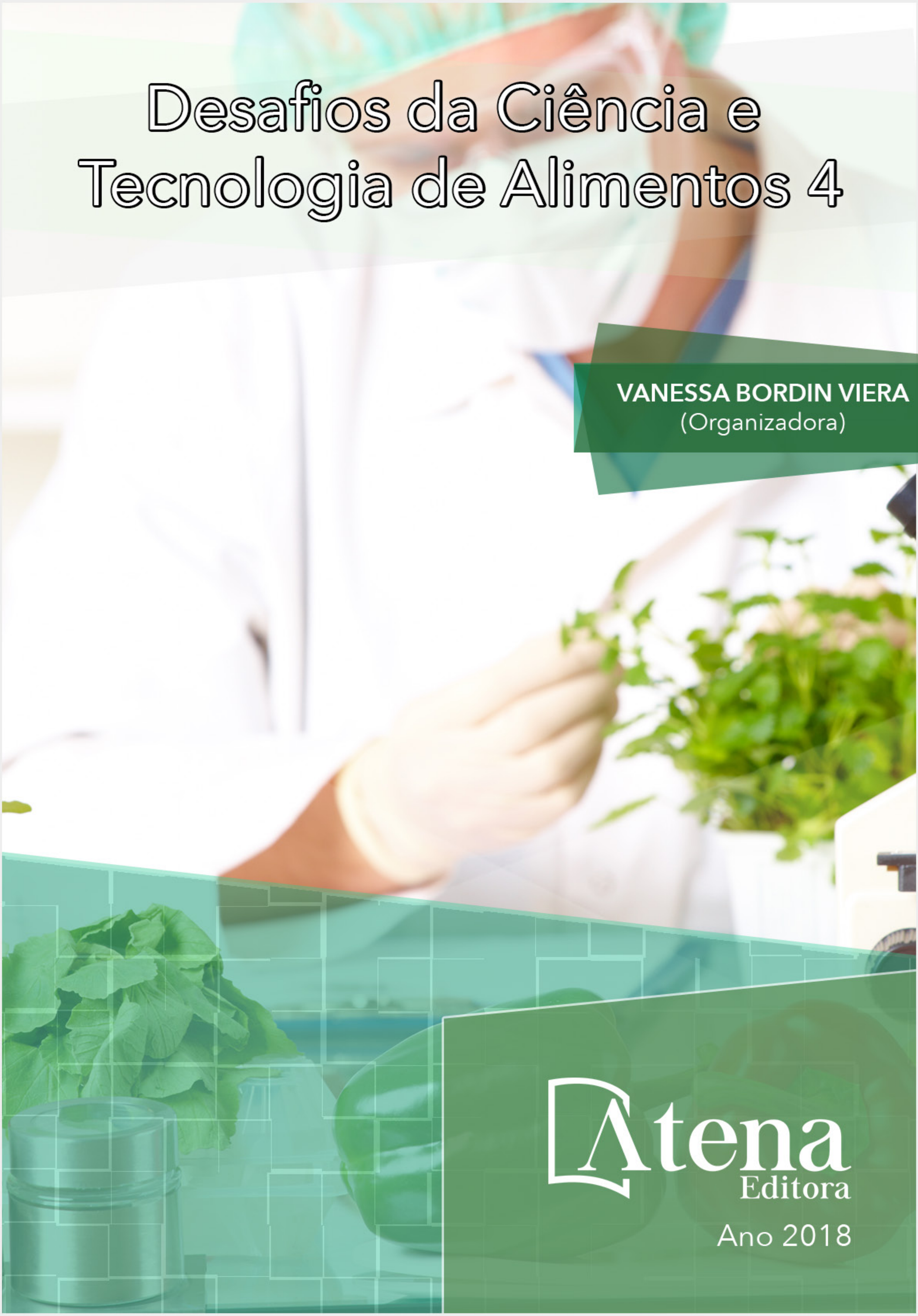

Desafios da Ciência e Tecnologia de Alimentos 4

VANESSA BORDIN VIERA
(Organizadora)

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Vanessa Bordin Viera

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APRESENTAÇÃO

A Ciência e Tecnologia de Alimentos é uma área que envolve o conhecimento da fabricação dos alimentos. Para isso, torna-se necessário e imprescindível o conhecimento acerca das propriedades físico-químicas, nutricionais, microbiológicas e sensoriais das matérias-primas, ingredientes e dos produtos elaborados.

A Coletânea Nacional “Desafios da Ciência e Tecnologia de Alimentos” é um e-book composto por 10 artigos científicos que abordam assuntos atuais, como a análise sensorial de alimentos, análises microbiológicas, determinação de pesticidas em alimentos, utilização de novos ingredientes e/ou matérias-primas no processamento de produtos, avaliação de rotulagem, entre outros.

Mediante a importância, necessidade de atualização e de acesso a informações de qualidade, os artigos elencados neste e-book contribuirão efetivamente para disseminação do conhecimento a respeito das diversas áreas da Ciência e Tecnologia de Alimentos, proporcionando uma visão ampla sobre esta área de conhecimento.

Desejo a todos uma excelente leitura!

Prof. Dra. Vanessa Bordin Viera

SUMÁRIO

CAPÍTULO 1

A NEW AND SENSITIVE GC-ITD-MS METHOD FOR DETERMINATION OF 37 PESTICIDES IN FRUIT JAMS

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ABSTRACT: A novel GC-ITD-MS method have been developed and successfully validated for the determination of 37 pesticides in fruit jams. In order to facilitate the sample handling and to reduce the interference of the high sugar content of the jams the samples were slurried with water. The pesticides extraction was done with the sulfate QuEChERS method using PSA for clean-up. The method was validated by the analysis of spiked samples at the concentrations of 10, 20 e 50 µg kg^{-1} (n=6). In total 41 pesticides were studied and 37 fulfilled all the requirements for the validation (recoveries from 70-120% and RSD ≤ 20%). So, the reporting limit (RL) was established at 10, 20 e 50 μg kg^{-1} for 26 (64%), 4 (10%) e 7 (17%) pesticides, respectively. Three compounds (7%) were not detected at the studied concentrations levels and one pesticide (2%) was detected but did not meet the requirements for validation. The method is easy to implement, uses equipments commonly available in laboratories and can be recommended for routine multiresidue analysis of jams.

KEYWORDS: Fruit Jams. Gas chromatography. Mass spectrometry. Residues. QuEChERS.

1 I INTRODUCTION

Pesticides are chemical substances applied to crops at various stages of cultivation and during post-harvest storage of crops. The use of pesticides is intended to prevent the destruction of food crops by controlling agricultural pests or unwanted plants and to improve plant quality (EUROPEAN COMMISSION, 2018; REICHERT et al., 2015). In Brazil, one of the world's major food producers, over 90% of farmers rely on pesticide use and the country has ranked first in pesticide use worldwide in recent years, with 936 thousand tons used from second semester of 2010 until the end of the first semester of 2011 (JARDIM AND CALDAS, 2012; CARNEIRO et al., 2015; REICHERT et al., 2015). Even when pesticides are applied in accordance with good agricultural practices they can leave residues. Therefore, many countries have established legal guidelines and monitoring programs to control the use of pesticides in agricultural crops and verify if the residue concentrations are in compliance with the maximum residue limits (MRL) (WALORCZYK, 2007).

Jams are processed food products, originated as food preserving processes of fruits during off-season and also a way to add economic value to the fruits. Jams became very popular because of its low cost, all year long availability and pleasant organoleptic properties (MOHD NAEEM et al., 2017; TAUATI et al., 2014). Jams are prepared mixing sugar, pulp and/or puree of one or more fruits and water and cooking it to a suitable gelled consistency (ABID et al., 2018; COUNCIL OF THE EUROPEAN UNION, 2004).

According to the Guidance Document SANTE/11813/2017, fruit jams are classified as high sugar and low water content commodities, together with honey and dried fruits and these characters of the fruit jams can represent a challenge in pesticide determination in such matrices (EUROPEAN COMMISSION, 2017).

Considering that fruits and vegetables are susceptible to pesticides application during their cultivation and that they are essential ingredients to the jams production, it is of great interest to measure the contamination level of the jams with these toxic compounds, because the presence of contaminants, depending on the concentration, can be dangerous for human consumption.

Every year, several new multiresidue methods are developed to determine pesticides in raw food. But the same is not true when it comes to monitor pesticides and their metabolites in processed foods like jams. Cooking might alter and degrade the chemical structure of analytes. So, in order to evaluate in detail the hazardous effects of pesticides on human health, cooked foodstuffs appear to be a more reasonable choice of sample (PARK et al., 2011; MARTIN et al., 2013).

Gas chromatography tandem mass spectrometry with ion trap detector (GC-ITD-MS) is a very sensitive, selective and well-established analytical technique. It is frequently applied to determine pesticide residues in different types of matrixes (PIZZUTTI, 2006). Therefore, this study aimed to develop and validate a multirresidual method for pesticides determination in jams using GC-ITD-MS.

2 I MATERIAL AND METHODS

2.1 Reagents, Solvents, Standards and Instrumentation

Acetonitrile and toluene (purity ≥ 99.5%) were acquired from Mallinckrodt (USA). Acetic acid HPLC grade 99.9% was purchased from J.T. Baker (USA). Sodium sulfate ($MgSO_4$) (98.0%) was obtained from Sigma-Aldrich (Japan). sodium acetate (99.0%) from Vetec (Brazil) primary and secondary amine (PSA) from Supelco (USA). The solid pesticides standards, purity > 98%, were obtained from Dr. Ehrenstorfer (Germany) and stored in freezer at -30 ° C.

Individual standard stock solutions of the 41 pesticides were prepared in toluene at 1000 mg L^{-1} and stored in amber glass vials at -20 ° C. Posteriorly, by dilutions of the individual stock solutions a new standard solution containing a mixture of the 41 pesticides was prepared at 500 μg L^{-1}. This mixture solution was used as spiking solution in the method development studies and for the validation.

The GC-ITD-MS instrument consisted of a CP 3800 gas chromatograph (Varian, EUA), equipped with a CP 8400 autosampler (Varian, USA), a 1079 programmable temperature vaporizing (PTV) injector with silanized glass liner containing a carbofrit of 0.5 cm. The injection volume was 5 μL, at the initial temperature of 80 ºC and final temperature of 300 ºC.

The pesticides were separated on a fused silica capillary column FactorFour VF-5ms (5% phenyl 95% methylpolysiloxane), 30 m length, 0.25 mm i.d. and 0.25 μm of film thickness (Varian, The Netherlands). Helium was used as mobile phase at a flow rate of 1.2 mL min^{-1}. The column oven operated with a linear temperature program starting at 80 °C (1 min), followed by an increase of 25 °C min^{-1} to 180 °C; 5° C min^{-1} to 280 °C and 10 °C min^{-1} to 300 °C.

The GC was coupled to an ion trap mass spectrometer Saturn 2000 (Varian, USA) operated in the positive electron impact ionization mode (EI) and full scan acquisition mode. The chromatographic parameters of the pesticides are shown in Table 1. The total analysis time was 37 min and data acquisition was performed with MS Workstation 6.5 software (Varian, USA).

2.2 Samples

Fruit jam samples were purchased in local markets of Santa Maria, South of Brazil. The samples consisted of jams made from three different fruits (pineapple, strawberry and grape) and from 3 different brands. For the preliminary tests and for the validation just the grape jam was used.

2.3 SLURRY PREPARATION

Fruit jams are difficult to manipulate because of its high sugar content and pasty consistency. Therefore, the use of pure jam and jam slurries, at different ratios, was evaluated to select the most adequate one. The preparation of the slurries was performed homogenizing the jams with ultrapure water in an Ultra-Turrax for 5 min. Slurries of three different ratios were prepared, 1:1. 1:0.5 and 1:0.25 (grape jam:water, m/m). Selection of the best ratio of slurry was done based on the its consistence, homogeneity, accuracy tests (recovery% and RSD%) of spiked samples and based on matrix effects for the studied pesticides.

2.4 QUECHERS SAMPLE EXTRACTION

Sample extraction was done with the modified QuEChERS method as described following. Slurry portions of 10 g were weighted into 45 mL centrifuge tubes. For recovery studies the samples were spiked with the pesticide standard mixture solution (500 μg L^{-1}) and homogenized in Vortex for 1 min. For the extraction, 10 mL of acetonitrile containing 1% acetic acid and the procedure internal standard (tris(1,3-dichloroisopropyl)phosphate) at 200 μg L^{-1} were added to the tubes and automatically shaken for 2 min. After that, 3 g of anhydrous $MgSO_4$ were added to each tube followed by 2 min shaking. Then, 1.7 g of sodium acetate was added and the samples were shaken for more 2 min. The tubes were taken to centrifugation. The upper layer (4 mL) was transferred into other tubes containing a mixture of 600 mg of anhydrous $MgSO_4$ and 50 mg of PSA. The tubes were shaken again for 2 min and centrifuged. Finally, 990 μL of the upper layer was pipetted to a vial and mixed with the instrument internal standard (bromophos-ethyl) at 50 μg L^{-1}. The vials were then capped and taken to the GC-ITD MS.

Pesticide	Molecular mass (g)	Rt (min)	Quantification ion (m/z)
Propham	179.2	6.43	179.0
Tecnazene	260.8	7.75	261.0
Clorpropham	213.5	8.28	213.0
HCH-alpha	290.8	8.96	181.0
Hexachlorobenzene	284.7	9.05	284.0
Dicloran	207.0	9.27	206.0
HCH-beta	290.8	9.53	181.0
Quintozene	295.3	9.61	295.0
Diazinon	304.3	9.73	304.0
HCH-gamma (Lindane)	290.8	9.76	183.0
Chlorpyrifos-ethyl	322.5	11.12	288.0
Promethryn	241.3	11.55	241.0
Heptachlor	373.3	11.59	272.0
Pirimiphos-methyl	305.3	11.82	290.0
Chlorpyrifos-ethyl	350.6	12.41	316.0
Aldrin	364.9	12.65	293.0

Dicofol*	370.4	12.97	139.0
Heptachlorepoxide	389.3	13.84	289.0
Phenthoate	320.3	13.93	274.0
Quinalphos	298.2	13.97	146.0
Bromofos-ethyl (P.I.S.)	394.0	14.39	303.0
DDE-2.4	318.0	14.59	247.0
Endosulfan-alpha	406.9	15.00	241.0
Fludioxonil	248.1	15.42	248.0
DDE-4.4	318.0	15.65	318.0
DDD-2.4	318.0	15.88	237.0
Dieldrin	380.9	16.58	279.0
Endrin	380.9	16.60	281.0
Endosulfan-beta	406.9	16.95	267.0
DDD-4.4	318.0	17.03	235.0
DDT-2.4	352.0	17.13	235.0
TDCPP (P.I.S.)	430.9	17.72	191.0
Quinoxyfen	308.1	18.18	272.0
Endosulfan-sulfate	422.9	18.25	387.0
DDT-4.4	354.4	18.33	235.0
Methoxychlor	345.6	18.80	227.0
Propargite	350.4	18.83	135.0
EPN	323.3	20.05	169.0
Tetramethrin	331.4	20.07	164.0
Tetradifon	356.0	21.02	356.0
Phosalone	367.8	21.18	182.0
Pyrazophos	373.3	22.16	221.0
Azoxystrobin	403.3	29.65	344.0

Table 1. Chromatographic parameters of the pesticides determined by GC-ITD-MS analysis.

*degradation product of dicofol, not included in the standard pesticide mixture solution

2.5 Method Validation

To assess the method linearity and linear range, analytical solutions were prepared at the concentrations of 2.5; 5; 10; 20; 40; 50 and 65 µg kg^{-1} (2; 4; 8; 16; 32; 40; 52 *µ*g L^{-1}) in acetonitrile and matrix extract (matrix-matched calibration standards). These solutions were obtained by dilution of the standard solution containing the mixture of the pesticides (500 µg L^{-1}) with acetonitrile and blank grape jam extract, respectively. The linearity was determined by the calculation of the correlation coefficient (r) of analytical curves, obtained based on the areas of the chromatographic peaks. The matrix effects (%) were calculated for each compound based on the slopes of the calibration curves in matrix extract and in organic solvent, according to the Equation 1.

Accuracy and precision were accessed by the analysis of spiked samples at the concentrations of 10, 20 e 50 *µ*g kg^{-1} with 6 replicates at each concentration (n=6) and the reporting limit (RL) was set based on the lowest spiked concentration that presented recoveries between 70-120% and RSD ≤ 20%.

$$\text{Matrix effects (\%)} = \left[\left(\frac{\text{slope curve, standard in matrix}}{\text{slope curve, standard in acetonitrile}}\right) - 1\right] \text{x}\,100 \qquad (1)$$

3 I RESULTS AND DISCUSSION

As explained in Section 2.3, fruit jams present a pasty consistence and are difficult to handle during extraction. So, studies were performed using pure jam and slurries (ratios, 1:1, 1:0.5 and 1:0.25, m/m). Pure jam was difficult to weight, did not mix completely with the extraction solvent (acetonitrile 1% acetic acid) and it was then considered inadequate. The slurry of ratio 1:1 (m/m) was to liquid and therefore not suitable. Slurries of ratios 1:0.5 and 1:0.25 (w/w) were completely homogeneous and shown a good consistence. The slurry of ratio 1:0.25 (m/m) was selected for the validation study because it presented the best performance on the accuracy study, with recoveries within 70-120% and RSD ≤ 20% for the majority of the pesticides.

The results of the method accuracy and precision are reported in Table 2. As demonstrated for the spike concentrations of 10 20 and 50 μg kg^{-1}, the number of pesticides which presented recoveries between 70-120% and RSD ≤ 20% were, respectively, 26 (64%), 21 (51%) and 37 (90%), RL was 10, 20 e 50 μg kg^{-1} for 26 (64%), 4 (10%) and 7 (17%) pesticides, respectively. Three compounds (7%) were not detected at the studied concentrations and one (2%), namely phenthoate, was detected at 50 μg kg^{-1}, but did not fulfill the requirements for validations.

Method linearity was evaluated based on calibration curves prepared in matrix extract and in acetonitrile. For the matrix-matched calibration curves, 38 (93%) pesticides had an r > 0.990, azoxystrobin (2%) presented an r = 0.975, endossulfan-alpha (2%) was not detected at any level studied and propargite (2%) did not had areas at least at 3 different concentration levels. For the calibration curves in acetonitrile, just 6 (15%) compounds showed an r > 0.990; 21 (51%) had

Pesticide	**Spike concentration (μg kg^{-1})**						**RL (μg kg^{-1})**
	10		**20**		**50**		
	Recovery (%)	**RSD (%)**	**Recovery (%)**	**RSD (%)**	**Recovery (%)**	**RSD (%)**	
Aldrin	94	19	82	17	79	13	10
Azoxystrobin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorpropham	112	13	82	18	72	15	10
Chlorpyrifos-ethyl	95	20	76	20	75	12	10
Chlorpyrifos-methyl	95	9	75	20	71	8	10
DDD-2.4	90	5	72	31	80	11	10
DDD-4.4	94	16	79	18	78	11	10
DDE-2.4	100	5	81	28	79	10	10
DDE-4.4	95	16	77	33	75	9	10
DDT-2.4	n.d.	n.d.	80	19	71	13	20

DDT-4.4	n.d.	n.d.	75	18	78	19	20
Diazinon	88	7	76	28	73	8	10
Dicloran	112	5	76	15	75	14	10
Dicofol*	n.d.	n.d.	81	20	71	10	20
Dieldrin	n.d.	n.d.	43	26	71	14	50
Endosulfan-alpha	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Endosulfan-beta	n.d.	n.d.	n.d.	n.d.	72	12	50
Endosulfan-sulfate	n.d.	n.d.	97	28	79	16	50
Endrin	n.d.	n.d.	n.d.	n.d.	80	16	50
EPN	118	14	87	14	87	12	10
Fludioxonil	127	30	79	18	84	16	20
HCH-alpha	85	10	74	14	71	8	10
HCH-beta	72	18	59	32	71	13	10
HCH-gamma (Lindano)	91	15	80	18	80	12	10
Heptachlor	93	15	76	12	74	5	10
Heptachlorepoxide	n.d.	n.d.	n.d.	n.d.	74	11	50
Hexachlorobenzene	98	9	79	15	74	10	10
Methoxychlor	93	16	74	29	78	19	10
Phenthoate	n.d.	n.d.	n.d.	n.d.	70	32	n.f.r.
Phosalone	88	19	62	12	73	15	10
Pirimiphos-methyl	97	9	73	37	75	8	10
Promethryn	94	10	74	19	76	11	10
Propargite	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propham	117	6	84	15	78	5	10
Pyrazophos	94	12	68	5	83	15	10
Quinalphos	91	13	71	20	70	4	10
Quinoxyfen	106	23	74	27	81	11	50
Quintozene	88	11	77	20	81	11	10
Tecnazene	99	8	80	18	78	9	10
Tetradifon	n.d.	n.d.	88	33	80	11	50
Tetramethrin	89	9	83	5	89	13	10

Table 2. Average recoveries (%), RSD% (n=6) and RL for the pesticides spiked to blank grape jam at 10, 20 e 50 μg kg-1 (n=6). Analysis performed by GC-ITD-MS.

n.d.: not detected; n.f.r.: not fulfilling requirements for validation (recovery 70-120% and RSD ≤ 20%)

*Identified and quantified indirectly by dichlorobenzophenone-4.4.

an r between 0.900-0.990; 4 (10%) presented an r < 0.900; 2 (5%) pesticides did not have areas at least at 3 different concentrations and 8 (20%) compounds were not detected.

Another parameter evaluated were the matrix effects (%). It is defined as the influence of one or more co-extracted matrix compounds on the measurement of the analyte concentration or mass. It may be observed as an increased or a decreased (enhancement or suppression, respectively) of detector response, in comparison with that produced by solvent solutions of the analyte (EUROPEAN COMMISSION, 2017). In this study, a clean-up step (with 50 mg of PSA) was applied to sample extracts before the GC-ITD-MS analysis, aiming to reduce the matrix interference.

The calculated matrix effects were prevalently positive (enhancement) and was ≤ 20% for just 8 (20 %) pesticides. Thus, to avoid erroneous quantifications of the pesticides it is advisable to prepare the calibration curves in matrix extract (EUROPEAN COMMISSION, 2017). The positive matrix effects can be seen in Fig. 1, which shows the total ion chromatograms of two standard solutions at 52 μg L^{-1}. A prepared in blank grape jam extract (matrix-matched standard), and B prepared in neat organic solvent. So, the higher intensity of the chromatographic peaks when in the presence of matrix extract evidences the positive matrix effects.

The retention time of the analytes is an important criterion for identification and for the selectivity of the analytical method. Thus, the method selectivity can be clearly visualized in Fig. 2, which represent the selective chromatograms of tequinazene, DDD-4,4, phosalone, free of interfering.

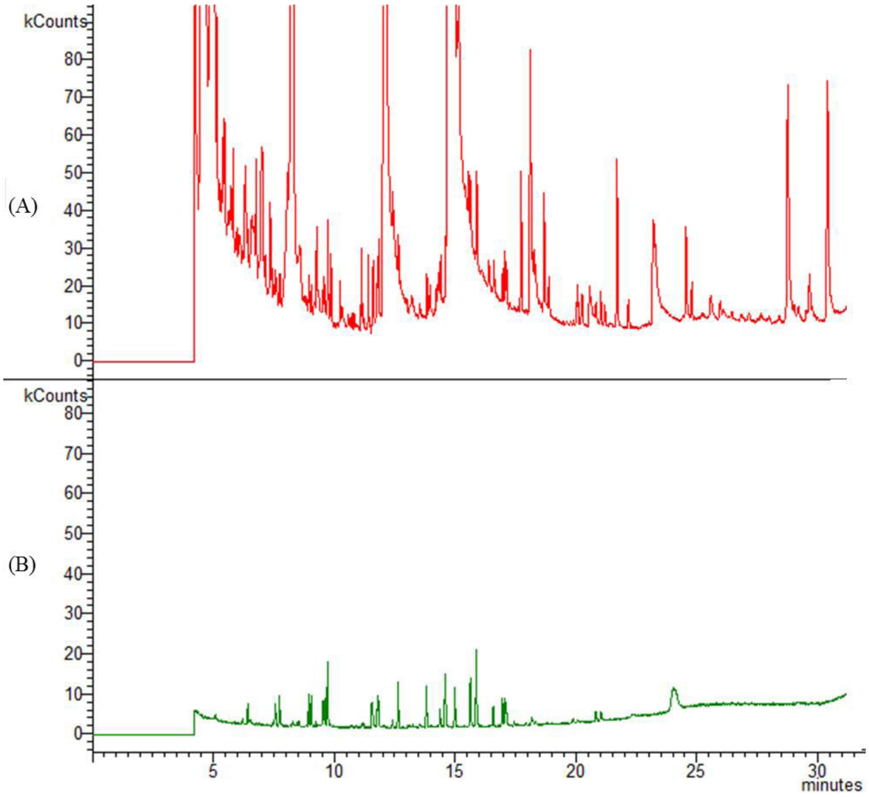

Fig. 1. Total ion chromatograms of a standard solution prepared in blank grape jam extract at 52 μg L^{-1} (A) and a standard solution prepared in neat acetonitrile at 52 μg L^{-1} (B) demonstrating the positive matrix effects of the grape jam.

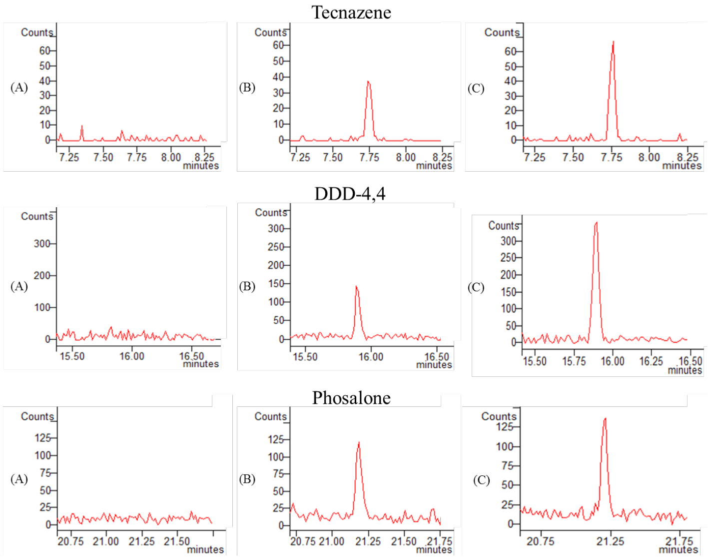

Fig. 2. Selective chromatograms of tecnazene, DDD-4.4 and phosalone obtained by GC-ITD-MS analysis of (A) blank grape jam extract, (B) standard pesticide solution in matrix at 4 µg L-1 (5 µg kg-1) and (C) grape jam sample spiked at 10 µg kg-1 (8 µg L-1).

4 I CONCLUSIONS

According to the results presented in this study, it is possible to conclude that the sulfate QuEChERS method is suitable for the pesticide residues extraction from fruit jams and that PSA was effective for clean-up the acetonitrile jam extracts before the chromatographic analysis, due the fact that it was observed minimal interference in the analytes detection.

In the method validation study, 41 pesticides were evaluated and 37 (90%) were successfully validated. The matrix effects were higher than 20% for 33 (80%) compounds, so, it is preferably use matrix-matched calibration to avoid incorrect quantification of the pesticides. The RL was 10, 20 and 50 µg kg^{-1} for, 26 (64%), 4 (10%) and 7 (17%) pesticides, respectively. Three (7%), (azoxystrobin, endosulfan-alpha and propargite), were not detected at the studied concentrations and phenthoate (2%) was detected at the spike level of 50 µg kg^{-1} but did not fulfill the validation requirements.

Whereas the majority of the pesticides studied are prohibited or are not allowed in Brazil in the fruits used in the jams production, the developed method has been proved to be successful as a real quantitative multi-residue method for pesticide determination in fruit jams, and can be recommended for routine application in monitoring studies or surveys.

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