)	101.7 (4.8)	98.0 (4.0)	18.2	12.1	11.4	11.3	5.0	10.0	[b]	50
Phosalone	WLS	98.6 (5.4)	113.1 (4.0)	109.8 (6.1)	99.2 (4.4)	34.3	15.1	12.0	11.7	5.0	10.0	[b]	50
Phosmet	WLS	97.4 (4.4)	105.5 (5.7)	101.4 (3.1)	98.8 (2.9)	17.3	12.0	11.3	11.3	5.0	10.0	[b]	50
Pirimiphos methyl	WLS	103.1 (5.8)	109.2 (5.8)	103.0 (7.1)	101.9 (5.9)	19.0	12.3	11.5	11.4	5.0	10.0	[b]	50
Prochloraz	WLS	92.2 (7.1)	108.3 (7.7)	107.4 (4.9)	96.7 (4.7)	37.6	16.0	12.0	11.9	5.0	10.0	[b]	50
Propargite	WLS	98.7 (6.2)	109.3 (3.5)	101.3 (12.9)	94.4 (2.5)	30.3	14.2	12.4	11.5	5.0	10.0	[b]	10
Propiconazole	WLS	101.1 (4.7)	107.8 (7.6)	103.9 (4.7)	97.9 (4.8)	26.5	13.7	11.6	11.5	5.0	10.0	100	100
Propoxur	WLS	96.0 (3.8)	102.1 (4.1)	101.1 (4.5)	96.0 (3.0)	19.1	12.2	11.4	11.3	5.0	10.0	[b]	50
Propyzamide	WLS	95.8 (3.4)	105.8 (5.3)	104.0 (6.2)	97.9 (4.4)	15.7	11.8	11.4	11.3	5.0	10.0	[d]	20
Prosulfuron	WLS	95.5 (4.4)	105.1 (5.8)	100.5 (5.7)	96.3 (4.5)	17.9	12.1	11.4	11.3	5.0	10.0	[d]	20
Pyraclostrobin	WLS	95.8 (9.3)	112.9 (8.2)	110.3 (4.1)	98.1 (5.1)	36.1	15.7	11.9	11.8	5.0	10.0	500	20
Pyrazophos	WLS	98.4 (8.9)	116.9 (6.1)	109.3 (5.5)	100.0 (3.7)	33.6	15.0	11.9	11.7	5.0	10.0	[b]	50
Pyridaben	WLS	89.5 (14.8)	107.8 (8.5)	106.4 (5.0)	90.9 (5.5)	39.0	16.3	12.1	11.9	5.0	10.0	[b]	500
Pyridate	WLS	91.8 (10.3)	106.2 (10.1)	102.3 (12.3)	97.1 (11.1)	36.6	15.9	12.6	12.3	5.0	10.0	[c]	50
Pyrifenox	WLS	82.0 (11.6)	93.3 (10.3)	90.7 (10.2)	85.4 (9.6)	45.9	18.2	12.8	12.5	5.0	10.0	[c]	–
Pyrimethanil	WLS	97.1 (3.8)	99.2 (4.9)	98.2 (4.7)	97.5 (3.2)	14.6	11.6	11.3	11.2	5.0	10.0	100	100
Quinalphos	WLS	94.8 (4.4)	106.9 (8.0)	103.1 (5.2)	96.7 (5.4)	23.3	13.1	11.5	11.5	5.0	10.0	[c]	50
Tebuconazole	WLS	94.5 (8.6)	107.1 (5.7)	103.7 (6.8)	96.4 (5.1)	26.5	13.5	11.7	11.5	5.0	10.0	50	50
Tebufempirade	WLS	99.3 (15.2)	106.1 (12.4)	101.1 (13.9)	91.7 (11.0)	27.6	14.2	12.4	12.0	5.0	10.0	[d]	50
Tebufenozide	WLS	84.7 (7.8)	106.8 (4.4)	105.0 (5.7)	92.9 (2.4)	46.4	18.0	12.5	12.1	5.0	10.0	[b]	50
TEPP	WLS	81.9 (4.3)	98.6 (3.6)	104.5 (7.2)	99.7 (6.4)	38.8	16.1	12.2	12.0	5.0	10.0	[d]	10
Thiacloprid	WLS	87.5 (4.9)	104.0 (4.1)	102.9 (7.3)	95.7 (4.0)	34.8	15.2	12.0	11.7	5.0	10.0	50	20
Thiamethoxam	WLS	87.3 (10.0)	99.4 (6.1)	98.7 (7.9)	94.7 (4.9)	47.5	18.4	12.7	12.3	5.0	10.0	[b]	50
Thiodicarb	WLS	87.4 (4.9)	93.5 (2.5)	94.3 (5.5)	90.4 (3.0)	18.7	12.1	11.4	11.3	5.0	10.0	[b]	20
Tiabendazole	WLS	89.5 (13.0)	89.5 (13.6)	101.0 (15.0)	95.5 (13.0)	31.6	15.1	12.7	12.3	5.0	0.01	3000	5000
Tifensulfuron methyl	WLS	91.2 (8.9)	99.2 (14.9)	96.4 (14.1)	99.6 (8.9)	27.7	14.5	12.5	11.8	5.0	10.0	[d]	50
Tolylfluanid	WLS	70.0 (5.5)	75.4 (10.1)	85.3 (10.6)	85.4 (7.4)	24.8	13.5	12.0	11.6	5.0	10.0	[d]	50
Triadimefon	WLS	97.2 (5.0)	107.3 (6.7)	104.0 (6.9)	98.7 (5.0)	23.4	13.0	11.6	11.5	5.0	10.0	[b]	1000
Triadimenol	WLS	97.0 (5.0)	105.0 (5.4)	102.2 (4.8)	99.8 (5.0)	15.9	11.8	11.3	11.3	5.0	10.0	200	1000
Triassulfuron	WLS	97.0 (9.6)	111.3 (9.5)	103.0 (7.0)	95.0 (4.4)	36.0	15.7	12.1	11.8	5.0	10.0	[d]	50
Triazophos	WLS	93.6 (4.2)	106.6 (4.3)	106.0 (5.4)	93.8 (3.5)	22.5	12.8	11.5	11.4	5.0	10.0	[b]	10
Trichlorfon	WLS	90.0 (4.9)	102.6 (4.7)	100.8 (6.3)	96.1 (3.6)	34.0	15.1	12.0	11.7	5.0	10.0	[c]	500
Tridemorph	WLS	96.3 (4.0)	97.0 (3.4)	101.1 (5.5)	96.8 (4.4)	18.9	12.1	11.4	11.3	5.0	10.0	[a]	50
Triflumizole	WLS	89.6 (8.0)	107.0 (4.7)	107.4 (5.0)	97.0 (3.4)	35.1	15.3	11.9	11.7	5.0	10.0	[b]	100
Triforin	WLS	92.1 (5.3)	98.7 (5.2)	96.9 (4.2)	96.5 (3.2)	15.1	11.7	11.3	11.2	5.0	10.0	[b]	10

*Brazilian legislation.
**European Community legislation. The unsatisfactory values are shown in bold.
[a] Active ingredient not included in Instruction Normative No. 27, December, 2012.
[b] Product not allowed for cultivation of banana.
[c] Product with prohibited use in Brazilian agriculture.
[d] product not still authorized in Brazil.

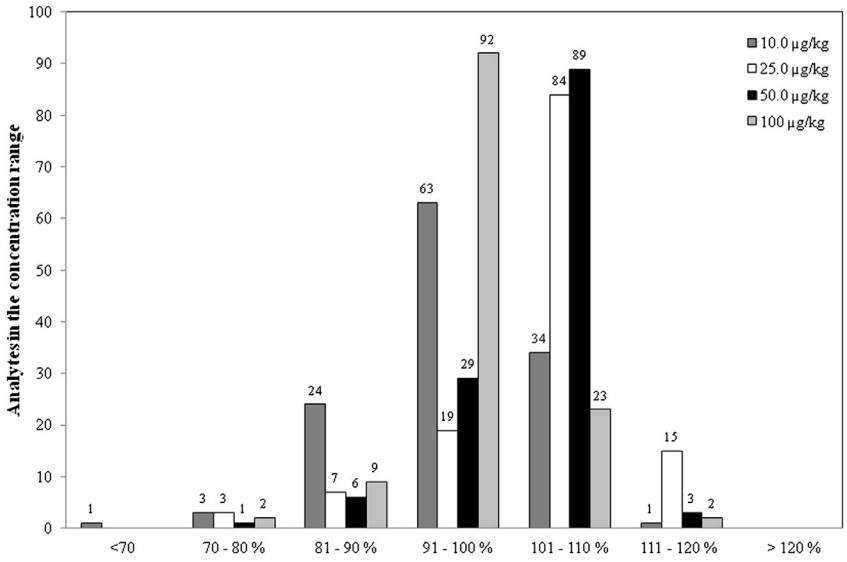

Fig. 2. Recovery range of analytes validated at each level of concentration evaluated.

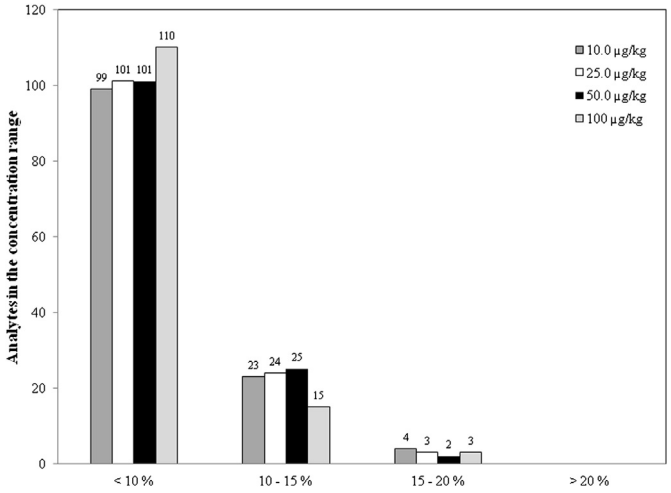

Fig. 3. Intervals coefficients of variation of analytes validated at each level of concentration evaluated.

(4) the MMC curves and (5) intermediate precision. Uncertainties related to measurements of volume and mass are negligible compared to other sources raised. For all pesticides validated, the main contribution to the total uncertainty arises from the MMC curves, because these last encompass all steps from the weighing of standards for preparation of solutions until the final quantification step, including the whole extraction process, the instrumental analysis and statistical processing of data. The expanded uncertainty, expressed as percentage (MU %, Table 2), for each pesticide was determined in each one of the fortification levels for which the assessment of repeatability and reproducibility have been performed. As it can be seen in Table 2, the MU calculated for each pesticide showed values below 50%. The uncertainty values at all levels studied were in the range 11.2%–48.4%. These results agree with the acceptable criteria established in SANCO/12495/2011 document (European Union, 2011).

3.3. Sample analysis

The validated method was applied to detect and quantify residues of the pesticides in ten different kinds of banana samples acquired from different retailers in Minas Gerais state (Brazil). In order to ensure the quality of the results and evaluate the stability of the method proposed, an internal quality control was carried out on every batch of samples. This quality control required the construction of MMS analytical curves for each analyte. Furthermore, to meet the criteria established by Manual of Analytical Quality Assurance (Brasil, 2011a), the retention time of each analyte and the relative intensities of the quantification and confirmation product ions (SRM transitions) in the actual samples were compared to those of spiked blank samples (at 10 and 100 µg kg^{-1}). By following these criteria, traces of azoxystrobin, carbendazin and tebuconazole were detected in four samples of banana, i.e., at levels below the respective LOQs, whereas boscalid, carbendazin and imidacloprid were quantified, respectively, at the sample one (31.0 ± 4.12 µg kg^{-1}), sample seven (24.0 ± 3.65 µg kg^{-1}) and sample nine (13.0 ± 5.17 mg kg^{-1}), as shown in Table 3. Fig. 4 shows the extracted ion chromatograms for the positive samples. The samples one and seven are non-compliant because boscalid and

Table 3
Concentration of pesticide residues (µg kg^{-1}) found in banana samples acquired from different retailers in Minas Gerais state (Brazil).

Compound	S^*_1	S^*_2	S^*_3	S^*_4	S^*_5	S^*_6	S^*_7	S^*_8	S^*_9	S^*_{10}
Azoxystrobin	–	–	–	–	–	<LOQ	–	–	–	<LOQ
Boscalid	31.0 ± 4.1	–	–	–	–	–	–	–	–	–
Carbendazin	–	–	<LOQ	–	–	–	24.0 ± 3.7	–	–	–
Imidacloprid	–	–	–	–	–	–	–	–	13.0 ± 5.2	–
Tebuconazole	–	<LOQ	<LOQ	–	–	–	–	–	<LOQ	–

*Sample.

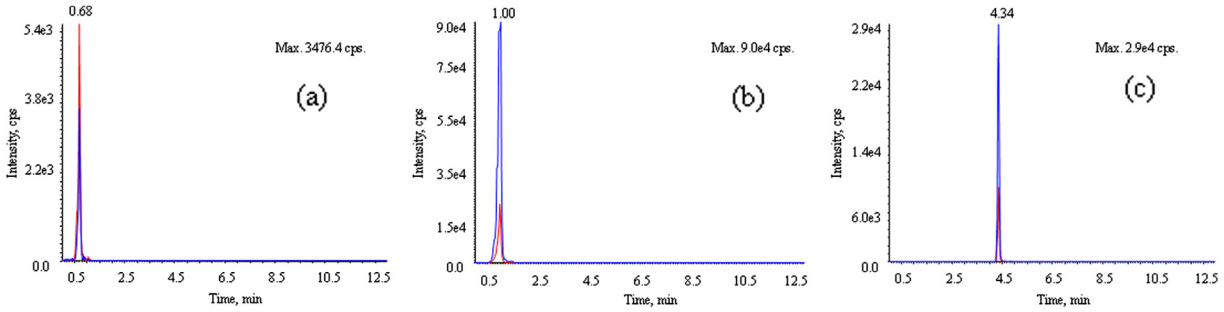

Fig. 4. UHPLC–MS/MS chromatogram for positive samples: (a) imidacloprid (13.0 ± 5.17 μg kg^{-1}); (b) carbendazin (24.0 ± 3.65 μg kg^{-1}) and (c) boscalid (31.0 ± 4.12 μg kg^{-1}).

carbendazin are not allowed for use in banana crops according to the Brazilian legislation, whereas the sample nine is positive but with a concentration of imidacloprid less than the MRL.

4. Conclusions

A multiresidue method was developed for rapid and simultaneous determination of 128 pesticides in bananas by a modified QuEChERS procedure and UHPLC–MS/MS analysis. The whole analytical procedure was validated according to European Union SANCO/12495/2011 guidelines (European Union, 2011), and the normative instruction number 24/2009 (Brasil, 2009). Furthermore, the method proved to be simple and gave quantitative results for the assayed analytes, providing good validation parameters, such as linearity, limits of detection and quantification and precision. The uncertainties values obtained for each pesticide were below 50% at all the fortification levels, which complies with the requirements of SANCO/12495/2011 (European Union, 2011) document. The applicability of the method was demonstrated by analysis of ten banana samples. A good performance of the method was observed, allowing the reliable determination of the target compounds in real samples. Finally, the results presented in this report demonstrate that the validated method is feasible to be applied in pesticide routine analysis carried out to attend the Brazilian National Plan for Residues and Contaminants (PNCRC) in matrices with high water content.

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