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Article

Analysis of Residues of Pesticides in Tomato Processed Foods

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The tomato (*Solanum lycopersicon* L.) crop has great economic relevance, being one of the most processed agricultural products worldwide. Some pesticides are chemically stable and can remain in food even after processing. In this context, the objective of this work was to analyze food products derived from tomatoes (extract, sauce and ketchup), regarding the levels of pesticide residues. Fifteen samples were acquired from Vale do Jaguaribe, Ceará, Brazil. Six pesticides (bifenthrin, chlorothalonil, chlorpyrifos, cyfluthrin, pyriproxyfen, trifluralin) authorized by Agência Nacional de Vigilância Sanitária (Anvisa) for tomato cultivation were selected for the study. QuEChERS (quick, easy, cheap, effective, rugged, safe) extraction and gas chromatography coupled to mass spectrometry (GC-MS) were used in method validation, according to the recommendations of SANTE 11312/2021 guidelines. Statistical analyses of linearity showed that the six pesticides studied were classified as heterocesdastic. Limits of detection (LOD) and quantification (LOQ) values (0.01-0.03 and 0.03-0.10 mg kg^{-1}, respectively) were below the established maximum residue limits (MRLs) for tomatoes. Accuracy and precision (78-121 and 2.3-16.7%, respectively) were satisfactory. The results indicated that among the 15 analyzed samples, one active ingredient was detected (0.05 mg kg^{-1}) in a tomato sauce sample, lower than MRLs (Anvisa 0.15 mg kg^{-1} and FAO 0.3 mg kg^{-1}). The results show the relevance of monitoring pesticide residues in tomato-derived products and the validation of new methodologies for food control.

Keywords: extract, ketchup, tomato sauce, multiresidue, QuEChERS

Introduction

The tomato production chain has stood out for its economic relevance in the food industry of ready-to-eat products, in addition to inputs for other chains. Because it is a very perishable product, part of this production reaches the consumer's table in a processed form. According to the Instituto Brasileiro de Geografia e Estatística (IBGE),[1] around 35% of the production is destined to handling tomatoes for industrialization, with the remainder for fresh consumption.

According to the Food and Agriculture Organization of the United Nations (FAO),[2] the largest producer of the vegetable is China (31% of world production), surpassing a territory with more than one million cultivated hectares, resulting in more than 56 million tons. Brazil occupies the 9th place (2.5%), producing 4,167,629 tons in an area of 63,980 hectares, reaching an average productivity of 65.14 tons *per* hectare.

The food market has been increasingly concerned with controlling the quality of commercial products. If a raw material contaminated by pesticide residues is used in the preparation of food, it may also be contaminated by these compounds. Several studies[3-6] in recent years have reported traces of pesticides in different food matrices.

A survey conducted by the Food and Agriculture Organization of the United Nations (FAO) in 2018, informs that Brazil occupied the third position regarding the consumption of pesticides in tons, behind only China and the United States, with the first and second place, respectively.[7] Each year, new chemical groups have been released. In Brazil, from January 2021 to December 2021, 500 active principles were registered, considered the highest

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number verified by the Ministry of Agriculture. Approvals of these inputs have been increasing, resulting in impacts in the environmental and social areas, in addition to increasing the risk of contamination.[8-10] Arias *et al.*[11] analyzed the presence of pesticide residues in tomatoes produced in Bogotá, Colombia, evaluating the presence of 24 active ingredients in fresh tomatoes. At least one pesticide was detected in 70.5% of the samples, with acephate, dimethomorph, pyrimethanil and carbendazim being the most common. Lozowicka *et al.*[12] detected pyrethroids in fresh tomato samples. Li *et al.*[13] verified that bifenthrin and cypermethrin were the most detected pyrethroids in samples of fruits and vegetables, representing about 69% of all pesticides studied for these matrices. Although international research has been reported in recent years, citing the investigation of pesticides in tomatoes, in Brazil these studies are still insufficient.

The resistance of some of them in cultures and their difficult degradation can contaminate processed foods derived from the product *in natura*, even after the industrialization process.[11-14] The levels of these residues found in processed products can be influenced by several factors after processing such as evaporation, boiling, thermal degradation, dissolution (washing with water or solvents), mechanical removal (peeling of vegetable peel), volatilization and weight changes.[15]

QuEChERS (quick, easy, cheap, effective, rugged, safe) method associated with detection by mass spectrometry coupled to gas chromatography (GC-MS) has shown high efficiency and numerous advantages in the analysis of contaminants in food, such as high selectivity and sensitivity.[16] Some research[17,18] have reported the application of the QuEChERS method to food products. Abd-elhaleem[18] analyzed 412 pesticide residues in more than 22 tomato samples, including tomato paste and ketchup collected in local markets (Majmaah, Saudi Arabia), using the modified QuEChERS method, followed by liquid chromatography tandem mass spectrometry (LC-MS/MS) and GC-MS/MS. Around eight active ingredients were detected in 36% of the analyzed samples. All detected residues were below the maximum residue limits (MRLs). Corrias *et al.*[19] determined and validated a modified QuEChERS method, analyzing 186 active ingredients in raw tomatoes and derivatives after processing, proving to be convenient and practical for checking possible residues in market samples. Among the 186 analyzed samples, 46 presented residues of azoxystrobin and chlorantraniliprole as the most represented in the samples of raw tomatoes. Processed products, on the other hand, showed no pesticide residues. According to the authors,[19] the industrial processing coupled with the dilution effect allowed to decrease pesticide residues found in the raw material below the LOD.

Given this context, this research aims to analyze pesticide residues in industrialized tomato products (tomato extract, tomato sauce and ketchup), using the multiresidue methodology associated with QuEChERS and GC-MS, followed by statistical analysis. The choice by tomato-derived products is related to the popularity of these foods and the susceptibility of tomato contamination, used as raw material.

Experimental

Sample collection

Industrialized samples of tomato paste, tomato sauce and ketchup produced in other states of the country (Southeast and South of Brazil) were collected in March 2020 in different supermarkets in Quixeré and Limoeiro do Norte, Vale do Jaguaribe, Ceará, Brazil. Five (5) brands of tomato paste, tomato sauce and ketchup were selected from random lots of products and taken to carry out the analyzes at the Núcleo de Tecnologia e Qualidade Industrial do Ceará (LQI-NUTEC), Ceará, Brazil.

Reagents

Pesticides chromatographic standards (purity > 98%) bifenthrin (Sigma-Aldrich, SP, Brazil); chlorothalonil (Sigma-Aldrich, SP, Brazil); chlorpyrifos (Sigma-Aldrich, SP, Brazil), cyfluthrin (Sigma-Aldrich, SP, Brazil); priproxyfen (Sigma-Aldrich, SP, Brazil) and trifluralin (Sigma-Aldrich, SP, Brazil) were used in the analyses. The reagents anhydrous magnesium sulfate 98% P.A. (Vetec, RJ, Brazil); sodium chloride 99% P.A. (Vetec, RJ, Brazil); tribasic sodium citrate 99% P.A. (Vetec, RJ, Brazil); sodium hydrogen citrate sesquihydrate 99% P.A. (Sigma-Aldrich, SP, Brazil); secondary primary amine (PSA) 40 µm particle (Supelco, SP, Brazil); acetonitrile 99.9% UV/HPLC/Spectroscopic grade (Vetec, RJ, Brazil); formic acid 85% P.A. (Vetec, RJ, Brazil); acetone 99.9% UV/HPLC/Spectroscopic grade (Vetec, RJ, Brazil); helium gas 99.999% (White Martins, CE, Brazil); ultrapure water (Milli-Q Direct UV3 system, SP, Brazil) were used in the experiments.

Preparation of analytical solutions

Stock solutions (1000 mg L^{-1}) of individual standards of pesticides were prepared for method validation experiments. Then, by dilution, a 10 mg L^{-1} mixture containing all analyzed compounds was obtained. Solvent (methanol, Sigma-Aldrich, SP, Brazil) and matrix-matched (extract) curves in the range of 0.01 to 2.0 mg kg^{-1} were used in the tests to determine the validation parameters, using the quantification method by external standard.

QuEChERS method

The samples of tomato products were submitted to the extraction procedures according QuEChERS method proposed by Anastassiades *et al.*[20] Initially, the samples were previously homogenized and then 10 g of the homogenized sample were weighed in the 50 mL Falcon tube. Soon after, 10.0 mL of acetonitrile were added and subsequent stirring for 1 min in a vortex shaker. Then, 4.0 g of anhydrous magnesium sulfate were added; 1.0 g tribasic sodium citrate; 1.0 g of sodium chloride and 0.5 g of sodium hydrogen citrate sesquihydrate were added, followed by manual shaking of the tube, again vortexing for 1 min and centrifuged for 5 min at 3600 rpm. Then, an aliquot of 4.0 mL of the supernatant was removed to carry out the cleaning step. In the cleaning step by dispersive solid phase extraction (d-SPE), 0.6 g of magnesium sulfate and 0.1 g of PSA solvent were added, followed by vortexing for 30 s. Then, they were centrifuged for 5 min. Subsequently, an aliquot of 1.0 mL was removed and transferred to the 2 mL vial to be further analyzed by GC-MS.

Chromatographic conditions

A gas chromatograph coupled to a single quadrupole mass spectrometer (GC-Q-MS, model DSQII, Thermo, Washington, USA) was used in the multiresidue analyses. Pesticide separation was performed using the RTX-5ms (30 m, 0.25 mm internal diameter, 0.25 µm stationary phase film thickness) capillary column and helium carrier gas (99.99%) at a constant flow of 1 mL min^{-1}. The injection temperature was 250 °C, in splitless mode (1 min). The oven temperature program was as follows: initial temperature 100 °C for 1 min, 15 °C min^{-1} to 180 °C, then 4 °C min^{-1} to 280 °C and held for 14 min (total time: 45.33 min).

The conditions of the mass spectrometer were defined as follows: ionization mode by electronic impact (EI), 70 eV, ion source temperature 270 ºC and transfer line temperature 270 °C. The analysis was performed in the selected ion monitoring mode (SIM) based on the use of one ion target (Q_1) and two qualifier ions (Q_2 and Q_3) (Table 1).

Method validation

Selectivity, linearity, LOD and LOQ

The selectivity of the method is important to justify that the chromatographic peak is associated with an analyte. Thus, the selectivity of the method was evaluated by comparing the chromatograms obtained through the blank extract and the spiked sample.

Linearity was evaluated through of the analytical curves of pesticides at five concentration levels 0.01; 0.03, 0.05; 0.1; 1.5 and 2 mg kg^{-1}, as recommended by Agência Nacional de Vigilância Sanitária (Anvisa)[21] and guidelines SANTE.[23] Despite not being a requirement of regulatory agencies, statistical tests for homocestacicity analysis have proved to be of great relevance. The definition of homoscedasticity is that the standard deviation of signal intensities at different concentrations is constant. Thus, the calibration equation and correlation coefficient (r) for each analyte were initially obtained by ordinary least squares (OLS). OLS assumes that the residuals are normally distributed, but it also means that the data are linear. Then, residual graphs were obtained to evaluate the residual distribution of the analytical signal (y_i, peak area) on the concentration values (x_i values). Hartley's *F* test was performed to assess homoscedasticity. In case of heteroscedasticity (no homoscedasticity), the calibration curve equation and correlation coefficient (r) were obtained by the weighted least squares (WLS).[24-27]

Hartley's *F* test was conducted by calculating the F_{max}

Table 1. Physical chemical parameters of the analyzed pesticides

Pesticide	Chemical formula	Chemical group	Class	Solubility[a] / (mg L^{-1})	pK_a (25 ºC)	K_{ow} (pH 7, 20 °C)	Fragments (*m*/*z*)		
							Q_1	Q_2	Q_3
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	dinitroaniline	H	0.221	N.A.	1.86×10^5	306	264	290
Chlorothalonil	$C_8Cl_4N_2$	isophthalonitrile	F	0.81	N.A.	8.71×10^2	264	268	–
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	organophosphate	I	1.05	N.A.	5.01×10^4	97	197	199
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	pyrethroid	A/I	0.001	N.A.	3.98×10^6	181	165	166
Pyriproxyfen	$C_{20}H_{19}NO_3$	pyridyloxypropyl ether	I	0.37	6.87	2.34×10^5	136	96	226
Cyfluthrin	$C_{22}H_{18}Cl_2FNO_3$	pyrethroid	I	0.0066	N.A.	1.00×10^6	163	164	206

[a] In water at 20 °C. N.A.: not applicable; A: acaricide; F: fungicide; I: insecticide; H: herbicide; K_{ow}: octanol-water partition coefficient at pH 7, 20 °C. Adapted from Anvisa[21] and PPDB.[22]

(equation 1) and comparing them with the critical value of Hartley's $F_{tab.}$[24-28]

$$F_{max} = \frac{s^2_{max}}{s^2_{min}} \quad (1)$$

where s^2_{max} and s^2_{min} are the largest and smallest variances of the calibration data, respectively. F values less than or equal to the critical value indicate that the regression residuals are homoscedastic. In situations that the errors showed systematic deviations, the linear model for the calibration curve was considered inadequate and a nonlinear model was evaluated. When the regression residuals indicated heteroscedasticity, the slope (b_w), intercept (a_w), and correlation coefficient (r_w) were estimated.[29]

The limit of detection (LOD) and limit of quantification (LOQ) were estimated for each compound by the signal/noise ratio method (LOQ = 3 × LOD). These limits were compared with the maximum residue limits (MRL) allowed by Anvisa[30] and *Codex Alimentarius*-FAO[31] to verify the proposed analytical method.

Accuracy and precision

Accuracy was verified through the recovery rate of spiked samples in three concentration levels: low (0.05 mg kg^{-1}), medium (0.5 mg kg^{-1}) and high (1.5 mg kg^{-1}). The precision of the method in terms of repeatability was calculated and expressed as a coefficient of variation (CV, in percentage) (n = 7). The analytical procedures followed the recommended by SANTE.[23]

Results and Discussion

Validation parameters

Selectivity, linearity, LODs and LOQs

Initially, the validation of the method was carried out in order to ensure the reliability of the results, guaranteeing more precision and adequacy to the analyses. As shown in Figure 1, the selectivity was satisfactory, assuring that the chromatographic peaks are associated with a single analyte. Thus, the selective method guarantees the absence of interferents in the peaks from the residues.[22,32]

The linearity of the compounds studied is shown in Table 2. All compounds were classified as heteroscedastic ($F_{cal} > F_{tab}$), requiring linearity adjustment using the WLS, based on obtaining the weighted coefficients (b_w and a_w).[23] The analytical curves (OLS and WLS models) and residual graphs obtained by statistical analysis of linearity are shown in Figure 2.

Table 2 also shows the LOD and LOQ values obtained for the 6 pesticides analyzed in the multiresidue method. It was verified that the method reached low values in the interval between 0.01-0.03 and 0.03 and 0.10 mg kg^{-1} for the determination of LODs and LOQs, respectively. The values found were below the MRLs established by Anvisa[21] and FAO,[31] therefore being acceptable. When comparing Anvisa and FAO limits, there is a variation in terms of the MRLs required by the agencies. Therefore, it is important

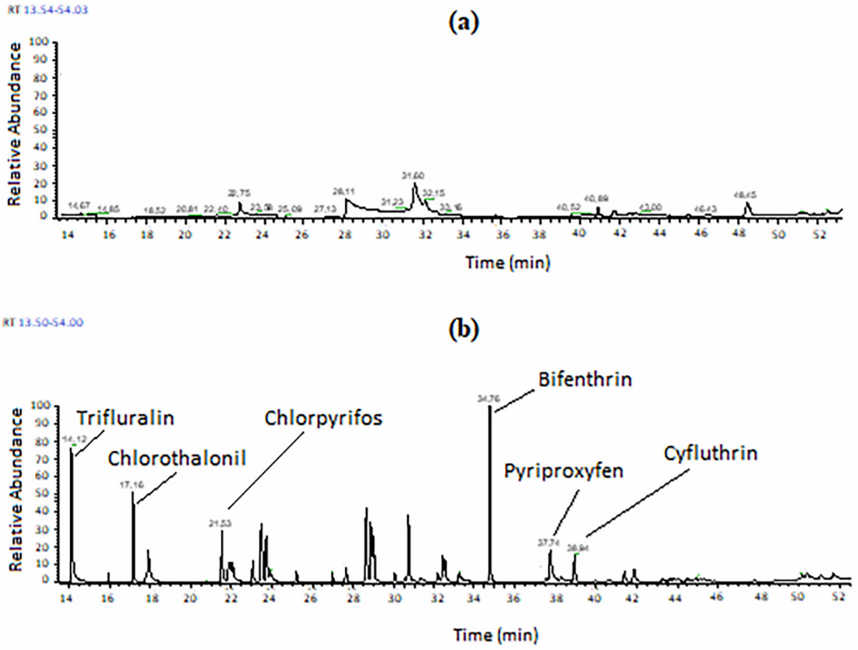


Figure 1. Chromatogram of (a) tomato matrix blank; (b) standard solution of pesticides (2 mg kg^{-1}) in the matrix.

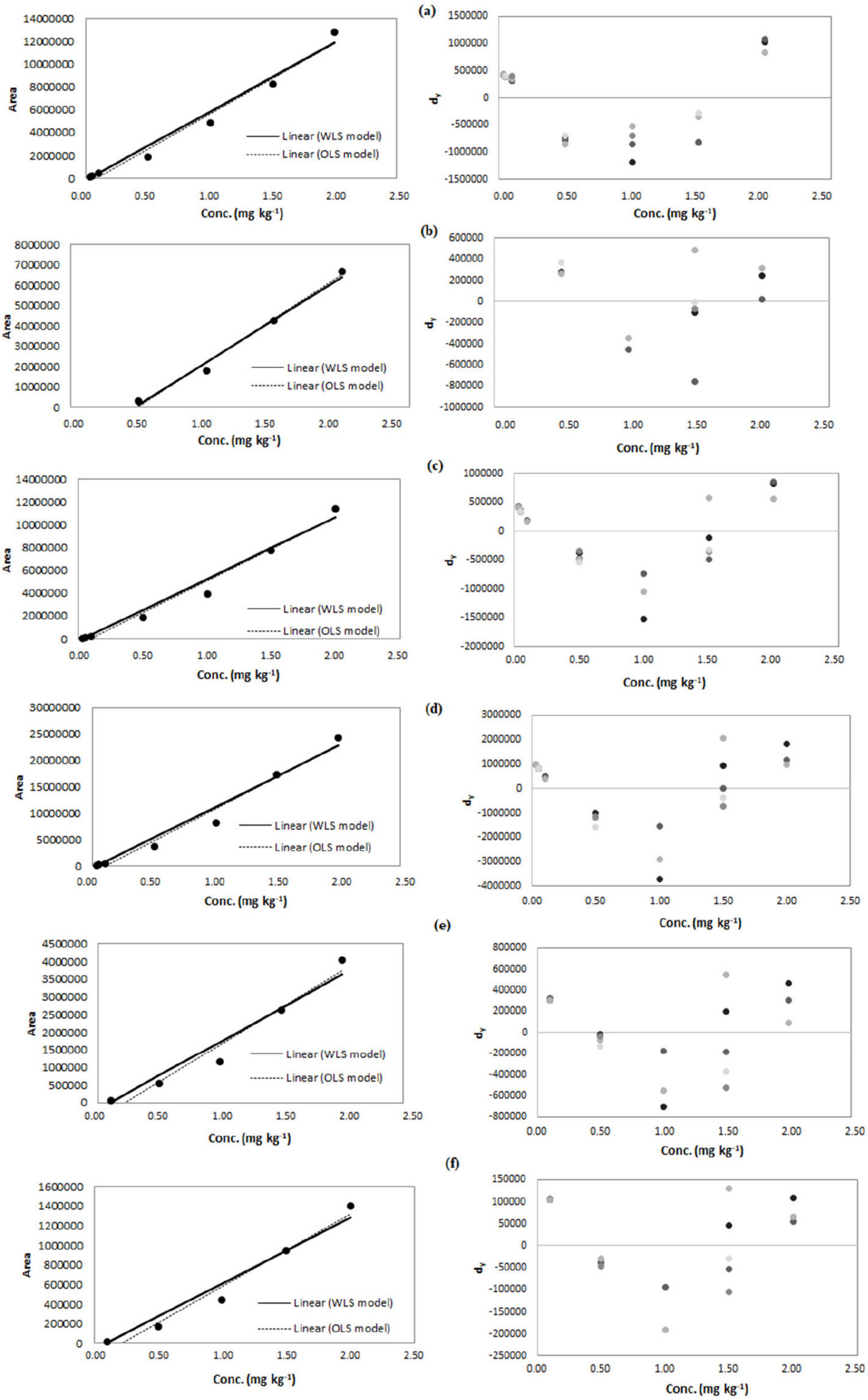


Figure 2. Analytical curves (OLS and WLS models) and residuals graphs obtained by statistical analysis of linearity: (a) trifluralin, (b) chlorothalonil, (c) chlorpyrifos, (d) bifenthrin, (e) pyriproxyfen, (f) cyfluthrin.

Table 2. Linearity ($y = a + bx$), statistical test and limits (LODs, LOQs and MRLs) of pesticides

Pesticide	Concentration range / (mg kg^{-1})	Statistical test								LOD / (mg kg^{-1})	LOQ / (mg kg^{-1})	MRL^c / (mg kg^{-1})	
		Ordinary coefficients^a		r	*F* calc	Classification	Weighted coefficients^b		r_w			Anvisa[30]	FAO (Codex)[31]
		b	a				b_w	a_w					
Trifluralin	0.03-2.00	6185377	−513585	0.979	64.44	heterosedastic	6016586.4	−138016.5	0.990	0.01	0.03	0.05	NA
Chlorothalonil	0.03-2.00	3953716	−104286	0.988	34.81	heterosedastic	3774128.4	−29493.1	0.999	0.02	0.05	3	5
Chlorpyrifos	0.03-2.00	3953716	−104286	0.980	34.81	heterosedastic	3774128.4	−29493.1	0.999	0.02	0.05	0.5	1
Bifenthrin	0.03-2.00	12066786	−1225876	0.977	124.12	heterosedastic	11566296.1	−371173.4	0.998	0.01	0.03	0.15	0.3
Pyriproxyfen	0.1-2.00	2104501	−464603	0.960	43.77	heterosedastic	1905624.4	−181740.8	0.990	0.03	0.10	0.2	0.4
Cyfluthrin	0.03-2.00	740415	−158311	0.970	86.10	heterosedastic	671939.4	−59441.6	0.995	0.03	0.10	0.2	0.1

[a]Coefficients obtained by OLS: slope (b), intercept (a), correlation coefficient (r); [b]weighted coefficients obtained by WLS: slope (b_w), intercept (a_w), correlation coefficient (r_w); [c]MRLs established for tomato crop. $F_{tab\ (\alpha = 0.05)} = 19$; LOD: limit of detection; LOQ: limit of quantification.

to control these data in order to seek means for greater standardization of the limits required by regulatory agencies in different countries.

Therefore, it is up to government agencies to adopt more restrictive monitoring and similar requirements, including a greater number of active ingredients inserted in crops that are not inspected and analyzed.

Accuracy and precision of the method

Accuracy was verified using the recovery rate of spiked samples at 3 levels (0.05, 0.5, 1.5 mg kg^{-1}). The precision of the method in terms of repeatability was calculated and expressed as relative standard deviation (RSD) in percentage.

The values for the accuracy and precision of the method are described in Table 3. Anvisa[21] establishes limits of 70 to 120% for recovery rates. According to SANTE[23] a practical standard range of 60-140% can be used for individual recoveries in routine analyses. The precision (RSD) must not exceed 20%, in the concentration range used.[21,23] The recovery rates and CV ranged from 78-121% and 2.3-16.7%, respectively. According to the results, the precision and accuracy values remained within the recommended limit for the applied concentration levels for the compounds.

Table 3. Accuracy and precision of the method

Pesticide	Accuracy (Precision / %) / %		
	0.05 mg kg^{-1}	0.5 mg kg^{-1}	1.5 mg kg^{-1}
Trifluralin	105 (3.7)	101 (3.6)	106 (3.2)
Chlorothalonil	78 (15.7)	84 (4.0)	86 (2.3)
Chlorpyrifos	112 (8.2)	107 (4.4)	121 (5.5)
Bifenthrin	107 (5.4)	98 (6.0)	118 (6.6)
Pyriproxyfen	90 (16.6)	98 (8.9)	114 (16.7)
Cyfluthrin	80 (4.3)	109 (15.6)	112 (9.7)

Analysis of tomato products

Commercial samples were analyzed after the development and validation of the method for determining pesticide residues under study. Among the 15 samples analyzed, only bifenthrin (t_R = 34.65 min) was detected in one tomato sauce sample, but none of the samples showed quantifiable levels (< LOQ). The concentration detected in the sample was 0.05 mg kg^{-1}, therefore below the MRL established by Anvisa (0.15 mg kg^{-1})[30] and FAO (0.3 mg kg^{-1}).[31]

Figure 3 shows the chromatogram representing the component identified in the sample and then the mass spectrum of the bifenthrin compound detected. Bifenthrin is a pyrethroid insecticide, toxicological classification III-moderately toxic. In tomato plants, a period of 6 days must be respected after using the bifenthrin compound in the crop, in order to prevent the harvested food from having residues above the limit determined by legislation.[22] The main characteristics of the compound are detailed in Table 4.

If the individual becomes intoxicated with the exposure or consumption of these components, it generates subacute intoxication that occurs due to moderate or mild exposure to these highly or moderately toxic products. According to Table 4, bifenthrin has a lipophilic character ($\log K_{ow} = 6.6$) and tends to accumulate in body fat. In general, substances with $\log K_{ow}$ greater than 3 have a tendency to bioaccumulate.[33] The degree of toxicity of this compound varies according to the metabolism and cellular components of the individual. Studies[34] indicate that, even though the exposure of humans and mammals to these compounds is low, it can cause neurotoxic symptoms. Chronic exposure can develop symptoms such as headache, nausea and dizziness, as well as damage to the spleen and lymph nodes, increasing the risk of developing cancer. The presence of pyrethroid metabolites is also associated with an increased risk of brain tumors and addition to heart problems.[34]

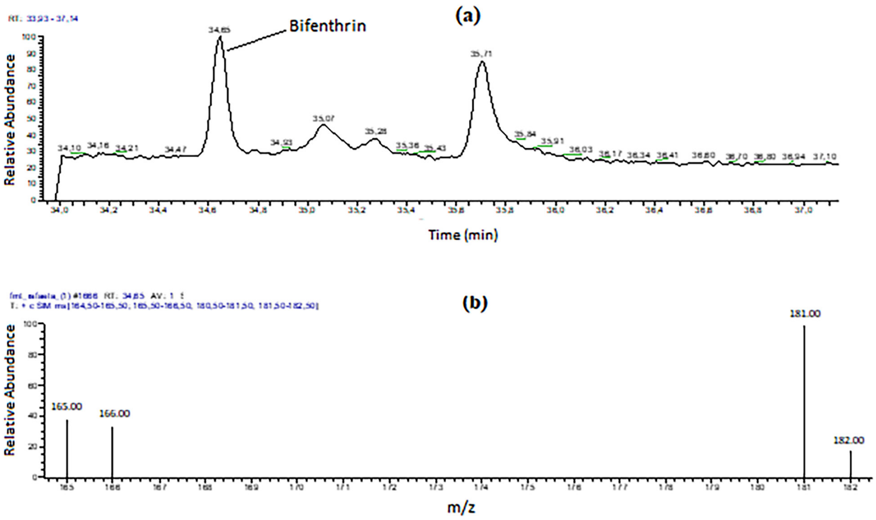
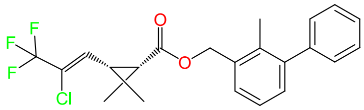


Figure 3. Mass spectrum of the bifenthrin compound identified in the tomato sauce sample.

Table 4. Bifenthrin compound classification

	Bifenthrin
Chemical name	2-methylbiphenyl-3-ylmethyl (*Z*)-(1*RS*,3*RS*)-3-(2-chloro3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
Structural formula	
Chemical formula	$C_{23}H_{22}ClF_3O_2$
Chemical group	pyrethroid
Toxicological classification	III-moderately toxic
Class	insecticide, acaricide
Application	foliar
MRL for tomato crop / (mg kg^{-1})	0.15
Security interval / days	6
Log K_{ow}	6.6
Acceptable daily intake (ADI) / (mg kg^{-1} b.w)	0.02
Acute reference dose (ARfD) / (mg kg^{-1} b.w)	0.01

Adapted from Anvisa[30] and PPDB.[22] MRL: maximum residue limits; b.w: body weight.

Some ways to mitigate the problem of the presence of pesticides in food are: Good Agricultural Practices (GAPs) from suppliers in crops, the insertion of inspection programs regarding the levels of these active principles in inputs purchased by companies, routinely carrying out analysis of residues, control of entry of raw materials into stocks and processing areas and management programs including audits and certifications.[35]

The strengthening of public policies such as the Programa Nacional de Redução de Agrotóxicos (PNARA)[36] and the Política Nacional de Agroecologia e Produção Orgânica (PNAPO)[37] in order to make farmers aware of the need to reduce the use of these inputs or avoid their use is a means of stimulating the search for less toxic crops and more sustainable management.[38] Sustainable means such as agroecology, integrated pest management and biological control are used to control pests in crops, mitigating the impacts caused by pesticides.[39]

One way to investigate the quality of processed products, with raw material from agricultural fields, would be the implementation of laws, standards and maximum limits of contaminants for the processing industries of these commodities. The system that assesses the risks caused by pesticides is based on ensuring only primary agricultural products, without taking into account the impacts of processing in different ways and the variation of residues in these final products.[40,41]

Conclusions

The validation of the QuEChERS extraction associated with the quantification by GC-MS showed satisfactory for compounds regarding the parameters established by regulatory agencies: selectivity, LOD, LOQ, linearity, precision and accuracy. The six compounds (bifenthrin, chlorothalonil, chlorpyrifos, cyfluthrin, pyriproxyfen, trifluralin) were classified as heterocesdastic and required curve fitting. The values found were in accordance with those specified in the technical standards and corroborated with data from the literature for chromatographic methods, indicating that their use is reliable in monitoring pesticide residues in industrialized products derived from tomatoes.

Regarding the application of the GC-MS method, it was found that among the 15 samples analyzed, bifenthrin was detected in one sample of tomato sauce, but according to parameters established by regulatory agencies (Anvisa and FAO). Bifenthrin is an insecticide of the pyrethroid group of moderately toxic classification. However, a continuous monitoring control of these pesticide residues in tomato products is essential to ensure quality to consumers, in view of the lack of studies on processed products regarding the detection and quantification of pesticide residues. The method can help control the quality of products derived from tomatoes, in order to ensure food safety for consumers.

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Author Contributions

Fátima R. S. Costa was responsible for literature review, definition of methodology, participation in laboratory analysis, tabulation and statistical analysis of data, interpretation of data, preparation of the original draft and formatting of the article; Priscilla L. Maia for preparation of the original draft and formatting of the article; Felipe S. da Silva for participation in laboratory analysis, tabulation and statistical analysis of data, interpretation of data; Crisiana A. Nobre for participation and guidance of chromatographic analyzes interpretation of data; Renata O. Silva for participation in laboratory analysis, tabulation and statistical analysis of data, interpretation of data; Maria A. L. Milhome for formal analysis, supervision, visualization and writing-review and editing, project administration.

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