

Headspace Solid Phase Microextraction in Pesticide Residues Analysis: 2. Apple Samples

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SUMMARY

Headspace solid phase microextraction method (HS/SPME), optimised previously for pesticide water solutions, was applied to trace residues of the pesticides chlorpyrifos, fenthion and bifenthrin in apple samples. One-hour extraction procedure was performed at 60°C extraction temperature. Nonpolar polydimethyl siloxane (PDMS) fiber was used. Detection and quantification were carried out by gas chromatography/mass spectrometry (GC/MS).

A non-pesticide treated apple sample was fortified with the pesticides over a 0.025-1.25 mg/kg concentration range in order to determine analytical parameters of the method applied. Linearity with regression coefficient (R) values higher than 0.99 were obtained over the whole concentration range investigated for chlorpyrifos and fenthion, while linear dependence was observed in the 0.1-1.25 mg/kg range for bifenthrin. Relative recovery values for samples fortified at different levels were in the 56.68-82.91% range. Limit of detection (LOD) values were determined as follows: 0.014 mg/kg for chlorpyrifos, 0.021 mg/kg for fenthion and 0.053 mg/kg for bifenthrin. Relative standard deviation (RSD) values obtained for multiple analysis of the sample fortified at 0.6 mg/kg level were not higher than 20%.

Keywords: HS/SPME; Pesticide residues; Apple samples

INTRODUCTION

Unlike the direct SPME mode, headspace SPME analysis can shorten the time of extraction significantly owing to faster analyte diffusion in the gas than in the liquid phase (Lambropoulou and Albanis, 2002). Additionally, as the fibre has no direct contact with a sample during HS/SPME analysis, its life can be prolonged and matrix effects reduced. Apart from these evident benefits of the headspace mode, its applica-

bility to pesticide residues analysis of complex matrix samples is still not fully investigated. Besides pesticide residue analysis of water samples (Lambropoulou and Albanis, 2002; Sakamoto and Tsutsumi, 2004), HS/SPME has also been applied to wine (Bellavia et al., 2000; Correia et al., 2000; Navalón et al., 2002), strawberry fruit and cherry juice samples (Lambropoulou and Albanis, 2002).

In a previous experiment (Đurović et al., 2007), the HS/SPME method was successfully applied to simul-

taneous determination of various pesticides in water solutions. Temperature and time extraction profiles were inspected and optimisation of extraction parameters was done. Chlorpyrifos, fenthion and bifenthrin were among the pesticides selected for the study. Since these insecticides are widely used in insect pests control of pome fruits, the HS/SPME method developed and optimised for simple water matrix was then applied to determine chlorpyrifos, fenthion and bifenthrin residues in apple samples with a complex fruit matrix.

MATERIAL AND METHODS

Standards

Pesticide standards for chlorpyrifos, fenthion and bifenthrin (Dr Ehrenstorfer, Germany) were of 98.4, 92.5 and 97% purity, respectively.

Stock standard solutions of 1 mg/ml of each pesticide were prepared in acetone (J.T. Baker, USA). Mixed working standard solutions were made by diluting the stock solution with acetone. Highly purified deionized water (Purelab Option – R7, Elga, UK) was used in sample preparation.

Samples

Untreated apple samples originating from Gornji Branetići, Gornji Milanovac, were used. Commercial apple samples of unknown origin were randomly selected at the Zemun market.

Material and instruments

A 100 μm polydimethylsiloxane (PDMS) fibre (Supelco, Sigma-Aldrich, Germany) was used for HS/SPME measurements.

Extraction, with mixing included, was performed in 4 ml vials.

A gas chromatograph/mass spectrometer (GC/MS) was used as a detection device (CP-3800/Saturn 2200, Varian, Australia). Experimental parameters and conditions of GC/MS measurements performed have been described in detail elsewhere (Đurović et al., 2007). One specific pesticide ion was selected for MS detection and quantification, while another one was used for confirmation. The ions inspected were as follows: 314

(286) for chlorpyrifos, 278 (109) for fenthion and 181 (165) for bifenthrin.

Sample preparation and analysis

One kilogram of fresh apples was sliced and homogenized for approximately one minute using a home blender. The amount of 80 ml of water was added into each 20 g portion and the samples were homogenised for one hour using a mechanical stirrer. After centrifugation for 60 minutes at 10000 rpm (Sorvall, Superspeed RC2 – B), supernatant was collected and diluted 25 times with water before extraction.

HS/SPME measurements were performed at 60°C with an extraction time of 60 minutes. Sample supernatant solution for headspace extraction was adjusted to 2 ml in all measurements.

For analytical parameters determination and quantification, the untreated apple sample was fortified using mixed standard solution to obtain series of standard samples with 1.25, 0.6, 0.25, 0.1 and 0.025 mg/kg concentration of each pesticide studied. The fortified samples were left to rest for 24 hours and the same sample preparation and analysis procedure was applied.

RESULTS

A HS/SPME – GC/MS chromatogram of standard apple samples fortified at 0.6 mg/kg concentration level is shown in Figure 1.

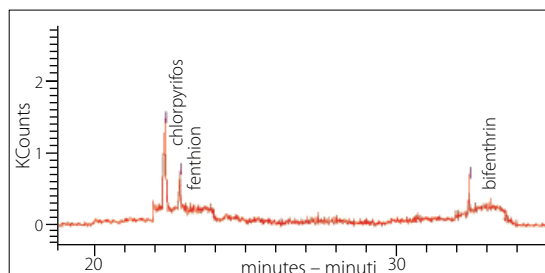


Figure 1. HS/SPME – GC/MS chromatogram of standard apple sample fortified with pesticides at 0.6 mg/kg level concentration

Slika 1. Hromatogram referentnog uzorka jabuka obogaćenog pesticidima do koncentracija od 0.6 mg/kg

Concentration linearity was attained in the following ranges: 0.025-1.25 mg/kg for chlorpyrifos,

0.025-1.25 mg/kg for fenthion and 0.1-1.25 mg/kg for bifenthrin. Correlation coefficient (R) values obtained were 0.9978 for chlorpyrifos, 0.9983 for fenthion and 0.9948 for bifenthrin. Precision of the extraction procedure applied was determined by performing three consecutive measurements of the standard apple sample fortified at 0.6 ppm level for three days. Relative standard deviation (RSD) values calculated are presented in Table 1. To determine the confidence of method, relative recovery values, determined as the peak areas ratio of standard apple sample and water standard solution fortified at the same level, were computed. The relative recovery values determined are summarised in Table 2. The limit of detection (LOD) values, computed as three times the base line noise of the blank sample, are presented in Table 2 as well.

The content of chlorpyrifos, fenthion and bifenthrin in the commercial apple samples analysed was below detection limit of the method applied.

DISCUSSION

The linear concentration dependences and corresponding correlation coefficient values obtained in the concentration range studied confirm that the extrac-

tion parameters optimised previously were suitable for extraction of chlorpyrifos, fenthion and bifenthrin from the complex apple matrix. RSD values (Table 1) calculated for a series of consecutive analyses, emphasizing a precision of the measuring procedure applied, are in accordance with literature data published for headspace extraction from the fruit matrix (Lambropoulou and Albanis, 2002). It is evident (Table 2) that the relative recovery values for the apple sample fortified at different levels were in the 56.68-82.91% range, which may be considered adequate for screening analysis of complex fruit matrix samples. Comparing the LOD values obtained (Table 2) with the MRL values cited in the relevant EU regulation for chlorpyrifos, fenthion and bifenthrin in apple samples (Council Directive 90/642/EEC, 1990), it is obvious that the procedure applied is sensitive enough to monitor residues of the pesticides studied within the concentration range well below the requested MRL values.

Summarizing the results presented, it can be concluded that the most important extraction parameters (extraction temperature and time), optimised previously for pesticide water samples, can be used for efficient and selective headspace extraction of chlorpyrifos, fenthion and bifenthrin from complex matrix apple samples. In order to maintain the precision, con-

Table 1. Relative standard deviation values in three consecutive measurements of the standard apple sample fortified at 0.6 mg/kg level over three days (RSD₁, RSD₂ and RSD₃), RSD_{AV} - mean value of nine consecutive measurements

Tabela 1. Relativne standardne devijacije izračunate na osnovu tri merenja uzorka jabuka obogaćenog sa 0.6 mg/kg svakog pesticida u toku tri dana (RSD₁, RSD₂ i RSD₃) i RSD vrednosti svih merenja (RSD_{AV})

Pesticide – Pesticid	RSD ₁	RSD ₂	RSD ₃ (%)	RSD _{AV} (%)
Chlorpyrifos – Hlorpirifos	8.36	10.85	9.18	11.91
Fenthion – Fention	5.76	19.75	7.91	13.31
Bifenthrin – Bifentrin	19.01	12.28	19.81	17.14

Table 2. Relative recovery values (%) for the apple sample fortified over 0.025-1.25 mg/kg range, and limit of detection (LOD) values for the pesticides studies

Tabela 2. Prinosi ekstrakcije (%) iz uzoraka jabuka obogaćenih pesticidima u opsegu 0.025-1.25 mg/kg, i granice detekcije (LOD) ispitivanih pesticida

Pesticide – Pesticid	Pesticides fortified – Dodato pesticida (mg/kg)					Limit of detection Granice detekcije (mg/kg)
	0.025	0.1	0.25	0.6	1.25	
Recovery – Prinosi ekstrakcije (%)						
Chlorpyrifos Hlorpirifos	60.98	66.06	64.34	70.22	76.18	0.014
Fenthion Fention	75.57	79.66	82.91	71.38	73.26	0.021
Bifenthrin Bifentrin	–	56.68	61.19	62.97	66.07	0.053

fidence and sensitivity of the method, the once optimized extraction parameters need to be controlled carefully. Having the benefits of shorter extraction time and reduced matrix effects, HS/SPME could become a reliable technique for sample preparation in pesticide residues analysis.

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Mikroekstrakcija u čvrstoj fazi – uzorkovanje iz gasovite faze: 2. Uzorci jabuka

REZIME

Metoda mikroekstrakcije u čvrstoj fazi – uzorkovanje iz gasovite faze (HS/SPME) optimizovana sa mešanim standardnim rastvorima hlorspirifosa, fentiona i bifentrina je testirana na uzorcima jabuka. Ekstrakcija u trajanju od 60 minuta je izvršena na temperaturi od 60°C sa 2 ml pripremljenog uzorka. Korišćeno je nepolarno 100 µm polidimetilsiloksansko (PDMS) vlakno. Detekcija i kvantifikacija su izvršene metodom gasno-masene spektrometrije (GC/MS).

U cilju određivanja analitičkih parametara, pravljena je serija obogaćenja referentnog uzorka jabuka mešanim standardnim rastvorom pesticida tako da finalne koncentracije budu u rasponu 0.025-1.25 mg/kg. Linearnost ($r^2 > 0.99$) je dobijena za ceo ispitivani koncentracioni opseg. Prinosi ekstrakcije za sve pesticide i sve koncentracije uključene u ispitivanje su u rasponu 56.68-82.91%. Granice detekcije metode (LOD) su bile 0.014 mg/kg za hlorspirifos, 0.021 mg/kg za fention i 0.053 mg/kg za bifentrin. Preciznost, odnosno ponovljivost merenja je određena na uzorku obogaćenom sa 0.6 mg/kg svakog pesticida. Izračunate RSD vrednosti su uvek bile ispod 20%.

Ključne reči: HS/SPME; ostaci pesticida; jabuke