

A Matrix Solid-Phase Dispersion Method for the Extraction of Seven Pesticides from Mango and Papaya

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Abstract

A simple and effective extraction method based on matrix solid-phase dispersion was developed to determine trichlorfon, pyrimethanil, methyl parathion, tetraconazole, thiabendazole, imazalil, and tebuconazole in papaya and mango using gas chromatography–mass spectrometry with selected ion monitoring. Different parameters of the method were evaluated, such as type of solid-phase (silica-gel, neutral alumina, and Florisil), the amount of solid-phase, and eluent [dichloromethane, ethyl acetate–dichloromethane (4:1, 1:4, 1:1, 2:3, v/v)]. The best results were obtained using 2.0 g of mango or papaya, 3.0 g of silica as dispersant sorbent, and ethyl acetate–dichloromethane (1:1, v/v) as eluting solvent. The method was validated using mango and papaya samples fortified with pesticides at different concentration levels (0.05, 0.10, and 1.0 mg/kg). Average recoveries (4 replicates) ranged from 80% to 146%, with relative standard deviations between 1.0% and 28%. Detection and quantification limits for mango and papaya ranged from 0.01 to 0.03 mg/kg and 0.05 to 0.10 mg/kg, respectively. The proposed method was applied to the analysis of these compounds in commercial fruit samples from a local market (Aracaju/SE, Brazil), and residues of the pesticides were not detected on the samples.

Introduction

Brazil plays an important role in the worldwide production of fresh fruit, which is seriously affected by the occurrence of pests and diseases. The mango (*Mangifera indica* L.) and papaya (*Carica papaya* L.) fruits are one of the most important components of the human diet in different countries, where it is consumed in its raw form, home-cooked, or processed as juice or paste. Mango and papaya are considered to be a good source of natural antioxidant for foods and they are considered to be a good food source to prevent cancer and heart disease (1). Pesticides are extensively used on this crop at various stages of cultivation to control pests and diseases that might cause yield reduction. As a result, the Brazilian government has established maximum residue limits for 64 compounds in mango. Among these different products used to control phytophagous insects and fungal pathogens on mango and papaya, thiabendazole (a

benzimidazole fungicide) is currently used to control powdery mildew caused by *Oidium mangiferae*, a plant pathogen on mango and papaya. Pyrimethanil, tebuconazole, imazalil, and tetraconazole, an anilinopyrimidine, as well as triazole, imidazole, and azole fungicides are used to control antracnose (*Colletotrichum gloeosporioides*) on mango and papaya in the Northeastern part of the Brazil (2). Following application, pesticide residues may remain in the crop and constitute a health risk due to their toxicity. Therefore, the monitoring of pesticide residues in mango and papaya is of particular concern from the consumer safety perspective.

The determination of pesticides in foodstuffs is usually accomplished using chromatographic techniques and involves many preliminary steps including sampling, extraction, and clean-up (3). Several multi-residue methods for the determination of pesticide residues in fruits including papaya and mango are mainly based on liquid–liquid extraction by organic solvents (such as acetone, petroleum ether, and dichloromethane) solid-phase extraction (SPE) using sorbents (such as Florisil, silica gel, C18, and amino), and supercritical fluid extraction (SFE). The clean-up step is based on solid-phase extraction (3–7). Final determinations are carried out using liquid chromatography (LC) with diode array detection (DAD) or mass selective detection (8–11) and gas chromatography (GC) with electron capture detection or mass selective detection. Matrix solid-phase dispersion (MSPD) is an extraction method that provides a good alternative to traditional extraction techniques for chromatographic analysis (11–13). MSPD can be carried out simultaneously with sample homogenization, extraction and clean-up, and it requires only a small sample size and small amounts of solvent. It avoids the drawbacks generally associated with liquid–liquid extraction (such as the use of large volumes of solvent), the occurrence of troublesome emulsions, and slow speed (12–16). Thus, MSPD is an analytical technique used for the extraction of analytes from semi-solid and viscous samples. The principle of this technique is based on the use of the same bonded-phase solid supports as in solid-phase extraction (SPE), which also is used as grinding material for producing the disruption of sample matrix. During this procedure, the bonded-phase support acts as an abrasive, and the sample disperses over the surface of the support. The classic methods used for sample disruption, such as mincing, shredding, grinding, pulverizing, and pressuring are avoided in this procedure. The MSPD technique has many applications to

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the processing of samples of biological origin (animal tissues, plant materials, fats, etc.) (17–19). The sample is placed in a mortar containing the sample and a bonded phase material. The mixture is then crushed with a pestle. During this operation, the bonded phase and its support serve several functions. (i) It is an abrasive that promotes mechanical disruption of the sample structure. (ii) It assists in sample disruption and analysis of cell membranes similar to a solvent. (iii) It adsorbs the analytes or other compounds of interest from the sample. After this step, the material containing the sample and the solid sorbent are transferred into an SPE column. The selection of sorbent to be mixed with the sample depends on the nature of the material to be analyzed (20).

The present work reports a simple methodology for simultaneous determination of trichlorfon, pyrimethanil, methyl parathion, tetraconazole, thiabendazole, imazalil, and tebuconazole in mango and papaya fruit by means of matrix solid-phase dispersion and gas chromatography using mass selective detection. The method developed was applied to determine pesticide residues in mango and papaya from a local market.

Experimental

Standards, reagents, and supplies

Dichloromethane, ethyl acetate, and n-hexane were HPLC grade (Tedia, Fairfield, OH). Certified standards of trichlorfon, pyrimethanil, methyl parathion, tetraconazole, thiabendazole, imazalil, and tebuconazole were purchased from Dr. Ehrenstorfer (Augsburg, Germany). All standards were at least 99% pure. The individual standard stock solutions of the analytes were prepared in dichloromethane at 500 µg/mL and stored at –18°C. The working standard solutions were prepared by diluting the stock solutions as required in dichloromethane. Matrix-matched standards were prepared at the same concentration as those of calibration solutions by adding appropriate amounts of standards to the control the matrix extract. Analytical grade anhydrous sodium sulfate was supplied from Mallinckrodt Baker (Paris, KY). Research-grade Florisil (80–100 mesh) was supplied from Sigma (Büchs, Switzerland), neutral alumina from Macherey-Nagel (Düren, Germany), and silica-gel 60 (70–230 mesh) from Merck (Darmstadt, Germany).

Table I. Time Scheduled and Ions Monitored to Determine the Selected Pesticides in Mango and Papaya Samples by GC–MS (SIM Mode)

Pesticide	Time (min)	SIM ion (<i>m/z</i>)*
Trichlorfon	7.0–14.0	109, 185, 220
Pyrimethanil	14.0–27.0	183, 198 , 199
Methyl Parathion	14.0–27.0	109, 125, 263
Tetraconazole	14.0–27.0	171, 336, 338
Thiabendazole	14.0–27.0	130, 174, 201
Imazalil	14.0–27.0	173, 215 , 217
Tebuconazole	14.0–27.0	125, 250, 252

* values of *m/z* in bold type correspond to the quantification ion for each analyte.

Apparatus

A Shimadzu system (Kyoto, Japan), consisting of a QP-2010plus mass spectrometer equipped with a GC-2010 gas chromatograph with a split/splitless injector, was used for the identification and quantification of the pesticides studied. A fused-silica column RTX-5MS (5% phenyl–95% polydimethylsiloxane; 30 m × 0.25 mm i.d., 0.25 µm), supplied by Restek (Bellefonte, PA), was employed. Helium (purity 99.995%) was used as the carrier gas at a flow-rate of 1.8 mL/min. The column temperature was programmed as follows: 60°C for 1 min, then increased to 280°C at 10°C/min, and held for 3 min. The solvent delay was 5 min. The injector port was maintained at 250°C, and 1-µL sample volumes were injected in splitless mode (0.7 min). The data were acquired and processed using Shimadzu GC Solution software. The total analysis time was 27 min. The eluent from the GC column was transferred via a transfer line heated at 280°C and fed into a 70 eV electron ionization source, also maintained at 280°C. The acquisition modes used were: scan (mass range 50–400) and selected ion monitoring (SIM). The time scheduled and ions monitored for quantification are given in Table I.

Sample preparation and fortification

The papaya and mango samples used for method development were obtained from an organic farm (pesticide free) in pesticide free crops located in the municipality of Aracaju, state of Sergipe, Brazil, from November 2007 to March 2008. A representative portion of sample (500 g) was chopped with a stainless-steel knife and homogenized using a household blender and stored in jars at –18°C until used for analysis. Fortified samples were prepared by adding 500 µL of different standard multi-component solutions to 2 g of sample resulting in the levels of 0.05 to 1.0 mg/kg. The fortified fruits were left to stand for a 30 min before extraction to allow the spike solution to penetrate into the matrix. Four replicates were analyzed at each fortification level. The extraction procedure was as described below.

Extraction procedure

An aliquot of papaya or mango (2.0 g) was placed into a glass mortar (ca. 50 mL) and 3.0 g of silica-gel was added. The fruit was then gently blended into the silica material with a glass pestle, until a homogeneous mixture was obtained (ca. 3 min). The

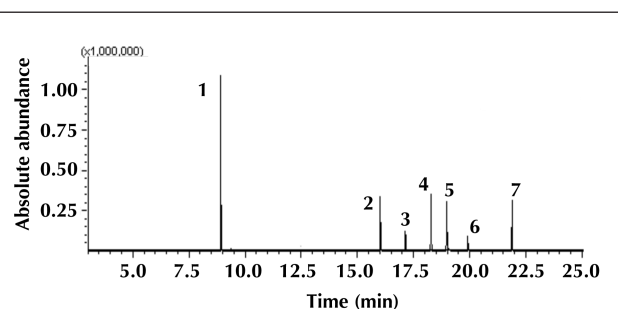


Figure 1. GC–MS (SIM mode) chromatogram of a standard solution in dichloromethane at 1.0 mg/kg. The numbered peaks are as follows: 1, trichlorfon; 2, pyrimethanil; 3, methyl parathion; 4, tetraconazole; 5, thiabendazole; 6, imazalil; and 7, tebuconazole. See Experimental section for details on GC–MS system and operating conditions.

homogenized mixture was introduced into a 100 x 20 mm I.D. polypropylene column filled with 0.1 g of silanized glass-wool at the base and 1.0 g of Na₂SO₄ anhydrous, respectively. A 40-mL portion of ethyl acetate–dichloromethane (1:1, v/v) was added to the column, and the sample was allowed to elute dropwise. The eluent was collected into a graduated conical tube and concentrated to a volume of 1 mL, using first a rotary vacuum evaporator (45 °C), followed by a gentle flow of nitrogen. A 1 µL portion of the extract was then directly analyzed by GC–MS

Results and Discussion

GC–MS conditions

Pesticide peak retention times and resolutions were optimized in full scan mode, using a 10 µg/mL standard solution and varying the oven temperature and carrier gas flow rate (Figure 1). In these evaluations, the characteristic ions were chosen for quantification of each pesticide. Matrix components can provide variation in the detector response to pesticides. Therefore, the matrix effect was evaluated by comparing the detector response for pesticide standards prepared in dichloromethane with that for standards prepared in extract of fruits. When standards were prepared by spiking blank mango and papaya samples with known amounts of pesticides, higher peak areas were obtained for the same pesticide concentrations. Consequently, the quantification of pesticide residues was carried out through matrix-matched standards. Selection of the ions for SIM acquisition was based on the best S/N ratios.

Optimization of the MSPD procedure

The extraction method proposed is based on the MSPD procedures developed and validated in our group (17–19). The most suitable extraction parameters were evaluated to achieve the

highest recovery for trichlorfon, pyrimethanil, methyl parathion, tetraconazole, thiabendazole, imazalil, and tebuconazole from the mango and papaya fruit. The polarities of the sorbent and the elution solvent are known to be key factors in MSPD because they determine both the efficiency of the extraction and the purity of the final extracts. Preliminary investigations for optimization of the MSPD procedure for the extraction of pesticides from mango were performed using fruit samples spiked with pesticides at 1.0 mg/kg, and either the Florisil, neutral alumina, or silica-gel as the solid-phase sorbent. To evaluate the influence of the eluting solvent, n-hexane–dichloromethane (1:1, v/v) were tested using a fruit matrix to solid-phase sorbent ratio of 1:2 (m/m). When comparing the data obtained, rather different results were found for the system tested. With neutral alumina, it was noted that all compounds gave very low recovery (< 17%), while the use of Florisil as extracting material of the MSPD column produced recovery values that ranged from 29% to 66% for these compounds, and a higher background and more interfering peaks compared to neutral alumina. On the other hand, the MSPD procedure prepared with silica-gel–mango or papaya matrix blend produced an extract that shows minimal interferences for most of the pesticides studied and recovery values ranged from 9% to 96% (Table II). Based on these experiments, other eluting solvents were investigated to optimize the extraction of the pesticides. The solvents tested were dichloromethane and ethyl acetate–dichloromethane (1:1, 1:4, 4:1, 2:3, v/v). Table III shows the influence of different eluting solvent on pesticide recoveries. The MSPD procedure prepared with silica-gel–mango or papaya matrix blend produced an extract that shows minimal interferences for most of the pesticides studied, while the use of dichloromethane for MSPD method produces the lowest recoveries (18–65%) for all pesticides. However, ethyl acetate–dichloromethane (1:4, v/v) provided recovery values for trichlorfon, pyrimethanil, and thiabendazole similar to the ones obtained with silica-gel and ethyl acetate–dichloromethane (4:1, v/v), except for methyl parathion, tetraconazole, imazalil, and tebuconazole.

Overall results indicate that the combination of silica as solid-phase and ethyl acetate–dichloromethane (1:1, v/v) as elution solvent is a suitable extraction procedure for determination of trichlorfon, pyrimethanil, methyl parathion, tetraconazole,

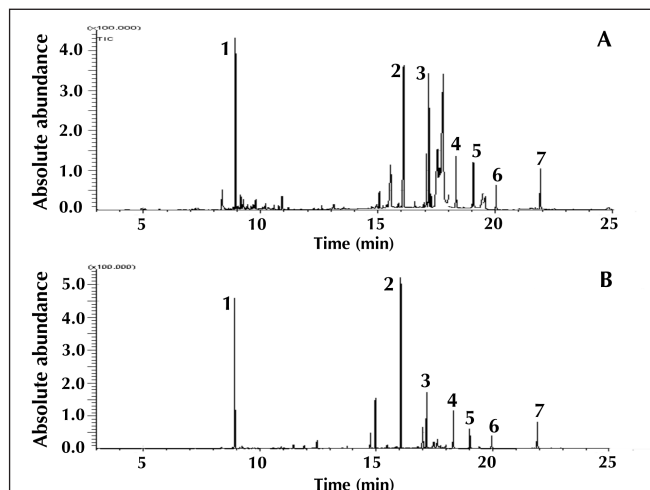


Figure 2. GC–MS (SIM mode) chromatograms of typical papaya (A) and mango (B) extracts fortified at a concentration level of 1.0 mg/kg, using 2.0 g of fruit + 3.0 g of silica-gel and ethyl acetate–dichloromethane (1:1, v/v, 40 mL). The numbered peaks are as follows: 1, trichlorfon; 2, pyrimethanil; 3, methyl parathion; 4, tetraconazole; 5, thiabendazole; 6, imazalil; 7, tebuconazole. See Experimental section for details on GC–MS system and operating conditions.

Table II. Influence of Different Solid-Phase Sorbents and Elution Solvent on Pesticide Recovery*

Pesticide	Recovery (%) [†] , 1.0 mg/kg <i>n</i> -Hexane–Dichloromethane (1:1, v/v)		
	alumina	Florisil	silica-gel
Trichlorfon	17; 8	62; 7	15; 2
Pyrimethanil	13; 2	49; 4	85; 3
Methyl parathion	6; 4	34; 6	96; 4
Tetraconazole	8; 11	42; 5	74; 5
Thiabendazole	9; 12	66; 3	61; 5
Imazalil	3; 5	29; 12	9; 8
Tebuconazole	5; 9	36; 10	78; 6

* Using the MSPD procedure using 2.0 g of mango + 3.0 g of sorbent. Mango sample fortified at 1.0 mg/kg (*n* = 2)*.

[†] Mean (%); RSD (%); DCM = dichloromethane.

thiabendazole, imazalil, and tebuconazole from fruit matrices such as mango and papaya.

Validation of the MSPD method

Recovery study

Once the factors that affect the MSPD procedure had been optimized, validation of the method was performed. Recovery data were calculated by comparison with the appropriate working standard solutions. The mango and papaya samples free from pesticides were fortified at different concentrations (0.05, 0.1, and 1.0 mg/kg) and residues were quantified by using the

Pesticide	Recovery (%) [†] , 1.0 mg/kg with silica-gel ethyl acetate–DCM (v/v)				
	DCM	(1:1)	(1:4)	(4:1)	(2:3)
Trichlorfon	65; 3	74; 2	62; 3	62; 2	66; 5
Pyrimethanil	42; 4	64; 4	49; 7	49; 1	62; 6
Methyl parathion	43; 6	56; 3	18; 9	34; 2	60; 12
Tetraconazole	45; 6	61; 7	60; 8	42; 4	56; 8
Thiabendazole	39; 5	100; 8	77; 11	66; 11	104; 7
Imazalil	18; 8	45; 7	33; 10	29; 9	47; 4
Tebuconazole	48; 10	66; 9	68; 7	36; 10	62; 9

* Mean (%); RSD (%); DCM = dichloromethane.
[†] Using the MSPD procedure using 2.0 g of mango + 3.0 g of sorbent. Mango sample fortified at 1.0 mg/kg (*n* = 2).

Pesticide	Recovery (%) [†]					
	Spiked level of Pesticide (mg/kg) in					
	Mango			Papaya		
	0.05	0.10	1.0	0.05	0.1	1.0
Trichlorfon	101; 6	99; 5	108; 7	85; 11	96; 11	82; 19
Pyrimethanil	115; 16	103; 12	99; 6	87; 6	98; 6	100; 12
Methyl parathion	121; 6	114; 9	122; 8	129; 6	132; 13	107; 5
Tetraconazole	98; 2	94; 8	97; 9	87; 10	104; 6	95; 17
Thiabendazole	146; 9	111; 15	144; 8	116; 6	89; 11	120; 9
Imazalil	80; 28	97; 13	108; 7	105; 14	121; 9	94; 11
Tebuconazole	116; 15	100; 8	108; 4	105; 12	117; 12	98; 1

* Using the MSPD procedure and GC/MS analyses (*n* = 4)*.
[†] Mean (%); RSD (%).

Pesticide	Retention time (min)	Linear range (mg/kg)	Calibration data		LOD (mg/kg)	LOQ (mg/kg)
			Equation	Correlation coefficient		
Trichlorfon	8.9	0.05–5.0	$y = 45230x - 3153$	0.999	0.02	0.05
Pyrimethanil	16.6	0.05–5.0	$y = 63176x - 4384$	0.998	0.02	0.05
Methyl parathion	17.1	0.05–5.0	$y = 7538x - 819$	0.997	0.01	0.05
Tetraconazole	18.2	0.05–5.0	$y = 8473x - 1220$	0.996	0.03	0.05
Thiabendazole	18.9	0.05–5.0	$y = 8473x - 1220$	0.962	0.03	0.05
Imazalil	19.9	0.05–5.0	$y = 771x - 63$	0.992	0.03	0.10
Tebuconazole	21.8	0.05–5.0	$y = 6157x - 1303$	0.988	0.03	0.05

external standards method. Fortification concentrations were selected to reach the maximum residue levels (MRLs) for pesticides in mango and papaya, according to Brazilian legislation and the Codex Alimentarius values, which range from 0.1 to 10.0 mg/kg (2, 21). Average recoveries ranged from 80% to 146% (*n* = 4), with relative standard deviations (RSD) values of 1.0% to 28% (Table IV). The precision and accuracy were considered adequate for validating the method according to the validation criteria. Accuracy was calculated as the percent ratio between the measured and the known concentrations and precision was determined as the percentage in relative standard deviation (%RSD), which is the ratio between standard deviation and mean measured concentration (22). Furthermore, considering mango fruit, the comparison between the extraction efficiency of proposed MSPD procedure with that of the Banerjee et al. (23) demonstrates that the average recovery value for 0.05 mg/kg was 98% for tetraconazole, which was similar than that obtained by the authors, 77%. However, the concentration level of this last method was 0.025 mg/kg, using 10 grams of homogenized sample and analysis by LC–MS–MS. On the other hand, considering papaya fruit, the comparison between the proposed MSPD procedure with our previous work (24) demonstrates that the same average recovery value of 87% was obtained for pyrimethanil at 0.05 mg/kg, using five grams of sample and analysis by HPLC–UV.

Selectivity

Figure 2 shows chromatograms of the spiked papaya and mango extracts, demonstrating the selectivity of the MSPD method developed. The chromatographic profiles show the importance of choosing the type of sorbent and eluting solvent for the removal of matrix interferences, while the high recoveries (Table IV) indicate the presence of matrix components, which were not properly extracted.

Linearity and detection and quantification limits

The detector response was linear within the concentration range studied. Linearities for all compounds were determined using blank mango and papaya samples fortified at eight concentration levels (0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 4.0 and 5.0 mg/kg). At each analyte amount, two replicate measurements were made. The slope and intercept values, together with their standard deviations, were determined using applying regression analyses. Linear regression coefficients for all pesticides ranged from 0.962 to 0.999.

The limits of detection (LOD) for the pesticides studied were calculated considering the standard deviation of noise (a value of 7 times the standard deviation of the blank) and the slope of the regression line, and ranged from 0.01 to 0.03 mg/kg. The limits of quantification (LOQ) were determined as the lowest concentration of still responsive compounds that could be quantified with an RSD of less than 15% and a recovery at least 70%. The LOQ values for these compounds were 0.05 mg/kg (22). This data is summarized in Table V.

Real sample analysis

The MSPD method developed was applied to determine the pesticides selected in four mango and papaya samples obtained from local market in the city of Aracaju (Sergipe, Brazil), and originating from conventional agriculture, were analyzed using this procedure. No pesticide residues, at concentrations above the detection limit, were found in these samples.

Conclusions

The proposed MSPD procedure followed by GC–MS (SIM mode) can be applied to determine trichlorfon, pyrimethanil, methyl parathion, tetraconazole, thiabendazole, imazalil, and tebuconazole in mango and papaya. The method uses a silica-based on the MSPD column and ethyl acetate–dichloromethane (1:1, v/v) as elution solvent. The results demonstrate that the accuracy, precision, and selectivity of the proposed method are acceptable for multi-residue analyses of pesticides, and that the LOQs achieved by the method are in good agreement with the limit values established by Brazilian and Codex legislations. In addition, the method requires a small sample size and offers considerable savings in terms of solvent consumption, cost of materials, sample manipulation, and analysis time. With regards to the mango and papaya samples from a local market, no detectable residues of the pesticides were found.

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