# Comparison of HS-SDME with SPME and SPE for the Determination of Eight Organochlorine and Organophosphorus Pesticide Residues in Food Matrices

**Chai Mee Kin**[1,2,*] and **Tan Guan Huat**[2]

[1]Dept. of Science and Mathematics, College of Engineering, Universiti Tenaga Nasional, Km 7, Jalan Kajang-Puchong, 43009 Kajang, Selangor, Malaysia; [2]Dept. of Chemistry, Faculty of Science, Universiti Malaya, Lembah Pantai, 50603 Kuala Lumpur, Malaysia

## Abstract

**A headspace single-drop microextraction (HS-SDME) procedure is optimized for the analysis of organochlorine and organophosphorous pesticide residues in food matrices, namely cucumbers and strawberries by gas chromatography with an electron capture detector. The parameters affecting the HS-SDME performance, such as selection of the extraction solvent, solvent drop volume, extraction time, temperature, stirring rate, and ionic strength, were studied and optimized. Extraction was achieved by exposing 1.5 µL toluene drop to the headspace of a 5 mL aqueous solution in a 15-mL vial and stirred at 800 rpm. The analytical parameters, such as linearity, correlation coefficients, precision, limits of detection (LOD), limits of quantification (LOQ), and recovery, were compared with those obtained from headspace solid-phase microextraction (HS-SPME) and solid-phase extraction. The mean recoveries for all three methods were all above 70% and below 104%. HS-SPME was the best method with the lowest LOD and LOQ values. Overall, the proposed HS-SDME method is acceptable in the analysis of pesticide residues in food matrices.**

## Introduction

Organophosphorus (OP) and organochlorine (OC) pesticides are widely used in agriculture as insecticides and leave residues to varying extents in agricultural produce, such as fruits and vegetables. Due to their toxic properties and potential risk to consumers, their residues in food commodities is an issue of public concern and are controlled by legislation (1).

OC and OP pesticides can be extracted from fruits and vegetables using a variety of conventional techniques. The most commonly-employed techniques for extracting pesticides are liquid–liquid extraction (LLE) and solid-phase extraction (SPE). These techniques, especially LLE, is considered time-consuming and expensive, which is hazardous to health due to the high volume of potentially toxic solvents used. Because of the disadvantages of conventional extraction techniques, solvent-free sample preparation methods or those employing less organic solvents became of great importance.

Modern trends in analytical chemistry are directed towards the simplification, miniaturization, and improvement of the sample extraction and cleanup methods with universal microextraction procedures (2–3). Solid-phase microextraction (SPME) and single-drop microextraction (SDME) are easy and fast techniques, which avoid or use only microliters of toxic solvents.

SPME is a solvent-free extraction technique (1–3), which represents a convenient alternative to the conventional extraction methods. This technique has become increasingly popular in the extraction of organic compounds (2–6). It is an inexpensive, solvent-free, and reliable technique with high sensitivity and good selectivity.

SPME has been applied extensively to determine pesticide residues in food samples (7–10). Kataoka et al. (3) and Beltran et al. (9) have reported the determination of pesticide residue analysis in water, soil, food, and biological samples by using the SPME techniques.

Single-drop microextraction (SDME) has been recently developed as an alternative extraction technique. SDME provides analyte extraction in a single drop of organic solvent; therefore, small volumes of organic solvent are used. When the extraction is finished, the single drop of organic solvent is injected into the gas chromatography (GC) port for analysis. SDME avoids the problems of solvent evaporation, as encountered in LLE and SPE, as well as fiber degradation of SPME; it is also fast, inexpensive, and employs simple equipments such as microsyringe, hot-plate magnetic stirrer, clamp, and stand.

Generally, SDME has been employed in the extraction of various types of pesticide residues from different water samples (11–15). However, only a very limited number of studies have been performed on fruit juices (16) and traditional Chinese medicines (17). To our knowledge, there is no report employing

*Author to whom correspondence should be sent: email ghtan@um.edu.my

headspace (HS)-SDME on the extraction of pesticide residues from complex food matrices such as fruits and vegetables.

The main objective of this study is to apply HS-SDME followed by GC with electron capture detector (ECD) to determine eight OC and OP pesticide residues in food matrices, namely cucumbers and strawberries. The parameters affecting the extracting process of HS-SDME were studied and optimized. The performance of the optimized HS-SDME was compared to that of the HS-SPME and SPE methods.

## Materials and Methods

### Chemicals and standard solutions

All the solvents used were HPLC-grade. Acetone, ethyl acetate, *n*-hexane, isooctane, methanol, and toluene were purchased from Fisher Scientific (Longhborough, U.K.). Eight pesticides standards > 95% pure (diazinon, chlorothalonil, malathion, chlorpyrifos, quinalphos, prefenofos, α-endosulfan, and β-endosulfan), which are commonly used by local farmers in fruit and vegetable cultivation (18), were purchased from AccuStandard Inc. (New Haven, CT). A range of standard mixture stock solutions containing 50–5000 mg/L were prepared in methanol and stored at 4ºC. Different concentration levels of stock solution were employed due to their sensitivity to the ECD detector. Working standard solutions of a mixture of pesticides were freshly prepared daily by volume dilution in distilled water. 1-chloro-4-fluorobenzene (98.0%) purchased from AccuStandard Inc. was used as the internal standard to compensate for sample and injection volume changes and was added to the vial prior to GC–ECD analysis.

### Sample preparation

In the multiclass and multiresidue analysis of pesticides in food matrices, pesticide-free organic fruits (strawberry) and vegetables (cucumber) were obtained from a pesticide-free farm in the Malaysian Agricultural Research and Development Institute (MARDI, Selangor, Malaysia). For HS-SDME and HS-SPME methods, fruit and vegetable samples (100 g) were weighed and finely chopped. A subsample of 30 g was accurately weighed and placed in a 150-mL beaker. Three concentration levels (low, medium, and high) were spiked into the samples drop by drop to provide the spiked control samples. After being kept at room temperature for 1 h, the spiked samples were added with 30 g of distilled water, blended, and homogenized in a food processor. Then, the samples were placed in separate vials.

### HS-SDME analysis

Before each extraction, a 10-µL microsyringe (Hamilton), obtained from Supelco (Bellefonte, PA) was washed at least 10 times with the extraction solvent. Then, a specific volume of extraction solvent is drawn into the microsyringe before the extraction. The microsyringe, which is clamped to a stand, is then inserted through the septum of the sample vial (15 mL capacity), and the end of needle was located about 1 cm above the surface of the stirred solution. The plunger is pushed down to expose a few µL of microdrop in the stirred solution for a certain period. After the extraction is finished, the microdrop was retracted into the microsyringe and injected directly into the GC–ECD inlet for further analysis.

### HS-SPME analysis

The HS-SPME procedure for extracting the same investigated pesticide residues in fruits and vegetables had been developed and optimized in a previous work (19). The procedure was performed using a 100-µm film thickness poly (dimethylsiloxane) PDMS-coated fiber mounted in a manual syringe holder, which was obtained from Supelco. A homogenized spiked sample was added with 2% (vol/weight) of methanol–acetone (1:1), and optimum dilution was made with distilled water containing 10% NaCl until the total sample in the vial was equal to 5.00 g. Then, the internal standard was added, and the sample was extracted by HS-SPME with a 100-µm PDMS fiber at 60ºC for 30 min with sample agitation at 800 rpm without pH adjustment. Desorption was done at 240ºC for 10 min.

### SPE analysis

The SPE procedure for extracting the same investigated pesticide residues in fruits and vegetables was based on that developed by Asha et al (20). In this method, acetone–ethyl acetate–*n*-hexane (10:80:10, v/v/v) is used as the extraction solvent. A 5% acetone in *n*-hexane was used as the eluent on a RP-$C_{18}$ SPE cartridge (Supelco) and GC–ECD was used for determination of the investigated pesticides.

### GC–ECD

A Shimadzu GC 17A version 2.21 gas chromatograph coupled with an ECD was used. A SGE BPX5 (30 m × 0.32 mm i.d. capillary column with a 0.25-µm film depth) was used in combination with the following oven temperature program: initial temperature 120°C, then heated at 7°C/min to a final temperature of 250°C, and then held for 4.5 min. The total run time was 23.07 min. A silanized narrow-bore injector liner (0.75 mm i.d.) for the SPME injections was installed, and the fiber was inserted into this injector using the splitless mode. The injector temperature was held at 240°C, and the detector temperature was at 300ºC. Nitrogen gas (99.999%) was used as the carrier gas with a flow rate of 24.4 cm/s linear velocity, and the gas pressure was kept at 94 kPa.

## Results and Discussion

### HS-SDME optimization

In order to perform the HS-SDME for the extraction of OC and OP pesticide residues in fruits and vegetables efficiently, several parameters that influence the extraction efficiency were studied and optimized. These factors included effects of solvent types and drop volume, effects of extraction time and temperature, effect of stirring rate, and effect of ionic strength.

### Effects of solvent types and drop volume

The first step in the HS-SDME method is the selection of an appropriate extraction solvent. Selection of a suitable solvent is

very important to achieve good selectivity and improve extraction efficiency. The selection of the extraction solvent was based on the principle of "like dissolves like". The extraction solvent must have low water solubility, extract analytes well, have good drop stability during stirring, and have a low level of toxicity (21). Several types of organic solvents including *n*-hexane, isooctane, and toluene were tested. Solvent selectivity was evaluated by exposing 1.5 µL solvent drop in 5 mL distilled water samples for 15 min, stirred at 800 rpm, and spiked at the mid-concentration level, 0.2–25 mg/L, with all the investigated pesticides. Figure 1 shows the effect of the extraction solvent on extraction efficiency. The results showed that toluene exhibited the highest extraction efficiency for all the analytes when compared with the other solvents. It was also found that toluene is more stable and less toxic than other organic solvents tested. Toluene is also a very suitable solvent for pesticide GC injection (22). Thus, toluene was selected for the subsequent HS-SDME experiments.

Generally, the use of a large organic drop results in an increase in the analytical response of the instrument. However, larger drops are difficult to manipulate and are less reliable. In addition, the analytes diffuse into the drop through the diffusion process when the drop volume increases, and it takes a longer time to reach equilibrium. Therefore, in order to increase the sensitivity of the SDME procedure, the organic drop volume must be optimized experimentally. For this set of experiments, 5 mL distilled water samples spiked at the mid-concentration level of pesticides and stirred at 800 rpm were extracted for 15 min with toluene drop volumes ranging from 0.5–2.5 µL. The results from Figure 2 show that the analytical signal increased with increasing drop volume from 0.5 to 1.5 µL. After that, it levels off, and after 2.0 µL the peak areas for all the investigated pesticides decrease with any further increase in the drop volume. Therefore, the toluene drop volume of 1.5 µL was used to ensure the formation of a stable and reproducible microdrop and to allow fast stirring.

### Effects of extraction time and temperature

The effect of extraction time on extraction efficiency was investigated with the time varying from 5–30 min to 5 mL distilled water samples spiked at the mid-concentration level and stirred at 800 rpm. The extraction efficiency increases with longer extraction time in HS-SDME method. The extraction time should be sufficient for the microdrop to extract a finite quantity of the target analytes. Figure 3 shows that equilibrium has not yet been attained for all the investigated pesticides with a 30 min extraction time, which means that it will not be practical to make use of the full capacity of the microdrop in 30 min. One possible reason for this may be the slow equilibrium rate between the sample solution and the organic drop. However, longer extraction times were avoided as they typically resulted in significant solvent evaporation. Nonetheless, for quantitative HS-SDME analysis, it is not necessary for the analytes to have reached the equilibrium, only to allow sufficient mass transfer into the microdrop and exact reproducible extraction time (23–24). Moreover, a phenomenon of microdrop dissolution was observed with approximately 0.5 µL organic solvent being lost in the 30 min extraction experiment due to longer exposure times. Therefore, the extraction time for all subsequent experiments was fixed at 15 min.

Temperature has a significant effect on both kinetics and thermodynamics of the extraction process. The results showed that the extraction efficiency of most pesticides decreased as the temperature increased. It may be due to the fact that the high temperature can cause solvent drop damage and loss, which will

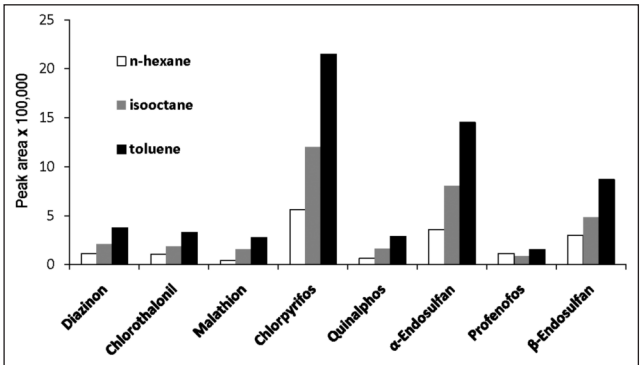


**Figure 1.** Effect of solvent types on peak area in HS-DSME.

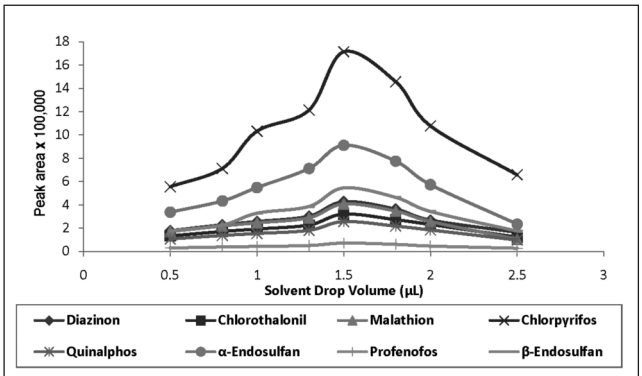


**Figure 2.** Effect of solvent drop volume on peak area in HS-SDME.

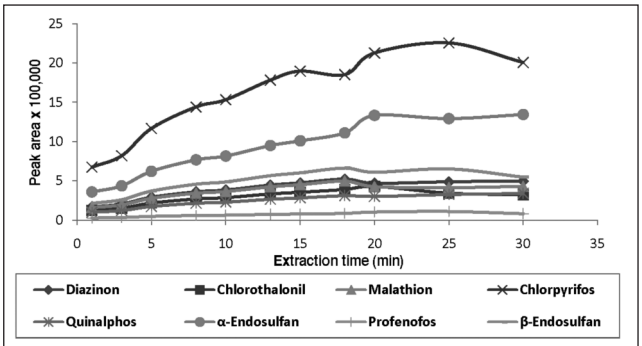


**Figure 3.** Effect of extraction time on peak area in HS-SDME.

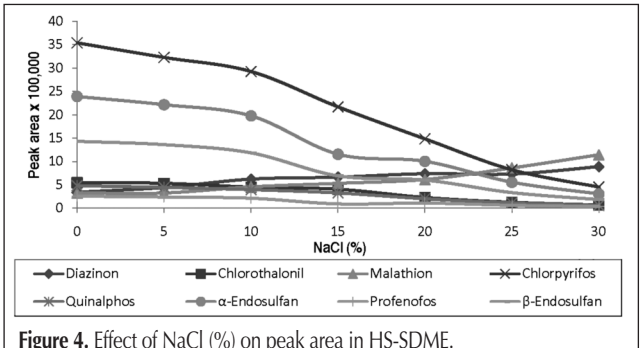


**Figure 4.** Effect of NaCl (%) on peak area in HS-SDME.

then decrease the response. To simplify the method, further experiments were performed at room temperature.

### Effect of stirring rate

The effect of agitation on the extraction of pesticides was also studied. Fast agitation of the sample could be employed to enhance the extraction efficiency because agitation permits continuous exposure of the extraction surface to fresh aqueous sample. To evaluate the effect of stirring rate, a 1.5 µL toluene drop was used to extract the same spiked level distilled water samples for 15 min and stirred at different agitation rates from 400 to 800 rpm. The results showed that the relative peak areas of all the analytes increased with the increase of stirring rate from 400 to 1000 rpm. However, when the stirring rate is greater than 800 rpm, the precision is unacceptable with the relative standard deviation (RSD) value greater than 20%, and the microdrop in the needle is also unstable. Nonetheless, at speeds greater than 800 rpm, the formation of air bubbles was promoted, thus increasing the incidents of drop loss or dislodgement. Therefore, the optimum stirring rate was selected at 800 rpm, and this was used in all subsequent experiments.

### Effect of ionic strength

Addition of salt to the sample may have several effects on SDME (21). It can improve the extraction of analytes because high ionic strength reduces water solubility due to the salt addition. However, the presence of salt was found to restrict extraction of nitroaromatic explosives (23). Based on the previous study (19), NaCl was most effective in increasing the amount of the investigated analytes extracted by HS-SPME. Thus, NaCl was chosen in this study. The effect of salt concentration on the extraction efficiency of pesticides is illustrated in Figure 4. As can be seen, the addition of salt caused little reduction in the extraction efficiency for the majority of investigated analytes, which is more pronounced for the less polar compounds except for diazinon and malathion. A possible explanation for this observation may be that apart from the salting-out effect, the NaCl dissolved in the aqueous solution may have changed the physical properties of the Nernst diffusion film and reduced the rate of diffusion of the investigated analytes into the drop (21). This means that with increased salt concentration the diffusion of analytes towards the organic drop becomes more difficult thus limiting the extraction. In contrast, the extraction efficiency for diazinon and malathion increased with increasing salt content from 0 to 30% of NaCl due to its high water solubility behavior. Based on the above experimental results, analysis of the direct sample without the addition of salt was employed in this study.

Overall, the optimum extraction conditions found in the present HS-SDME studies are: a 1.5 µL toluene microdrop was

**Table I. Monitoring Parameters: Linearity Ranges, Correlation Coefficients, and Mean RSD (%) for HS–SPME, SPE, and HS–SDME**

| | Linear ranges (µg/L) | | | Correlation coefficients ($r^2$) | | | Precision (RSD%, $n$ = 5) | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | HS-SPME | SPE | HS-SDME | HS-SPME | SPE | HS-SDME | HS-SPME | SPE | HS-SDME |
| Diazinon | 10–1000 | 100–10000 | 1000–100000 | 0.9985 | 0.9996 | 0.9876 | 1.30 | 1.61 | 8.33 |
| Chlorothalonil | 10–1000 | 100–10000 | 1000–100000 | 0.9977 | 0.9991 | 0.9912 | 5.93 | 2.17 | 12.46 |
| Malathion | 50–5000 | 500–50000 | 5000–500000 | 0.9973 | 0.9981 | 0.9966 | 3.93 | 2.69 | 12.31 |
| Chlorpyrifos | 0.5–50 | 5–500 | 50–5000 | 0.9969 | 0.9986 | 0.9834 | 5.71 | 1.29 | 13.15 |
| Quinalphos | 50–5000 | 500–50000 | 5000–500000 | 0.9972 | 0.9992 | 0.9949 | 4.82 | 1.91 | 5.88 |
| α-Endosulfan | 0.1–20 | 1–200 | 10–2000 | 0.9982 | 0.9987 | 0.9945 | 4.25 | 1.25 | 15.15 |
| Profenofos | 1–100 | 10–1000 | 100–10000 | 0.9990 | 0.9996 | 0.9946 | 2.75 | 0.70 | 7.44 |
| β-Endosulfan | 1–100 | 10–1000 | 100–10000 | 0.9990 | 0.9987 | 0.9918 | 2.30 | 1.39 | 10.20 |

**Table II. Monitoring Parameters: Limits of Detection, Limits of Quantification, and Mean Recovery (%) for HS-SPME, SPE, and HS-SDME**

| | LOD, µg/L(LOQ, µg/L) | | | Mean Recovery % (RSD%, $n$ = 3 × 3 levels) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Cucumber | | | Strawberry | | |
| Compound | HS-SPME | SPE | HS-SDME | HS-SPME | SPE | HS-SDME | HS-SPME | SPE | HS-SDME |
| Diazinon | 0.2 (1) | 2.0 (25) | 200 (600) | 96.0 (1.4) | 90.0 (0.9) | 76.7 (6.7) | 90.4 (2.1) | 104.0 (2.3) | 75.0 (8.5) |
| Chlorothalonil | 0.2 (1) | 2.0 (25) | 200 (600) | 89.9 (2.2) | 92.4 (1.6) | 77.4 (7.3) | 96.1 (1.6) | 96.5 (1.2) | 81.6 (6.8) |
| Malathion | 1.0 (5) | 10.0 (125) | 1000 (3000) | 88.3 (1.5) | 97.1 (1.0) | 91.9 (6.4) | 86.7 (1.5) | 94.5 (1.9) | 84.7 (13.6) |
| Chlorpyrifos | 0.02 (0.1) | 0.2 (1.25) | 2 (30) | 90.7 (2.5) | 86.5 (1.8) | 81.9 (9.6) | 84.2 (1.2) | 88.8 (2.0) | 75.7 (6.7) |
| Quinalphos | 1.0 (5) | 10.0 (125) | 1000 (3000) | 92.3 (1.8) | 89.5 (3.0) | 77.0 (4.7) | 91.9 (3.0) | 92.3 (2.3) | 87.8 (6.0) |
| α-Endosulfan | 0.01 (0.05) | 0.1 (0.25) | 1 (6) | 95.4 (1.5) | 102.1 (1.8) | 95.8 (8.1) | 86.9 (1.9) | 94.5 (1.0) | 89.0 (12.7) |
| Profenofos | 0.1 (0.5) | 1.0 (2.5) | 10 (60) | 88.8 (2.2) | 98.5 (2.7) | 89.5 (4.8) | 96.6 (2.6) | 95.5 (1.9) | 85.3 (8.4) |
| β-Endosulfan | 0.01 (0.5) | 1.0 (2.5) | 10 (60) | 95.1 (2.2) | 92.6 (0.9) | 93.0 (10.0) | 94.9 (1.7) | 94.8 (1.0) | 71.8 (4.8) |

exposed for 15 min to the headspace of a 5 mL aqueous sample in a 15-mL vial at room temperature and stirred at 800 rpm.

**Comparison of HS-SDME performance vs. HS-SPME and SPE**

The analytical parameters for the HS-SPME, SPE, and HS-SDME procedures were obtained by the analysis of different spiked cucumber and strawberry samples using the internal calibration curves for three concentration levels of the standard pesticide mixtures. The linearity of the detector's response using all three extraction techniques was verified in the concentration ranges from 0.0001–500 mg/L. Triplicate analyses were run for each of the six concentration levels chosen within these ranges. However, the precision (repeatability) of each method was determined by performing five consecutive extractions at the mid-concentration level.

**Linearity and precision**

The results of linearity and precision studied are summarized in Table I. For HS-SPME, the correlation coefficient ($r^2$) ranged from 0.9969–0.9990; for SPE, the $r^2$ ranged from 0.9981–0.9996. However, for HS-SDME, the values ranged from 0.9834–0.9966. Overall, the repeatability expressed as the RSD was found to be satisfactory for HS-SPME ranging from 1.30–5.93% with a mean value of 3.87%; for SPE, values ranged from 0.70–2.69% with a mean value of 1.63%. However, the RSD values of HS-SDME were less precise and varied between 5.88–15.15% with a mean value of 10.62%. An additional consideration for the HS-SPME and HS-SDME extraction techniques is that higher RSDs are expected when, as in this study, extractions are carried out under non-equilibrium conditions. It is evident that, with HS-SPME and SPE, better precision and linearity are obtained for all the investigated pesticides compared to HS-SDME. This observation reflects the fact that HS-SDME requires more elaborate manual operations, giving rise to less repeatable results.

**Limits of detection, limits of quantification, and recovery**

The limits of detection (LOD) and quantification (LOQ) for all the investigated pesticides using three methods were also determined. The results from Table II clearly show that, under the present experimental conditions, HS-SPME is the most sensitive technique among the three techniques. The LOD for HS-SPME is one order of magnitude lower than that for SPE, although a 10-fold sample volume was used for SPE. This can be overcome by increasing the volumes for SPE, but in the present study where sample volume is limited, a higher sensitivity would be a considerable advantage. Compared to HS-SPME, the LOD and LOQ of HS-SDME for all the investigated pesticides are 10–100 times higher than HS-SPME. For HS-SDME, the lower LOD are expected by prolonging the extraction times. However, prolonged sampling times may result in drop dissolution and dislodgment for HS-SDME.

Pesticide-free cucumber and strawberry samples were spiked at three concentration levels and analyzed using SPE and HS-SDME methods in order to evaluate the effect of the matrix and to compare the results with those obtained with HS-SPME. Similar to HS-SPME, HS-SDME is an equilibrium technique and not an exhaustive method such as SPE. Hence, in SPE the absolute recovery is measured, whereas for HS-SDME, the relative recovery was used. For SPE, the average recoveries ranged from 86.5–104.0% with the RSD values, which were less than 3%. The relative recoveries of HS-SPME and HS-SDME ranged from 84.2–96.6% and 71.8–95.8%, respectively. However, the RSD values obtained with the HS-SDME method (4.7–13.6%) were higher than those obtained with HS-SPME (1.2–3.0%), reflecting once again the fact that HS-SDME is a more elaborate method.

With regard to sample preparation time, which depends mainly on the extraction time, it can be controlled by the analyst in the case of HS-SPME. The equilibrium is barely achieved in less than 1 h, and quite often it takes several hours to be established. But for practical reasons, the extraction time employed is between 20 min and 1 h. Quite often, the extraction time chosen depends on the duration of a GC run to shorten the overall time of analysis. In this study, this was also the main reason for choosing an extraction time of 30 min, as equilibrium was reached only after an extraction time of 60 min and the sensitivity was sufficient after 30 min. Sample preparation by SPE takes about 2 h with a greater number of steps to be carried out in that time. On the other hand, it was possible to prepare several samples simultaneously, which was not quite possible without high expenses in SPME. HS-SDME is a much faster extraction method given that the results were obtained after sampling for only 15 min instead of 30 min as it were in the case of HS-SPME.

## Conclusions

In the present study, the alternative method HS-SDME, which can be employed for the determination of pesticide residues in the food matrices, was evaluated. Headspace analysis enables more complex matrices to be extracted than by direct analysis, and it can also be applied for the determination of semi-volatile analytes in complex food matrices, such as fruits and vegetables. HS-SPME and SPE are more efficient than HS-SDME in the present system because it has better linearity, precision, LOD, and LOQ. However, the HS-SDME is simpler to perform, being free from memory effects and also is cost effective. In addition, the disposable nature of the droplet would eliminate the problems commonly encountered with SPME, such as limited lifetime and fragility of the fiber. However, the HS-SDME method requires more elaborate manual operations, whereas the HS-SPME is easier to perform. Overall, both HS-SDME and HS-SPME techniques represent powerful alternatives to the conventional extraction method due to their speed, simplicity, cost, and solvent-free nature compared to SPE.

## Acknowledgement

The authors would like to acknowledge the financial support given by Universiti Tenaga Nasional and University Malaya. In addition, the authors would also like to thank the Malaysia Toray Science Foundation for financial support.

## References


1. D.A. Lambropoulou and T.A. Albanis. Headspace solid-phase microextraction in combination with gas chromatography-mass spectrometry for the rapid screening of organophosphorus insecticide residues in strawberries and cherries. *J. Chromatogr. A* **993:** 197–203 (2003).
2. J. Beltran, F.J. Lopez, and F. Hernandez. Solid-phase microextraction in pesticide residue analysis. *J. Chromatogr. A* **885:** 389–404 (2000).
3. H. Kataoka, H.L. Lord, and J. Pawliszyn. Application of solid-phase microextraction in food analysis. *J. Chromatogr. A* **880:** 35–62 (2000).
4. L.J. Krutz, S.A. Senseman, and A.S Sciumbato. Solid-phase microextraction for herbicide determination in environmental samples. *J. Chromatogr. A* **999:** 103–121 (2003).
5. M.A. Farajzadeh and M. Hatami. Solid-phase microextraction gas chromatography for determination of some organophosphorus pesticides. *Chromatographia* **59:** 259–262 (2004).
6. C.G. Zambonin, M. Quinto, N.D. Vietra, and F. Palmisano. Solid-phase microextraction-gas chromatography mass spectrometry: A fast and simple screening method for the assessment of organophosphorus pesticides residues in wine and fruit juices. *Food Chem.* **86:** 269–274 (2004).
7. Y.I. Chen, Y.S. Su, and J.F. Jen. Determination of dichlorvos by on-line microeave-assisted extraction coupled to headspace solid-phase microextraction and gas chromatography-electron capture detection. *J. Chromatogr. A* **976:** 349–355 (2002).
8. C.G. Zambonin, A. Cilenti, and F. Palmisano. Solid-phase microextraction and gas chromatography-mass spectrometry for the rapid screening of triazole residues in wine and strawberries. *J. Chromatogr. A* **967:** 255–260 (2002).
9. J. Beltran, A. Peruga, E. Pitarch, F.J. Lopez, and F. Hernandez. Application of solid-phase microextraction for the determination of pyrethroid residues in vegetable samples by GC-MS. *Anal. Bioanal. Chem.* **376:** 502–511 (2003).
10. L. Cai, S. Gong, M. Chen, and C. Wu. Vinyl crown ether as a novel radical crosslinked sol-gel SPME fiber for determination of organophosphorus pesticides in food samples. *Anal. Chim. Acta* **559:** 89–96 (2006).
11. M.C. Lopez-Blanco, S. Blanco-Cid, B. Cancho-Grande, and J. Simal-Gandara. Application of single drop microextraction and comparison with solid phase microextraction and solid phase extraction for the determination of alpha and beta endosulfan in water samples by gas chromatography electron capture detection. *J. Chromatogr. A* **984:** 245–252 (2003).
12. D.A. Lambropoulou, E. Psillakis, T.A. Albanis, and N. Kalogerakis. Single drop microextraction for the analysis of organophosphorus insecticides in water. *Anal. Chim. Acta* **516:** 205–211 (2004).
13. Q. Xiao, B. Hu, C. Yu, L. Xia, and Z. Jiang. Optimization of a single drop microextraction procedure for the determination of organophosphorus pesticides in water and fruit juice with gas chromatography-flame photometric detection. *Talanta* **69:** 848–855 (2005).
14. F. Ahmadi, Y. Assadi, S.M.R.M. Hosseini, and M. Rezaee. Detemination of organophosphorus pesticides in water samples by single drop microextraction and gas chromatography flame photometric detector. *J. Chromatogr. A* **1101:** 307–312 (2006).
15. E. Zhao, W. Shan, S. Jiang, Y. Liu, and Q. Zhau. Determination of the chloroacetanilide herbicides in waters using single drop microextraction and gas chromatography. *Microchemical J.* **83:** 105–110 (2006).
16. E. Zhao, L. Han, S. Jiang, Q. Wang, and Z. Zhou. Application of a single drop microextraction for the analysis of organophosphorus pesticides in juice. *J. Chromatogr. A* **1114:** 269–273 (2006).
17. C. Deng, N. Yao, B. Wang, and X. Zhang. Development of microwave-assisted extraction followed by headspace single drop microextraction for fast determination of paeonal in traditional Chinese Medicines. *J. Chromatogr. A* **1103:** 15–21 (2006).
18. T. Suzuki. Imported Pesticide Amounts as an active ingredients in Malaysia at 1998 to 2001. Residue Section, Pesticides Control Division, Department of Agriculture, Malaysia (2003).
19. M.K. Chai, G.H. Tan, and A. Lal. Optimization of headspace solid-phase microextraction for the determination of pesticide residues in vegetables and fruits. *Inter. J. Anal. Sc.* **24(2):** 273–276 (2008).
20. A. Lal, G.H. Tan, and M.K. Chai. Multiresidue analysis of pesticide in fruits and vegetables using solid-phase extraction and gas chromatographic method. *Inter. J. Anal. Sc.* **24(2):** 231–236 (2008).
21. E. Psillakis and N. Kalogerakis. Development in single drop microextraction. *Trends Anal. Chem.* **21(1):** 53–63 (2002).
22. K. Mastovska, J. Hajslova, and S.J. Lehotay. Ruggedness and other performance charactieristics of low-pressure gas chromatography-mass spectrometry for the fast analysis of multiple pesticide residues in food crops. *J. Chromatogr. A* **1054:** 335–349 (2004).
23. E. Psillakis and N. Kalogerakis. Application of solvent microextraction to the analysis of nitroaromatic explosives in water samples. *J. Chromatogr. A* **907:** 211–219 (2001).
24. Y. Yamini, M. Hojjati, M. Haji-Hosseini, and M. Shamsipur. Headspace solvent microextraction. A new method applied to the preconcentration of 2-butoxyethanol from aqueous solutions into a single microdrop. *Talanta* **62:** 265–270 (2004).


Manuscript received July 18, 2008;
Revision received November 19, 2008.