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Headspace Solid Phase Microextraction Application for Pesticide Residues in Fruits and Vegetables

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ABSTRACT

Headspace solid phase microextraction, fundamental& principle with its application on the determination of various pesticides are reviewed in this article. Pesticides extraction as a sample preparation step prior to subsequent analysis is aimed to achieve a reliable and accurate determination of this contaminants residue in food. Fast and high efficiency extraction process with free solvent consumption and overall cost is achieved through headspace solid phase micro extraction. HSPME is an equilibrium process which depends on the physio-chemical properties of the analyte to be extracted. Sample preparation and extraction condition such as fiber coating, temperature, time etc, have a direct impact on the extraction efficiency and sensitivity of headspace technique.

Keywords*: Pesticides, vegetables, Fruit, Headspace Solid Phase Microextraction*

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Introduction

Pesticides are various chemical compounds, with different functional groups, forming various types of isomeric compound. They differ in their substitution groups, degree of ionization, octanol/water coefficient, polarity, volatility and their solubility (Aulakh *et al*., 2005). Agriculture pesticides are used by farmers to attacks insects and other harmful organisms in many agriculture crops. They qualify the quantities and the quality of cultivated crops and help to prevent plant and human diseases transmission by insect. In contrast, some of pesticides are highly toxic and mobile substances in the environment, however and their accumulation in living organisms can be cause of serious diseases(Cairns & Sherma, 1992).Therefore, determination the residues of pesticide in agriculture products such as food, vegetables and so on is an important aspect of food safety and public concern because of their residues constitute a potential risk to human health (Hogendoorn, *et al*.,2000).

Most existing analytical methods used to control levels of residues in commodities typically require excessive time, highly cost, labor-intensive, complicated equipment, and/or required large quantities of organic solvent that may be harmful to humans and the environment which means to be discarded(Fiedler,*et al*., 2002).Analyses of chlorinated pesticides, in food, or environmental samples usually are extracted by liquid-liquid extraction, which required a time up to 18 hours per each sample to be extracted. In addition, liquid-liquidextraction can produce contaminants and introduce errors into the final sample, along with the analyses of interest, producing a high background in the analysis, due to the multi-stage operations of LLE.

Solid-phase extraction is still requiring large volumes of organic solvents to extract the sample from the column, before it can be injected into a separation method. However, the requirement of an organic solvent is eliminated in SPME method (Lord, and Pawliszyn, 2000; Zhang*, et al*., 1994).Solid-phase microextraction (SPME) technique was developed by Pawliszyn, 1989 to reform limitations inherent in SPE or LLE. SPME is a novel and very successful new technique to integrates sampling, extraction, concentration, can alsoachieve sampling, clean-up, and concentration in the same step, offers a simple, solvent-free with comparison to the traditional methods (Kataoka ., *et al*., 2000). In addition, interferences is eliminated in this technique, because the fiber is not contact with the sample matrix(Ng *et al.,* 1999; Mestres, *et al*., 2002).Since the fiber is not in contact with the sample, background adsorption and matrix effects can be reduced, which also increase the lifetime of SPME fiber(Ruey& Pei-Lin, 2001).The main object of this article is to describe the basic of headspace technique as a rapid and reliable extraction method for the determination of pesticides in vegetables and fruit sample.

Head space Solid Phase Microextraction (HS-SPME)

Headspace solid-phase microextraction (HS-SPME) is a solvent-free sampling, sensitive, eliminates the interferences and the need for complicated apparatus for extraction and concentrating of analyte by exposure to gaseous phase (Aurther, *et al*., 1992). An extraction mechanism is based on the sorption characteristics (adsorption or absorption) of fiber coating materials (Rocha*et al*., 2001). It offers uncomplicated manual sampling and thermal desorption in one syringe-like device, which can be used with all GC and GC/MS systems

HSPME is a modifications of solid extraction technique, but with a small amount of organic solvents and a high efficiency of extraction capacity fiber, in which fused-silica fibers coated with a thin layer of selective coating is used for the identification of organic volatile and semi-volatile constituents in complex matrices directly from the headspace (Hayasaka,*et al*., 2003).The constituents (volatiles or semi volatiles) from gaseous, liquid, or solid matrices are first released from the matrices and sorted onto a fiber coated with an adsorbent/ absorbent polymer introduced into the headspace. Polydimethysiloxane (PDMS) fiber coating is used following the detection by the chromatography coupled to mass spectrometry, either thermally desorbed onto a gas chromatographic (GC) inlet or solvent desorbed into a high-performance liquid chromatographic(HPLC) inlet (Arthur, & Pawliszyn,, 1990).

Fundamental Theory of HS-SPME

The concept of HS- SPME has been derived from the idea of SPE. It is a modified on gas–liquid or liquid–liquid partitioning. The theory of SPME as described by Pawliszyn and his coworkers (Arthur *et al*., 1992; Arthur & Pawliszyn, 1990; Pawliszyn,, 2012) indicates that there is partition of analyte between the coated fiber and the sample matrix and then the amount of analyte extracted by the fiber and the initial concentration of the analyte present in the sample matrix. This will enable the partition process to achieve quantitative extraction.

HS-SPME involves three phases (fiber coating, head space gas and the sample matrix) with two interfaces, so the mass balance is more complex (Pawliszyn, 1997). HS-SPME involves connecting of the liquid phase and fiber coating by gaseous phase (Katoaka *et al*., 2000). Where the analyte are extracted from the gas phase equilibrated with sample matrix (Pawliszyn, 1999). Typically, the extraction is considered to be achieved when the analyte concentration has reached distribution equilibrium between the sample, in the headspace above the sample, and in the coating on fiber (Pawliszyn, 1997).

The adsorbed amount of analyte depends on the thickness of the coating fiber and on the distribution constant for the analyte. The extracted amount of analyte at equilibrium can be determined using the thermodynamic principle, which is based on the partition equilibrium (Ai 1997). For every compound, there is a thermodynamic energy associated with its presence in the headspace phase and in the liquid phase. These thermodynamic properties dictate how the molecules will ultimately distribute themselves between the two phases. The most convenient way of representing this distribution is through the equilibrium constant

$X_S \longleftrightarrow X_h$ (1)

The distribution coefficient or equilibrium constant (K) is proportional to the ratio of the concentration of molecules between the two phases when at equilibrium. This value is called the partition ratio, or distribution constant, or equilibrium constant and is expressed as the concentration of the analyte in the fiber coating (C_f), the concentration of analyte in the sample matrix (C_s) and concentration of analyte in the head space (C_h). The analyst's function is to optimize extracting conditions so that the distribution of solute between phases lies far to the right in equation (1) and the resulting value of K is large, indicating a high degree of extraction from phase X_S into phase X_f.. Conversely, if K is small, less chemical X is transferred from phase X_S into phase X_f. If K is equal to 1, equivalent concentrations exist in each phase.

The equilibrium constant expression, referred to as the Nernst distribution law between the SPME fiber and the sample matrix interface is

$K_{fs} = C_f / C_s$ or $= C_f \times V_f / C_s \times V_s$

While the equilibrium constant between the headspace/ sample matrix and the fiber coating/headspace interface are defined as

$K_{hs} = C_h / C_s$ or $= C_h \times V_h / C_s \times V_s$

The equilibrium constant between the headspace and the fiber coating interface is expressed as

$K_{fh} = C_f / C_h$ or $= C_f \times V_f / C_h \times V_h$

The amount of analyte distributed between the three phases as following

$$C_o V_s = (Cs \times V_s) + (C_h \times V_h) + (C_f \times V_f)$$

Where C_o is the concentration of the analyte in the sample with volume V_s and Cs, C_h , C_f, are the concentration of the analyte at equilibrium in liquid phase (sample matrix), gaseous phase (headspace) and fiber with volumes, V_s, V_h, V_f respectively.

The equilibrium constants (K) generally affected by the molecular weight and boiling point, of the analyte, where it increase with increasing molecular weight and boiling point of the analyte. Selectivity can be altered by changing the type of polymer coating on the fiber, or the coating thickness, to match the characteristics of the analytes of interest. Mass of the analyte extracted into the fiber can be calculated by

$$W_f = (C_o \times V_s \times V_f \times K_{fh} \times K_{hs}) (K_{fh} \times K_{hs} \times V_f) + (K_{hs} \times V_h) + (V_h). \quad (2)$$

The mass of the analyte extracted into the fiber which is then injected to the GC is a function of nearly all variables that may occur in the vial. If the small fiber volume long with possible cases of K_{hs} is considered simplified to two cases:

When K_{hs} is large (low volatility or semi volatility analytes) the mass extracted is essentially related to the headspace – fiber partition constant which is likely to also be large and When K_{hs} is small (volatile analytes) the mass is related to both partition constants. For example, heating the vial may drive more analyte into the headspace phase from the sample, but reduce extraction efficiency from the vapor to the fiber(Colin, 2012).). K_{fh} is highly dependent on the molecule and can be accurately estimated by its retention index on a column coated with a polymer corresponding to the fiber. Those compounds with high values of K_f will have a large adsorption capacity on the fiber as compared to those compounds with low values (Pawliszyn, 2012). In practice, the migration of compounds into the headspace phase does not just depend on their volatility but more on their affinity for the original sample phase. Furthermore, if the contents inside the sample vial are left long enough, the relative concentrations of a compound between the two phases will reach a steady value (or equilibrium) (Andrew, 2013).

The equilibrium conditions are described by the following equation:

$$N = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s}$$

or $n = K_{fs} V_f C_o$ (3)

where n is the amount extracted by the coating, K_{fs} is a fiber coating/sample matrix equilibrium constant, V_f is the fiber coating volume, V_s is the sample volume, and C_o is the initial concentration of a given analyte in the sample (Pawliszyn, 1997)

The above Equation indicate that the extraction efficiency is dependent on the fiber coating/sample matrix distribution constant. This is a characteristic parameter that describes properties of a coating and its selectivity toward the analyte of interest versus other matrix components (Pawliszyn, 1997). Kinetic theory of an extraction, demonstrates that coating volume is another parameter affecting the sensitivity of the SPME method. However, the use of thicker coatings to compensate for this effect will also result in longer equilibration times. In the other hand, an extraction phase with a large surface area accelerates the extraction rate as described in Equation (4) which demonstrates that the initial extraction rate (dn/dt) is proportional to the surface area of the extraction phase (A).Therefore, the extraction phase should have a large surface area-to-volume ratio, to enhance the sensitivity. This can be achieved by using, a thin film with a large surface area-to-volume ratio results in enhancement of the extraction efficiency without sacrificing the extraction time assuming the same convection conditions. $dn/dt = (DA / \delta) Cs$ (4)

The above equation applied in TFME, where δ is the thickness of the boundary layer; and, D is the diffusion coefficient (Jiang & Pawliszyn 2012).

Headspace solid phase micro extraction sampling techniques

Direct headspace injection, also called purge and trap, or dynamic HS-solid-phase extraction are extraction techniques widely applied for the determination of volatile fraction and semi-volatile composition of many different samples (Beltrán *et al.*, 2005). In static headspace, the sample is in contact and in equilibrium with the extractant gas, where in dynamic headspace can be extracted by a steady stream of inert gas. Therefore, the headspace solid phase sampling techniques can be classified into one-step procedures, such as static headspace, where an aliquot of the vapor phase is transferred in a closed container directly to the gas chromatograph, or dynamic headspace which include, two-step procedures, where the analytes are transferred from the matrix of the headspace to a "trap" where they are released by the action of heat or by a stream of carrier gas, and transferred to the gas chromatograph(Kolb, 1999). The fiber can also be desorbed into liquid chromatography eluent using a static or dynamic mode (Ridgway *et al.*, 2007).

Dynamic headspace sampling (figure 1), is a process that uses a flow of inert gas through the sample container to enhance the headspace size and thus, transferring the analytes from a solid or liquid matrix to the headspace phase by heating, and back flushed the adsorbed compounds from the headspace to the carrier gas without the use of solvent extraction(Smith, 2003). Instead of allowing the sample to come to equilibrium in a sample vial, the sample is warmed and the headspace atmosphere process is continues purged out of the sample vessel and through a trap (Colin, 2012).

Figure (1),
(A) Dynamic headspace&
(B) Static headspacesampling (Drawing from Chromservis s.r.o & Hachenberg & Schmidt 1977)

Static headspace sampling, or equilibrium headspace extraction is one of the methods that have been used for qualitative and quantitative analysis of many pesticides residue in several vegetables and fruit. Static headspace process, involves placing the sample in a closed vial, and then releases the volatile analytes into the headspace of the vial. After reaching the equilibrium between concentration of the analyte in the headspace and concentration of the analyte in the sample, a portion of the headspace is then injected into the gas chromatograph; this can be done manually or with an auto sampler, this process will be usually carried out at a pressure and temperature above ambient conditions (Slack *et al.,* 2003).

The preferable technique depends on the type of the desired analysis to be quantitative or qualitative analysis, sensitivity, automation and budget. The ability and time required to extract analyte are depend on the equilibrium constant and volume of gas passed through the sample. Following extraction the following gas contains the extracted analytes is passed over sorbent trap to collect them (Colin, 2012).

HS-SPME device
Fused Silica fiber device

The fiber HSSPME device consists of fiber holder and fiber assembly with built-in fiber inside the needle. The fiber holder consists of a spring-loaded plunger, a stainless-steel barrel. Stationary phase is a1cm length of fused silica fiber, coating with a various thickness and polarity characteristic, which is bonded to a stainless steel support tube and installed in a assembly that looks like a syringe like device or modified microliter syringe. The plunger moves the fused silica fiber pierced the rubber septum of the vial and the fiber immersed directly in the head space of the spiked sample, where the analytes are concentrated (supelco, 1998; Jolanta *et al*., 2011).

Fiber coating

Several SPME fibers have been used for the extraction of pesticides residues from vegetables and fruit samples. In general, SPME coating can be categorized into liquid polymer, solid sorbent or a combination of both with a two mechanisms of extractions, absorption or adsorption according to the nature of the fiber (Liquid or sold) (Kumar *et al*., 2008). If the fiber coating is liquid, the extraction of interest analyte is achieved by absorption process, in which the analytes partition from the surface into the coatings, such as polydimethylsiloxane (PDMS) and polyacrylate (PA). Solid coating is used to extract the analyte of interest by adsorption process, where the analyte bind to the porous surface of coating (Pawliszyn, 1999). PDMS–divinylbenzene (DVB), carbowax–DVB, carbowax–templete resin are solid coatings with porous surfaces. Adsorption extraction mechanism is more complex than absorption extraction. a stationary phase is immobilized on the support particles by various coating method such as partially or highly cross-linking, bonded, and non-bonded (Kataoka *et al*., 2000).Therefore, different coating procedures have been applied to expand coating types in the commercially applicable and reproducible SPME devices. A variety of different fibers, with different polarities and thickness reported in a review of SPME in food analysis by Kataoka *et al* and various of coating procedures including: dipping and physical agglutinating methods.

Sample preparation and extraction

Food is a complex non-homogenous mixture of a wide range of chemical substances that makes it hard to isolate and determine the analyte of interest. Analyses of pesticide residues in solid food samples is difficult due to the interfering compounds present in the matrix. To conquer this problem it is necessary to use appropriate sample preparation and extraction method (Blasco, *et al*., 2005).The pre-treatment or cleanup of the sample prior to SPME may include, such as, centrifugation, dilution or pre-extraction in organic solvent, is necessary to obtain reliable results, protect the fiber coating and avoid the fouling of the extraction phase by irreversible adsorption of macromolecules from the sample matrix, which could not only lead to a substantial decrease in the fiber lifetime, but also could possibly change the coating extraction properties (Érica *et al.,* 2014). .

HS-SPME, sample preparation process involve, weighting of the sample, cutting into uniform wedges as a solid samples can usually be prepared by grinding directly, followed by solvent or liquid extraction and be well homogenized. After that, chopped sample is spiked with appropriate amount of the pesticides standard. Finally, a chopped sample is then placed in separate sealed vials for pesticide isolation. The spiked sample should immediately be stored in the dark at room temperature, or frozen until they can be processed it for analysis. Also each sample should be clearly labeled as permanently as possible to be identified and correlated to the correct sample. Vegetables and fruit samples preparations for pesticides determination by HSSPME have been reported by (Chai , and Tan 2009; Chai *et al*., 2008; Crentsil *et al*., 2012;, Érica A. *et al*., 2014;).

Extraction procedure

Sample extraction is carried out for separation or transferring the desired pesticides from the sample matrix to the headspace device with the limitation of interferents and enrichment of the pesticides in sample to a level above the LOD of the applied analytical method, because pesticides concentrations in the various compartments of the environment are low (Pourya and Amir 2012). Extraction of an analyte is therefore influenced by solubility, penetration of the sample by the solvent (mass transfer) and matrix effects. However, many conventional solvents have been used for the HS-SPME extraction of various pesticides, which are added to the homogenised spiked sample. An optimum additives and dilution might make with a distilled water containing NaCl(Chai& Tan, 2009; Zi-Ye Sang *et al*., 2013; Jun Song *et al*., 2014; Sivaperumal *et al*., 2015).

After equilibrium has been reached (from a few minutes to several hours depending on the properties of the analytes, extraction process is then performed by depressing the needle of the fused silica fiber, through the rubber septum of the vialand the fiber immersed directly in the head space of the spiked sample, where the analytes are concentrated. Then, the needle is withdrawn from the sample vial, where the desired pesticides adsorbed to the coating on the fiber(figure2). Finally, the needle is introduced into the gas chromatograph injector port, where the adsorbed analytes are thermally desorbed and delivered to the GC column, or into the SPME/HPLC interface (Jolanta *et al*., 2011; Zi-Ye *et al* 2013).

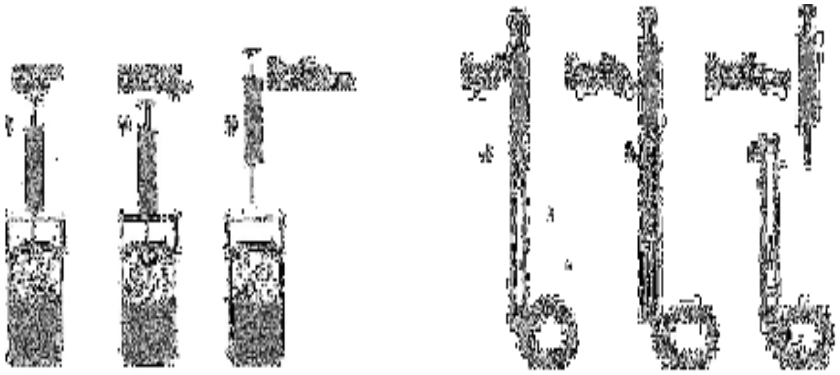

Figure 2; Steps in headspace analysis; 1-3 extraction and 4-6 desorption (Drawings courtesy of supelco, Inc)

Condition optimization of HS-SPME

Fiber coated selection

Selection of a suitable fiber coating (type and thickness) is the first step in headspace extraction and has a direct impact on the extraction efficiency. Typically itdepends on the characteristics of analyte (absorption or adsorption) from the sample matrix. Probably the most important feature determining the analytical performance of HS SPME is the type and thickness of the coating material. The HS-SPME fibers for fruit and vegetables are coated with a liquid polymer, solid sorbent or a combination of both (Kumar *et al*., 2008). Single-phase or absorption-based coatings such as nonpolar polydimethylsiloxane (PDMS) provide high capacity for the extraction of a polar (such as many pesticides compounds) from vegetables and fruits (Katoka*et al.,* 2000). The efficiency of PDMS and PDMS/ DVB for the extraction of pesticides residues in vegetables and fruit have investigated in many previous studies to have better performance characteristics of the extraction of wide range of pesticides (Bagheri *et al*, 2012; Lukman & Tan 2013).The efficiency and effectiveness of the fiber coating depend on the type, thickness and coating volume of the fiber (Lord & Pawliszyn, 2000). The polarity of the fiber coating may enhance the attraction of an analyte to that particular coating, but it is the thickness of the fiber that retains the analytes (Saraullo *et al*., 1997).

Agitation conditions

Sample agitation is another important parameter that has to be optimized. It can increase extraction efficiency, because, agitation of the sample assists the mass transport between the sample and the fiber coating and the time required to reach equilibrium can be reduced by using an agitation method (Pawliszyn, 2007; Chai and Tan , 2008;). The more effective the stirring, the shorter the extraction times required to achieve equilibrium or enhance sensitivity in pre-equilibrium conditions (Pawliszyn, 2007; 1997). The magnetic stir bar with a constant stirring rate is the most common agitation mechanism used inSPME for pesticide residues analysis in fruits and vegetables. It has been observed that the higher stirring rates cause the formation of air bubbles which can reduce the efficiency of extraction (Lukman and Tan 2013).

Sample volume

The optimization of sample volume is also an important factor that must be considered. The sample volume also determines the amount of the extracted analyte. The sensitivity of the method is directly dependent on the number of moles (n) extracted from the sample at equilibrium as described in equation 3 (Pawliszyn, 2007). The concentration of a compound in the headspace vapor phase is proportional to its original concentration in the sample and the reciprocal of the distribution constant. The amount of analytes with a high distribution constant is dependent on sample volume, while analytes with a low distribution constant are independent on sample volume. When dealing with complex multiphase systems typically encountered in HS-SPME mode of extraction, the situation is more complex since the analytes partition to the headspace phase as well as to the coating. Under these circumstances, volatile analytes prefer to condense in the headspace, resulting in a substantial loss of sensitivity when the headspace volume is very large. For this reason, the volume of the gaseous phase should be minimized for high sensitivity headspace extraction (Pawliszyn, 1997).

Headspace Volume

In HS_SPME , the total amount of analyte distributed among the fiber coating, the headspace and the sample. The smaller headspace is the higher the concentration of analyte in the headspace, so that the diffusion toward the fiber is enhanced. From a kinetic point of view, the smaller is the headspace volume/sample volume ratio, the faster is the analyte transport from the sample to the fiber (Colin 2012).

Extraction conditions

Extraction time is one of the most crucial steps in SPME method development. One of the most popular SPME approaches involves reaching a partitioning equilibrium between the sample matrix and extraction phase (Lord & Pawliszyn., 2000). The time between extraction and analysis should be

reduced in order to avoid analyte losses especially for more volatile compound. Furthermore, pesticides with high molecular masses are expected to require longer equilibrium times, due to their lower diffusion coefficients (the equilibrium time is inversely proportional to the diffusion coefficient) (Bras *et al*., 2000). Mohamed *et al*., 2014 found that, a 10 min of extraction with DVB/PDMS fiber coating is the optimal extraction time for the analysis of diazinon and chlorpyrifos by HS-SPME. The time of extraction (until equilibrium) may be decreased with use of any type of agitation method (stirring, ultrasonics, etc.) and in the case of perfect agitation, the extraction time depends only on the geometry of the fiber and the analyte diffusion coefficients in the fiber (Ulrich, 2000).

Optimization of the temperature is another parameter that can affect the extraction of the analyte in HS-SPME and that needs to be carefully considered when optimizing SPME methods. An extraction temperature increase causes an increase in mount of analyte in the vapor phase and hence gives improved sensitivity; with HS-SPME, and simultaneously a decrease in the distribution constant between the sample matrix and the fiber coating, which decreases analyte recovery at equilibrium, method sensitivity (Lord & Pawliszyn., 2000).

Previous studies, have investigated that, increasing the temperature improves the mobility of the pesticides through the liquid and gas phase and better recoveries were obtained up to 75 o C. At higher temperatures the ability of the SPME fiber to adsorb the tested pesticides begins to decrease. Moreover, extraction of pesticides at elevated temperatures decrease the extraction efficiency as a result of enhanced hydrolysis of OPPs (Chai and Tan , 2008; Dimitra and Triantafylloa, 2002, Lukman and Tan 2013).

Theoretically, manipulation of the pH of the sample can improve the sensitivity of the method and can change the solubility of analytes in water, thus affecting their extraction efficiency. This is related to the fact that unless ion-exchange coatings are used, SPME can only extract neutral nonionic species from water. By properly adjusting the pH, weak acids and bases can be converted to their neutral forms, in which case they can be extracted by the SPMEfiber. To make sure that at least 99% of the acidic compound is in the neutral form, the pH should be at least 2 units lower than the pKa of the analyte. For the basic analytes, the pH must be larger than pKa by 2 units

Salting out is also a parameter that can affect the extraction efficiency by altering the ionic strength and partition constant of the evaluated pesticides, because pesticides are more soluble in water and have a lower affinity for the fiber coating. Many subsequent research have reported that the amount of these pesticides extracted by the fiber can be increased and release more analyte into the headspace, if the solubility of the analytes in water is decreased by adding sodium chloride (Jeannot *et al*., 2010; Chai *et al*., 2010;Tan and Lukman 2012 Érica A et al., 2013)

Effects of Water and Organic Solvent

HS-SPME seems to be affected by the suspended matter and dissolved compound contained in vegetables and fruit such as sugar, pectin's, pigments, could adsorb the analytes, forming micelles and thus making it difficult for the analytes to reach the fiber (interfering with diffusion). Therefore, the addition of water and hydrophilic solvents on the samples would dilute the concentration of analyte from the matrix and then can promote the release of analyte from the matrix (aqueous phase) to the gaseous phase. Despite of that, adding water would cause decrease when the amount of water added exceeded a certain level. This discrepancy may probably be attributed to the different water solubility and vapor pressures of the pesticides. Several researches have demonstrated that the high concentration of organic solvent led to a significant decrease in extraction efficiency of analytes. Therefore, only a small amount of solvent was recommended for use as amendment (Ruey & Pei-Lin, 2001; Hernandez, *et al*., 2000; Dimitra 2003; Pawliszyn 1997)

Solution washing treatment

Washing with water or detergent can remove or reduce the level of pesticide residues in fruits and vegetables. The efficiency of the washing treatments on pesticide removal depends on the washing solution, the physicochemical properties of the pesticide, the surface area, the nature of the food, the length of time the pesticide is in contact with the food, and the formulation and application method of the pesticide. However, several studies that have examined the effects of washing on removing

pesticide residues and reported that, washing can be an effective method to reduce the intake of pesticide residues from these food samples(Cengiz, Certel, Karakas, & Gocmen, 2007; Kumari, 2008;Chai & Tan, 2010; Fadwa*et al*., 2014).

Conclusion

The determination of trace organic contaminations in various samples is an important aspect of interest. Headspace microextraction is a kind of SPME extraction, which is simple, fast and a solvent-minimized sample extraction procedure prior to a qualitative and quantitative analysis of pesticides in several of food samples. Most of SPME applications in pesticide residue analysis have been focused on liquid samples, such as drinking water, fruit and vegetable juices or soft drinks and the number of methods dealing with solid samples is limited. Disadvantageous of this method is related to the limitations of the current commercial devices to qualify multiclass pesticides determinations with a high efficiency. Coating of HS- devices became an important interest in laboratory researches. Current researches are focused on the improving the performance of HS-SPME for food and environmental samples analysis by introducing new coating phases to increase the selectivity, accuracy and efficiency of extraction. Most of the extracted analyst are detected using Gas Chromatography which is unsuitable for low thermal stability and non-volatile compounds.

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