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Review

Headspace–based approaches for volatile analysis: A review

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Abstract: This review examines the analytical techniques based on static and dynamic headspace for extracting volatile compounds. The discussed techniques include headspace stir bar sorptive extraction (HSSE), solid–phase microextraction (SPME), solid–phase microextraction arrow (SPME–Arrow), and dynamic headspace sampling (DHS). HSSE, SPME, and SPME–Arrow are categorized as static headspaces (SHS) compared to DHS, which relies on continuous airflow. For each technique, the used equipment for the extraction of the analytes and the major parameters for optimizing the analytical technique are described. Furthermore, we review recent studies (2015 – 2025) on the diverse applications of each technique in food science, environment, medicine, and pharmaceutical. The review is expected to offer a valuable reference for the selection of appropriate analytical techniques that enable the rapid, sensitive, and accurate analysis of volatile compounds in unknown samples.

Key words: headspace, headspace stir bar sorptive extraction, solid–phase microextraction, solid–phase micro-extraction arrow, dynamic headspace sampling

1. Introduction

Analysis of volatile compounds is of great interest across various fields, including the characterization of flavor profiles in food, authentication of agricultural products, environmental monitoring, and assessment of impurities in biomedical and pharmaceutical samples. However, applying these analyses to real samples encounters challenges in identifying typical volatile compounds at low concentrations within complex matrixes.[1] Gas chromatography coupled with mass spectrometry (GC/MS) is typically the general system for analyzing volatile compounds in real samples.[2] For GC/MS analysis, isolation and preconcentration of volatile compounds from the matrix are required prior to extraction.[3] Headspace (HS) extraction techniques are frequently utilized with GC/MS due to their advantages of simplicity and versatility. Additionally, these techniques are environmentally sustainable, as they minimize the use of solvents traditionally required for volatile extraction.[4]

The extraction method for the volatile compounds can be selected based on the analyzed samples. For example, understanding chemical volatility requires knowledge of the parameters that influence the distribution of volatile compounds between the

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gaseous phase and the sample matrix at equilibrium.[5] Among various parameters, such as matrix affinity, volatility, and polarity of volatile compounds, temperature of sample and sample–to–headspace volume ratio are the most important factors in determining equilibrium conditions.[5] To achieve this equilibrium condition, the characteristics of volatile compounds, such as their stability at high temperatures and affinity for water in liquid–type samples, should be considered. HS techniques have garnered increasing attention in recent research owing to their extraction efficiency and analytical precision with GC/MS. Additionally, a variety of fields have applied HS techniques to analyze volatile compounds in food, environmental, biomedical, and pharmaceutical samples due to their convenience and precision. For example, SPME–Arrow techniques have been utilized in flavor profiling in foods, such as a comparison of volatile compounds from edible insect oils[6] and plant–based patty.[7] In recent years, DHS has been used to analyze trace volatile compounds in rubber[8] and plastic,[9] as well as volatile impurities in blood[10] and urine.[11] This review discusses how HS techniques have been modified and advanced in recent studies conducted between 2015 and 2025.

2. Headspace Techniques

The term “headspace” (HS) describes the gaseous phase, whether in equilibrium or not, with the solid or liquid matrix located above a sample placed in a closed container, typically a vial sealed with a septum. HS techniques are classified into static (SHS) and dynamic (DHS) (*Fig.* 1).[5]

2.1. SHS technique

SHS is implemented at an equilibrium temperature, time, and agitation, considering the evaporative characteristics of volatile compounds, allowing volatiles to partition between the sample matrix and the gas phase to be in equilibrium. Under equilibrium conditions, considerable amounts of volatile compounds are present in the headspace prior to extraction because the diffusion coefficients of the gas phase are higher than those of the liquid–type samples.[6] SHS techniques facilitate the adsorption of volatile compounds compared to direct extraction under agitation.[5] In which a fiber coated with a suitable absorbent is positioned in the headspace above the sample. Subsequently, the loaded fiber is used to extract volatile compounds from the headspace and is directly injected into the GC, where the analytes are carried to the MS detector by a carrier gas, such as helium.[13]

2.1.1. SHS extraction equipment

The extraction equipment for SHS is straightforward, easily automated, and typically requires a sealed container, such as a vial with silicon/polytetrafluoroethylene septa, along with a heating system to control the temperature of the sample.[13] Through the heating process, the sample evaporates and volatile compounds from the sample matrix move to the headspace in the vial. When using adsorption–type fibers, volatile compounds in the headspace are adsorbed by porous materials consisting of fiber.[14] PAL (prep and load), an autosampler system, facilitates the automatic injection of the fiber–containing volatile compounds into the inlet of GC equipped with an inert liner.[7,8] Pawliszyn's research team was the first

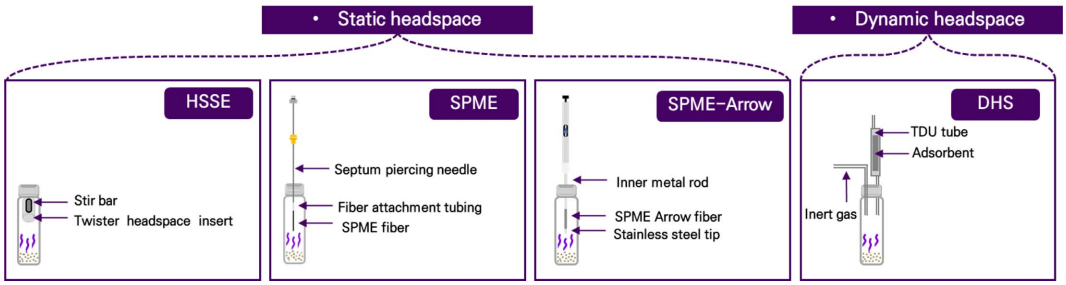

Fig. 1. SHS (HSSE, SPME, SPME-Arrow) and DHS for the analysis of volatile compounds.

to perform the SPME, which is necessary for reducing preparation time, is solvent–free, and allows for immediate sample readiness in fields like environmental research.[14] In addition to SPME, various devices are utilized according to different trapping designs and materials, using a concentration of volatile compounds in high concentration capacity HS (HCCHS) techniques, such as single–drop microextraction (SDME) and headspace sorptive extraction (HSSE).[8,15,16,17]

HSSE is a developed version of the stir–bar sorptive extraction (SBSE) technique. Tienpont *et al*. and Bicchi *et al*. first conducted HSSE to extract volatile compounds from water and plant samples in 2001[18] and 2000.[19] HSSE is based on the absorption of volatile compounds onto a thick layer (e.g., polydimethylsiloxane (PDMS) and ethylene glycol (EG) silicone) coated on a stir bar.[2,20] In SBSE, the stir bar is placed directly on a liquid sample and agitated until equilibrium is reached. For GC, the samples were thermally desorbed or back–extracted with solvents. In contrast, HSSE is performed by exposing the stir bar in the headspace above the solid, liquid, and gaseous samples.[20,21] After the samples are placed in the headspace vial, a twisting headspace insert is positioned on the upper part of the vial. A stir bar was then placed in the insert, and the HS vial was sealed with a cap. The vial with the stir bar was heated with a heating block or agitator to extract the volatile compounds. The stir bar with the volatile compounds in the samples was directly moved into a twister desorption liner to thermally desorb the volatile compounds.[21]

2.1.2. SHS experimental parameters

Different parameters should be optimized for the SHS technique, such as the temperature and time of equilibrium, as well as the extraction and headspace–to–sample volume ratios. Regarding temperature control, a range of 45 to 150 °C is typically utilized, depending on the stability of target volatile compounds and the characteristics of the sample matrix. Additionally, achieving equilibrium time and temperature is essential to guarantee accuracy in the SHS technique.[5] In liquid–type samples, the diffusion coefficients of headspace, water, and fiber coating, as well as distribution constants of headspace–water and fiber–headspace, are considered extraction parameters without agitation. With agitation, efficient flows in water, such as laminar and turbulent flows, should be considered for extraction optimization.[6]

Extraction optimization depends on the properties of the volatile compounds (e.g., matrix affinity, polarity, and volatility) and sample matrix (e.g., texture). For example, strategies are differentiated according to complicated food compositions (combination of carbohydrates, lipids, proteins, sugars, and water) to avoid the matrix effect.[13] The presence of lipids in a sample can interfere with the extraction of lipophilic volatiles by GC. Additionally, proteins serve as effective emulsifiers and foam stabilizers, complicating the diffusion of volatile compounds from the sample to the headspace. Similarly, carbohydrates contribute to the viscosity, foaming, and emulsification properties of the samples, further complicating the isolation of volatile compounds.[13]

As the sensitivity of headspace analysis is influenced by the combined effects of the partition coefficient and distribution factor (for a detailed explanation, see previous research), improving the sensitivity is crucial.[5] The detection sensitivity might be enhanced using high sample–to–headspace volume ratios or solvents to dissolve the sample, typically for analytes with low solubility. Furthermore, the salting out effect induces the dissolution of salts into an aqueous solution, improving the extraction efficiency of volatile compounds from liquid–type samples. Specifically, this technique increases the ionic strength of aqueous solutions, which reduces the solubility of hydrophobic volatile compounds. This leads to an elevated concentration of the target volatile compounds in the headspace.[4,6,22,23]

1) HSSE

The HSSE technique is primarily used to identify volatile compounds in the headspace. This method is characterized by extracting volatile compounds from all phases of samples (solid, liquid, and gaseous samples) through thick magnetic bars (twisters) coated with adsorbents.[2] Every sample has different

volatile compound chemical properties; a stir bar is an important parameter for effectively extracting the volatile compounds. PDMS is the most commonly used polymer in the HSSE technique. PDMS is easily synthesized and has good extraction efficiency. The degradation products are easily identified by MS.[21] The sensitivity of HSSE is 50 – 250 times higher than that of SPME because the stir bar can absorb a greater volume of PDMS. The PDMS extraction capacity is limited in the detection of polar volatile compounds due to its selective affinity for nonpolar compounds.[21,24] Stir bars featuring polar coatings, such as EG silicone or polyacrylate (PA), have recently emerged.[24,25] They can attach to polar compounds based on their thermal desorption compatibilities. The EG stir bar could break easily; therefore, its lifespan was shorter than that of the PDMS. Stir bar optimization is essential for the efficient extraction of target compounds from samples. Stir bar coating evaluation for the analysis of volatile compounds was performed in various samples, such as honey,[24] wine,[26] omija,[2] dry–cured ham,[27] and finger paint[28] comparing the peak areas detected by the MS detector.

2) SPME

SPME is the most frequently used technique for volatile compound extraction and involves diverse materials used as sorbent coatings. SPME fibers can be classified into four categories: type of coating, thickness, polarity, and whether the coating characteristics are absorbent or adsorbent. Commercially available SPME fiber coatings include PA, PDMS, divinylbenzene/PDMS (DVB/PDMS), carboxen/PPDMS (CAR/PDMS), and DVB/CAR/PDMS.[4,29] The thickness of the coating influences the extraction capacity of the fiber, and a thicker coating results in a longer extraction time, which is required to reach equilibrium when the fiber is exposed to the headspace. Additionally, the polarity of the coating enhances the affinity between the fiber and the volatile compounds, providing selectivity based on the polarity of the volatile compounds.[30] The initial fiber coatings for SPME were developed with an absorbent–type phase consisting of 'liquid–like' polymers. With absorbent–type fiber coatings, such as PA (polar type) and PDMS (non–polar type), volatile compounds can migrate in and out of the phase coatings. Cha *et al*. reported that PA (polar type) fibers exhibited a higher affinity for the acid group compared to other fibers, which are relatively nonpolar and semi–polar.[31] The adsorbent–type coatings, suspended in a liquid polymer and coated on the fiber, interact with solid materials and are generally composed of porous polymers, such as CAR/DVB and PDMS/DVB (semi–polar types). During extraction, volatile compounds migrate into the pores of the adsorbent.[32]

3) SPME–Arrow

SPME–Arrow, a novel extraction technology, was developed to combine the advantages of SPME and SBSE. The SPME–Arrow technique provided considerably larger peak areas for extracted volatile compounds, such as those extracted from soy sauce (4 – 40 times)[2] and brown rice vinegar (1.3 – 2 times)[4] compared to traditional SPME. Although the sorbent materials were optimized differently for the extraction method, SPME–Arrow (CAR/PDMS) demonstrated 5 – 10 times better LOQ values than SPME (DVB/CAR/PDMS) from wastewater samples.[33] The larger peak areas indicate that the SPME–Arrow technique improves volatile extraction efficiency. The fiber of SPME–Arrow is safeguarded by an outer metal tube and supported by an inner metal rod, which enhances its stability and extends its lifetime, consequently addressing the limitations associated with conventional SPME. Like HSSE, SPME–Arrow utilizes larger sorbent phase volumes, which help it absorb more volatile compounds from the sample.[34] Although SPME–Arrow fibers of increased diameter and length, the system does not necessitate a thermal desorption unit, enabling full automation similar to conventional SPME.[35] Nam *et al*. reported that the CAR/PDMS fiber efficiently extracted volatile compounds with low molecular weights, such as acids, alcohols, and aldehydes from brown rice vinegar.[4] In Korean distilled spirit, the total normalized peak area of volatile compounds showed high values in the following order: CAR/PDMS, DVB/CAR/PDMS, PDMS, and DVB/PDMS, exhibiting a wide range of

Table 1. Recent applications of SHS technique for analysis of volatile compounds in different fields

Sample	Objective	SHS extraction procedure	Instrumental conditions	Method validation				Ref.
				LOD/LOQ	R^2	IS	Recovery (%)	
Food samples								
Edible insect oils	Characterization of volatile profiles followed by HS-SPME-Arrow-GC/MS	– Sample: 0.5 g in 20 mL vials – Equilibration: 40°C, 10 min, 500 rpm – Extraction: 40°C, 30 min, 1000 rpm – Desorption: 220°C, 5 min.	Injector temperature: 220 °C; Splitless mode; Column: HP-5MS (60 m × 0.25 mm × 0.25 µm); SPME-Arrow fiber: DVB/CAR/PDMS; Oven program: 45 °C (10 min) – 2 °C/min, 100 °C – 3 °C/min, 230 °C (3 min); MS detector.	– LOD: 1.01–593.79 ng/g – LOQ: 3.36–1979.32 ng/g	0.9961–0.9999	– 2,2–dimethyl–propanoic acid – 1–hexyl alcohol–d13 – octanal – 2–methylpyrazine – phenyl acetate – toluene–d8 – 3–octanone – 3,4–dimethyl phenol	–	[9]
Plant–based patties supplemented with biji powder	Characterization of volatile profiles followed by HS-SPME-Arrow-GC/MS	– Sample: 1 g in 20 mL vials – Equilibration: 50 °C, 10 min, 500 rpm – Extraction: 50 °C, 30 min, 1000 rpm – Desorption: 220 °C, 5 min.	Injector temperature: 220 °C; Split mode (5:1); Column: HP-5MS (60 m × 0.25 mm × 0.25 µm); SPME–Arrow fiber: DVB/CAR/PDMS; Oven program: 35 °C (5 min) – 4 °C/min, 215 °C – 7 °C/min, 250 °C (5 min); MS detector.	–	–	– 2,2–dimethyl–propanoic acid – 1–hexyl alcohol–d13 – octanal – 2–methylpyrazine – phenyl acetate – toluene–d8 – 3–octanone – 3,4–dimethyl phenol	–	[10]
Rice cultivated from China, Vietnam, and India	Analysis of volatile compounds to identify geographical origins followed by HS-SPME-GC/MS	– Sample: 3 g in 20 mL vials – Equilibration: 75 °C, 6 min – Extraction: 75 °C,5 min – Desorption: 270 °C, 2 min.	Injector temperature: 250 °C; Splitless mode; Column: DB-5MS (30 m × 0.25 mm × 0.25 µm); SPME fiber: DVB/CAR/PDMS; Oven program: 50 °C (1 min) – 10 °C/min, 170 °C (2 min)–30 °C/min, 280 °C (1 min); MS detector.	–	–	–	–	[39]
Brown rice vinegar	– Optimization and comparison of HS-SPME and HS-SPME-Arrow techniques – Characterization of volatile profiles	– Sample: 1 mL in 20 mL vials – Equilibration: 40 °C – Extraction: 50 °C, 30 min – Desorption: 250 °C, 2 min.	Injector temperature: 250 °C; Split mode (5:1); Column: DB-WAX (60 m × 0.25 mm × 0.25 µm); SPME-Arrow fiber: CAR/PDMS; Oven program: 50 °C (2 min) – 2.5 °C/min, 210 °C (2 min); MS detector.	–	–	– 4–methyl–2–pentanol	–	[25]
Omija (*Schisandra chinesis Baillon*)	– Characterization of volatile profiles followed by HS–SBSE–GC/MS – Correlations between volatile profiles and human sensory perceptions	– Sample: 0.9 g in vials – Extraction: 50 °C, 2.5 hours.	TDU: Desorption: 50 °C – 60 °C/min, 220 °C for 5 min; Desorption flow: 50 mL/min; Splitless mode CIS: Cooled temperature: -20 °C N_2; 12 °C/s, 220 °C (2 min) GC: Split mode (20:1); Column: DB-WAX (60 m × 0.25 mm × 0.25 µm); Stir-bar: EG silicone; Oven program: 50 °C (1 min) – 3 °C/min, 210 °C; MS detector.	–	–	phenethyl alcohol	–	[43]

Table 1. Continued

Sample	Objective	SHS extraction procedure	Instrumental conditions	Method validation				Ref.
				LOD/LOQ	R^2	IS	Recovery (%)	
Environmental samples								
Water obtained experimental profiles with benzene, ethylbenzene, m–xylene, o–xylene, and toluene	– Development COMSOL Multiphysics® (CMP) model from water followed by HS-SPME-GC/MS	– Sample: 5 mL in 20 mL vials – Stirring speed: 2000 rpm – Fiber insertion depth: 40 mm – Pressure in vial: 0.0313 atm – NaCl concentration: 6 mol/L – Extraction time: from 0 to 60 min.	Injector temperature: 250 °C; Split mode (10:1); Column: DB-VRX (30 m × 0.25 mm × 1.4 µm); SPME fiber: CAR/PDMS; Oven program: 40 °C (3 min) – 20 °C/min, 150 °C; MS detector.	–	–	–	–	[6]
Wastewater and atmospheric air	– Optimization and comparison of HS-SPME and HS-SPME-Arrow techniques – Determination of alkylamines within wastewater and air	– Wastewater sample: 5 mL in 20 mL vials – Atmospheric air sample: collected by a peristaltic pump with a flow rate of 1.5 m^3/ stir bar for 2 hours and flushing denuder with 10 mL of ultra-pure water; 5 mL in 20 mL vials – NaCl content: 2 g – Extraction: 40 °C, 30 min, 1400 rpm – Desorption: 250 °C, 40 s.	Injector temperature: 250 °C; Split mode (10:1); Column: InertCap for Amines (30 m × 0.25 mm); SPME-Arrow fiber: CAR/PDMS; Oven program: 40 °C (5 min) –30 °C/min, 250 °C (4 min); MS detector.	– LOQ Wastewater: 10 µg/L (DMA), 0.13 µg/L (DMA)	–	– DMA (purity 99 %) – TMA (purity 98 %)	– SPME–Arrow DMA (88 %) – SPME DMA (75 %),	[30]
Polychlorinated biphenyls in soils	– Development of stir bar coated with HB-Apt using HCR – Identification of PCB in soils followed by HS-SBSE–GC/MS	– Sample: 10 g with 10 mL deionized water in 50 mL vials – Sample pH: pH 7 – Extraction: 50 °C, 40 min – Magnetic separation: 20 min, 600 rpm in 1.0 mL ethanol.	Injector temperature: 280 °C; Splitless mode; Column: HP-5MS (30 m × 0.25 mm × 0.25 µm); Stir-bar: AuMNPs@ HB-Apt coating; Oven program: 110 °C (2 min)–20 °C/min, 230 °C (1 min); MS detector.	– LOD: 0.003–0.005 ng/g	0.994	–	– PCB72 (90.4–96.2 %) – PCB106 (91.3–96.4 %)	[50]
Biomedical and Pharmaceutical samples								
Human plasma and serum	– Simultaneous analysis of anesthetic agents (Ket and Mdz) followed by HS–SPME–GC/IMS	– Sample: 5 mL in 10 mL vials – Sample pH: pH 10 – NaCl concentration: 3 mol L^{-1} – Equilibration: 75 °C, 5 min – Extraction: 75 °C, 25 min – Desorption: 220 °C, 2 min.	Injector temperature: 220 °C; positive mode; corona discharge ionization source using ammonia as a dopant; SPME fiber: Polypyrrole doped with dodecylbenzene sulfonate (PPy-DBS) film; IMS detector.	– LOQ: 8.9 µg/L (Ket) 52 µg/L (Mdz)	–	– Ket and Mdz	– Plasma: 85–95 % – Serum: 83–92 %	[19]
Commercial ranitidine	– Determination of NDMA impurity within ranitidine followed by HS-SPME-GC/MS	– Sample: 5 mL in 20 mL vials – Equilibration: 45 °C, 45 min, 600 rpm – Extraction: 45 °C, 45 min, 600 rpm – Desorption: 220 °C, 2 min.	Injector temperature: 220 °C; Split mode (5:1); Column: DB–WAX (30 m×0.25 mm × 0.5 µm); SPME–fiber: Poly Acrylate (PA); Oven program: 70 °C (4 min)–20 °C/min, 230 °C (4 min); MS detector.	–	–	–	–	[56]
Human airway cell cultures	– Development of noninvasive diagnostic platforms with volatile profiling followed by HSSE–GC/MS – Optimization of HSSE–GC/MS techniques	– Sample: Transwell containing confluent cell cultures in sterile borosilicate glass jars filled with 5 mL of OptiMEM® (OPT) medium – Equilibration: 37 °C – Extraction time: 24 hours – Desorption: 300 °C, 7 min.	TDU: Desorption: 30 °C (0.5 min) – 60 °C/min, 250 °C (1 min) CIS: Cooled temperature: -80 °C He; 12 °C/s, 260 °C (3 min) GC: Splitless mode; Column: DB-5 ms (30 m × 0.25 mm × 0.25 µm); Stir-bar: Twisters®; Oven program: 35 °C (3 min) – 5 °C/min, 75 °C –2 °C/min, 220 °C–30 °C/min, 300 °C (3 min); MS detector.	–	–	deuterated decane	–	[57]

LOD: limit of detection, LOQ: limit of quantification, IS: internal standard, Ref.: reference, HS: headspace, SPME: solid–phase microextraction, GC: gas chromatography, MS: mass spectrometry, DVB: divinylbenzene, CAR: carboxen, PDMS: polydimethylsiloxane, SBSE: stir–bar sorptive extraction, TDU: thermal desorption unit, CIS: cooled injection system, EG: ethylene glycol, DMA: dimethylamine hydrochloride, TMA: trimethylamine hydrochloride, HB-Apt: hyperbranched aptamer, HCR: hybridization chain reaction, AuMNPs: Fe_3O_4@AuNPs, Ket: ketamine, Mdz: midazolam, IMS: ion mobility spectrometry, NDMA: N–nitrosodimethylamine

molecular weights.[31] As a result, SPME–Arrow implements high sensitivity and extensive extraction benefits through recent research comparing two SPME methods, such as polycyclic aromatic hydrocarbons in water,[33] alkylamines in wastewater and atmosphere,[22] and volatile compounds in food.[4,29,31]

2.1.3. Applications

HS techniques are frequently used across various disciplines to extract volatile compounds before chromatographic analysis. Although numerous applications can be found in diverse fields, these techniques are predominantly applied in the food, environmental, and pharmaceutical industries. The primary objectives and specific experimental parameters for combining the SHS technique and GC analysis across the reviewed studies are summarized in *Table* 1.

1) Food samples

Different sorbents for SPME and SPME–Arrow were evaluated to determine the most effective fiber for headspace analysis in various samples, such as soy sauce,[35] brown rice vinegar,[29] salt–fermented fish sauce,[4] and Korean distilled spirit.[31] In general, DVB/CAR/PDMS fibers effectively identify a wide spectrum of volatile and semi–volatile compounds when demonstrating the volatile compound profiles of foods.[36] SPME–Arrow fibers coated with CAR/PDMS[4] and DVB/PDMS[37] extracted each group of volatile compounds with a significantly higher normalized peak area compared to other fibers. Additionally, optimization of the SPME–Arrow fiber can be achieved by focusing on the efficiency of extraction of major volatile compounds in fish with PA,[37] and in salt–fermented fish sauce with CAR/PDMS.[29] CAR/PDMS is a porous coating sorbent that enables the selective and sensitive absorption of semi–polar compounds, making it highly effective for extracting compounds with low molecular weight and low boiling points. Comparing SPME and SPME–Arrow with the same fiber coating (CAR/PDMS) revealed that the SPME–Arrow method detected a wider range of volatile compounds than the conventional SPME method.[38] In addition, SPME–Arrow fiber provided relatively high reproducibility, a lower standard deviation with relative standard deviation (RSD), which was under 5 % more than conventional SPME fibers (<8 %).[4]

To demonstrate volatile profiles, similar food products were compared based on HS–SPME–Arrow techniques.[8,31,39] According to HS–SPME–Arrow–GC/MS analysis, the volatile profiles of edible insect oils were determined, and the volatile compounds were quantified using the ratio of the peak areas (analyte/internal standard) by extracting the quantifier ions of each compound. Notably, all regression equations showed high correlation coefficients (R^2), and LODs and LOQs achieved as low as 10 ng/g and 20 ng/g, respectively.[8] Based on these results, the high sensitivity and accuracy of the HS–SPME–Arrow techniques can be emphasized.

The food industry has focused on vegan products; however, replicating meat products characteristic attributes (e.g., taste and flavor) remains challenging for food scientists.[40,41,42] Recently, plant–based patties supplemented with biji (okara or soybean curd residue) powder have been studied by comparing their quality characteristics and volatile compounds based on variations in the supplementary content. The volatile compounds in the plant–based patties were analyzed using HS–SPME–Arrow method coupled with GC/MS. Biji powder could mask off–flavors and function as an additive that can provide desirable meat flavors, including compounds such as 2–undecanone (fresh, orange, pineapple), 1–octanol (fruit and citrus), and 1–pentanol (almond and fruit).[7]

For discrimination of geographical origin, in particular, HS–SPME facilitates extracting a wide range of volatile compounds with varying molecular weights in agriculture. The profiles of non–target volatile compounds present a highly effective approach for distinguishing agricultural products, such as rice,[43] sesame seeds,[44] wheat,[45] and potatoes.[46] For example, volatile compound profiles of rice samples correctly classified geographical origins, such as China, Vietnam, and India, achieving 100 % accuracy. Based on highly predictive partial least square discriminant analysis (PLS–DA), the discrimination models identified five volatile compounds (dodecane–

5–methyl, octane–4–methyl, nonane–4–methyl, nonane–2,5 dimethyl and hexane–2,3,4–trimethyl) were identified potential markers for geographical discrimination.[43]

HSSE combined with GC/MS was employed to analyze the volatile compounds of frozen omija (FO), frozen–blended omija (FBO), and freeze–dried omija (FDO). Kim *et al*. investigated the correlation between device–based flavor characterization and human sensory analysis of a food product.[47] 28 volatile compounds were qualified and quantified in omija fruits using HSSE–GC/MS. The representative aroma–active volatile compounds of omija fruits, such as α– pinene, α–terpinene, and (E)–β–ocimene, showed significant differences in concentrations of three omija samples. Three major compounds were detected highly in freeze–dried omija.[48] As heating was not performed in FDO, the flavor profiles were similar to those of the other two samples (FO and FBO). Three sensory features included, ginger, pine needle, and wet grassy aromatics, exhibited significant differences among the samples. Cross–validation through the principal compound analysis (PCA) revealed that FBO and FDO had similar flavor characteristics, whereas FO contained distinguishing flavor characteristics. The establishment of the omija volatile compound profile using HSSE–GC/MS confirmed the efficiency of the freeze–drying pretreatment technique.[47]

2) Environmental samples

The identification of volatile compounds in water and the atmosphere is an important aspect of research in environmental monitoring aimed at minimizing human health risks *in vivo*.[6,33,49] Analysis of volatile compounds with toxicity in ecological matrixes is needed because they are ecotoxicants, such as carcinogens. For example, the extraction of benzene, ethylbenzene, m–xylene, o–xylene, and toluene from samples to simulate water pollutant conditions was conducted by HS–SPME–GC/MS using CAR/PDMS SPME fiber. The extraction method was optimized through numerical modeling with COMSOL Multiphysics, which is an effective approach for determining extraction parameters (e.g., stirring speed and fiber location). Notably, HS–SPME under vacuum conditions accelerated the extraction of 95 % of the equilibrium concentration of benzene compared to HS–SPME under normal atmospheric pressure.[6]

Determining low molecular weight alkylamines is challenging due to their reactivity, volatility, and wide range of concentrations.[50] To enhance the sensitivity of HS–SPME–GC/MS, derivatization is an essential procedure that improves the detectability of low–level amines by increasing their retention in the GC column.[51] When wastewater samples received from the Viikinmäki municipal wastewater treatment plant were analyzed using HS–SPME–GC/MS, the concentrations of DMA and trimethylamine hydrochloride were detected to be similar in both effluent and influent. The extraction of DMA using the SPME–Arrow fiber (PDMS/CAR) achieved 88 % recovery, which was significantly higher than the 57 % recovery from the SPME fiber (DVB/CAR/PDMS). TMA peak area decreased by 13 % with the SPME fiber in the DMA spiked samples and remained stable with SPME–Arrow.[22]

HSSE is an advantageous analysis technique for tracing a variety of compounds in environmental samples because of its adsorption capacity and high recovery with an automation system.[52] Polychlorinated biphenyls (PCBs) are persistent organic contaminants known for their cancer–causing effects and toxicity.[53] To trace ultra–fine amounts of highly toxic PCBs in soil samples, the HSSE–GC/MS technique using a stir bar coated with a hyperbranched aptamer (HB–Apt) was developed. The original aptamer is a type of single–stranded DNA or RNA that binds with high affinity to its target. However, the original aptamers were vulnerable to the extraction capacity and physicochemical stability of the restriction to detect trace levels of PCB. HB–Apt, which has extreme effectiveness and bioactivity characteristics, was produced using a hybridization chain reaction (HCR).[54] HSSE–GC/MS combined with the HB–Apt stir bar assay is an eco–friendly and accurate method that provides other ultrafine pollutant residues to be analyzed.[54] Furthermore, HSSE–GC/MS is used in water quality tests of water samples such as tap

water,[55] wastewater,[52] and river water. [52]

3) Biomedical and pharmaceutical samples

To date, diverse analytical techniques have been developed to detect pharmaceuticals in formulated products or biological samples; however, they often require large amounts of solvents and complex preparation procedures.[56,57] HS–SPME is generally used in the pharmaceutical industry for the separation and determination of analytes, as it makes the process more rapid, reliable, sensitive, and simple than other extraction and sample preparation methods.[58] Nakhodchi and Alizadeh recently optimized the HS–SPME method for simultaneous analysis of ketamine (Ket) and midazolam (Mdz) in human plasma samples by adjusting extraction time, extraction temperature, pH, stirring rates, and salt concentration. Among these parameters, pH strongly influenced the extraction of Ket and Mdz by supporting ionization and volatilization. The use of HS–SPME coupled with ion mobility spectrometry in human plasma samples achieved R^2 greater than 0.99, quantitative recoveries from 85 to 95 %, and LODs for Ket and Mdz were 8.9 and 52 μg L^{-1}, respectively. Consequently, this method eliminated the need for labor–intensive pretreatment or derivatization procedures, with a total analysis time of approximately 25 min.[23]

Nitrosamine contamination in medicines is an emerging hazard in the pharmaceutical industry, particularly highlighted by the European Medicines Agency, which screens suspected medicines. In 2019, the United States Food and Drug Administration informed the public that ranitidine medication had been contaminated with the carcinogenic impurity N–nitrosodimethylamine (NDMA).[59] Liquid chromatography coupled with mass spectrometry is generally used to analyze NDMA in ranitidine, whereas GC/MS, when implemented at high temperatures, may release NDMA from ranitidine itself, leading to potentially inaccurate measurements. Alshehri *et al*. demonstrated that HS–SPME coupled with GC/MS could effectively extract NDMA at 45 °C from commercial ranitidine samples. This optimized method yielded negative results for four ranitidine brands, consistent with the results obtained using LC–MS/MS techniques, indicating its potential for analyzing impurities in pharmaceutical products.[60]

Human respiratory diseases and illnesses were identified by HSSE–GC/MS analysis of the captured volatile metabolites. This technique can be used to promptly diagnose and treat conditions that enhance clinical outcomes. Human airway cells, a crucial cell type associated with respiratory tract diseases, exhibit considerable biological complexity and release volatile compounds at notably low concentrations.[61] Arthur and Pawliszyn's research on airway–relevant cell culture volatile compounds was performed using SPME fibers.[62] The SPME fiber is typically limited in its ability to detect analytes because of the small amount of sorbent on the fiber.[61] The HSSE showed a high recovery of 52 times and detected 97 more volatile compounds than the SPME model. Optimization of the HSSE analytical parameters, including extraction time (24 hours), desorption time (7 min), and desorption temperature (300 °C), were carried out.[61] This analytical process would be helpful for allergic sensitization, bacterial or viral infection, and exposure to a variety of topical drugs.[63]

2.2. DHS technique

The dynamic headspace sampling (DHS) technique is a solvent–free method. In DHS, continuous gas extraction is performed to completely extract volatile compounds from the sample using an inert gas flow.[63] After being preconcentrated into an adsorbent or a cryogenic trap, these volatile compounds are desorbed and heated for transfer into the GC/MS system for analysis.[5]

2.2.1. DHS extraction equipment

A DHS mainly consists of a sample vessel, a trap, and various tools such as probes, valves, and flow pressure regulators.[64] They are used for the control and regulation of temperature and purge gas. After incubating the prepared sample in a headspace screw–cap glass vessel, volatile compounds are formed in the headspace above the sample. The headspace is then purged with nitrogen gas, and the volatile compounds are transferred into the trapping glass

tube. The Purge and Trap (P&T) stir bar technique is one of the most widespread applications of DHS. The gas purge flow was pumped through the bulk of the sample to improve volatile recovery. Subsequently, the mixture is swept into an analytical trap, where the volatile compounds are absorbed and adsorbed. After purging and trapping, an additional gas flow dries the trapping pack to remove the remaining water that accompanies target volatile compounds.[64] This step prevents water from blocking the gas flow and destabilizing the GC stationary phase.[65,66] The trapped volatile compounds are released into a thermal desorption unit (TDU) by increasing the temperature. After thermal desorption (primary trap) in the TDU, a cryogenic trap (secondary trap) is created by transferring the trapped volatile compounds to a cooled injection system. This is typically accomplished in fused–silica traps with N_2 and CO_2.[67] The cryogenic trap proceeds fast, improves peak sharpness, and enhances sensitivity and separation.[68] Finally, the volatile compounds are separated and detected from the GC/MS system.

2.2.2 DHS experimental parameters

The optimization of several parameters for DHS is essential for the accurate analysis of samples. Depending on the analyte characteristics (e.g., polarity, volatility, and matrix affinity) and sample matrix type, several parameters should be set for headspace sampling, including sampling time, sample temperature, and sample volume ratio. Equilibrium time and temperatures in the range of 45 – 150 °C, based upon the targets' stability and the sample matrix, are required to offer reproducibility in headspace sampling. The time and temperature conditions for extraction and desorption should also be optimized.[9,69] Furthermore, using low sample volume ratios and solvents to solubilize the analytes could enhance the sensitivity, particularly for low–solubility samples. Adding salts to the sample decreases the solubility of analytes in water, resulting in higher concentrations of volatile compounds in the headspace.[69] Depending on the chemical and matrix characteristics of the sample, a high–viscosity sample may be diluted, or an antifoam agent may be added.[70,71]

DHS must optimize additional factors in comparison with other headspace techniques. Parameters such as purge volume and desorption temperature should be considered the 'purge and trap' application.[64] Dry gas, TDU, and cooling injection system (CIS) options (e.g., temperature, flow, rate) are also the parameters for the optimization samples using the DHS technique.[72] To ensure the comprehensive capture of volatile compounds in the headspace, inert gas flow (15 – 45 mL/min) and purge time (2–15 min) should be optimized. It is necessary to consider the breakthrough volume, which is the maximum volume per gram of adsorbent that can be coated without considerable loss of the sample from the trap. In addition, different sample vials (e.g., a purge tube with frit, fritless purge vial, or needle sparge vial) are used following the sample and extraction modes. Various traps and cartridges with different diameters, thermal stabilities, desorption properties, and sorbent compositions (e.g., Silica gel, Tenax, Chromosorb, carbon molecular sieves, or graphitic carbons (Carbotrap)) are available for volatile preconcentration.[73]

Tenax sorbent, a porous hydrophobic polymer, is the most used owing to its low water retention and suitability in detecting a wide range of volatile compounds.[74] When comparing water adsorption, Tenax showed the lowest water absorption (1 – 3 mg water per g adsorbent), an important characteristic for analyzing water–based samples.[73] In comparing the capability of mainly used solid absorbents, the trap containing Tenax displayed the greatest performance of trapping esters, aldehydes, and aromatic hydrocarbons.[75] Additionally, the Tenax trap is widely used because of the capacity for samples with high boiling points and extended shelf life.[64,74] Meanwhile, Carbotrap and carbon molecular sieve materials are regarded for their high capacity in adsorbing volatile compounds with low boiling points.[74] Chromosorb exhibits a higher artifact signal in the 5 – 10 ng range compared to other adsorbents. Moreover, it has low thermal stability, with a maximum operational temperature of 225 °C.[76] The optimization of adsorbent is essential and should be based on the chemical properties of the target compounds.

Table 2. Recent applications of DHS technique for analysis of volatile compounds in different fields

Sample	Objective	DHS extraction procedure	Instrumental conditions	Method validation				Ref.
				LOD/LOQ	R^2	IS	Recovery (%)	
Food samples								
Orange juices	– Characterization of volatile profiles followed by DHS-GC/MS – Correlations between volatile profiles and human sensory perceptions	– Sample: 3 mL in 10 mL vials – Equilibration: 60°C, 10 min, 400 rpm – Purge flow: 70 mL/min N_2 (3 min) – Dry purge flow: 40 mL/min N_2 (2.5 min).	TDU: Desorption: 25 °C (0.2 min) – 720 °C/min, 250 °C CIS: Cooled temperature: -10 °C N_2; 12 °C/s, 250 °C (5 min) GC: Split mode (50:1); Column: DB-WAX (60 m × 0.25 mm × 0.25 μm); Trap: Tenax TA; Oven program: 50 °C (2.5 min) – 4 °C/min, 200 °C; MS detector.	–	–	tetradecane	–	[76]
Botrytized wine	Optimization and characterization of volatile profiles followed by DHS-GC/MS techniques	– Sample: 5 mL in 20 mL vials – NaCl content: 1 g – Equilibration: 54°C, 20.17 min, 500 rpm – Extraction: 80°C – Purge flow: 16 mL/min He (21.52 min) – Dry purge flow: 5 mL/min He (2 min).	TDU: Desorption: 40 °C (10 min) – 120 °C/min, 110 °C (1 min) – 120 °C/min, 300 °C (10 min); Solvent vent mode CIS: Cooled pressure: 0 psi; 12 °C/s, 20 °C – 300 °C GC: Solvent vent mode; Column: DB-FFAP (30 m × 0.25 mm × 0.25 μm); Trap: Carbopack B/Carbopack X and Tenax TA; Oven program: 40 °C (10 min)–2 °C/min, 220 °C (5 min); MS detector.	– LOD: 0.2–2.0 μg/L – LOQ: 0.5–5.0 μg/L	0.884–0.997	benzophenone	–	[73]
Environmental samples								
Raw rubber	Identification of volatile compounds followed by DHS–GC/MS techniques	– Sample: 4 g in 20 mL vials – Equilibration: 30°C, 5 min, 500 rpm and 60°C, 5 min – Extraction: 35°C – Purge flow: 100 mL/min He – Purge volume: 500, 1000, 1500, and 2000 mL – Dry purge flow: 100 mL/min He (5 min).	TDU: Desorption: 50 °C (1 min)–720 °C/min, 300 °C (8 min) CIS: 10 °C/s, 20 °C – 300 °C GC: Split mode (20.7 mL/min); Column: DVB-RX; Trap: Tenax TA; Oven program: 50 °C (2 min) – 15 °C/min, 200 °C (5 min) – 5 min; MS detector.	–	–	–	–	[65]
Additives in plastic samples	– Development of additives tracing model with volatile profiles followed by ITEX–DHS–GC/MS – Optimization of ITEX–DHS–GC/MS techniques	– Sample: 0.5 g in 20 mL vials – Equilibration: 200°C, 30 min – Extraction: 95°C, aspiration (150 strokes), 250 μL/s, 1000 μL – Desorption: 300°C, 300 μL/s, 1000 μL (gas).	Injector temperature: 320 °C; Split mode (10:1, 12.29 mL/min); Column: HP-5 MS UI (30 m × 0.25 mm × 0.25 μm); Trap: Tenax TA 80/100 mesh; Oven program: 80 °C (2 min)–5 °C/min, 220 °C –7 °C/min, 340 °C; MS detector.	– LOQ < 0.1 μg/g	0.981–0.999	–	70–128%	[77]
Biomedical and Pharmaceutical samples								
DMTS (cyanide antidote)	– Analytical technique development of identifying DMTS in blood with DHS–GC/MS techniques – Optimization of DHS–GC/MS techniques	– Sample: 900 μL in 20 mL vials – Equilibration: 40°C, 1 min – Trapping: 28°C, 10 min	TDU: Desorption: 30 °C (1 min)–12 °C/s, 280 °C, 275°C CIS: Colded temperature: -100°C; 12 °C/s, 275 °C GC: Column: DB5-MS (30 m × 0.25 mm × 0.25 μm), 10 psi; Trap: Tenax TA; Oven program: 30 °C (1 min)–120 °C/min, 250 °C (2 min); MS detector.	– LOD: 0.04–0.06 μg/L – LOQ: 0.2–50 μM	0.9962–0.9989	dimethyl-d_6 trisulfide	–	[78]
Aromatic and chlorinated compounds in urine	– Determination of aromatic and chlorinated compounds in urine followed by DHS–GC/MS	– Sample: 2, 5, 10 mL in 20 mL vials – Extraction: 80 °C, 30 min, 30 psi – Dry purge: 5 min – Desorption: 280°C, 25 psi	Column: DB-5MS (60 m × 0.25 mm × 1.0 μm); Trap; Air monitoring trap; Oven program: 40 °C (5 min)–8 °C/min, 85 °C (20 min)–45 °C/min, 250 °C (5 min); MS detector.	– LOD: 5 ng/L – LOQ: 10–15 ng/L (styrene: 50 ng/L)	0.991–0.998	toluene-d_8	–	[80]

LOD: limit of detection, LOQ: limit of quantification, IS: internal standard, Ref.: reference, DHS: dynamic headspace sampling, GC: gas chromatography, MS: mass spectrometry, ITEX: in–tube extraction, TDU: thermal desorption unit, CIS: cooled injection system, DMTS: dimethyl trisulfide

2.2.3. Applications

The DHS method is an analytical technique applied in a wide range of fields. DHS is a formally recommended technique developed to detect hazardous volatile compounds in soil and water samples.[77] In addition to legal purposes, DHS proved useful in evaluating food certification and the quality of pharmaceuticals.[78] In addition to analyzing volatile compounds in animal feed and strawberry honey to identify zoological and botanical origin markers.[10,79] *Table* 2 summarizes the main samples and specific experimental parameters used in combining DHS and GC analysis throughout the study.

1) Food samples

As DHS is a free solvent and is faster, it provides better results in managing food and beverage quality.[69] Different processing conditions, such as thermal processing temperatures, greatly affect the flavor profile of food. The research of Kim *et al*. showed the correlation between the instrumental and sensory flavor profiles of commercial orange juice (OJ) products with different processing methods.[11] The room temperature OJ contained more favorable volatile compounds including β–pinene, decanal, dl–limonene, linalool, and nonalool. Meanwhile, OJ that needed to be refrigerated showed a high concentration of α– and β–terpineol. Sensory analysis characterized room–temperature storage samples as having a cooked orange flavor ($p < 0.05$). The flavor of refrigerated storage samples was defined as orange peel characteristic ($p < 0.05$).[11] The research on correlation between sensory evaluation and instrumental volatile compounds identified by HSSE–GC/MS greatly improves our capacity to distinguish between different commercial juices.

The transfer of volatile compounds from the sample to the adsorbent with a constant flow of inert gas is a major characteristic of the DHS technique.[64] Recently, multiple volatile models using the DHS technique have been developed. This mode is based on the multi–step fractionation of samples at different extraction temperatures. Two adsorbents (Tenax® TA and Carbopack B/Carbopack X) were applied to the wine sample at varying extraction temperatures to maximize the extraction of volatile compounds.[78] The analytical technique was developed using the following optimized extraction conditions: 54 °C incubation temperature, 20.18 min for incubation time, 16.0 mL/min purge flow rate, and 344.3 mL purge volume. In wine samples, α–terpineol, γ–hexalactone, ethyl phenylacetate, and linalool oxide showed significant differences ($p < 0.05$), which could be key aroma chemicals of botrized wine.[78] The development of the dual adsorption mode DHS was influential in determining the characteristics of wine sort and maturation.

2) Environmental samples

A stench that occurs during rubber production is an emerging environmental and public health problem. The analysis of volatile compounds in rubber is indispensable for solving rubber–derived odor emissions and discomfort. Four headspace technologies: SHS, DHS, HS–SPME, and micro-chamber/thermal extractor (μ–CTE) were used to detect volatile compounds in rubber.[9] Compared to SHS, DHS has a superior detection ability to detect low concentrations of volatile compounds.[9] A total of 23 new compounds were identified using DHS compared to the conventional SHS techniques. Meanwhile, a similar number of volatile compounds was detected when compared to HS–SPME. Due to high trapping temperature and thermal desorption limitations, the number of volatile compounds with DHS was lower than those detected using μ–CTE. The main compounds identified in rubber extracts were pentanoic acid, D–limonene, and phenol. In contrast to SHS and HS–SPME, DHS was used for the first time to analyze rubber extracts.[9]

Because plastic additives produce many harmful substances, an analysis process is essential for evaluating the risk of plastic pollution. Plastic additives have mostly been analyzed using techniques with high detection limits and toxic solvents. However, Concha–Graña *et al.* developed a non–solvent, environmentally safe method for automatically analyzing plastic additives.[80] 47 additives in plastic were quantified through the in–tube extraction DHS (ITEX–DHS) combined with GC–MS/MS. ITEX–

DHS is the process of repeatedly pumping headspace using gas–tight syringes into connected tubes packed with Tenax TA 80/100 mesh sorbents, which are capable of a wide range of volatility and polarity characteristics.[80] In contrast to typical DHS, ITEX–DHS can easily analyze large solid samples. The developed method can be used for microplastic monitoring programs, plastic quality control, and leaching research.[80]

3) Biomedical and Pharmaceutical samples

Toxic and fast–spreading cyanide causes cell hypoxia and cytotoxic anoxia, resulting in death. Recently, dimethyl trisulfide (DMTS) has gained attention as an antidote for cyanide. DMTS has been analyzed using high–performance liquid chromatography–ultraviolet (HPLC–UV), SBSE–GC/MS, and HS–SPME–GC/MS. SBSE is expensive and time–consuming. HPLC–UV is an inexpensive and simple method, but it is 193 times less sensitive than SBSE.[12,81] HS–SPME is relatively expensive for extracting fiber, and its sensitivity is 25 times less sensitive than SBSE.[12,81] However, the DHS technique is very simple, involving only acidification of samples, internal standard addition, and instrumental analysis.[12] The inter–trial accuracy was 100 ± 15 %, the intra–trial accuracy was 100 ± 9 %, and the RSD was less than 9 %, demonstrating accurate analytical values.[12] Furthermore, blood samples collected at 60 days of age could also be used to evaluate DMTS. This technique is suitable for DMTS blood concentration analysis in drug development studies.

Although less toxic alternatives have replaced many hazardous chemicals that are widely used in the industry, they are still in use. Erb *et al*.'s research established the rapid simultaneous detection of 11 aromatic and chlorine compounds as harmful contaminants (e.g., toluene, chloroform, and trichloroethylene) identified in urine.[82] In contrast of SHS, volatile compounds present in urine were more efficiently extracted and concentrated in adsorption traps using DHS–GC/MS.[64,82] The conditions of extracting 11 urinary volatile compounds in urine samples were optimized at 80 °C for 30 min. The method was validated with good precision, with inter–day precision values between 2.1 % and 5.5 % and intra–day precision values ranging from 2.7 % to 8.5 %. These results were consistent at the lowest concentration within the established linear range among the 11 spiked volatile compounds.[82] Although the concentrations of the 11 targeted volatile compounds in urine were generally low, significant differences were observed in urine samples from workers before and after their factory tasks. The high sensitivity of DHS can be used to check for exposure to harmful chemicals in human bodily fluids.

3. Conclusions and Future Trends

This review provides an overview of the recent developments and applications of HS techniques for extracting volatile compounds in various fields. Both SHS and DHS are commonly used to analyze volatile compounds in food, environmental, biomedical, and pharmaceutical samples. The primary advantages of these techniques are their improved recovery and sensitivity, along with their straightforward and rapid implementation. Furthermore, HS techniques eliminate the need for solvents or other potentially hazardous chemicals, safeguarding the environment and human health. These advantages have emphasized environment–friendly approaches as viable alternatives to traditional methods, such as distillation and solvent–based extraction, across various applications.

The lack of sensitivity and discrimination in extracting low–volatility compounds is typically identified as the primary limitation of SHS. In contrast, DHS combines the benefits of SHS, such as the extraction of high–volatility compounds with high sensitivity. The high recovery is attributed to the alteration of the thermodynamic equilibrium, shifting the gas phase above the sample, utilizing a larger volume of the extractant gas phase, and complete transfer of all volatile compounds into the GC instrument. Additionally, it is essential to recognize that the extraction efficiency of volatile compounds is significantly influenced by the experimental parameters and characteristics of the sample matrix.

Recent advancements in SHS and DHS extraction

equipment have primarily focused on developing systems or devices that enable faster and more sensitive determination of targets or non–targets. Advanced SPME, SPME–Arrow, HSSE, and DHS can play a key role in extracting trace analytes such as active ingredients, toxic compounds, and impurities from food, environmental, and pharmaceutical samples. However, their applications remain limited to routine analysis to achieve reproducibility, efficiency, practicality, and accuracy. In addition, method validation, including acceptable selectivity, linearity, precision, detection and quantitation limits, robustness, and stability, should be conducted to demonstrate the reproducibility and accuracy of this method. Consequently, in line with the current analysis trend, the parameters for headspace extraction must be optimized in detail for each technique for different purposes.

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