Determination of Metolcarb and Diethofencarb in Apples and Apple Juice by Solid-Phase Microextraction–High Performance Liquid Chromatography

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Abstract

A method for the determination of metolcarb and diethofencarb in apples and apple juice is developed using solid-phase microextraction (SPME) coupled with high-performance liquid chromatography (HPLC). The experimental conditions of SPME, such as the kind of extraction fiber, extraction time, stirring rate, pH of the extracting solution, and desorption conditions are optimized. The SPME is performed on a 60 µm polydimethylsiloxane/divinylbenzene fiber for 40 min at room temperature with the solution being stirred at 1100 rpm. The extracted pesticides on the SPME fiber are desorbed in the mobile phase into SPME–HPLC interface for HPLC analysis. Separations are carried out on a Baseline C18 column (4.6 i.d. × 250 mm, 5.0 µm) with acetonitrile–water (55/45, v/v) as the mobile phase at a flow rate of 1.0 mL/min, and photodiode-array detection at 210 nm. For apple samples, the method is linear for both metolcarb and diethofencarb in the range of 0.05–1.0 mg/kg ($r > 0.99$), with a detection limit (S/N = 3) of 15 and 5 µg/kg, respectively. For apple juice, the method is linear for both metholcarb and diethofencarb over the range of 0.05–1.0 mg/L ($r > 0.99$) with the detection limit (S/N = 3) of 15 and 3 µg/L, respectively. Excellent recovery and reproducibility values are achieved. The proposed method is shown to be simple, sensitive, and organic solvent-free, and is suitable for the determination of the two pesticides in apples and apple juice.

Introduction

Metolcarb and diethofencarb are the most widely used Carbamates pesticides in fruits and vegetables due to their high effectiveness. Therefore, it is necessary to develop fast, simple, and sensitive analytical methods for their quantitation, in order to guarantee the safety of our food supplies. The most commonly used analytical methods for the analysis of Metolcarb and diethofencarb are chromatographic methods (1–4). Sample preparation procedures prior to chromatographic analysis are one of the most critical steps in the whole analytical process. Until now, some sample preparation techniques, such as liquid–liquid extraction (3) and solid-phase extraction (4) have been commonly used in the determination of metolcarb and diethofencarb. However, these methods are tedious, time-consuming, and often require large volumes of toxic organic solvents. Solid-phase microextraction (SPME) (5) is a relatively new sampling method. It integrates sampling, extraction, and concentration into a single procedure and is almost organic solvent-free. To date, SPME coupled with gas chromatography (GC) has been widely investigated for the analysis of a wide variety of semi-volatile compounds, including pesticides, agrochemicals, and other compounds (6–10). On the other hand, the research on SPME coupled with liquid chromatography (LC) (11) has also been progressing, especially for the determination of low volatile or thermal unstable compounds of environmental concern, such as polychlorinated biphenyls (12), phenolic compounds (13), and pesticide residues (14–18). However, to date, the reports describing SPME coupled with high-performance liquid chromatography (HPLC) for the analysis of pesticides in food matrices are still very few (18). Concerning the determination of metolcarb and diethofencarb (their chemical structures are shown in Figure 1), there has been no report about the determination of metolcarb by SPME–HPLC, and the analysis of diethofencarb by SPME–HPLC has been only reported for strawberry samples (19). Here, we present a novel method for

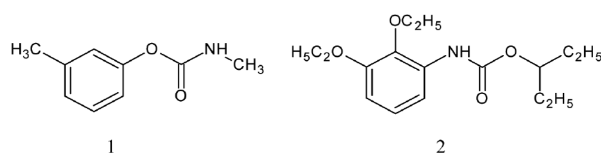

Figure 1. Structures of metolcarb (1) and diethofencarb (2).

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the determination of metolcarb and diethofencarb in apples and apple juice by SPME coupled with HPLC. To our knowledge, this is the first report about the determination of metolcarb and diethofencarb in apples and apple juice by SPME–HPLC.

Experimental

Apparatus

The SPME fiber assembly and SPME–HPLC interface were purchased from Supelco (Bellefonte, PA). The SPME–HPLC interface consisted of a six-port valve and a desorption chamber which replaces the injection loop of a six-port injection system. SPME fibers coated with carbowax/templated resin (CW/TPR, 50 µm) and polydimethylsiloxane/divinylbenzene (PDMS/DVB, 60 µm) (Supelco) were used in this work. The HPLC system, assembled from modular components (Waters, Milford, MA), consisted of an in-line degasser, a 600E pump, and a 996 photodiode-array detector (DAD). A Millennium^{32} workstation (Waters) was utilized for the acquisition and analysis of data and to control the system. All separations were carried out on a Baseline C_{18} column (250 mm × 4.6mm, 5 µm).

Reagents and Chemicals

Metolcarb (no less than 99.5% pure) and diethofencarb (no less than 99.5% pure) were kindly donated by Prof. Fu Cheng Guang (Hebei University, Baoding, China). Acetonitrile (HPLC-grade) was obtained from Kermel (Tianjin, China). Deionized water was prepared by a Milli-Q purification system (Millipore, Milford, MA) and filtered through a 0.45 µm membrane before use.

Stock solutions of metolcarb and diethofencarb were prepared at 1.0 mg/mL by weighing 100 mg of the pesticides, dissolving them in methanol (100 mL), and storing them at 4°C in the dark. The standard mixture solution at the concentration of 0.05 mg/mL was prepared by dilution of stock solution with methanol.

For optimization studies, a mixture of pesticides and water containing 100 µg/L of metolcarb and 20 µg/L of diethofencarb was used.

HPLC conditions

Separations were carried out on a Baseline C_{18} column (4.6 i.d. × 250 mm, 5.0 µm) with acetonitrile–water (55:45, v/v) as the mobile phase at a flow rate of 1.0 mL/min, and DAD detection at 210 nm.

SPME procedure

New fibers were conditioned with the mobile phase until no interfering peak appeared prior to use. Old fibers were conditioned with the mobile phase for 20 min before the first use of the day. The conditioned fibers were allowed to air dry for 2 min before each SPME. A 4 mL aliquot of the sample extracting solution was transferred to a 5-mL Teflon-lined septum cap vial, equipped with a glass-coated magnetic bar. The depth of immersion of the fiber was kept constant. The SPME extraction was performed on a 60 µm PDMS/DVB fiber for 40 min at room temperature (approximately 20°C), with the solution being stirred at 1100 rpm. After extraction, the extracted analytes on the SPME fiber were desorbed into HPLC for analysis with an SPME–HPLC interface (with Rheodyne valve). The fiber was allowed to desorb for 6 min in the mobile phase before starting the analysis. Then the fiber was held in the interface until the entire separation run was completed (approximately 15 min).

Calibration curve

For apples, a five-point calibration curve (0.05, 0.1, 0.2, 0.5, 1.0 mg/kg) was prepared by adding 25, 50, 100, 250, and 500 µL, respectively, of the mixed standard solution at 0.05 mg/mL to 25 g of the mashed apples in a 50-mL Teflon tube. The tube was first vortexed for approximately 30 s and then centrifuged at 3000 rpm for 20 min. The resultant supernatant was collected in a 50-mL volumetric flask. Another 15 mL H_2O was added to the Teflon tube and the previous extraction procedures were repeated, except centrifuging was done for 10 min. The final volume of the combined extract was adjusted to the mark with water. Then an aliquot of 4 mL of the extracted solution was subjected to SPME and HPLC analysis according to the previously mentioned procedures.

For apple juice, a five-point calibration curve (0.05, 0.1, 0.2, 0.5, 1.0 mg/L) was prepared by adding 25, 50, 100, 250, and 500 µL, respectively, of the mixed standard solution at 0.05 mg/mL to 25 mL apple juice in a 100-mL volumetric flask and then adding water to the mark. Then an aliquot of 4 mL of the extracted solution was subjected to SPME and HPLC analysis according to the previously mentioned procedures.

Results and Discussion

HPLC conditions

For the separation of carbamate pesticides, reversed-phase HPLC has been the most commonly employed method (19,20). In this study, for the separation of metolcarb and diethofencarb in apple and apple juice samples, different ratios of acetonitrile to water as the mobile phase were investigated on a Baseline C_{18} column (4.6 i.d. × 250 mm, 5.0 µm). As a result, the best separation was achieved with acetonitrile–water (55/45, v/v) as the mobile phase at a flow rate of 1.0 mL/min. Because the maximum absorption wavelengths of the two pesticides were both at 210 nm, the DAD monitoring wavelength was chosen at 210 nm for quantitation data handling. In these conditions, there were no interfering peaks coming from sample co-extractives.

Optimization of the SPME conditions

Comparison of two SPME fiber selection

In this study, two different kinds of commercial fibers (i.e., a 50 µm CW/TPR and a 60 µm PDMS/DVB) were evaluated for their extraction efficiency. Figure 2 shows that for both metolcarb and diethofencarb, the PDMS/DVB fiber had a better extraction efficiency than the CW/TPR fiber. Therefore, the

60 µm PDMS/DVB fiber was selected for further investigations.

Effect of extraction time

Figure 3 shows the effect of extraction time on the signal when the SPME extraction time was changed from 10 to 90 min using the 60 µm PDMS/DVB fiber. It can be seen in Figure 3 that the extraction efficiency for both pesticides was increased as extraction time increased, and the extraction equilibrium was not reached even at 90 min. Ai (21) shows that in SPME, a short extraction time can be used as long as sufficient sensitivity is achieved and the experimental conditions are well controlled. As a compromise between analytical time and sensitivity, an extraction period of 40 min was chosen for the experiment.

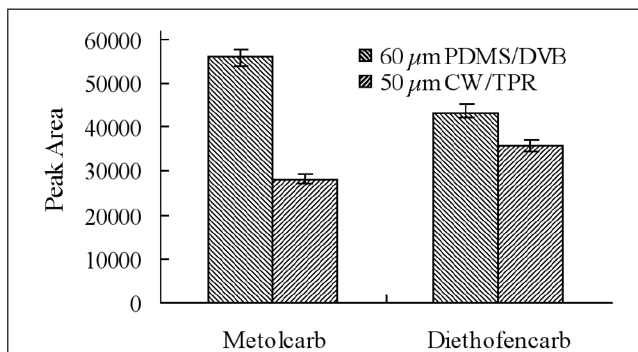

Figure 2. Comparison of two SPME fibers. Conditions: concentration, 100 µg/mL of metolcarb and 20 µg/mL of diethofencarb; extraction time, 50 min; desorption mode, static, 6 min; stirring rate, 1100 rpm; room temperature.

Effect of stirring rate

Fast agitation of the sample solution can be employed to enhance the extraction efficiency because agitation permits the continuous exposure of the fiber coating to fresh sample solution. In this study, the effect of sample agitation rate was evaluated between 0 and 1100 rpm. Figure 4 shows that the extraction efficiency was increased as the stirring rate increased to 1100 rpm, which is the highest speed that could be achieved by our magnetic stirrer. Therefore, 1100 rpm was selected for further investigation.

Effect of pH value

Because metolcarb and diethofencarb are unstable in alkaline environments, pH values in the range between 3 and 7 were evaluated. As shown in Figure 5, when the pH value was lower than 6, pH had no significant effect on the extraction efficiency for both of the analytes; when the pH value was increased from 6 to 7, the extraction efficiency for both analytes

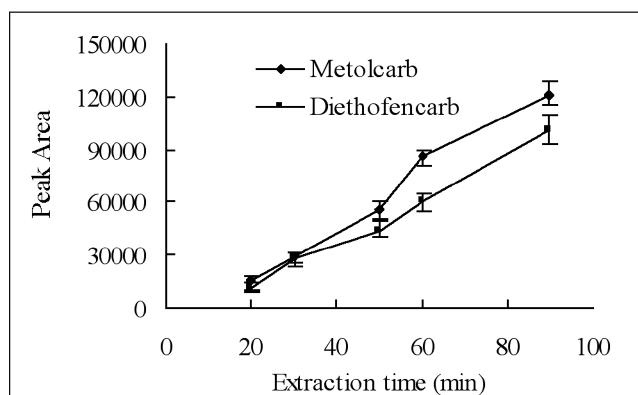

Figure 3. Effect of extraction time on SPME efficiency. Conditions: 60 µm PDMS/DVB filter, other conditions were the same as in Figure 2.

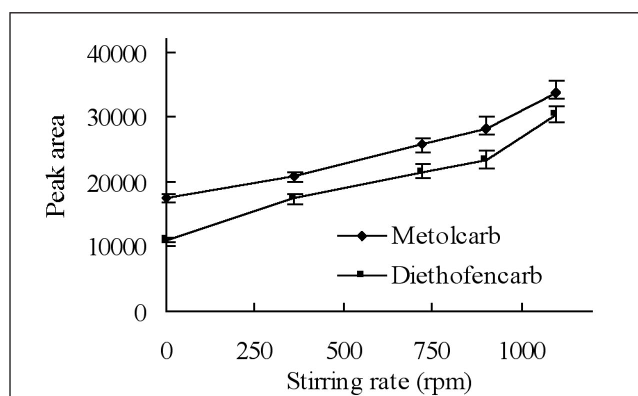

Figure 4. Effect of stirring rate on SPME efficiency. Conditions: extraction time, 40 min; other conditions were the same as in Figure 3.

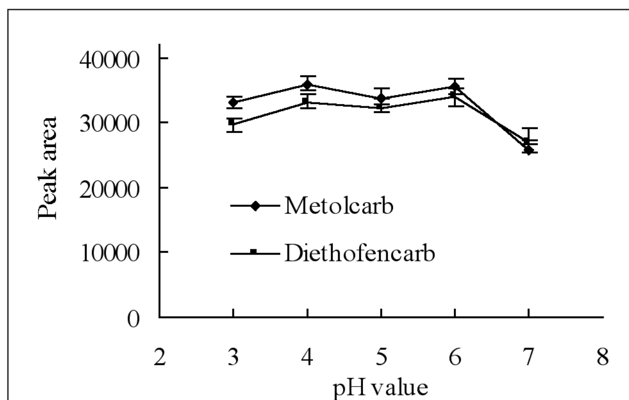

Figure 5. Effect of pH value on SPME efficiency. Conditions: stirring rate, 1100 rpm; other conditions were the same as in Figure 4.

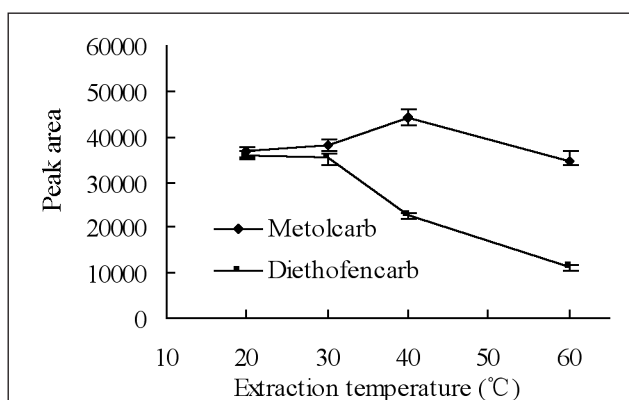

Figure 6. Effect of extraction temperature on SPME efficiency. Conditions were the same as in Figure 5.

was decreased. Based on this result and considering that the pH value of either apple sample solution or apple juice sample solution was approximately 5–6, the pH of the sample solutions was not adjusted.

Effect of temperature

The temperature of the extraction influences the extraction efficiencies in two different ways: kinetic and thermodynamic. Kinetically, a higher temperature increase the diffusion rate of the analytes, thus the extraction efficiencies may increase at a high temperature. Thermodynamically, because absorption is generally an exothermic process, the amount of analytes absorbed decreases when temperature is increased (22). These two effects compete with each other and different analyses may be affected in different ways. It can be seen from Figure 6 that the extraction efficiency of metolcarb was increased as the temperature was increased from 20°C to 40°C then decreased from 40°C to 60°C, but for diethofencarb, the extraction efficiency was almost unchanged as the temperature increased from 20°C to 30°C then decreased from 30°C to 60°C. As a compromise for the two compounds, 20ºC was selected for further study. Because ambient temperature was approximately 20ºC, the extraction temperature was not adjusted.

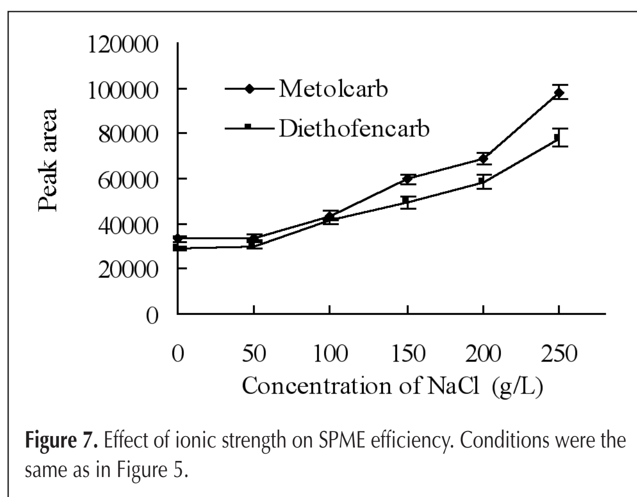

Figure 7. Effect of ionic strength on SPME efficiency. Conditions were the same as in Figure 5.

Effect of ionic strength

Figure 7 shows the effect of sodium chloride (NaCl) concentration on the extraction efficiencies of the two pesticides using the PDMS/DVB fiber. As illustrated in Figure 7, the extraction efficiencies for the two pesticides were both increased as the concentration of NaCl was increased. However, when SPME was performed at a high salt concentration, it may facilitate crystal formation, thus blocking the fiber protection mechanism and producing a mechanical failure (23), resulting in a shortened lifetime of fibers (24). Considering that the sensitivity was good enough even without addition of the salt in the experiment and for the protection of the fibers, the ionic strength of sample solutions was not adjusted.

Desorption conditions

There are two kinds of desorption mode: one is static and the other is dynamic. For static mode, the fiber was soaked in the desorption chamber for several minutes, then the injector was switched to the inject position and the analytes were delivered

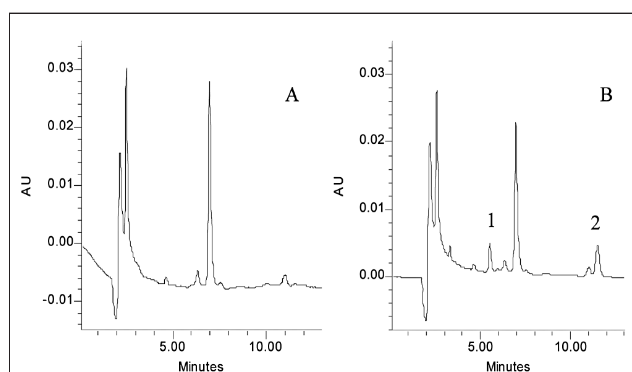

Figure 8. Chromatograms of blank apple sample (A) and apple sample spiked with metolcarb (1) and diethofencarb (2) at each concentration of 0.05 mg/kg (B). Conditions: 60 µm PDMS/DVB filter; extraction time, 40 min; stirring rate, 1100 rpm; desorption mode, static, 6 min; room temperature. Baseline C18 column (250 mm × 4.6 mm, 5 µm); mobile phase: acetonitrile–water mixture (55/45 [v/v]); flow rate: 1.0 mL/min; detection wavelength: 210 nm.

Table I. The Linear Range, Limit of Detection, and Limit of Quantitation of the Method for Apple Sample

Insecticide	Concentration range (mg/kg)	Equation	Correlation coefficients (r)	LOD (µg/kg)	LOQ (µg/kg)
Metolcarb	0.05–1.0	y = 61654x + 6436	0.9950	15	50
Diethofencarb	0.05–1.0	y = 1340442x + 22967	0.9985	5	16

Table II. The Linear Ranges, Limits of Detection, and Limit of Quantitation of the Method for Apple Juice

Insecticide	Concentration range (mg/L)	Equation	Correlation coefficients (r)	LOD (µg/L)	LOQ (µg/kg)
Metolcarb	0.05–1.00	$y = 38416x + 2114$	0.9993	15	50
Diethofencarb	0.05–1.00	$y = 851540x + 9039$	0.9994	3	10

to the column. For dynamic mode, the fiber was not soaked in the desorption chamber, and the analytes were directly removed by mobile phase.

Our experiment showed that when the relative concentration of acetonitrile to water was changed from 40 to 60 (v/v), the desorption efficencies had almost no changes. However, using the mobile phase as the desorption solvent could avoid baseline disturbances and eliminate the extra step of injecting the desorption solvent into the desorption chamber. Therefore, the mobile phase (i.e., acetonitrile–water [55/45, v/v]) was selected as the desorption solvent.

Our results showed that the desorption efficiency for metolcarb remained almost unchanged when desorption time was changed between 2 and 10 min and that there was a maximum for the desorption efficiency of diethofencarb at approximately 6 min. As a result, the desorption was performed by allowing the fiber to soak in the mobile phase for 6 min before injection. After injection, the fiber was held in the desorption chamber for the whole HPLC separation run (approximately 15 min). In such a way, no detectable carry-over was found on the fiber, which could facilitate the next use of the fiber.

Calibration curve and limit of detection and quantitation

In this work, calibration curves for apple and apple juice sample were established with DAD detection at 210 nm, which was the maximum absorption wavelength for both metolcarb and diethofencarb. Three replicate experiments for each point were performed. The regression equations showed that within the concentration range investigated (0.05–1.0 mg/kg for apple samples; 0.05–1.0 mg/L for apple juice), there was a good linear relationship between the peak area (*Y*/arbitrary unit) and the concentration of the pesticides in apple and apple juice samples (*X*/mg/kg). The regression coefficients were higher than 0.99. The limit of detection (LOD) and limit of quantitation (LOQ) in this study was were defined as the content of compound in samples that gave rise to a signal-to-noise ratio of 3 and 10 within the window of its retention time. The results are shown in Tables I and II. The detection limits obtained with this method are at low µg/kg levels (15 and 5 µg/kg for metholcarb and diethofencarb in apple samples, and 15 and 3 µg/L in apple juice, respectively), which can satisfy the requirements set by European and international regulations for the limits of maximum residues, which are usually at the mg/kg level for the majority of pesticides and µg/kg for some others. The detection limit obtained here for diethofencarb is a little better than that obtained by Faiqui-cao et al. (19), where the detection limit for diethofencarb was 0.018 mg/kg for strawberry samples. Figures 8 and 9 show the representative chromatograms of the two pesticides from the extractions of both apple and apple juice samples.

Reproducibilities and recoveries

Recoveries were expressed as the percentage ratio between the amount found to the amount added. Blank samples were spiked with metolcarb and diethofencarb at three concentration levels, and five replicate analyses for each concentration level were performed. The results are shown in Tables III and IV. In apples, the average recoveries for metolcarb and diethofencarb ranged from 81.3% to 90.6% and from 83.8% to 90.0%, respectively, with relative standard deviations (RSD) of 2.7–4.2% and 2.5–7.1%. In apple juice, the average recoveries for metolcarb and diethofencarb were in the range from 83.5% to 103.8% and from 82.5% to 99.4%, with RSDs of 3.8–5.7% and 2.3–5.0%, respectively. The results indicated a good precision and accuracy for the method.

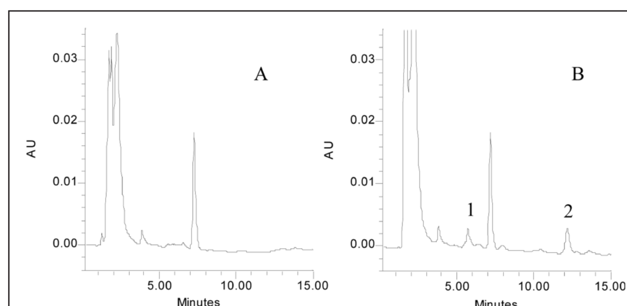

Figure 9. Chromatograms of blank apple juice sample (A) and apple juice sample spiked with metolcarb (1) and diethofencarb (2) at each concentration of 0.4 mg/L and 0.160.05 mg/L (B), respectively. Conditions were the same as in Figure 8.

Table III. Recoveries and Reproducibilities of Metolcarb and Diethofencarb in Apple Sample

Compound	Added (mg/kg)	Found (mg/kg)	Recovery (%)	RSD (%)
Metolcarb	0.08	0.065	81.3	4.2
	0.30	0.261	87.0	2.7
	0.80	0.725	90.6	4.1
Diethofencarb	0.08	0.067	83.8	7.1
	0.30	0.264	88.0	5.0
	0.80	0.720	90.0	2.5

Table IV. Recoveries and Reproducibilities of Metolcarb and Diethofencarb in Apple Juice

Compound	Added (mg/L)	Found (mg/L)	Recovery (%)	RSD (%)
Metolcarb	0.08	0.083	103.8	5.7
	0.20	0.167	83.5	5.1
	0.40	0.040	100.0	3.8
Diethofencarb	0.04	0.033	82.5	5.0
	0.08	0.067	83.8	4.8
	0.16	0.159	99.4	2.3

Conclusion

An SPME–HPLC method for the determination of metolcarb and diethofencarb in apples and apple juice was developed. Various parameters influencing the SPME were optimized. The method allows the detection limits down to 5 µg/kg and 3 µg/L (S/N = 3) for apple and apple juice samples, respectively. The method is simple, organic solvent-free, and sufficiently sensitive for pesticide residue analysis for fruit samples, suggesting that SPME–HPLC can be a good choice for the analysis of some compounds, especially those thermally labile and non-volatile pesticides that cannot be easily analyzed by GC.

Acknowledgements

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