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Review

Applications of solid-phase microextraction in food analysis

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Abstract

Food analysis is important for the evaluation of the nutritional value and quality of fresh and processed products, and for monitoring food additives and other toxic contaminants. Sample preparation, such as extraction, concentration and isolation of analytes, greatly influences the reliable and accurate analysis of food. Solid-phase microextraction (SPME) is a new sample preparation technique using a fused-silica fiber that is coated on the outside with an appropriate stationary phase. Analyte in the sample is directly extracted to the fiber coating. The SPME technique can be used routinely in combination with gas chromatography (GC), GC–mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC) or LC–MS. Furthermore, another SPME technique known as in-tube SPME has also been developed for combination with LC or LC–MS using an open tubular fused-silica capillary column as an SPME device instead of SPME fiber. These methods using SPME techniques save preparation time, solvent purchase and disposal costs, and can improve the detection limits. This review summarizes the SPME techniques for coupling with various analytical instruments and the applications of these techniques to food analysis.

Keywords: Reviews; Solid-phase microextraction; Headspace analysis; Direct immersion; Food analysis; Aroma compounds; Pesticides

Contents

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1. Introduction

Food analysis is important for the evaluation of nutritional value, the quality control of fresh and processed products, and the monitoring of food additives and other toxic contaminants. For example, flavor, being a combination of taste and olfaction, is a crucial factor in consumer acceptance of foods [1]. In general, flavor is sensitive to compositional alterations. In the case of fruit flavor, the volatile aromatic compounds are produced through metabolic pathways during ripening, harvest, post-harvest and storage, and their production depends on many factors related to the species, variety and type of technological treatment [2]. Therefore, it is important to know the typical chromatographic pattern of a fresh product and the modified pattern during processing or storage in order to identify changes in the volatile composition. In addition, monitoring of adulteration is vital to the industry as well as the health of the consumer. Foodstuffs are prone to deterioration by light, heat, oxidation and contamination from the container during storage. Many protein-containing foodstuffs are known to release ammonia and amines with spoilage through microbial deamination and decarboxylation of amino acids [3]. Early detection of the vapors from foodstuffs can be used to prevent widespread infections in stored food. Furthermore, carcinogenic *N*-nitrosamines [4–6] and heterocyclic amines [7–9] are known to be produced in the human diet. *N*-Nitrosamines are formed by the reaction of precursor secondary amines with nitrosating agents such as nitrite or nitrate in foods, and heterocyclic amines are formed during cooking of protein-containing foodstuffs. These amines are also produced during combustion processes [10,11]. Therefore, monitoring of these toxic compounds formed unintentionally in foods is very important for human health risk assessment. On the other hand, pesticides such as fungicides, insecticides and herbicides are widely used for agricultural and non-agricultural purposes throughout the world. Consequently, pesticide residues are currently detected in various foodstuffs, and cases of intoxication due to consumption of contaminated food products occurs from time to time. Analysis of pesticide residues is essential for food monitoring.

Although various methods, using highly efficient instruments such as gas chromatography (GC), high-performance liquid chromatography (HPLC) and their combination with mass spectrometry (MS), have been developed for food analysis, most analytical instruments cannot handle the sample matrices directly. In general, the analytical method involves processes such as sampling, sample preparation, separation, detection and data analysis, and more than 80% of the analysis time is spent on sampling and sample preparation steps such as extraction, concentration, fractionation and isolation of analytes. Therefore, it is not an exaggeration to say that the choice of an appropriate sample preparation method greatly influences the reliable and accurate analysis of food. In order to achieve a practical and reliable method for the analysis of complex matrices such as food samples, several sample preparation methods have been developed including steam distillation, extraction with organic solvents, surfactants and supercritical fluids, and solid-phase extraction. However, these methods involve some drawbacks, such as being tedious and time-consuming, and requiring large volumes of samples and solvents. For example, a long sample preparation time limits the number of samples and multi-step procedures are prone to loss of analytes. Furthermore, use of a large amount of

solvent influences trace analysis, and imposes environmental pollution, health hazard to laboratory personnel and extra operational costs for waste treatment. On the other hand, headspace sampling and purge-and-trap methods are simple, less laborious, faster and solvent-free techniques. Nevertheless, these methods have some disadvantages, such as the risk of cross-contamination and leaks, and the use of high flow-rates that can sometimes be incompatible with on-line operation.

Solid-phase microextraction (SPME), developed by Pawliszyn and co-workers in 1990 [12,13], is a new sample preparation technique using a fused-silica fiber that is coated on the outside with an appropriate stationary phase. Analyte in the sample is directly extracted and concentrated to the fiber coating. The method saves preparation time, solvent purchase and disposal costs, and can improve the detection limits [13–17]. It has been used routinely in combination with GC and GC–MS, and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semi-volatile organic compounds from environmental, biological and food samples [13–26]. SPME was also introduced for direct coupling with HPLC and LC–MS in order to analyse weakly volatile or thermally labile compounds not amenable to GC or GC–MS [17,22,26]. The SPME–HPLC interface equipped with a special desorption chamber is utilized for solvent desorption prior to HPLC analysis instead of thermal desorption in the injection port of the GC. Moreover, a new SPME–HPLC system known as in-tube SPME was recently developed using an open tubular fused-silica capillary column as the SPME device instead of the SPME fiber [27–33]. In-tube SPME is suitable for automation, and automated sample handling procedures not only shorten the total analysis time, but also usually provide better accuracy and precision relative to manual techniques.

In this article, we review recent advances in SPME techniques coupled with various analytical instruments and the applications of these techniques to food analysis. The review consists of two main parts. In the first part (Section 2), general aspects of SPME techniques are described for the selection of extraction mode and optimization of the SPME process which should be considered when developing SPME methods. In the second part (Section 3), applications of the SPME methods in food analysis are considered according to the food composition and contaminants. The details of SPME and its application are also summerized in SPME books [17,26] and well-documented reviews [13–16,18–25,28,29].

2. Solid-phase microextraction

2.1. Solid-phase microextraction device

The fiber SPME device consists of fiber holder and fiber assembly with built-in fiber inside the needle which looks like a modified syringe (Fig. 1). The fiber holder consists of a spring-loaded plunger, a stainless-steel barrel and an adjustable depth gauge with needle, and is designed to be used with reusable and replaceable fiber assemblies. The fused-silica fiber is coated with a relatively thin film of several polymeric stationary phases. This film acts like a ‘sponge’, concentrating the organic analytes on its surface during absorption or adsorption from the sample matrix. As shown in Fig. 2, seven kinds of fibers are commercially available. Stationary phases are immobilized by non-bonding, bonding, partial crosslinking or high crosslinking. Non-bonded phases are stable with some water-miscible organic solvents, but slight swelling may occur when used with non-polar solvents. Bonded phases are stable with all organic solvents except for some non-polar solvents. Partially crosslinked phases are stable in most water-miscible organic solvents and some non-polar solvents. Highly crosslinked phases are equivalent to partially crosslinked phases, except that some bonding to the core has occurred. Advantages of these phases for SPME applications are similar to the advantages in their use as GC stationary phases.

On the other hand, open tubular GC capillary columns are very stable and available as an SPME device in in-tube SPME coupled with HPLC or LC–MS. Although applications of GC capillary columns in in-tube SPME have not yet been investigated sufficiently, their properties are considered to be similar to those as for their use in GC analysis.

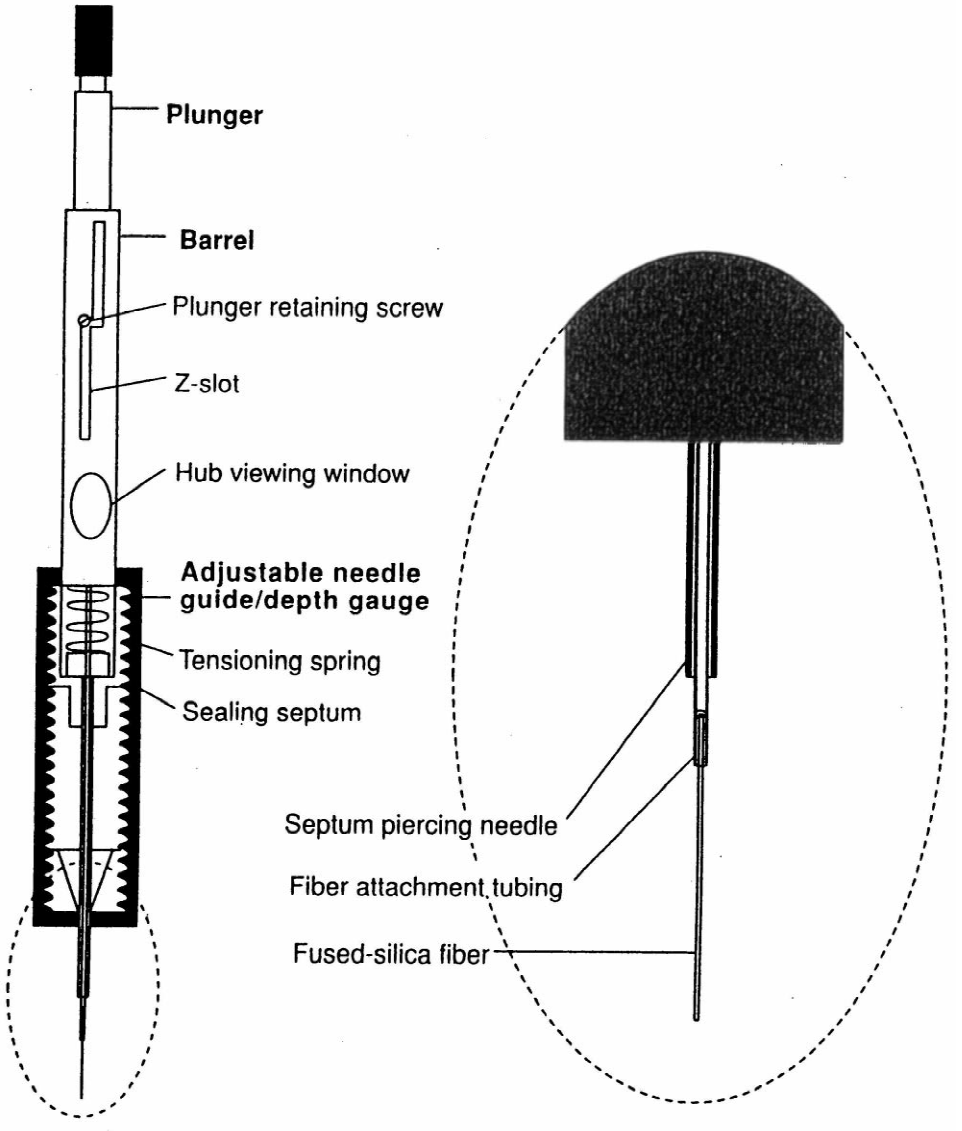

Fig. 1. Commercial SPME device made by Supelco. Reproduced from Ref. [13].

2.2. Solid-phase microextraction process

2.2.1. Fiber solid-phase microextraction

The process of fiber SPME is illustrated in Fig. 3. The sample is placed in a vial, which is sealed with a septum-type cap. The fiber should be cleaned before analyzing any sample in order to remove contaminants which give a high background in the chromatogram. Cleaning can be done by inserting the fiber in an auxiliary injection port or a syringe cleaner. When the SPME needle pierces the septum and the fiber is extended through the needle into the sample, the target analytes partition from the sample matrix into the stationary phase. Although SPME has a maximum sensitivity at the partition equilibrium, a proportional relationship is obtained between the amount of analyte adsorbed by the SPME fiber and its initial concentration in the sample matrix before reaching partition equilibrium [34,35]. Therefore, full equilibration is not necessary for quantitative

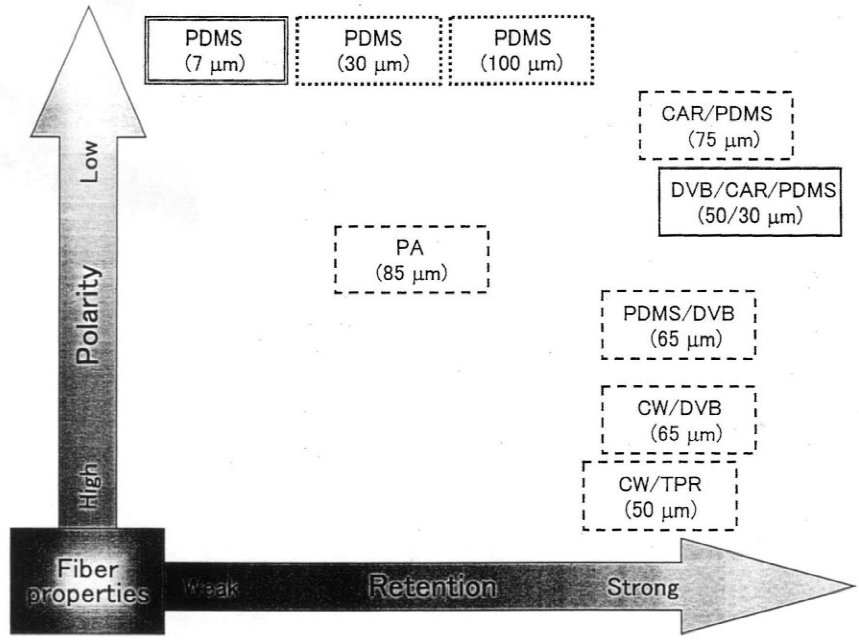

Fig. 2. Properties of commercially available SPME fibers. Bonded, non-bonded, partially crosslinked, highly crosslinked.

analysis by SPME. Two types of fiber SPME techniques can be used to extract analytes: headspace (HS)-SPME and direct immersion (DI)-SPME. In HS-SPME, the fiber is exposed in the vapor phase above a gaseous, liquid or solid sample. In DI-SPME, the fiber is directly immersed in liquid samples. Agitation of the sample is often carried out with a small stirring bar to increase the rate of equilibration. After a suitable extraction time, the fiber is withdrawn into the needle, the needle is removed from the septum and is then inserted directly into the injection port of the GC or the desorption chamber of the SPME–HPLC interface. HS- and DI-SPME techniques can be used in combination with any GC, GC–MS, HPLC and LC–MS system. The desorption of analyte from the fiber coating is performed by heating the fiber in the injection port of a GC or GC–MS, or by loading solvent into the desorption chamber of the SPME–HPLC interface, and then the analytes are transferred directly to the column for analysis. The HPLC interface consists of a six-port injection valve and a special desorption chamber, and requires solvent desorption of analyte prior to HPLC or LC–MS analysis. The desorption chamber is placed in the position of the injection loop. After sample extraction, the fiber is inserted into the desorption chamber at the 'load' position under ambient pressure. When the injector is changed to the 'inject' position, the mobile phase contacts the fiber, desorbs the analytes, and delivers them to the HPLC column for separation.

2.2.2. In-tube solid-phase microextraction

In-tube SPME using an open tubular capillary column as the SPME device was developed for coupling with HPLC or LC–MS. It is suitable for automation, and can continuously perform extraction, desorption and injection using a standard autosampler. With the in-tube SPME technique, organic compounds in aqueous samples are directly extracted from the sample into the internally coated stationary phase of a capillary column, and then desorbed by introducing a moving stream of mobile phase or static desorption solvent when the analytes are more strongly absorbed to the capillary coating. A schematic diagram of the automated in-tube SPME–LC–MS system is illustrated in Fig. 4. The capil-

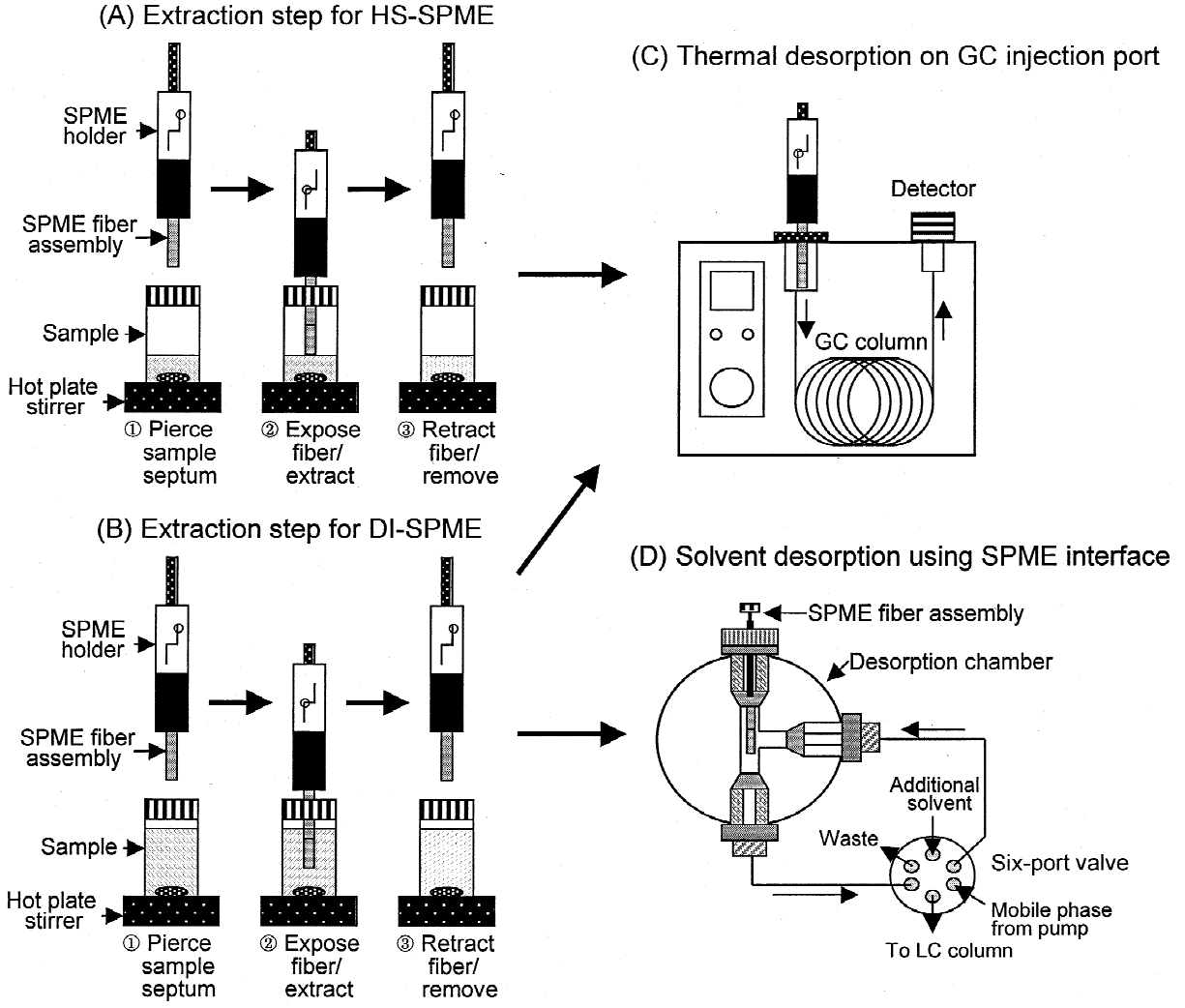

Fig. 3. Extraction process by headspace and immersion fiber SPME, and desorption systems for GC and HPLC analyses.

laries selected have coatings similar to those of commercially available SPME fibers. The capillary column is placed between the injection loop and the injection needle of the HPLC autosampler. While the injection syringe repeatedly draws and ejects samples from the vial under computer control, the analytes partition from the sample matrix into the stationary phase until equilibrium is reached. Subsequently, the extracted analytes are directly desorbed from the capillary coating by mobile phase flow or by aspirating a desorption solvent. The desorbed analytes are transported to the HPLC column for separation, and then detected with UV or mass-selective detection (MS).

2.2.3. Comparison of solid-phase microextraction techniques

For the GC and GC–MS analysis of volatile compounds in a complex sample matrix, fiber HS-SPME is a more appropriate sampling mode. In this SPME technique, the fiber is placed in the vapor phase of the liquid or solid sample and is not in contact with the sample, and therefore has a longer lifetime. On the other hand, in the DI-SPME sam-

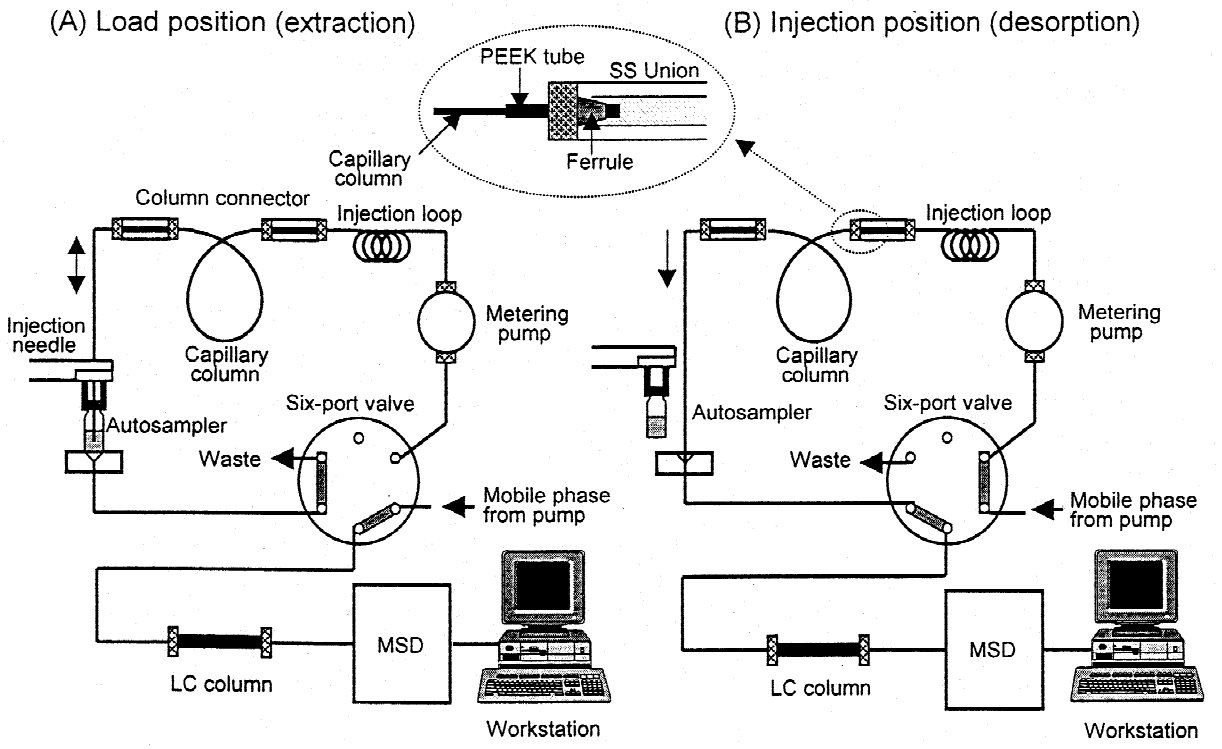

Fig. 4. Schematic diagram of the in-tube SPME–LC–MS system. (A) Load position (extraction phase); (B) injection position (desorption phase).

pling mode, the fiber is directly inserted into the sample so that its lifetime decreases. This decrease is caused by the influence of the addition of salts with supersaturation, pH adjustment or coexisting compounds of the complex matrix. Another problem is caused by the relatively high concentration of ethanol or any other compounds in the samples such as alcoholic beverages, which interfere with the extraction of the analytes. These problems will be encountered in both techniques (HS-SPME and DI-SPME).

Although the theories of fiber and in-tube SPME methods are similar, the significant difference between these methods is that the extraction of analytes is performed on the outer surface of the fiber for fiber SPME and on the inner surface of the capillary column for in-tube SPME. Therefore, with the in-tube SPME method it is necessary to prevent plugging of the capillary column and flow lines during extraction, and typically particles must be removed from samples by filtration before extraction. On the other hand, with the fiber SPME method it is not necessary to remove particles before extraction, because they can be removed by washing the fiber with water before insertion into the desorption chamber of the SPME–HPLC interface. However, the fibers should be carefully handled because they are fragile and can easily be broken, and the fiber coating can be damaged during insertion and agitation. Furthermore, high-molecular-mass compounds such as proteins can adsorb irreversibly to the fiber, thus changing the properties of the stationary phase and rendering it unusable. Another significant difference between in-tube SPME and manual fiber SPME–HPLC is the possible decoupling of desorption and injection with the in-tube SPME method. In the fiber SPME method, analytes are desorbed during injection as the mobile phase passes over the fiber. On the other hand, in the in-tube SPME method, analytes are desorbed by mobile phase or by aspirating a desorption solvent from a second vial, and then transfered to the HPLC column by mobile phase

flow. The fiber SPME–HPLC method also has the advantage of eliminating the solvent front peak from the chromatogram, but peak broadening is sometimes observed because analytes can be slow to desorb from the fiber. With the in-tube SPME method, peak broadening is comparatively small because analytes are completely desorbed before injection.

2.3. Optimization of solid-phase microextraction conditions

2.3.1. Selection of extraction modes

In fiber SPME, two main types of extraction modes, HS- and DI-SPME, are available. Extraction efficiency with each technique depends on the properties of the analytes and the sample matrix. Particularly, non-volatile compounds in the sample are concentrated and remain on the fiber, and can thus reduce the life-time of the fiber and the reproducibility of extraction. Therefore, the extraction technique should be selected relative to the nature of the sample matrix. In general, DI-SPME is more sensitive than HS-SPME for analytes predominantly present in a liquid. However, HS-SPME exhibits lower background than DI-SPME, and is suitable for the extraction of more-volatile analytes in most gaseous, liquid and solid samples. DI-SPME is suitable for the extraction of semi- or less-volatile analytes in liquid samples. Fiber SPME techniques in combination with GC or GC–MS are unsuitable for the extraction of less-volatile or thermally labile compounds. On the other hand, fiber SPME techniques in combination with HPLC or LC–MS can be used for the extraction of less-volatile or thermally labile compounds. Although the in-tube SPME technique is also available for these compounds, particles must be removed from samples by filtration prior to extraction in order to prevent plugging of the capillary column and flow lines during extraction. Therefore, in-tube SPME is preferred for the extraction from clean samples.

2.3.2. Selection of fiber coatings

As shown in Fig. 2, several types of coating fibers are currently available for the extraction of analytes. The affinity of the fiber for an analyte depends on the principle of ‘like dissolves like’, and coating fibers having different properties or thickness are selected in accordance with different compounds. For example, non-polar polydimethylsiloxane (PDMS) fiber is preferred for the extraction of non-polar analytes such as many volatile flavor compounds. However, it can also be applied successfully to more-polar compounds, particularly after optimizing extraction conditions. PDMS is very rugged and is able to withstand high injector temperatures, up to about 300°C. In general, volatile compounds require a thick polymer coat and a thin coat is effective for semi-volatile compounds. Furthermore, fibers coated with thicker films require a longer time to achieve extraction equilibrium, but might provide higher sensitivity due to the greater mass of the analytes that can be extracted. The more-polar polyacrylate (PA) fiber is preferred for the extraction of more-polar analytes, especially phenols and alcohols. Mixed coating fibers, containing divinylbenzene (DVB) copolymers, templated resin (TPR) or Carboxen (CAR: a porous activated carbon support), increase retention capacity due to the mutually potentiating effect of adsorption and distribution to the stationary phase. PDMS–DVB, CAR–DVB, Carbowax (CW: polyethylene glycol)–DVB and CW–TPR can be used for the extraction of volatile low-molecular-mass and polar analytes. CAR–PDMS fiber shows better extraction efficiency than a 100 μm PDMS fiber and similar fibers, but repeatability is poorer and equilibrium more time-consuming. Details of the properties of commercial SPME fiber coatings are also reviewed by Mani [36].

2.3.3. Optimization of extraction

In fiber SPME, the amount of analyte extracted onto the fiber depends not only on the polarity and thickness of the stationary phase, but also the extraction time and the concentration of analyte in the sample. Extraction of analyte is also typically improved by agitation, addition of salt to the sample, changing the pH and temperature. Extraction time is mainly determined by the agitation rate and the partition coefficient of the analyte between the fiber coating and sample matrix. Although SPME has a maximum sensitivity at the equilibrium point, full equilibration is not necessary for accurate and precise analysis by SPME because of the linear relationship between the amount of analyte adsorbed by the SPME fiber and its initial concentration in the

sample matrix in non-equilibrium conditions [34,35]. However, in such cases, the extraction time and mass transfer conditions have to be carefully matched across runs. Magnetic stirring is widely used for agitation in both HS- and DI-SPME. Agitation accelerates the transfer of analytes from the sample matrix to the coating fiber. Although the equilibration time progressively decreases with increasing agitation rate, faster agitation tends to be uncontrollable and the rotational speed might cause a change in the equilibration time and poor measurement precision. The extraction efficiency is also improved by adding soluble salts to the sample. Sodium chloride, sodium hydrogencarbonate, potassium carbonate and ammonium sulphate are generally used for this purpose. In principle, supersaturation of the sample with salts is most effective for the extraction of analytes onto the fiber due to the salting-out effect. However, the addition of salts is preferred for HS-SPME because fiber coatings are prone to damage during agitation by DI-SPME. The form of analytes present in the sample mainly depends on the pH of the matrix relative to the analyte and influences the extraction efficiency. In general, the sample is acidified for the extraction of acidic analytes and is made alkaline for the extraction of basic analytes. Furthermore, a volatile acid or base is used for DI-SPME, and a non-volatile acid or base is used for HS-SPME. In DI-SPME, contact of the fiber with high and low pH is prone to damage the coating. In order to increase the concentration of the analytes in the gaseous phase in HS-SPME, the sample is usually heated. An increase in extraction temperature causes an increase in extraction rate, and simultaneously a decrease in the distribution constant. Therefore, an adequate temperature which provides satisfactory sensitivity and extraction rate should be used. For accurate and precise analysis, a consistent extraction time and other SPME parameters are essential. Another critical point is that the vial size and sample volume should be the same during analysis by SPME.

In in-tube SPME, the amount of analyte extracted by the stationary phase of the capillary column depends on the polarity of the capillary coating, the number and volume of draw/eject cycles and the sample pH. A capillary column 50–60 cm long is optimal for extraction. Below this length, extraction efficiency is reduced, and above this length, peak broadening is observed. In general, complete equilibrium extraction is not obtained for any of the analytes, because the analytes are partially desorbed into the mobile phase during each eject step. The target analytes with higher K values need longer equilibration times. Although an increase in the number and volume of draw/eject cycles can enhance the extraction efficiency, peak broadening is often observed in this case. The optimal flow-rate of draw/eject cycles is 50–100 μL/min. Below this rate, extraction requires an inconveniently long time, and above this rate, bubbles form inside the capillary and extraction efficiency is reduced.

2.3.4. Optimization of desorption

Efficient thermal desorption of analyte in a GC injection port is dependent on the analyte volatility, the thickness of the fiber coating, injection depth, injector temperature and exposure time. A narrow-bore GC injector insert is required to ensure high linear flow and the fiber needs to be exposed immediately after the needle is introduced into the insert. Needle exposure depth should be adjusted to place the fiber in the center of the hot injector zone. Most injectors in modern GC instruments are suitable for direct introduction of the fiber. The liner volume affects the shape of the chromatographic peaks, for example larger volumes cause peak tailing. Split/splitless injectors should be operated in the splitless mode. Generally, the optimal desorption temperature is approximately equal to the boiling point of the least volatile analyte. To prevent peak broadening, the initial GC column temperature should be kept low, or even cooled (cryofocusing). Thus, concentration of analytes at the head of the column is achieved. The desorption time depends on the injector temperature and the linear flow-rate around the fiber.

In solvent desorption using the SPME–HPLC interface, two desorption techniques can be used to remove the analytes from the fiber: dynamic desorption and static desorption. In dynamic desorption, the analytes can be removed by a moving stream of mobile phase. When the analytes are more strongly adsorbed to the fiber, the fiber can be soaked in mobile phase or other strong solvent for a specified time by static desorption before injection onto the

HPLC column. In each desorption technique, rapid and complete desorption of analytes using minimal solvent is important for optimizing the SPME–HPLC or SPME–LC–MS methods.

On the other hand, the in-tube SPME technique does not need a special SPME–HPLC interface for desorption of analytes. The analytes extracted onto the capillary coating can be easily desorbed by a moving stream of mobile phase or an additional desorption solvent when the analytes are more strongly adsorbed to the capillary coating. Carryover in the in-tube SPME method is lower or eliminated in comparison with the fiber SPME method.

3. Applications in food analysis

SPME methods applied to the analysis of various components and contaminants in food samples are listed in Tables 1 and 2, according to the compound type, sample type, extraction device, extraction mode and associated analytical technique. The HS-SPME methods using 100 μm PDMS fibers in combination with GC or GC–MS are widely used for the analysis of various foods. The SPME methods coupled with HPLC or LC–MS are used for the analysis of less volatile or thermally labile compounds. Recently, some of these food analysis methods were also reviewed by Pawliszyn [17,26], Stevenson et al. [18], Harmon [19], and Mariaca et al. [20].

3.1. Flavors

Aroma and flavor are one of the most important quality criteria of fresh and processed foods, and both qualitative and quantitative information is desired for characterizing aroma-producing compounds. Aroma and flavor compounds usually occur at extremely low concentrations in complex food matrices and consist of a wide range of organic compounds possessing various polarities and reactivities. Fortunately, most aroma and flavor compounds are volatile, and procedures for their isolation from food samples have been established by taking advantage of this volatility. However, commonly used sampling methods, such as steam distillation, solvent extraction, trapping of the volatiles on adsorbents, or combinations of these methods with other techniques, require a long time prior to chromatographic separation. Furthermore, artifacts may be introduced from impurities in the solvents or through decomposition of the matrix or of the flavor compounds themselves during sampling with these techniques. The volatile aroma and flavor compounds are also analysed using either direct HS or dynamic HS purge-and-trap methods. While direct HS analysis is largely confined to higher concentration samples, purge-and-trap sampling can enhance sensitivity by enriching volatile components on a polymer bed. However, this technique is expensive, time-consuming and prone to loss analytes from the sample matrix. Ideally, sample preparation techniques should be fast, easy to use, inexpensive and compatible with a range of analytical instruments. SPME approaches this ideal and is applied to the analyses of various aroma and flavor compounds in food samples (Table 1).

3.1.1. Vegetables and fruits

SPME methods combined with GC–flame ionization detection (FID) and GC–MS are reported for the analysis of various volatile compounds in vegetables and fruits. Pelusio et al. [37] detected volatile organic sulphur compounds such as dimethyl mono-, di- and trisulphide and 1,2,4-trithiolane in aromas of truffles by HS-SPME–GC–ion trap MS (IT-MS). Jarvenpaa et al. [38] also identified a variety of volatile sulphur compounds in onions by HS-SPME–GC–MS using a PDMS fiber. The major sulphur constituents in onion aromas were diprop(en)yl disulphides. Essential oils are complex mixtures of fragrance and flavor substances originating in plants. Coleman and Lawson [39] applied the SPME technique for testing the origin and purity of menthol samples by HS-SPME–GC–MS. Among several coating fibers tested, CAR–PDMS fiber was most effective for the extraction of menthol. Miller et al. [40] developed an HS-SPME–GC–FID method for the classification of the botanical origin of cinamon. Volatile compounds in several fruits such as apples [41–44] and strawberry [40,45,46] were also analysed using fiber SPME techniques. Verhoeven et al. [42] used a PA fiber for the extraction of fruit flavors by DI-SPME. The artifact Maillard products produced from high concentrations of carbohydrates and amines in samples during thermal desorption and

Table 1
SPME methods for the analysis of flavor compounds in food samples

Analyte	Food sample	SPME conditions					Desorption temp. (°C)	Detection[c]	Ref.
		Fiber[a]	Extraction[b]	Temp. (°C)	Time (min)	Salt			
Vegetables and fruits									
Sulphur aroma	Truffle	95 μm PDMS	HS	80	30		200	GC–IT-MS	[37]
Sulphur volatiles	Onion	100 μm PDMS	HS		1		35	GC–MS	[38]
Menthol	Plant	65 μm CAR–PDMS	HS	50	10		250	GC–MS	[39]
Semi-volatiles	Cinnamon	100 μm PDMS	HS	70	5		275	GC–FID	[40]
Volatiles	Apple	100 μm PDMS	HS		5–90		200	GC–FID	[41]
Volatiles	Strawberry	85 μm PA	DI		0.5		250	GC–MS	[42]
Volatiles	Apple	100 μm PDMS	HS		2–30		250	GC–TOF-MS	[43]
Volatiles	Apple	100 μm PDMS	HS		20		275	GC–MS	[44]
Volatiles	Tomato Strawberry	65 μm PDMS–DVB	HS	23	12		200	GC–TOF-MS	[45]
Volatiles	Fruits	100 μm PDMS	HS	60	30		200	GC–FID	[46]
Juices and other soft drinks									
Volatiles	Fruit juice	85 μm PA	HS		40–60	NaCl	250	GC–FID	[47]
Volatiles	Beverages	100 μm PDMS	DI, HS		2, 60		200	GC–MS	[48]
Aroma volatiles	Cola	100 μm PDMS 85 μm PA	HS	60	30		250	GC–MS	[49]
Volatiles	Coffee	7, 100 μm PDMS	HS, DI	60, 40	120, 30		250	GC–FID	[50]
Orange flavor	Orange juice	100 μm PDMS	HS	40, 60	30, 20		220	GC–MS	[51]
Volatiles	Strawberry juice	100 μm PDMS	HS	50	5		250	GC–FID	[52]
Volatiles	Tomato juice	65 μm CW–DVB	HS	35	30	$CaCl_2$	260	GC–MS	[53]
Volatiles	Beverages	100 μm PDMS 65 μm PDMS–DVB	HS	49	30	NaCl	220	GC–IT-MS	[54]
Caffeine, etc.	Beverages	Uncoated	DI		5		300	GC–MS	[55]
Caffeine	Beverages	100 μm PDMS	DI		5		250	GC–MS	[56]
Alcohol beverages									
Alcohols, esters	Beer	85 μm PA	HS	50	60		240	GC–FID	[57]
Volatiles	Malt beverage	100 μm PDMS	HS	45	45–60		200	GC–FID	[58]
Bouquet	Wine	85 μm PA	HS, DI	60	15	NaCl	220	GC–FID	[59–61]
Sulphur aroma	Wine	100 μm PDMS 85 μm PA	HS	30	15		250 275	GC–FPD	[62]
Sulphur aroma	Wine	75 μm CAR–PDMS	HS	25	30		300	GC–FPD	[63,64]
Aroma volatiles	Wine	100 μm PDMS 85 μm PA	HS DI	22	10 60		250	GC–MS	[65,66]
Diacetyl	Wine	60 μm CW–DVB	HS	40	10	NaCl	200	GC–MS	[67]
Aroma volatiles	Wine	100 μm PDMS	HS	20	15	NaCl	250	GC–O	[68]
Esters	Vodka, rum	100 μm PDMS	DI	Room temp.	30		250	GC–MS	[69]
Dairy products									
Volatiles	Cheese	100 μm PDMS 85 μm PA	HS	60	20		220	GC–FID	[70]
Aroma	Cheese	85 μm PA	HS	40	30		2	GC–MS	[71]
Aroma	Cheese	100 μm PDMS 85 μm PA	HS, DI		4		200	GC–FID	[72]
Fatty acids, lactones	Cheese	85 μm PA	HS	60	30		250	GC–FID	[73]
Volatiles	Cheese	65 μm PDMS–DVB	HS		40		220	GC–FID	[74]

Table 1. Continued

Analyte	Food sample	SPME conditions					Desorption temp. (°C)	Detection[c]	Ref.
		Fiber[a]	Extraction[b]	Temp. (°C)	Time (min)	Salt			
Volatiles	Whey protein	100 μm PDMS	HS	23	120		220	GC–MS	[75]
Volatiles	Whey protein	85 μm PA		40	30		250	GC–MS	[76]
Volatiles	Whey protein	65 μm PDMS–DVB	HS	50	30		250	GC–MS	[77]
Volatiles	Whey protein	100 μm PDMS 65 μm CW–DVB	HS	40	30		220	GC–MS	[78]
Others									
Flavor ingredients	Beverages, chewing gum	100 μm PDMS	DI	100	10	Na_2SO_4	260	GC–MS	[79]
Menthole, menthone	Candy, tea, etc.	7 μm PDMS 10 μm PDES	HS	30	15		200	GC–FID	[80]
Aroma	Spaghetti	65 μm CW–DVB	DI		10	NaCl	200	GC–FID	[81]
Aroma	Rendered sheep fat	100 μm PDMS	HS		30		200	GC–FID	[74]
Volatiles	Meat	100 μm PDMS	HS	60	60		220	GC–MS	[82]

[a] PDMS, polydimethylsiloxane; PDES, ethoxypolydimethylsiloxane; PA, polyacrylate; CAR, Carboxen; CW, Carbowax; DVB, divinylbenzene.

[b] HS, headspace; DI, direct immersion.

[c] FID, flame ionization detection; FPD, flame photometric detection; IT-MS, ion trap mass spectrometry; TOF-MS, time-of-flight mass spectrometry; O, olfactometry.

remaining on the surface of the fiber were significantly reduced by rinsing the fiber with water prior to thermal desorption. Song et al. [43,45] examined an HS-SPME technique coupled with GC–time-of-flight MS (TOF-MS) for rapid sampling, separation and detection of fruit flavor volatiles using PDMS and PDMS–DVB fibers. Typical analysis times for complex matrix mixtures were 2–5 min as compared with 20–60 min required for purge-and-trap analyses. Ibanez et al. [46] developed a method for the analysis of volatile compounds in fruits by HS-SPME–GC–FID. Fig. 5 shows typical chromatograms obtained from berries, banana and mango. A variety of alcohols, esters and terpenic compounds were detected in these samples. This method can be used for fruit characterization and analyzing changes in key flavor compounds during processing or storage of different fruits.

3.1.2. Juices and other soft drinks

Steffen and Pawliszyn [47] developed a HS-SPME–GC–FID method for the analysis of 17 common flavor volatile compounds in fruit juices. PA fiber was found to extract more of the target flavor volatiles than the commonly used PDMS fiber, and addition of salt to the sample enhanced the amount of analytes extracted into both fiber coatings. The HS-SPME technique was also useful for the analysis of other fruit flavors and aroma volatiles in soft drinks [48–54]. The characteristic aroma in fruit is mainly determined by a complex mixture of aldehydes, alcohols, esters and sulphur compounds. Servili et al. [53] detected 190 volatile compounds in tomato juice by HS-SPME–GC–MS. Yang and Peppard [48] compared HS- and DI-SPME techniques for the sampling of 25 common flavor compounds in spiked water. The DI-SPME sampling was more effective for the extraction of most compounds than the HS-SPME sampling. Furthermore, the sensitivity of DI-SPME was comparable to or higher than that of conventional solvent extraction for most esters, terpenoids and lactones in fruit juice beverage (Fig. 6). The use of a GC injector liner with small diameter improved resolution and obviated the need for cryogenic focusing for thermal desorption following SPME. In addition to beverage analysis, the SPME method was applied to monitor flavor compounds in ground coffee and butter flavored vegetable oil. Hawthorne et al. [55] and Yang et al. [56] also developed a DI-SPME–GC–MS

Table 2
SPME methods for the analysis of off-flavors and contaminants in food samples

Analyte	Food sample	SPME conditions					Desorption temp. (°C)	Detection[c]	Ref.
		SPME device[a]	Extraction[b]	Temp. (°C)	Time (min)	Salt			
Off-flavors									
Volatiles	Sunflower oil	100 μm PDMS	HS	40	45		275	GC–IT-MS	[83,84]
Oxidized volatiles	Vegetable oil, meat	7, 100 μm PDMS 85 μm PA	HS	35	30		220	GC–MS	[85]
Oxidized products	Milk	75 μm CAR–PDMS	HS	45	12–15	NaCl	250	GC–MS	[86,87]
Cork taint	Wine	100 μm PDMS	HS, DI	20	20	NaCl	250	GC–MS	[88]
Cork taint	Wine	100 μm PDMS	HS	40	25		260	GC–MS	[89]
Geosmin, etc.	Catfish	100 μm PDMS	DI		25	NaCl	250	G–IT-MS	[90]
Methylisoborneol	Catfish	100 μm PDMS	HS	40	15	NaCl	270	GC–MS	[74,91]
Amine molodors	Spoiled foods	65 μm PDMS–DVB	HS	25	5		270	GC–MS	[92]
Sulphur volatiles	Butter	85 μm PA	HS	30–35	10		200	GC–MS	[93]
Pesticides and other agrochemicals									
Herbicides	Wine	65 μm PA	HS		50	NaCl	230	GC–MS GC–NPD	[94]
Pesticides	Wine	30, 100 μm PDMS	DI		30		250	GC–MS	[95]
Methylisothiocyanate	Wine	65 μm CW–DVB	HS		30	NaCl	230	GC–FID GC–NPD	[96]
Pesticides	Wine	100 μm PDMS	DI		30	$MgSO_4$	250	GC–MS	[97]
Pesticides	Honey	100 μm PDMS	DI	30	120	NaCl	260–270	GC–ECD	[98]
Pesticides	Potato, honey	100 μm PDMS	DI	25	50		250	GC–MS	[99]
Pesticides	Vegetable	100 μm PDMS	HS	25	5		250	GC–MS	[100]
Pesticides	Strawberry	100 μm PDMS	DI	Room temp.	45		270	GC–MS	[101]
Pesticides	Fruit juices	100 μm PDMS	DI	25	30	NaCl	260	GC–MS	[102]
Organophosphorous pesticides	Vegetables, fruits	100 μm PDMS	DI		90		270	GC–FPD	[103]
Organophosphorous pesticides	Fruits fruit juice	100 μm PDMS	DI	Room temp.	20		250	GC–FPD	[104]
Other contaminants									
Halogenated volatiles	Beverages	100 μm PDMS	HS		30	NaCl	250	GC–ELCD	[105,106]
MMT[d]	Beverages	100 μm PDMS	HS	25	35	NaCl	275	GC–AAS	[107]
Phenol	Honey	85 μm PA	HS	45	15	Na_2SO_4	250	GC–FID	[108]
Tetracycline antibiotics	Milk	50 μm CW–TPR	DI	65	15	KCl		LC–MS	[109]
Aromatic amines	Milk	65 μm PDMS–DVB	HS	45	15	NaCl	220	GC–MS	[110]
Nitrosamines	Smoked ham	85 μm PA	HS	80	60	NaCl	220	GC–TEA	[111]
Heterocyclic amines	Meat	Omegawax 250	IT		10			LC–MS	[31]

[a] PDMS, polydimethylsiloxane; PA, polyacrylate; CAR, carboxen; CW, carbowax; DVB, divinylbenzene; TPR, templated resin.
[b] HS, headspace; DI, direct immersion; IT, in-tube.
[c] FID, flame ionization detection; FPD, flame photometric detection; ECD, electron-capture detection; ELCD, electrolytic conductivity detection; NPD, nitrogen–phosporous detection; TEA, thermal energy analysis; AAS, atomic absorption spectrometry; IT-MS, ion trap mass spectrometry.
[d] MMT, methylcyclopentadienyl manganese tricarbonyl.

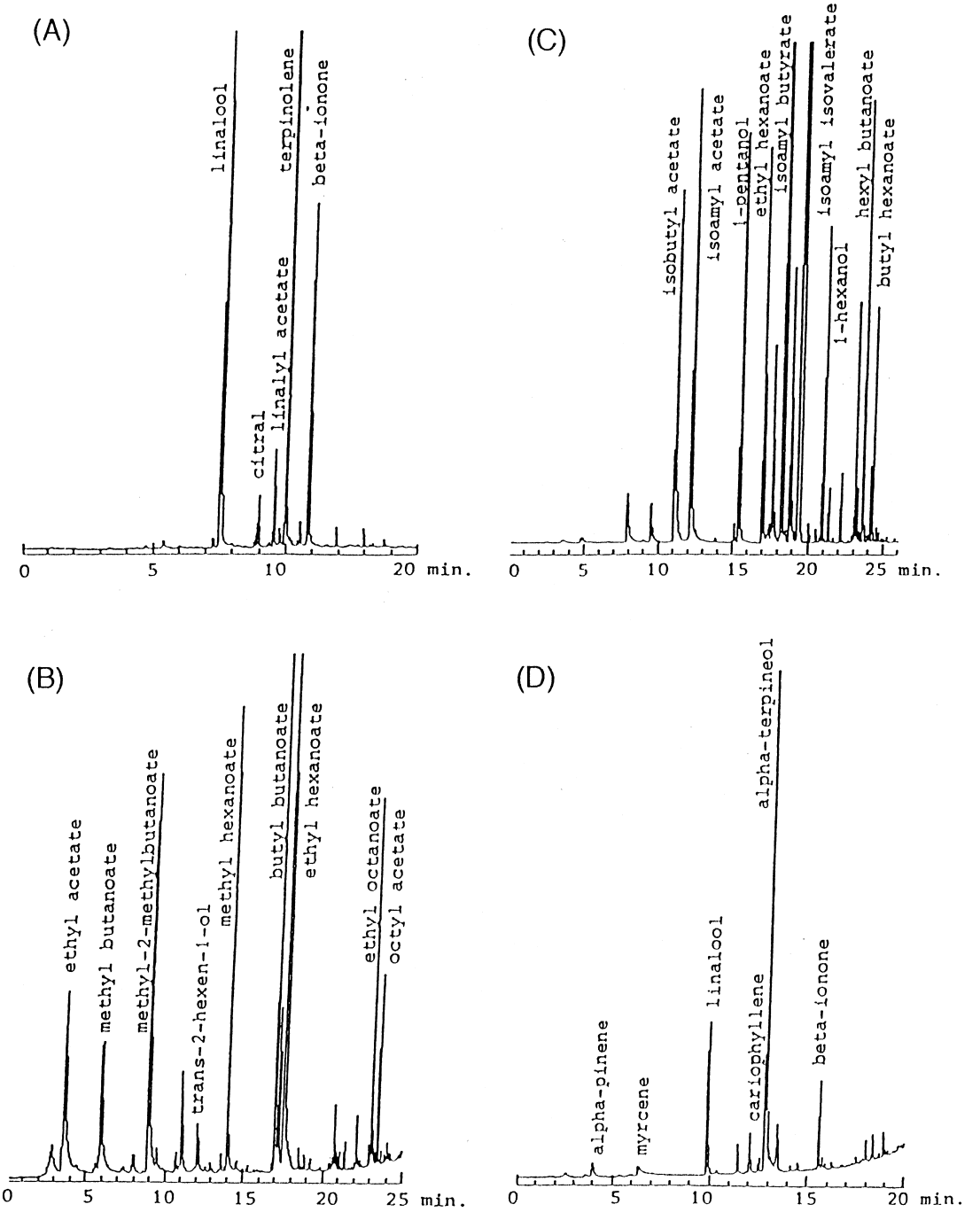

Fig. 5. Gas chromatographic patterns of the SPME extracts of (A) raspberry, (B) strawberry, (C) banana and (D) mango. SPME conditions: fiber, 100 μm PDMS; extraction mode, headspace; sample, solid (1 g); extraction, 60°C for 30 min; desorption, 200°C for 15 min. GC conditions: column, CP-Sil-5CB (50 m×0.25 mm I.D., 0.25 μm film thickness); column temperature, program from 50°C (3-min hold) to 250°C at 5°C/min and hold at 250°C for 17 min; injection temperature, 200°C; detector temperature, 250°C; detection, FID. Reproduced from Ref. [46].

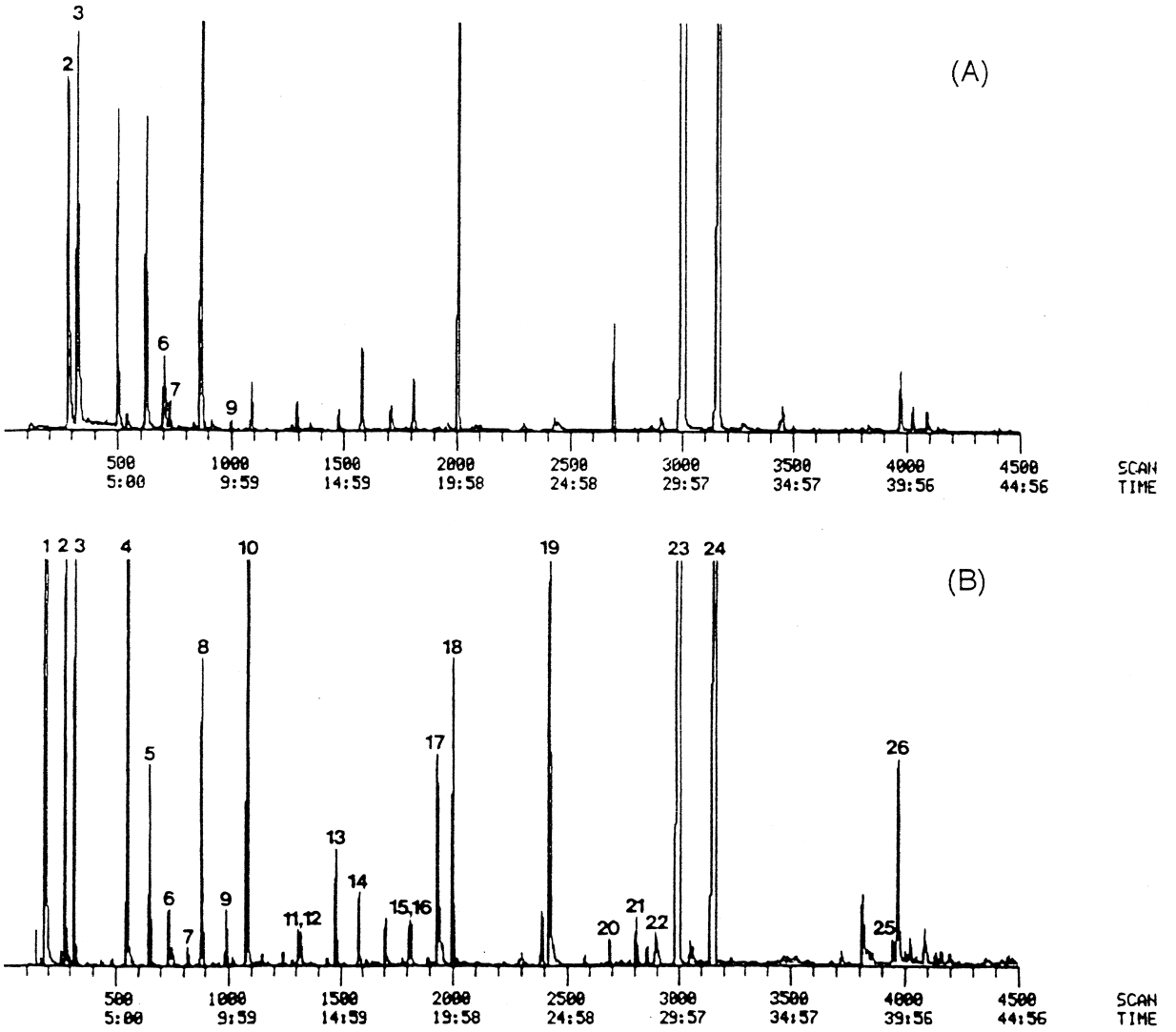

Fig. 6. GC–MS chromatograms of fruit juice beverage by (A) dichloromethane extraction and (B) SPME liquid sampling. Solvent extraction conditions: sample, 250 mL; extraction, three times with 50 mL of dichloromethane; concentration, Kuderna-Danish evaporator. SPME conditions: fiber, 100 μm PDMS; extraction mode, direct immersion; sample, liquid (3 mL) containing 0.6 g sodium chloride; extraction, 10 min; desorption, 200°C for 3 min. GC–MS conditions: column, DB-Wax (30 m×0.25 mm I.D., 1 μm film thickness); column temperature, program from 50°C (2-min hold) to 220°C at 4°C/min; injection temperature, 200°C; detector temperature, 220°C; detection, MS. Peaks: 1=dichloromethane, 2=ethyl butyrate, 3=ethyl isovalerate, 4=limonene, 5=ethyl hexanoate, 6=isoamyl butyrate, 7=hexanyl acetate, 8=*cis*-3-hexenyl acetate, 9=hexanol, 10=*cis*-3-hexenol, 11=*cis*-3-hexenyl butyrate, 12=furfural, 13=benzaldehyde, 14=linalool, 15=β-terpineol, 16=butyric acid, 17=2-methylbutyric acid, 18=α-terpineol, 19=hexanoic acid, 20=*cis*-methyl cinnamate, 21=1-(2-furyl)-2-hydroxyethanone, 22=furaneol, 23=*trans*-methyl cinnamate, 24=γ-decalactone, 25=dodecanoic acid, 26=(hydroxymethyl)-furfural. Reproduced from Ref. [48].

method for the determination of caffeine and flavor and fragrance compounds in various beverages including juice, cola, coffee, tea and brandy. Quantitative reproducibilities were ca. 5% and the entire scheme including sample preparation and GC–MS analysis was completed in ca. 15 min per sample [55].

3.1.3. Alcoholic beverages

Beer constituents comprise >800 compounds and

many of them contribute to its flavor characteristic such as bitterness, sweetness, acidity, hop character, carbonation, alcoholic flavor and fruity or estery flavor. Jelen et al. [57] used an HS-SPME technique for the determination of 12 alcohols and esters in beer, and made a comparison with the static HS sampling technique. As shown in Fig. 7, the HS-SPME method using a PA fiber was more sensitive for the extraction of most compounds tested than the static HS method. Both methods gave high repeatability and good linearity, and results of beer analyses obtained by these methods were highly correlated. Constant and Collier [58] also identified over 40 components in fruit-flavored malt beverages by HS-SPME–GC–FID. On the other hand, over 1000 aroma compounds have been identified as components of wine. Most of these compounds originate from the grapes and are formed at pre- and post-fermentation. Wine aromas contain various classes of compounds such as hydrocarbons, terpenoids, alcohols, esters, aldehydes and acids that present a large range of volatility and polarity. Although some components are present in high concentration (100 mg/L), most are found at the low μg/L or ng/L level. Therefore, extraction and concentration of most volatiles is usually necessary before analysis. The aromatic patterns are useful for the chemometric classification of wine varieties. De la Calle Garcia et al. [59–61] analysed wine bouquet components using DI- and HS-SPME coupled with GC–FID or GC–MS. PA fiber achieved the most complete bouquet profiles and HS-SPME gave some essential advantages such as longer lifetime of the fiber and higher sensitivity for terpenoids in comparison with DI-SPME. Mestres et al. [62–64] used an HS-SPME technique coupled with GC–flame photometric detection (FPD) for the analysis of thiols, sulphides and disulphides in wine aroma. As shown in Fig. 8, sulphur aroma compounds were selectively detected in the wine at a detection limit of 0.05–3 μg/L. Vas et al. [65,66] also studied an HS-SPME technique coupled with GC–MS for the determination of volatile wine components. The results obtained by these methods are suitable to compare and optimize fermentation conditions and can be correlated to sensory evaluation.

3.1.4. Dairy products

Cheese flavors consist of a heterogeneous mixture of compounds originating from milk, and over 200 compounds are present in cheese as the result of enzymatic and chemical reactions which lead to the formation of peptides, amino acids and volatiles through different pathways. Chin et al. [70] extracted cheese volatile compounds by HS-SPME using either PDMS or PA fiber. As shown in Fig. 9, the results with PA fibers were better than those with PDMS fibers. Major volatile components such as volatile fatty acids and lactones were readily extracted by both fibers, but minor components such as volatile sulphur compounds were not observed. Jaillais et al. [72] studied a new method based on SPME following an initial concentration step using cryo-trapping, and applied it to the analysis of cheese aromas. Cryo-trapping allows the extraction of volatiles from the solid matrix by changing the equilibrium between sample and headspace. The dairy industry handles large amounts of whey protein concentrate (WPC) during either casein or cheese whey processing. Due to its inherent functional properties, adhesive, foaming, gelling and emulsifying properties, WPC has been used as a nutritional source of protein for fortification of many products including cereals, beverages, and infant and weight-gain formulations, increasing the overall nutritional value of the product. Characterization of WPC's volatile profile is important for the manipulation of its flavor perception for various applications. A variety of volatile compounds, including acids, alcohols, aldehydes, hydrocarbons, esters, furans and amines, in WPC were identified by HS-SPME–GC–MS [75–78].

3.1.5. Others

Wang et al. [79] applied a DI-SPME technique to monitor the use of flavor ingredients, Veltol and Veltol-Plus, in food products including coffee, cola, potato chips, canned food and chewing gum. Menthol, the main component of peppermint essential oil, is used in confectionery, perfumery, cigarettes, nasal inhalers and cough drop production. Ligor and Buszewski [80] determined menthol and menthone in food products by HS-SPME–GC–FID. Fig. 10 shows typical chromatograms obtained from menthol candy and peppermint tea. A new type of fiber coated with laboratory-made organic phase ethoxypolydimethylsiloxane (PDES) was used for the extraction of these compounds. PDES fiber gave a higher extraction efficiency and good selectivity in

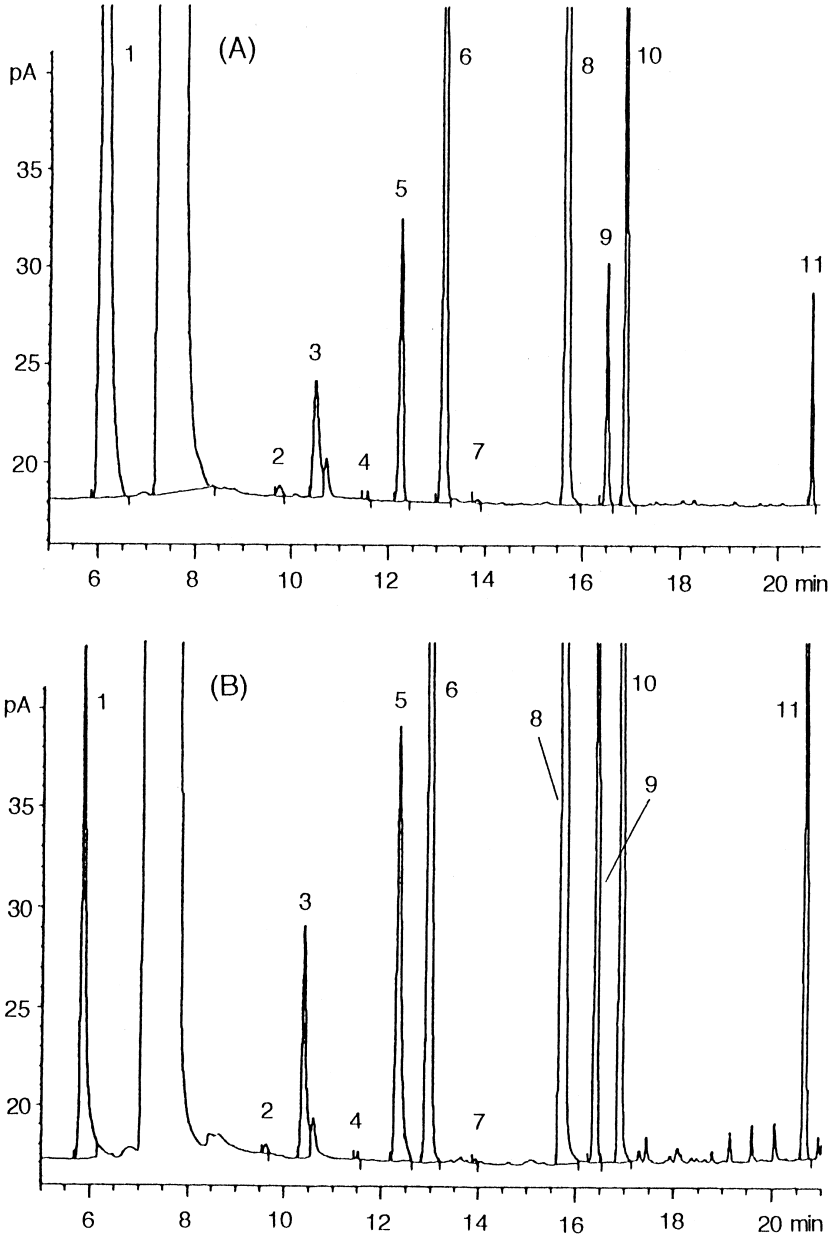

Fig. 7. Gas chromatograms of Pilsner-type beer alcohols and esters determined by (A) static headspace and (B) SPME methods. Static headspace conditions: sample heating, 50°C for 30 min. SPME conditions: fiber, 85 μm PA; extraction mode, headspace; sample, liquid; extraction, 50°C for 60 min; desorption, 240°C for 5 min. GC condition: column, Stabilwax (30 m×0.32 mm I.D., 1 μm film thickness); column temperature, program from 40°C (4-min hold) to 100°C at 5°C/min, then to 220°C at 10°C/min, and hold at 220°C for 7 min; injection temperature, 240°C; detector temperature, 260°C; detection, FID. Peaks: 1=ethyl acetate, 2=isobutyl acetate, 3=propanol, 4=butyl acetate, 5=isobutanol, 6=isoamyl acetate, 7=butanol, 8=methyl-1-butanol, 9=ethyl caproate, 10=1-pentanol (internal standard), 11=ethyl caprylate. Reproduced from Ref. [57].

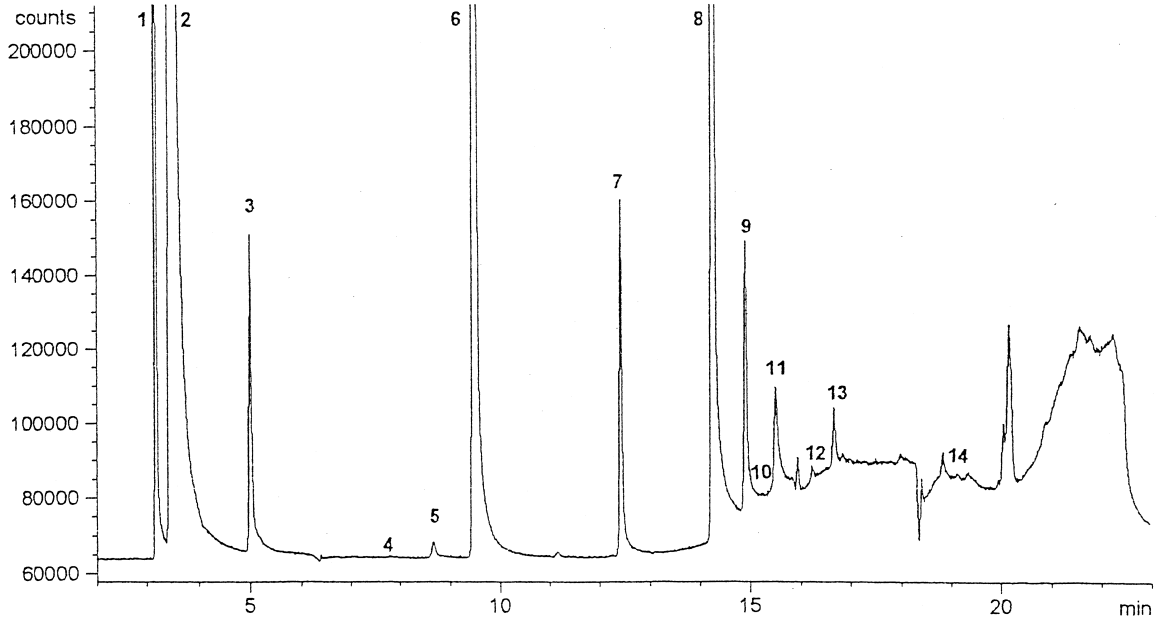

Fig. 8. Gas chromatogram of wine sample. SPME conditions: fiber, 75 μm CAR–PDMS; extraction mode, headspace; sample, liquid; extraction, 25°C for 30 min; desorption, 300°C for 1 min. GC condition: column, SPB-1 Sulphur (30 m×0.32 mm I.D., 4 μm film thickness); column temperature, program from 35°C (8-min hold) to 150°C at 15°C/min, then to 280°C at 40°C/min, and hold at 280°C for 5 min; injection temperature, 300°C; detection, FPD. Peaks: 1=hydrogen sulphide, 2=sulphur dioxide, 3=methanethiol, 4=ethanethiol, 5=dimethyl sulphide, 6=carbon disulphide, 7=ethylmethyl sulphide (internal standard), 8=thiophene (internal standard), 9=methyl thioacetate, 10=diethyl sulphide, 11=methylpropyl sulphide, 12=dimethyl disulphide, 13=ethyl thioacetate, 14=diethyl disulphide. Compounds 4 and 10 do not appear in this sample but their retention times are indicated. Reproduced from Ref. [64].

comparison with PDMS fiber. Selective losses of flavor components sometimes occur during processing. These losses can be detected by comparing chromatographic patterns for the final product with those for the flavor ingredients. The fiber SPME technique was also applied for the analysis of aroma release during microwave heating of frozen foodstuffs [81] and the analysis of volatile compounds in a dry-cured meat product [82].

3.2. Off-flavors

Polyunsaturated oils are susceptible to autoxidation over time to form hydroperoxides, and at accelerated rates on heating, exposure to sunlight or metals. The breakdown of hydroperoxides proceeds via peroxyl and alkoxyl radicals as intermediates. Increased levels of these oxidized volatile products are indicators of rancidity in oil samples. Keszler et al. [83,84] used a HS-SPME technique coupled with IT-MS in order to monitor oxidized volatile compounds in vegetable oil. Fig. 11 shows typical chromatograms obtained from sunflower oil samples. In strictly oxygen-free media, pure sunflower oil did not contain any volatile compounds, but 13 volatile products were detected in sunflower oil after 180 min of storage at 140°C in a nitrogen atmosphere containing trace oxygen. Marsili [86,87] developed a sensitive and rapid procedure for testing light-induced lipid oxidation products in milk by HS-SPME–GC–MS. In comparison with dynamic HS sampling, SPME is less expensive and demonstrates better precision and accuracy. SPME also has consistently better linearity and reproducibility than the dynamic HS method. Cork taint is a musty and moldy off-flavor in wine. 2,4,6-Trichloroanisole (TCA) is the major impact component in wine responsible for the characteristic unpleasant odor. It was automatically analysed by HS-SPME–GC–MS using a PDMS fiber and a Varian 8200 CX autosampler [88,89]. The detection limit of 2.9 ng/L TCA is low enough to detect the commercially most

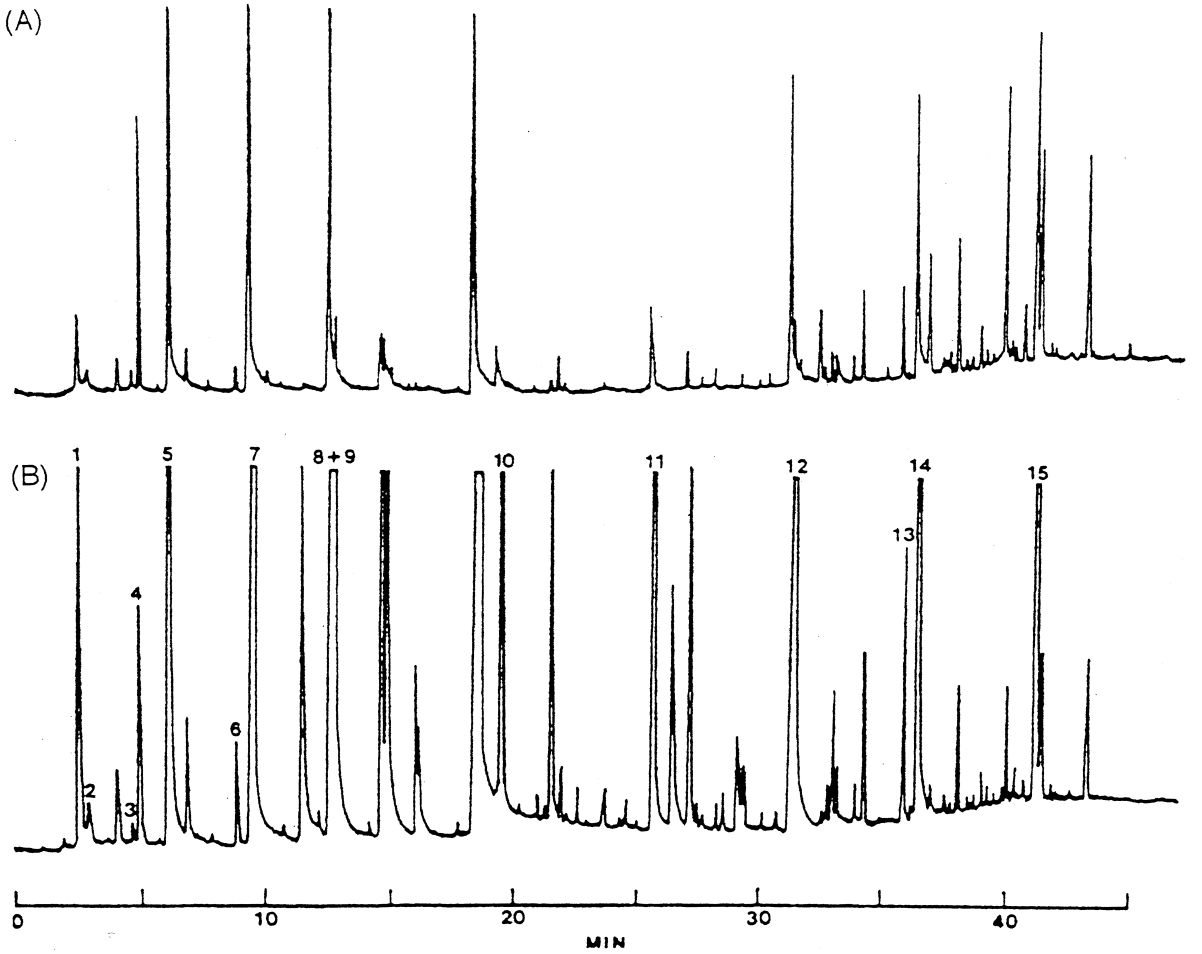

Fig. 9. SPME–GC chromatograms of Swiss cheese. SPME conditions: fiber, (A) 100 μm PDMS, (B) 85 μm PA; extraction mode, headspace; sample, solid; extraction, 60°C for 20 min; desorption, 220°C. GC conditions: column, DB-1301 (30 m×0.25 mm I.D., 1 μm film thickness); column temperature, program from 40°C (2-min hold) to 230°C at 5°C/min and hold at 230°C for 10 min; injection temperature, 220°C; detector temperature, 250°C; detection, FID. Peaks: 1=ethanol, 2=acetone, 3=diacetyl, 4=ethyl acetate, 5=acetic acid, 6=acetoin, 7=propanoic acid, 8=butanoic acid, 9=2,3-butanediol, 10=hexanoic acid, 11=octanoic acid, 12=decanoic acid, 13=δ-decanolactone, 14=dodecanoic acid, 15=δ-dodecanolactone. Reproduced from Ref. [70].

detrimental off-flavor in wine below its threshold range of 4–50 ng/L [88]. Planktonic and benthic algae, fungi, bacteria and actinomycetes are known to produce geosmin and 2-methylborneol, and these semi-volatile and lipophilic compounds have a muddy and musty odor perceived as disagreeable to consumers. These compounds are rapidly absorbed from water into the lipid tissues of fish and other aquatic organisms. Zhu at al. [90] analysed these compounds in catfish tissues by DI-SPME–GC–IT-MS using a PDMS fiber (Fig. 12). In addition, HS-SPME was applied to the extraction and identification of amine malodors from spoiled foodstuffs [92] and to the analysis of reduced sulphur volatile compounds in butter [93].

3.3. Pesticides and other agrochemicals

Pesticides, herbicides and other agrochemicals are widely used for agricultural and non-agricultural purposes worldwide. Consequently, health risks connected with the use of these chemicals and residues

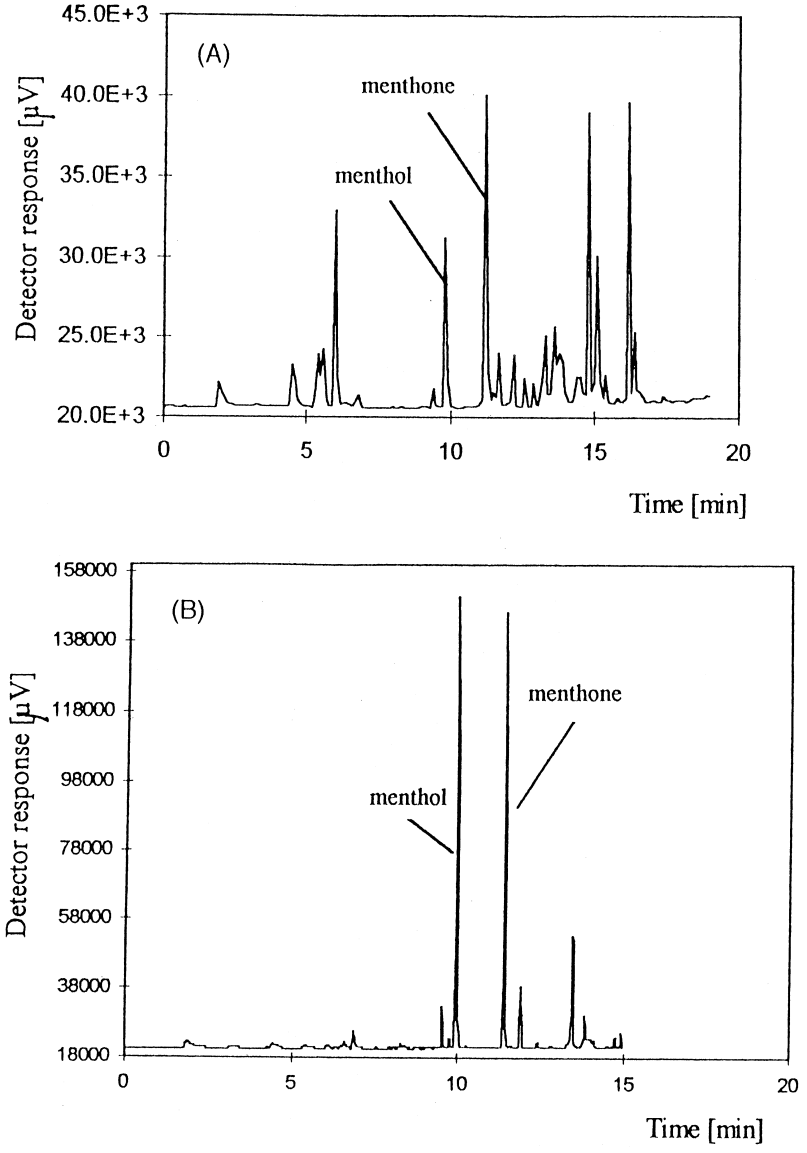

Fig. 10. Typical gas chromatograms obtained from (A) menthol candies and (B) peppermint tea samples. SPME conditions: fiber, 10 μm PDES; extraction mode, headspace; sample, liquid; extraction, 30°C for 15 min; desorption, 200°C for 2 min. GC conditions: column, RTX 200 (30 m×0.53 mm I.D., 0.25 μm film thickness); column temperature, program from 40°C (2-min hold) to 150°C at 10°C/min, hold at 150°C for 4 min, then to 225°C at 20°C/min, and hold at 225°C for 2 min; injection temperature, 200°C; detector temperature, 250°C; detection, FID. Reproduced from Ref. [80].

in foods have received a great deal of attention because they impact the daily life of people everywhere in the world. The residues of these chemicals in agricultural and agroindustrial samples should be monitored to determine that they are within specified limits. Therefore, there is an urgent need for an analytical method that is simple, rapid and applicable for a variety of food samples. Boyd-Boland and Pawliszyn [94] developed a HS-SPME method for the analysis of 22 nitrogen-containing herbicides by

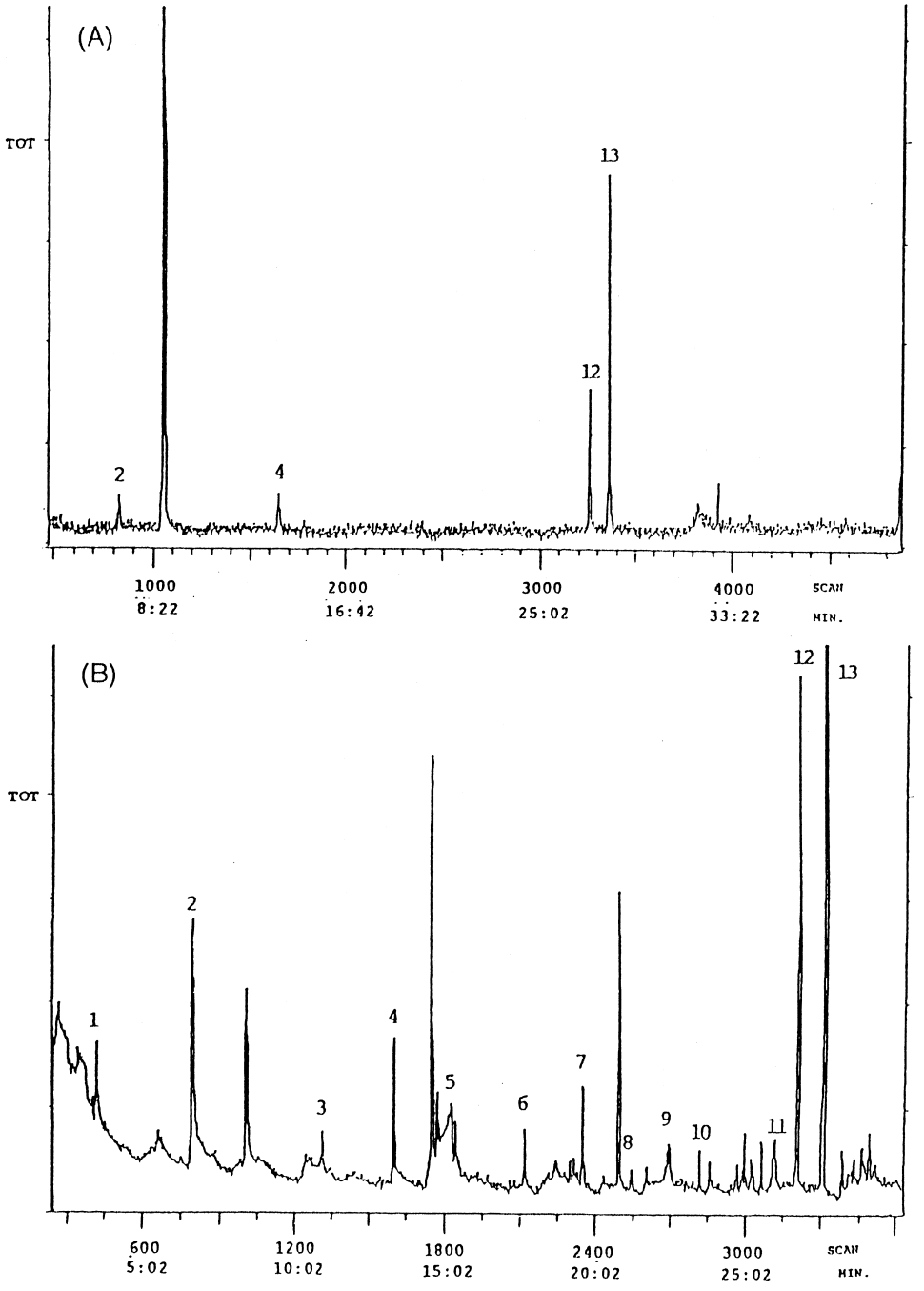

Fig. 11. Total ion chromatograms of sunflower oil samples. (A) In strictly oxygen-free medium after 180 min storage at 140°C, (B) in the presence of a trace of oxygen after 180 min storage at 140°C. SPME conditions: fiber, 100 μm PDMS; extraction mode, headspace; sample, liquid; extraction, 40°C for 45 min; desorption, 275°C for 1 min. GC–MS conditions: column, DB-5MS (30 m×0.25 mm I.D., 0.25 μm film thickness); column temperature, program from 40 to 220°C at 4°C/min, and hold at 220°C for 5 min; ionization, 70 eV; detector, MS-SIM. Reproduced from Ref. [84].

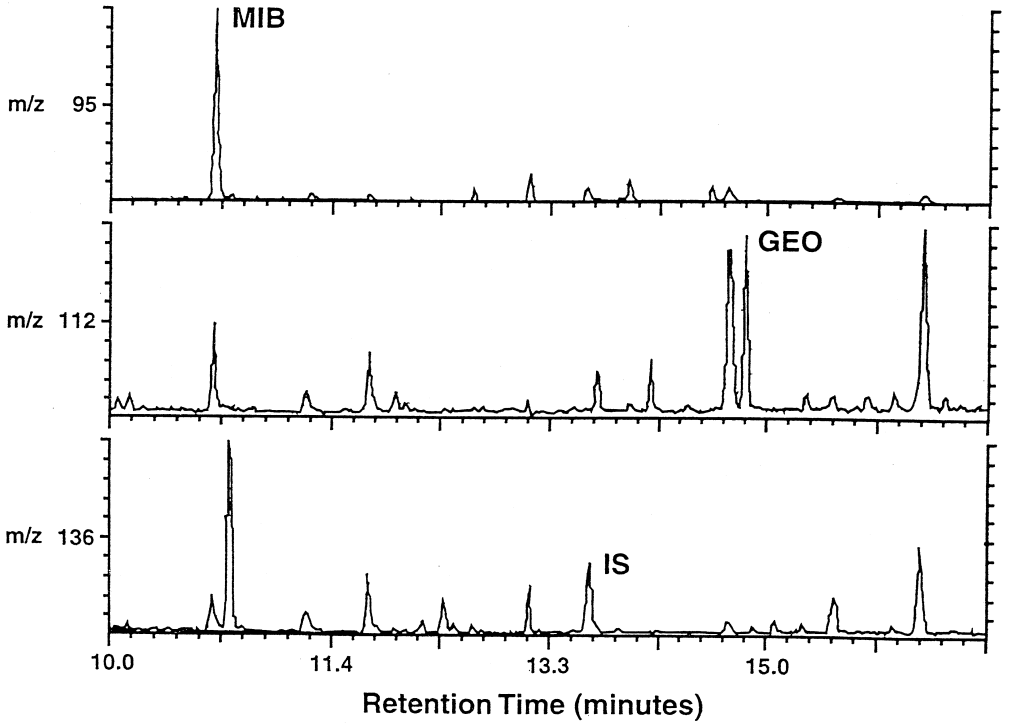

Fig. 12. Ion trace chromatograms from an 'off-flavor' channel catfish extract. SPME conditions: fiber, 100 μm PDMS; extraction mode, direct immersion; sample, liquid containing saturated sodium chloride; extraction, 45 min; desorption, 250°C for 3 min. GC–MS conditions: column, DB-5MS (30 m×0.25 mm I.D., 0.25 μm film thickness); column temperature, program from 60°C (4-min hold) to 200°C at 8.5°C/min, hold at 200°C for 16.5 min, then to 250°C at 20°C/min, and hold at 250°C for 3 min; injection temperature, 250°C; detector temperature, 250°C; ionization, 70 eV; detector, IT-MS-SIM. MIB, methylisoborneol; GEO, geosmin, IS, *cis*-decahydro-1-naphthol (internal standard). Reproduced from Ref. [90].

coupling GC–MS, GC–FID and GC with nitrogen–phosphorus detection (NPD), and applied it to the analysis of wine samples. Methyl isothiocyanate is used as a soil fumigant for nematodes, fungi and other diseases in vegetables and fruits. Gandini and Riguzzi [95] used a HS-SPME technique for the detection of this compound employed illegally as antifermentative agents in wine. A DI-SPME method combined with GC–MS was also developed for the determination of pesticide residues in wine [96,97]. Jimenez et al. [98] applied a DI-SPME technique to the extraction of 21 pesticides of different chemical families in honey, and selectively analysed by GC–electron-capture detection (ECD). As shown in Fig. 13, a large peak with a tail that decreases progressively until disappearing at approximately 50 min was observed using a 7 μm PDMS fiber, but a simple chromatogram was obtained from a multifloral honey sample using a 100 μm PDMS fiber. Various pesticide residues in vegetables and fruits were also analysed by SPME coupled with GC–MS [99–101]. Yang et al. [102] developed an automated DI-SPME–GC–MS method for the determination of pesticide residues in fruit juices using a Varian 8200 autosampler, which is specially designed for SPME. In the automated SPME method with fiber vibration, no operator is necessary for extraction and desorption steps. Moreover, the precision of extraction is substantially improved. Chen et al. [103] and Sinplicio and Boas [104] reported a DI-SPME–GC–FPD method for the determination of organophosphorous pesticide residues in food plants and fruit

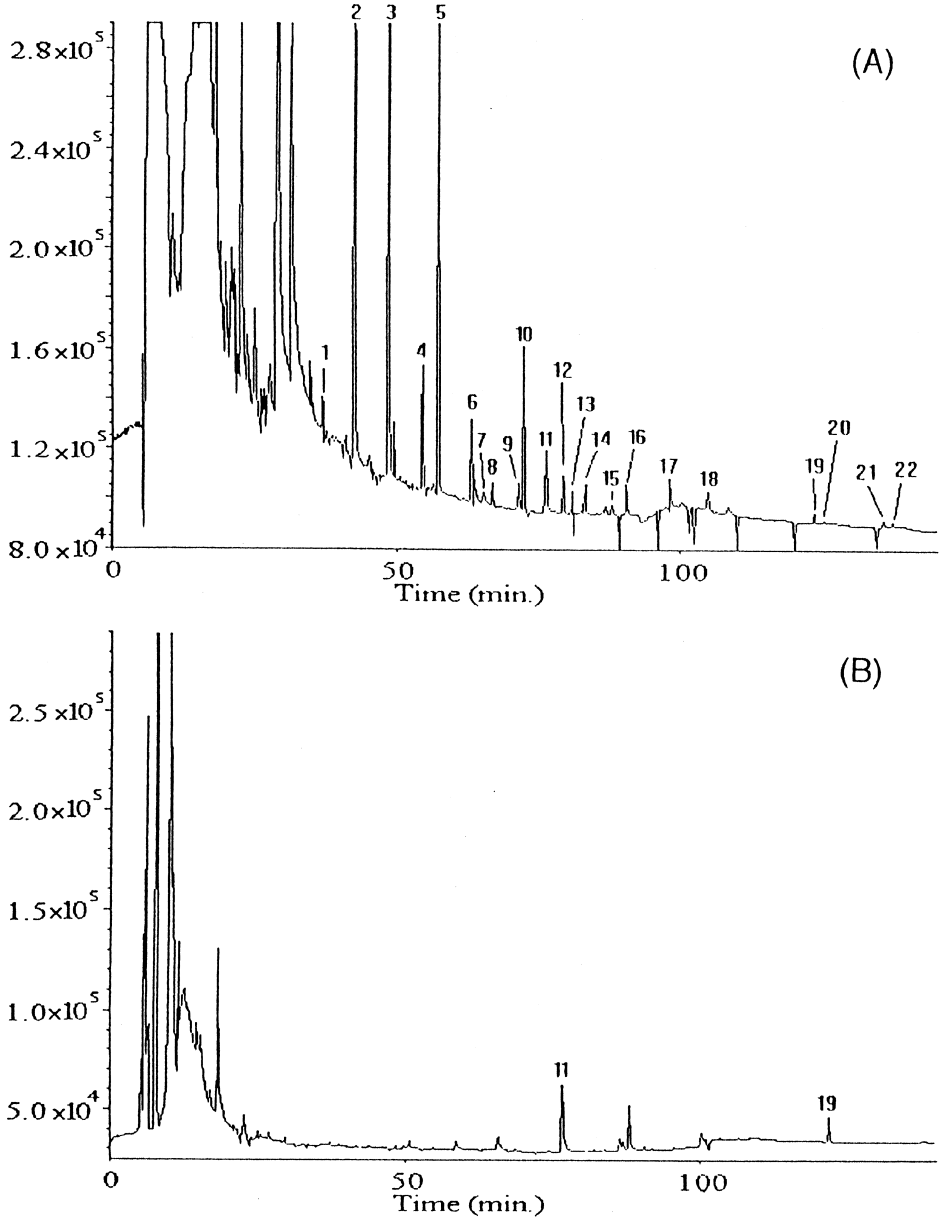

Fig. 13. Gas chromatograms obtained from (A) spiked and (B) non-spiked honey samples. SPME conditions: fiber, (A) 7 μm PDMS, (B) 100 μm PDMS; extraction mode, direct immersion; sample, liquid containing sodium chloride; extraction, 30°C for 120 min; desorption, (A) 270°C for 4 min, (B) 260°C for 4 min. GC conditions: column, 50% phenylmethylsiloxane (60 m×0.25 mm I.D., 0.25 μm film thickness); column temperature, program from 50°C (5-min hold) to 160°C at 25°C/min, to 260°C at 1.2°C/min, then to 275°C at 20°C/min, and hold at 275°C for 34 min; injection temperature, 270 or 260°C; detector temperature, 300°C; detection, ECD. Peaks: 1=demeton-*S*-methyl, 2=α-hexachlorocyclohexane, 3=lindane, 4=vinclozolin, 5=aldrin, 6=chlorpyrifos, 7=malathion, 8=parathion, 9=chlorfenvinphos, 10=endosulfan, 11=1,1′-(2,2-dichloroethenylidene)bis(4-chlorobenzene), 12=captan, 13=1,1′-(2,2-dichloroethylidene)bis(4-chlorobenzene), 14=endrin, 15=ethion, 16=1,1′-(2,2,2-trichloroethylidene)bis(4-chlorobenzene), 17=acrinathrin, 18=methoxychlor, 19=tetradifon, 20=phosalone, 21=fluvalinate-1, 22=fluvalinate-2. Reproduced from Ref. [98].

beverages. The method was selective and reproducible, and the detection limits were below 2 μg/kg for all pesticides [104].

3.4. Other contaminants

Foods are sometimes contaminated with environmental pollutants including a variety of naturally occurring and man-made hazardous chemicals. Therefore, monitoring of these contaminants in foods is very important for human health risks. Page and Lacroix [105,106] applied the HS-SPME technique to the analysis of 33 halogenated volatiles in selected beverages and finely divided dry foods. Halogenated hydrocarbons such as chloroform, trichloroethane and bromobenzene, extracted into PDMS fiber, were selectively analysed by GC–electrolytic conductivity detection (ELCD). Forsyth and Dusseault [107] used a HS-SPME technique to determine methylcyclopentadienyl manganese tricarbonyl (MMT), a gasoline antiknock additive, in beverages.

Tetracycline antibiotics have been used in veterinary practice and animal rearing for both therapeutic and prophylactic purposes, and have led to concerns about their contamination of animal products destined for human consumption. Tetracycline residues have been widely identified in meat products and commercial milk supplies. Lock et al. [109] developed a new SPME method combined with LC–MS for the analysis of seven tetracycline antibiotics in milk. After extraction with CW–templated resin (CW–TPR) fiber by direct immersion, the fiber was transferred to a desorption chamber previously filled with mobile phase for static mode desorption. Detection limits of tetracycline antibiotics were 4–40 ng/mL, and this method was efficiently applied to the analysis of 100 ppb level tetracycline in milk.

On the other hand, foods sometimes contain mutagenic and carcinogenic compounds produced from food components and packaging materials during cooking or storage. Therefore, monitoring of these toxic compounds in foods is very important for human health risks. Sen et al. [111] used a HS-SPME technique for the analysis of carcinogenic *N*-nitrosamines in smoked ham. As shown in Fig. 14, *N*-nitrosodibenzylamine (NDBzA), reflecting a change in the formulation of the rubber used in the manufacture of the nettings, was successfully extracted onto a PA fiber. NDBzA was selectively detected at a concentration of 39.8 μg/kg ham by GC–thermal energy analysis (TEA), and the detection limits were 1–3 μg/kg. Recently, Kataoka and Pawliszyn [31] developed a new SPME method (in-tube SPME) coupled with LC–MS for the analysis of carcinogenic heterocyclic amines. In-tube SPME is suitable for the extraction of less volatile or thermally labile compounds not amenable to GC or GC–MS. An Omegawax capillary column was used as a SPME device. This method is simple, rapid and automatic, and was successfully applied to the analysis of a food sample. As shown in Fig. 15, 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx), 2-amino-3-methyl-3*H*-imidazo[4,5-*f*]quinoline (IQ) and 2-amino-1-methyl-6-phenylimidazo-[4,5-*b*]pyridine (PhIP) were selectively detected from grilled beefsteak.

4. Conclusions

Food analysis is very important for the quality control of foodstuffs and the monitoring of harmful contaminants. The choice of analytical method depends on the presence of the target compounds in foods at low parts per billion or less and the variety and complexity of the sample. Therefore, sample preparation for a complex matrix greatly influences the reliable and accurate analysis of food samples. The SPME technique described in this review is very effective as a sample preparation technique for qualitative and quantitative analyses. As extraction and concentration are combined, all of the analyte extracted is introduced into the analytical system. The main advantages of SPME are simplicity, rapidity, solvent elimination, high sensitivity, small sample volume, lower cost and simple automation. SPME techniques can be successfully applied for polar and non-polar compounds in gaseous, liquid and solid samples, and can be easily coupled with various analytical instruments such as GC, GC–MS, HPLC and LC–MS.

Since 1992, a number of SPME methods have been developed to extract flavors, off-flavors, pesticides and other contaminants from various food samples such as vegetable, fruit, beverages, dairy products and meat. The affinity of the fiber coating

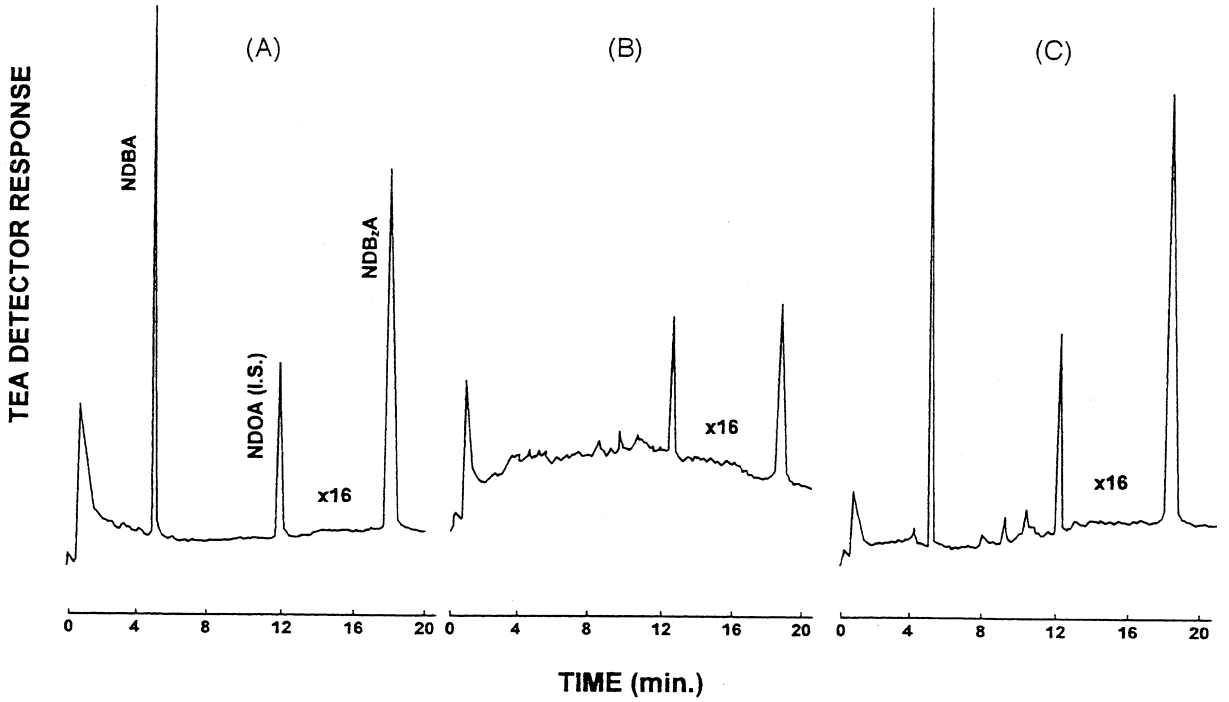

Fig. 14. Gas chromatograms of SPME analyses. (A) Standard solution, NDBA (14 ng), NDOA (4 ng) and NDBzA (8.1 ng). (B) A non-spiked ham extract (equivalent to 0.1 g of ham). (C) Same ham spiked with 140 μg/kg of NDBA and 81 μg/kg of NDBzA. SPME conditions: fiber, 85 μm PA; extraction mode, headspace; sample, liquid made up to 3 *M* KOH strength and saturated with sodium chloride; extraction, 80°C for 60 min; desorption, 220°C. GC conditions: column, Supelcowax 10 (30 m×0.53 mm I.D., 1 μm film thickness); column temperature, program from 40°C (1-min hold) to 160°C at 50°C/min, and then to 220°C at 6°C/min; injection temperature, 220°C; TEA furnace and interface temperatures, 800 and 375°C, respectively; detection, TEA. Peaks: NDBA=*N*-nitrosodibutylamine, NDOA=*N*-nitrosodioctylamine, NDBzA=*N*-nitrosodibenzylamine. Reproduced from Ref. [111].

for an analyte is the most important factor in SPME. As shown in Tables 1 and 2, fiber coatings of different polarity and thickness were selected for each compound. Most flavors in food samples were extracted with 100 μm PDMS for non-polar compounds and 85 μm PA for polar compounds by HS sampling, and analysed in combination with GC or GC–MS. On the other hand, most pesticide residues in food samples were extracted with 100 μm PDMS by DI sampling. In-tube SPME has not yet been extensively applied to food analysis. Although the theories of fiber and in-tube SPME methods are similar, the significant difference between these methods is that the extraction of analytes is performed on the outer surface of the fiber for fiber SPME and on the inner surface of the capillary for in-tube SPME. Commercially available SPME fibers for food analysis are limited, but GC capillary columns with a vast array of stationary phases are commercially available for in-tube SPME. Fiber HS-SPME is suitable for the extraction of compounds in gaseous, liquid and solid samples, and eliminates contact with an agressive matrix incompatible with the fiber. Fiber DI-SPME can extract compounds from clear and cloudy liquid samples. In-tube SPME is limited to the extraction of clear liquid samples, although samples can be centrifuged or prefiltered. However, in-tube SPME is important for the development of an automated SPME–LC method. The extraction efficiency of fiber SPME depends on the extraction time, agitation, heating, sample pH and salt concentration. For in-tube SPME, the number, volume and speed of draw/eject cycles, and sample pH are important factors for efficient extraction. On the other hand, the desorption of analyte from a fiber or capillary coating depends on the temperature of

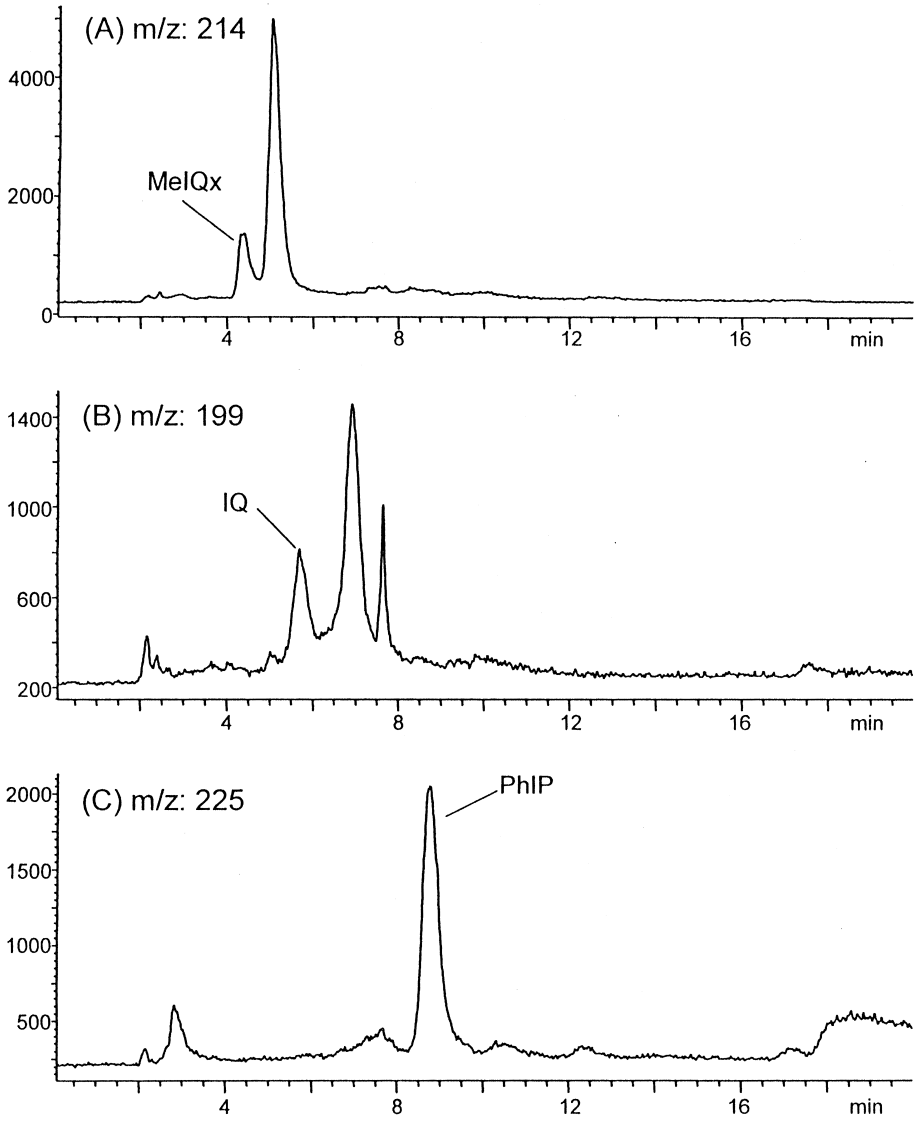

Fig. 15. SIM chromatograms obtained from grilled beefsteak by blue-rayon treatment and in-tube SPME–LC–MS analysis. In-tube SPME conditions: capillary, Omegawax 250 (60 cm×0.25 mm I.D., 0.25 μm film thickness); sample pH, 8.5; draw/eject cycles, 10; draw/eject volume, 30 μL; draw/eject flow-rate, 100 μL/min, desorption solvent, methanol (30 μL). LC–MS conditions: column, Supelcosil LC-CN (3.3 cm×4.6 mm I.D., 3 μm particle size); column temperature, 25°C; mobile phase, 15% acetonitrile–methanol (4:1)+85% 0.1 *M* ammonium acetate (pH 7.0); flow-rate, program from 0.2 to 0.8 mL/min for 20 min run; fragmentor voltage, 90 V; ionization mode, positive electrospray; SIM ion, $m/z = 214$ (MeIQx), 199 (IQ) and 225 (PhIP). Reproduced from Ref. [31].

the injection port and exposure time in combination with GC or GC–MS, or component and volume of solvent when used in combination with HPLC or LC–MS. Therefore, these SPME parameters should be optimized when developing a new SPME method for food analysis.

With further development of new coating materials such as affinity coatings for target analytes and chiral coatings for optically active analytes, further hyphenation with different analytical instruments such as capillary electrophoresis, improvement of the extraction and desorption conditions, and automation

of the SPME method coupled with analytical systems, the SPME technique is expected to be widely applied in the future for highly efficient extraction of food components and contaminants from various food samples.

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