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Research Article

Multi-residue analysis of pesticide residues in mangoes using solid-phase microextraction coupled to liquid chromatography and UV–Vis detection

A sensitive and efficient solid-phase microextraction method, based on liquid chromatography and UV–Vis detection, was developed and validated as an alternative method for sample screening prior to LC-MS analysis. It enables the simultaneous determination of ten pesticides in mango fruits. The fiber used was polydimethylsiloxane while optimum SPME conditions employed have been developed and optimized in a previous work. The desorption process was performed in static mode, using acetonitrile as a solvent. The results indicate that the DI-SPME/HPLC/UV–Vis procedure resulted in good linear range, accuracy, precision and sensibility and is adequate for analyzing pesticide residues in mango fruits. The limits of detection (0.6–3.3 µg/kg) and quantification (2.0–10.0 µg/kg) were achieved with values lower than the maximum residue levels (MRLs) established by Brazilian legislation for all pesticides in this study. The average recovery rates obtained for each pesticide ranged from 71.6 to 104.3% at three fortification levels, with the relative standard deviation ranging from 4.3 to 18.6%. The proposed method was applied for the determination of the aforementioned compounds in commercial mango samples and residues of azoxystrobin, fenthion, permethrin, abamectin and bifenthrin were detected in the mango samples, although below the MRLs established by Brazilian legislation.

Keywords: HPLC/UV–Vis / Mangoes / Pesticide residues / SPME
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1 Introduction

Mango (*Mangifera indica*) is one of the most common of tropical fruits. It has a pleasant flavor and color, is rich in carotenoids, minerals and carbohydrates and is part of a group of tropical fruits that are economically important in Brazilian and international markets [1]. Brazil's environmental conditions are favorable for mango cultivation, and the northeast and southeast regions of the country account for 89% of Brazil's production (Embrapa: <http://sistemasdeproducao.cnptia.embrapa.br/FontesHTML/Manga/CultivodaMangueira/socioeconomia.htm>). The fruit is consumed raw or processed into various products, such as juices, nectars, jellies and ice cream [2]. Mango crops are susceptible to pest attack in every season. Therefore, insecticides and fungicides are used extensively at several stages of cultivation to control pests and diseases that may reduce the crop yield. The use of pesticides increases

agricultural output, but pesticide residues may remain in the fruit, posing a risk to human health because of their toxicity [3]. Therefore, monitoring pesticide residues in mangoes is a particular concern from the standpoint of consumer safety.

Public awareness of health hazards posed by pesticide residues in fruits and vegetables has led to the development of many analytical methods [4, 5]. Pesticide residues in fruits and vegetables are usually determined using chromatographic techniques, which involve preliminary steps such as sampling, extraction and clean-up [6]. Sample preparation is essential to increase the sensitivity, efficiency, practicality and reliability of methods for the analysis of pesticide residues in fruit samples. Ideally, a sample preparation method should be fast, simple and able to isolate a wide range of compounds with very different chemical structures and properties [7]. Low concentrations of pesticide residues in fruits and vegetables require the use of sensitive techniques for trace analysis [8].

The solid-phase microextraction (SPME) method is a good alternative to eliminate or significantly reduce the use of organic solvents. This method can combine sampling, extraction, preconcentration and sample introduction in a single uninterrupted process that results in a high-sample throughput [9]. Moreover, it is easily automated and can

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improve the limits of detection (LOD) [10]. SPME extraction, followed by analysis by gas chromatography (GC) or liquid chromatography (LC) coupled to a variety of detectors, is very useful for determining pesticide residues in different matrices. GC-MS is a common technique for separating pesticide residues because of its sensitivity and selectivity and the easy identification of compounds through their mass spectra [7, 11].

SPME coupled with GC has been widely employed in the analysis of pesticide residues. Nevertheless, pesticides that are thermally unstable, such as carbofuran and carbosulfan, or those that decompose before reaching their boiling points (IUPAC: <http://sitem.herts.ac.uk/aeru/iupac/8.htm>), such as abamectin, are not suitable for separation and analysis by GC, although they can be easily separated by high-performance liquid chromatography (HPLC) [12]. Solvent desorption is thus proposed as an alternative for coupling SPME to HPLC, allowing for the chromatographic analysis of nonvolatile and/or thermally unstable compounds. In this case, an interface with an organic solvent inside (static desorption mode) or the mobile phase flowing through it (dynamic mode) is used to desorb the analytes from the SPME fiber [13].

The ideal methods for determining pesticide residues in foods make use of mass spectrometers as detection systems, in the MS or MS/MS mode, since they allow for the simultaneous identification and quantification of the analytes. Nevertheless, mass spectrometers are relatively expensive instruments and, due to their sensitivity, easily contaminated by matrix impurities. Therefore, a screening analysis with a more simple detector may be an attractive alternative to be applied for samples, in order to first select only those containing the target analytes.

Several methods have been described in the literature [7, 9, 14–22] for the analysis, in fruits and vegetables, of the pesticides abamectin, carbofuran, carbosulfan, bifenthrin, permethrin, thiaabendazole, prochloraz, clofentezine, fenthion and azoxystrobin, those which are being proposed in this work. Nevertheless, most of them were developed to analyze only one compound or a few compounds belonging to the same chemical class. To our present knowledge, there is no method yet that is able to simultaneously determine these ten compounds together, in fruits and vegetables.

This paper regards the development and validation of a simple method, based on SPME followed by LC and UV–Vis detection, as an alternative for sample screening prior to the confirmative LC-MS analysis. The developed method was optimized for the simultaneous determination of abamectin, carbofuran, carbosulfan, bifenthrin, permethrin, thiaabendazole, prochloraz, clofentezine, fenthion and azoxystrobin in mango fruits. These compounds were selected due to their extensive application in an irrigation project in the state of Sergipe, northeast of Brazil, and their authorized use by ANVISA, the Brazilian National Health Surveillance Agency.

The factors that may have influence on the desorption efficiency of the SPME interface were evaluated and the

analytical parameters were optimized. After validation, the method was applied to determine pesticide residues in fresh mango, purchased at different sales outlets in the city of Aracaju, state of Sergipe, Brazil.

2 Materials and methods

2.1 Standards, reagents and solvents

HPLC-grade acetonitrile was purchased from J. T. Baker (Phillipsburg, NJ, USA). Certified standards of abamectin, azoxystrobin, bifenthrin, carbofuran, carbosulfan, clofentezine, fenthion, permethrin, prochloraz and thiaabendazole were purchased from AccuStandard (New Haven, CT, USA). All the standards were at least 97% pure. Isopropanol was purchased from Merck (Darmstadt, Germany) and NaCl (99.0% pure) from Nuclear (São Paulo, Brazil). Individual stock solutions of the analytes in concentrations of 400 µg/mL were prepared in acetonitrile and stored in a freezer at -18°C . A working standard solution (10 µg/mL) was prepared by diluting the stock solution with acetonitrile and storing it at 4°C . This standard was used to spike the matrix in order to optimize the desorption conditions (50 µg/kg) and to validate the method at different concentrations (5–250 µg/kg). Calibration standards in concentrations of 2, 5, 10, 25, 50, 100 and 250 µg/kg were prepared by diluting the working standard directly in the matrix extract.

Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2 Equipment

HPLC analyses were carried out on an LC-ProStar liquid chromatograph (Varian, USA) with two 210/215 SD-1 pumps, a 325 LC UV–Vis detector and a MetaChem degasser (East Lyme, CT, USA). An SPME–HPLC interface equipped with a Rheodyne[®] valve (Supelco, Bellefonte, USA) and a 60-µL desorption chamber was also used. The separations were performed using an XTerra[®] MS C₁₈ column (250 mm × 2.1 mm id, 5 µm particle size) (Waters, Milford, USA). The separation gradient employed in this work was water (A) and acetonitrile (B), starting with 30% B, then linearly increasing up to 70% B in 6 min, followed by a slow increase to 80% B in 12 min, then an increase to 100% B in 4 min, holding at this composition for 10 min and returning to the initial condition in 10 min, with a total analysis time of 42 min at a flow rate of 0.25 mL/min. UV detection was performed at 203 nm (0–25.5 and 31–42 min) and 245 nm (25.5–31 min).

A fiber holder designed for autosampler and a 100-µm polydimethylsiloxane (PDMS) SPME fiber for autosampler, both supplied by Supelco, were used in the SPME analysis. The fiber was conditioned by exposing it to the SPME–HPLC interface while percolating the mobile phase through it for 42 min, running the gradient through the

entire cycle (dynamic mode), as recommended by the manufacturer.

2.3 Sample preparation and fortification

The mango samples used in the development of this method were obtained from an organic farm (pesticide free) located in the state of Sergipe (10°37'21"S and 37°28'56"W) in northeastern Brazil. A representative portion of mango (~500 g) was cut into small pieces with no pretreatment, blended in a food processor, placed in amber glass flasks and stored at –18°C until it was used.

Fortified samples were prepared by adding 3–75 µL of the work solution (10 µg/L) to 3 g of mango, resulting in final pesticide concentrations of 10–250 µg/kg in samples. Based on the previous results [11], the fortified samples were equilibrated in ambient conditions for 30 min prior to extraction.

2.4 DI-SPME analysis

This work was carried out using the extraction conditions previously optimized by Menezes Filho *et al.* [23] for the determination of pesticide residues in mango through the SPME extraction and GC/MS analysis. In this previous work, the polyacrylate (PA 85 µm) and PDMS (100 µm) fibers were tested and their conditions pre-optimized. Although the PA fiber was finally chosen to develop the method, since it gave better recoveries in the extraction of the 14 studied pesticides, carbosulfan was observed to be recovered only by the PDMS fiber. Besides, the abamectin, which has not been considered in that previous work, since it is not determined by GC, was now tested with the PA and PDMS fibers and the second was the only one with the ability to extract it. In this way, the PDMS fiber was chosen here, for the ability to extract carbosulfan and abamectin and for giving still acceptable recoveries for the remaining of the pesticides studied.

Extractions were performed with 3 g of mango and 10 mL of water in glass vials (20 mL) closed with caps and Teflon/Silicone septa purchased from UnitechUSA (Medley, FL, USA). The pesticides were extracted in the direct immersion mode (DI-SPME), at 50°C for 30 min and stirred at 250 rpm. The fiber (PDMS 100 µm) was then inserted into the desorption chamber in the “load” position and the chamber was filled with pure acetonitrile to allow static desorption to take place. Fiber soaking time at the SPME–HPLC interface was always 15 min. The fiber was removed from the SPME–HPLC interface and the injection valve was switched to the “injection” position, allowing the mobile phase to percolate through the chamber for 10 min. After this, the injection valve was returned to the “load” position. After each desorption cycle, the fiber was cleaned for 10 min with 10 mL of mobile phase and stirred at 300 rpm. Between each set of two samples, a blank of the

fiber was prepared to check for the absence of carryover effects.

3 Results and discussion

3.1 HPLC/UV–Vis conditions

The chromatographic conditions were optimized using a 1 µg/mL standard mixture. The chromatographic resolution obtained with the conditions described in Section 2.2 was considered satisfactory. Figure 1 shows the chromatogram obtained with DI-SPME–HPLC/UV–Vis, when standard mixtures were prepared in the matrix extract at a fortification level of 250 µg/kg.

The components of the matrix may cause variations in the detector's response to pesticides. This phenomenon was studied by comparing the calibration curves of each compound in solutions with and without the matrix extract. When standards were prepared in solutions with the matrix extract, higher peak areas were obtained. Therefore, the calibration curves were prepared in this way.

3.2 Selection of the desorption mode

The effect of the desorption mode was examined in the dynamic and static modes. In the dynamic mode, the fiber was placed in the desorption chamber and the valve was immediately switched to the “inject” position. After 15 min, the valve was switched back to the “load” position and the fiber was removed from the SPME–HPLC interface. This procedure resulted in saturation of the detector, due to the presence of interferents, such as polar carbohydrates, extracted from the matrix and washed away by the mobile phase (water/ACN, 70:30).

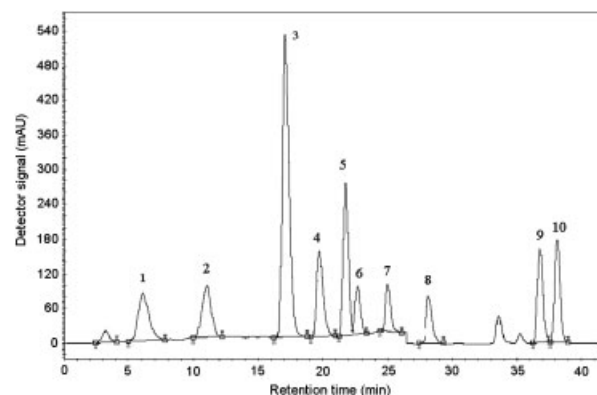


Figure 1. Chromatogram obtained in the DI-SPME–HPLC/UV–Vis with the standard mixture prepared in the matrix extract at a 250 µg/kg fortification level. Peak identification: 1, thiabendazole; 2, carbofuran; 3, azoxystrobin; 4, prochloraz; 5, fenthion; 6, clofentezine; 7, permethrin; 8, abamectin; 9, carbosulfan; 10, bifenthrin.

In the static mode, the fiber was placed in the desorption chamber previously filled with acetonitrile and held for 15 min in contact with this solvent. After that the fiber was removed and the extract was injected into the column. The best results were obtained in the static mode, since no detector saturation was observed. The static mode was then chosen for use in the remaining experiments and Fig. 2 shows a chromatogram obtained with this mode. Since it represents a preliminary evaluation and the desorption

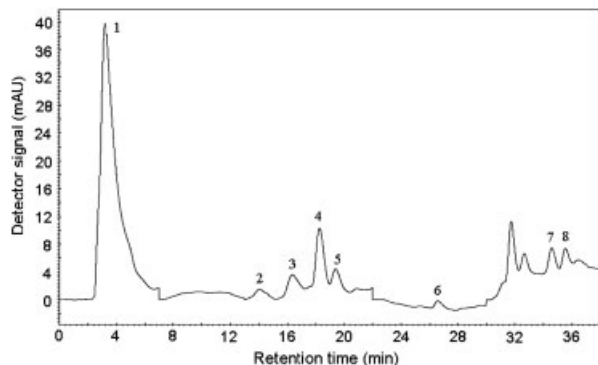


Figure 2. Chromatogram obtained in the DI-SPME–HPLC/UV–Vis and desorption in the static mode. Peak identification: 1, acetone; 2, azoxystrobin; 3, prochloraz; 4, fenthion; 5, clofentezine; 6, abamectin; 7, carbosulfan; 8, bifenthrin.

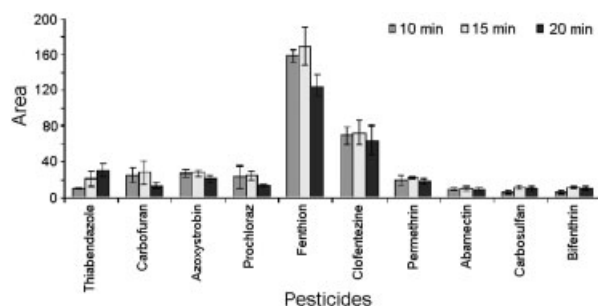


Figure 3. Influence of time on the desorption efficiency in the static mode, using acetonitrile as extracting solvent.

conditions had not been yet optimized, the retention times are different relative to the other chromatograms presented.

3.3 Selection of the desorption time

Desorption time was evaluated in the range of 10–20 min. Figure 3 shows the peak area for each pesticide as a function of desorption time. The peak areas did not increase significantly after 15 min, except for thiabendazole, which showed better results in 20 min. For permethrin, abamectin, carbosulfan and bifenthrin, no significant variations in the results were observed. The best results were attained in 15 min, and thus this desorption time was chosen.

3.4 Method validation

The detector response was linear for all the compounds studied and was determined based on external standard calibration curves constructed at seven concentration levels (2–250 µg/kg). Each level was analyzed in triplicate. Good determination coefficients, ranging from 0.9903 to 0.9997, were obtained for all the pesticides.

The LOD and LOQ were established using the signal-to-noise ratio for each compound, obtained through a standard for which a minimum signal was still measurable for each analyte. A 3:1 ratio was used as the LOD, whereas a 10:1 ratio was used as the limit of quantification (LOQ). The LOD for the pesticides under study ranged from 0.6 to 3.3 µg/kg, whereas the LOQ ranged from 2.0 to 10.0 µg/kg. These LOQ were lower than the maximum residue limits (MRLs) of all the determined pesticides, according to the values established by the Brazilian National Health Surveillance Agency (ANVISA) (Pesticide residues in food, <http://www.anvisa.gov.br/toxicologia/monografias/index.htm>).

Table 1 summarizes the data.

Regarding abamectin, the LOQ obtained (5.0 µg/kg) was similar to the values reported in the previous works [15, 16]. Nevertheless, while in these works a previous derivatization step with trifluoroacetic anhydride or *N*-methylimidazole

Table 1. Analytical figures of merit obtained and maximum residue limits (MRLs)

Pesticide	Linearity (µg/kg)	r^2	LOD (µg/kg)	LOQ (µg/kg)	MRL ^{a)} (µg/kg)
Thiabendazole	5.0–250.0	0.9997	1.6	5	2000
Carbofuran	10.0–250.0	0.9969	3.3	10	–
Azoxystrobin	2.0–250.0	0.9994	0.6	2	500
Prochloraz	5.0–250.0	0.9960	1.6	5	200
Fenthion	2.0–250.0	0.9961	0.6	2	50
Clofentezine	5.0–250.0	0.9988	1.6	5	–
Permethrin	5.0–250.0	0.9920	1.6	5	–
Abamectin	5.0–250.0	0.9992	1.6	5	10
Carbosulfan	5.0–250.0	0.9903	1.6	5	50
Bifenthrin	2.0–250.0	0.9917	0.6	2	100

a) Source: ANVISA, 2009.

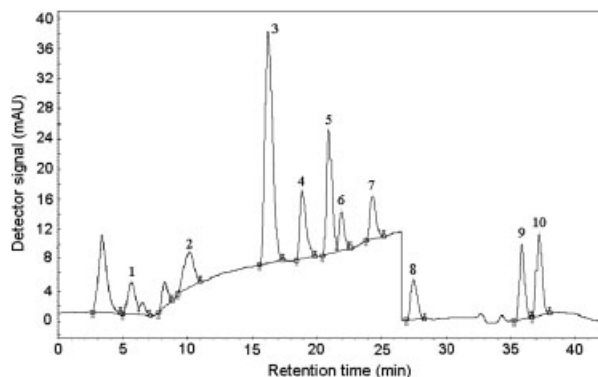


Figure 4. Chromatogram obtained in the DI-SPME–HPLC/UV–Vis with the standard mixture prepared in the matrix extract at a 10 µg/kg fortification level. Peak identification: 1, thiabendazole; 2, carbofuran; 3, azoxystrobin; 4, prochloraz; 5, fenthion; 6, clofentezine; 7, permethrin; 8, abamectin; 9, carbosulfan; 10, bifenthrin.

was necessary, no similar procedure was necessary here, thus reducing the sample manipulation and possible losses of the analytes. Figure 4 shows the chromatogram obtained with standards at the lowest fortification level (10 µg/kg).

To examine the accuracy and precision of the SPME method, the relative recovery rates and RSDs were determined by performing seven consecutive extractions on the same day at three different levels of fortification, and three extractions per day for five consecutive days at two different levels of fortification. The mean relative recoveries and the RSD values obtained from the analysis of fortified mango samples are listed in Table 2. These values can be deemed excellent when compared with the values usually obtained by SPME methods. In the first case, the relative recoveries ranged from 75.1 to 104.4% at the lowest concentration (10 µg/kg), with RSD values of 17.8 and 18.6% for carbofuran and bifenthrin, respectively, and from 73.3 to 86.1% at the highest concentration (250 µg/kg), with RSD values of 11.0 and 7.5% for thiabendazole and carbosulfan, respectively. In the second case, the relative recoveries ranged from 71.6 to 89.4% at the lowest concentration (10 µg/kg), with RSD values of 9.7 and 16.2% for carbofuran and bifenthrin, respectively, and from 72.9 to 88.3% at the highest concentration (100 µg/kg), with RSD values of 9.1 and 8.8% for carbofuran and fenthion, respectively.

The absolute recoveries were calculated by comparing the average ($n = 3$) detector signals produced when directly injecting a volume of standard mixture containing 30 ng of each pesticide, against the average ($n = 3$) detector signals produced by the DI-SPME analysis of samples to which the same amount (30 ng) of each pesticide was spiked into the sample matrix. Because SPME is a non-exhaustive extraction technique, recoveries are usually low [24]. Table 3 shows absolute recoveries obtained by this method. The values ranged from $4.6 \pm 0.7\%$ for carbofuran to $41.8 \pm 3.2\%$ for abamectin.

Table 2. Accuracy and repeatability of the developed method for samples spiked at three different levels

Pesticide	Spiking levels (µg/kg)	Intraday study ($n = 7$)		Interday study ^{a)} ($n = 15$)	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Thiabendazole	10	72.2	14.7	82.9	17.2
	100	75.9	8.9	81.8	5.4
	250	73.3	11	–	–
Carbofuran	10	72.7	15.7	71.6	9.7
	100	77	12.1	72.9	9.1
	250	81.5	11.1	–	–
Azoxystrobin	10	84.9	10.3	79.6	5.3
	100	75.3	6	81.5	4.5
	250	78.4	5.2	–	–
Prochloraz	10	88.8	9.6	78.3	10.6
	100	85	8.5	78.1	4.3
	250	75.9	5.6	–	–
Fenthion	10	89.6	9.5	83.6	8.2
	100	82.2	7.2	88.3	8.8
	250	76.6	8.1	–	–
Clofentezine	10	96.1	6.6	88.4	16.3
	100	84.5	9	84.4	18.1
	250	84.9	6.8	–	–
Permethrin	10	86.6	11.5	89	10.1
	100	79.3	8.7	84.5	12.8
	250	82.2	11.9	–	–
Abamectin	10	80.5	9.6	78.9	8.3
	100	75.8	6.8	82.4	4.6
	250	76	11.7	–	–
Carbosulfan	10	79.4	8.8	81.7	9.7
	100	81.8	13.4	86.2	11.5
	250	86.1	7.5	–	–
Bifenthrin	10	91.6	7.2	89.4	16.2
	100	82	4.3	85.8	10.1
	250	78.7	13.9	–	–

a) Interday ($n = 15$) in triplicates for five days.

Table 3. Absolute recoveries and relative standard deviations for the studied pesticides

Pesticide	Absolute recovery (%) and RSD (%) ($n = 3$)
Thiabendazole	26.9 ± 3.3
Carbofuran	4.6 ± 0.7
Azoxystrobin	12.2 ± 1.5
Prochloraz	12.9 ± 1.1
Fenthion	12.0 ± 0.8
Clofentezine	16.4 ± 2.0
Permethrin	18.7 ± 1.5
Abamectin	41.8 ± 3.2
Carbosulfan	23.1 ± 2.8
Bifenthrin	14.8 ± 1.5

3.5 Analysis of real samples

The effectiveness of the proposed method in determining the ten pesticides in mango samples was tested by

Table 4. Pesticides concentrations determined in commercial mango samples

Samples (collection points)		Pesticide level, µg/kg (RSD, %, <i>n</i> = 3)									
		Thb	Caf	Azo	Pro	Fen	Clo	Per	Aba	Cas	Bif
Point 1	Peel and pulp	n.d	n.d	3.5 ± 0.4	n.d	2.6 ± 0.3	n.d	16.3 ± 1.1	5.3 ± 0.4	n.d	4.2 ± 0.7
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	15.3 ± 1.0	n.d	n.d	n.d
Point 2	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	12.8 ± 1.3	n.d	n.d	n.d
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Point 3	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	10.7 ± 0.9	n.d	n.d	n.d
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Point 4	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	16.3 ± 1.3	n.d	n.d	n.d
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	8.9 ± 0.7	n.d	n.d	n.d
Point 5	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	7.8 ± 0.7	n.d	n.d	3.0 ± 0.5
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Point 6	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	8.9 ± 1.1
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	4.2 ± 0.7
Point 7	Peel and pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	8.2 ± 0.9
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.0 ± 0.6
Point 8	Peel and pulp	n.d	n.d	n.d	n.d	5.7 ± 0.6	n.d	6.9 ± 0.7	5.3 ± 0.6	n.d	10.6 ± 1.8
	Only pulp	n.d	n.d	n.d	n.d	n.d	n.d	3.7 ± 0.3	n.d	n.d	3.4 ± 0.6

Thb, thiabendazole; Caf, carbofuran; Azo, azoxystrobin; Pro, prochloraz; Fen, fenthion; Clo, clofentezine; Per, permethrin; Aba, abamectin; Cas, carbosulfan and Bif, bifenthrin.

performing analyses, in triplicate, of samples from eight different markets in the city of Aracaju, state of Sergipe (Brazil), and produced through conventional agriculture techniques. Each sample was analyzed both by processing together peel and pulp and only the pulp. Table 4 shows the results obtained. For samples where pesticide residues were found, the concentrations were lower than the values established by ANVISA. It should be warned, however, that, although permethrin is forbidden for mango cultivation, high concentrations of this pesticide were found in most of the samples. Permethrin and bifenthrin were detected in a great number of samples and were also the unique compounds detected in the pulps, maybe due to their affinity to the lipid-rich pulps of these fruits.

4 Concluding remarks

The developed method involving DI-SPME extraction and HPLC/UV-Vis has proved to be a simple alternative for simultaneous sample screening, prior to confirmative LC-MS analysis, of the ten target pesticides in mango fruits, namely abamectin, carbofuran, carbosulfan, bifenthrin, permethrin, thiabendazole, prochloraz, clofentezine, fenthion and azoxystrobin. It is simple, efficient, selective and sensitive and can also be applied for a variety of other fruits. The LOD and LOQ values obtained for each pesticide were lower than the MRLs established by the Brazilian legislation, while precision and accuracy render it suitable for its application.

Abamectin, in particular, is usually derivatized and analyzed separately or with chemically similar compounds. This method allows for the simultaneous analysis of

abamectin with the compounds carbofuran and carbosulfan (carbamates), bifenthrin and permethrin (pyrethroids), thiabendazole and prochloraz (imidazoles), clofentezine (tetrazine), fenthion (organophosphate) and azoxystrobin (strobilurin) without derivatization, obtaining similar results.

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The authors have declared no conflict of interest.

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