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November 2023

ADVANCES IN SAMPLE PREPARATION

A supplement to *LCGC North America*

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Cover Image: Poter - stock.adobe.com | Cover Cannabis flowering plant with artist's colorful background and lighting

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FROM THE GUEST EDITOR

Advances in Sample Preparation

Elefteria Psillakis

Sample preparation continues to rise in importance with greenness and sustainability issues guiding future developments and trends. This is certainly reflected in the articles included in this collection. The first contribution by Cecilia Cagliero discusses the importance of environmentally friendly and sustainable sample preparation methods in plant metabolomics. The author emphasizes the need to consider not only the environmental impact but also the productivity and analytical performance of the approach applied. This article also highlights the crucial role of sample preparation in obtaining reliable and comprehensive data.

In the second article by Francisco Antonio Casado-Carmona, Rafael Lucena, and Soledad Cárdenas, the relevance of extraction techniques in onsite strategies is discussed, particularly in the context of environmental studies. Their focus on stirred units and the impact of open-source technologies in their design provides valuable insights for analysts and researchers conducting ambitious sampling campaigns in large and heterogeneous environmental compartments.

In the field of food analysis, the article by Steven Mascrez, Juan Aspromonte, and Giorgia Purcaro sheds light on the great potential of vacuum-assisted and multiple-cumulative trapping approaches to improve the efficiency and broaden the applicability of headspace-solid-phase microextraction. The authors demonstrate the effectiveness of these techniques in characterizing complex olive oil samples in terms of quality.

Next up, the article by Amir Salemi and Torsten C. Schmidt highlights the unique capabilities of passive samplers and their utilization in various fields of study, including wastewater-based epidemiology and non-target analysis. This article serves as a valuable resource for researchers seeking to benefit from the advantages of passive sampling in their studies.

Lastly, Shannon L. Thomas and Kevin A. Schug elegantly summarize in their review article the most important features of vacuum-assisted headspace solid-phase microextraction, a "game changer" technology and approach to use during headspace sampling of semivolatiles. This review will prove valuable to both new and advanced users, and serve a quick guide for applications, and underlying fundamentals.

LCGC readership will undoubtably find the articles inspiring and benefit from the authors sharing their expertise. I am grateful to all authors for producing such exciting articles, and to the *LCGC* staff who worked hard to ensure that the articles are published in a timely manner.

Enjoy reading!

Elefteria Psillakis
Professor, Technical University of Crete, Greece

From "Green" to "Sustainable" Sample Preparation in Omics Studies in the Natural Product Field: Case Studies Dealing with *Cannabis sativa* L.

Cecilia Cagliero

Plant metabolomics requires that as many metabolites as possible are extracted to obtain a reliable picture of the sample under study. Therefore, sample preparation plays a crucial role. In recent years, several efforts have been made to improve the environmental friendliness of sample preparation, including in the plant sector. However, the environmental friendliness of a method cannot be evaluated without also considering its productivity and, more importantly, its analytical performance to ensure not only environmental friendliness but also the "sustainability" of sample preparation approaches.

Plants and natural products are rich sources of a variety of bioactive metabolites that can be used for several applications, such as food and health. Their analyses need to cover a wide range of topics, from metabolomics studies to quality and safety controls. In particular, metabolomics studies for medicinal plants are growing rapidly and aim, for example, to identify new bioactive compounds, determine balsam time, monitor plant quality, and correlate the chemical composition of a natural product with its quality. Despite the remarkable technological advances made in recent years, the chemical diversity of primary and secondary metabolites of complex natural products still poses challenges for analysis. They affect all analytical steps from sample collection and sample preparation to analysis and data processing (1).

The main challenges in the analysis of natural products are related to the complexity of the plant metabolome, which, in addition to the abundant primary metabolites, is characterized by the presence of hundreds of specialized (secondary) metabolites belonging to different chemical classes, which are often present in very different amounts and, in some cases, are susceptible to degradation. Some of these compounds (such as chlorophylls and other pigments in photosynthetic tissues) could also interfere with extraction or analysis of target compounds. It is also important to remember that the samples are mainly solids and that plant cells are protected by thick and robust lignocellulosic walls that should be disrupted if efficient extraction of intracellular metabolites is to be achieved. All these factors have led to the analysis of natural products being quite conservative, especially in terms of sample preparation, which still mainly uses traditional extraction techniques, such as liquid-liquid extraction (LLE) and Soxhlet extraction, and involves high consumption of toxic and volatile organic solvents.

The use of microextraction techniques and new classes of more sustainable extraction phases are gaining importance as they meet the criteria of green analytical chemistry (GAC) (2), particularly green sample preparation (GSP) (3,4), and are thusly applied in the plant field (5). In this sense, several metric tools have been developed in recent years to assess the greenness of a method and its compliance with GAC principles. Of fundamental importance was the development of the AGREEprep metric tool, which focuses on sample preparation and is based on the ten principles of GSP (6). At the same time, the need has arisen in recent years to conduct a holistic and comprehensive evaluation of an analytical methodology and to balance the environmental friendliness of a method with its analytical performance and practical efficiency (7,8). A global assessment of analytical methods would be beneficial to industry and quality control laboratories because, in addition to increasing interest in improving the environmental impact of analyses, industry and official laboratories are dealing with a multiplication of norms and quality standards that require accurate and reliable measurements, as well as practical considerations such as productivity, cost, and simplicity of methods. In addition, assessing the environmental impact of a method (which provides an ecological outcome) along with assessing its analytical performance (which ensures the quality of the results and thus the social impact) and its productivity (which measures the economic impact) would help to measure the degree of "sustainability" of a given method (8,9). Some tools have also been developed to critically and globally evaluate analytical methods by balancing considerations of a method's environmental friendliness

with its analytical efficiency and practical efficiency (7,10), but their application is rather scarce, particularly in the assessment of sample preparation methods. However, in plant-based metabolomics studies, reliable sample preparation is essential because, as Mushtaq and coauthors noted, "the value of the information obtained from a metabolomic study depends on how much of the metabolome is present in analyzed samples. Thus, only a comprehensive and reproducible extraction method will provide reliable data, because the metabolites that will be measured are those that were extracted and all conclusions will be built around this information" (11).

Two case studies dealing with *Cannabis sativa* L. will be presented here to demonstrate the importance of evaluating the overall performance of sample preparation methods, especially in the plant field.

Cannabis sativa L. is a fascinating plant that has been used for recreational, medicinal, textile, and food purposes since ancient times. From a chemical point of view, it is a very complex matrix, as it contains several classes of specialized metabolites, including more than 100 cannabinoids, 120 terpenoids (monoterpenes, sesquiterpenoids, and triterpenoids) and several flavonoids among the more than 500 compounds identified (12). The plant metabolome is highly variable depending on the part of the plant considered (Figure 1). Cannabinoids and terpenoids are produced and stored in the secretory cells of the glandular trichomes, which are located in the aerial parts of the cannabis plant and especially on the upper surfaces of the seedless female flowers. Therefore, they are mainly found in the inflorescences of the plant, while their content in the leaves decreases sharply, and they are almost absent in the barks of the stems and in the roots. In contrast, the content of flavonoids is highest in the leaves, while they are less present in the inflorescences and almost absent in the roots and stem barks (12).

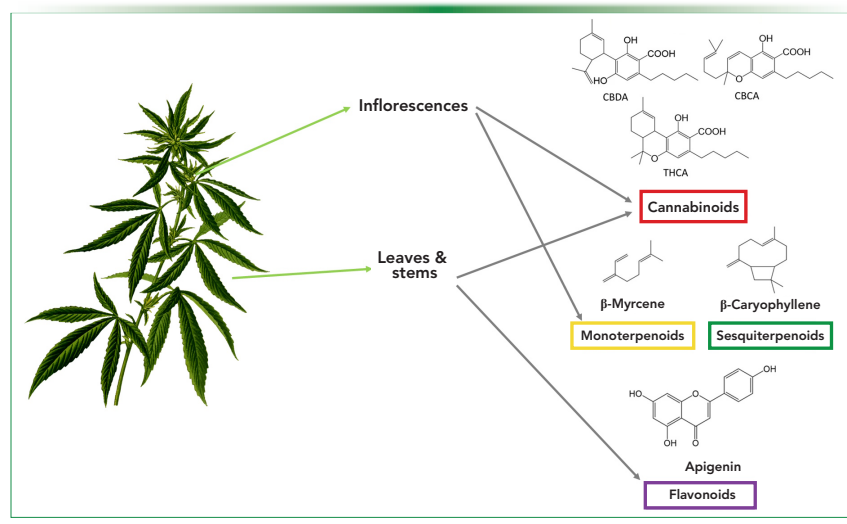


FIGURE 1: Main classes of specialized metabolites in *C. sativa* aerial parts (12).

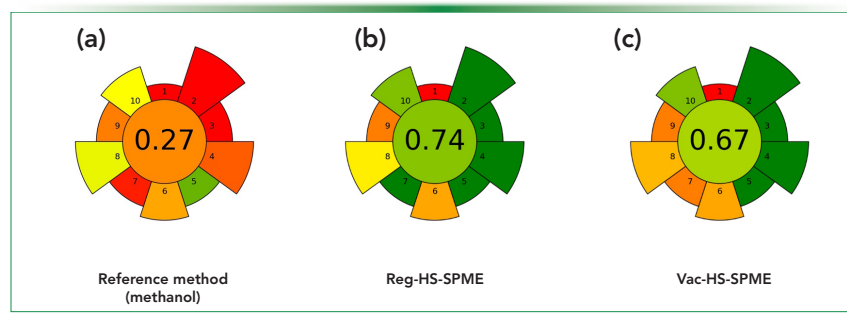


FIGURE 2: AGREEprep scores of the (a) reference method (12), (b) Reg-HS-SPME, and (c) Vac-SH-SPME methods (16) that can be adopted for the determination of terpenoids and cannabinoids from *C. sativa* L. inflorescences.

Classification and taxonomy of this plant is often difficult and ambiguous due to the high variability within the genus. Usually, a distinction is made between drug (cannabis) and fiber (hemp) types, based on the higher content of tetrahydrocannabinol (THC) and cannabidiol (CBD), respectively. Although attention has focused mainly on these two main markers, there is growing interest in exploring the bioactivity of *C. sativa* in terms of potential synergistic effects, the so-called entourage effect, which could contribute to or modulate the therapeutic properties of cannabis or hemp extracts. Synergistic effects have already been demonstrated in research on combinations of phytocannabinoids and phytocomplexes of cannabinoids and terpenoids. In addition, phenolic compounds are also known for their broad biological activity (13), and it is therefore important to determine the entire specialized metabolome to obtain an accurate characterization of the plant. In this sense, the extraction step is of fundamental importance, since significant differences in bioactive chemical profiles are observed in the extracts obtained with the different protocols (14).

As mentioned earlier, the inflorescences of cannabis are mainly characterized by the more volatile terpenoids and the semi-volatile cannabinoids. The most common method for extraction of cannabinoids is solid-liquid extraction (SLE) using organic solvents (such as ethanol, methanol, or acetone) coupled to high performance liquid chromatography (HPLC) or gas chromatography (GC) combined with mass spectrometry (MS). Organic solvents can also be used for the extraction of terpenoids (which are subsequently analyzed by GC), so that the two classes of compounds can be determined simultaneously by

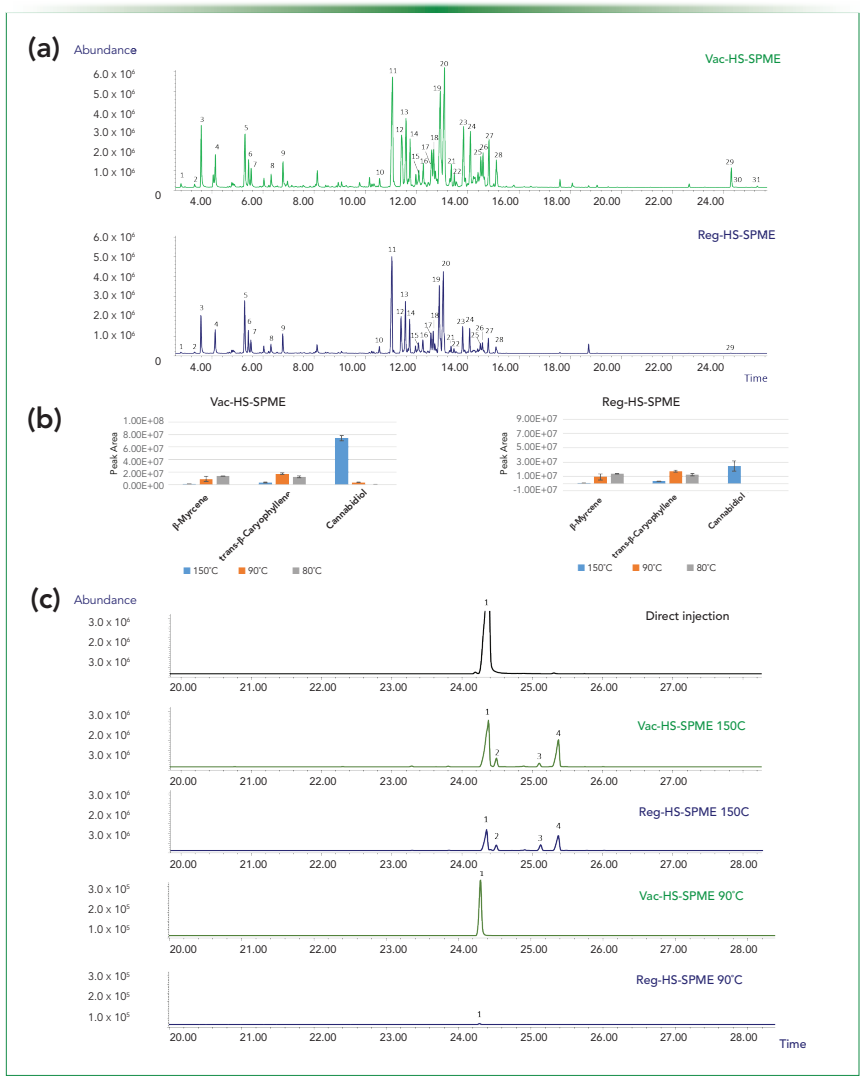
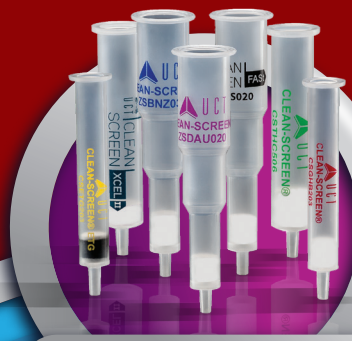


FIGURE 3: (a) HS-SPME GC–MS profiles obtained when sampling 10 mg of matrix at 90 °C for 5 min under reduced pressure (Vac-HS-SPME) and atmospheric pressure (Reg-HS-SPME) conditions. Legend: 1) α-Pinene, 2) β-Pinene, 3) β-Myrcene, 4) Limonene, 5) Linalool, 6) Fenchol, 7) cis-Pinene hydrate, 8) Borneol, 9) α-Terpineol, 10) β-Patchoulene, 11) *trans*-β-Caryophyllene, 12) *trans*-α-Bergamotene, 13) α-Humulene, 14) *trans*-β-Farnesene, 15) β-Selinene, 16) α-Selinene, 17) α-Farnesene, 18-19) Sesquiterpene, 20) Selina-3,7(11)-diene, 21) *trans*-Nerolidol, 22) Caryophyllene oxide, 23) Guaiol, 24) 10-epi-γ-Eudesmol, 25) β-Eudesmol, 26) α-Eudesmol, 27) Bulnesol, 28) α-Bisabolol, 29) Cannabidiol, 30) Cannabichromene, 31) Cannabinoid 2 (supposed Δ9-THC). (b) Extraction temperature profiles of CBD, β-myrcene and *trans*-β-caryophyllene obtained under Vac-HS-SPME and Reg-HS-SPME. C) GC–MS profiles of CBD standard solution under the following conditions: injection of 1 µL of CBD standard solution 1 mg/mL; 10 µL of CBD standard solution 1 mg/mL recovered by Vac-HS-SPME after 5 min at 150 °C and 90 °C; CBD standard recovered by Reg-HS-SPME after 5 min at 150 °C and 90 °C. Legend: 1) Cannabidiol, 2) Cannabichromene, 3) Cannabinoid 1 (supposed Δ^8-THC), 4) Cannabinoid 2 (supposed Δ^9-THC). Modified from (16). Axis labels for Figures 3a and 3c are Time (*x*-axis) and Abundance (*y*-axis). For Figure 3b, axis labels are Analyte with respect to Temperature (*x*-axis) and Peak Area (*y*-axis).

methods that can have strong environmental implications (15). Figure 2 shows the AGREEprep results for the method developed by Jin and coauthors to isolate terpenoids and cannabinoids using methanol as the extraction solvent (12). A final score of 0.27 is obtained, with several parameters showing very critical values.

Thanks to their volatile nature, the isolation of terpenes, especially mono- and sesquiterpenes, from plant raw materials can be performed by headspace solid-phase microextraction (HS-SPME) online combined with GC–MS analysis. Recovery of the semi-volatile cannabinoids from solid matrices by HS-SPME is also possible, but requires long sampling times due to their low volatility and low tendency to escape into the headspace. Indeed, poor recovery of cannabinoids is observed when using conventional sampling conditions (90 °C and 30 min) (Figure 3a) (16).

When investigating the possibility of sampling at higher temperatures, it is possible to observe that these conditions significantly discriminate against the recovery of more volatile markers (such as terpenoids) due to a reduction in the partition coefficient between the fiber and the headspace and an enhancement of competitive adsorption and displacement of low molecular weight analytes, given the extremely high amount of cannabinoids extracted (Figure 3b). Moreover, high temperature during sampling, especially when combined with relatively long extraction times, can lead to decomposition of cannabinoids and the formation of other components or artifacts (17). In fact, by submitting a CBD standard HS-SPME for only 5 min at 150 °C, it is possible to observe that the compound is degraded forming cannabinoids, including cannabichromene (CBC), Δ^9-THC, and Δ^8-THC (Figure 3c) (16). Thus, the HS-SPME method is certainly greener (Figure 2), but it can provide unreliable and misleading results. To maintain the optimal greenness of HS-SPME and avoid the risk of artifact formation, a very interesting option is the possibility of sampling at reduced pressure. As described in detail by Psillakis (18), vacuum is a powerful experimental parameter to consider to increase the extraction kinetic of semi-volatile compounds during the HS-SPME process. This is because, in the case of semi-volatiles and under non-equilibrium conditions, reduced pressure in the sample container decreases the resistance to mass transfer in the gas zone at the interface between the solid and the headspace. As a result, higher extraction efficiencies for semi-volatile compounds can be achieved in shorter sampling times and at milder extraction temperatures. Indeed, it can be observed that when sampling at a mild temperature (90 °C), regard-



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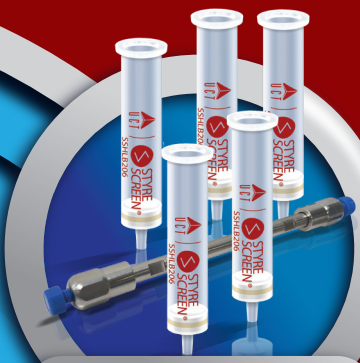

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less of the sampling time, the amount of CBD extracted with vacuum is several times higher than the amount obtained under regular conditions. In only 5 min, a sufficient amount of CBD could be extracted with vacuum to achieve an acceptable instrument sensitivity and to obtain a good picture of CBD abundance in inflorescences (Figures 3a and 3b). Moreover, no degradation of CBD can be observed at this temperature (Figure 3c) (16). This approach somewhat reduces the environmental friendliness of the method (Figure 2), since an additional step is introduced, but it also allows reliable results to be obtained. The three methods can be evaluated in terms of their overall performance. Among the available tools, the RGB model was chosen because it is flexible in the selection of parameters to be evaluated and the assignment of their relative weights, making it easier to adapt to the scope of the analysis and the objectives to be achieved. The name RGB is derived from the three primary colors that correspond to the three main parameters of each analytical method. The red color represents the analytical performance of the method, the green color represents its safety and greenness, and the blue color represents its productivity and practical effectiveness. An overall method score (called method brilliance) is calculated by combining the results of the three attributes, also taking into account the relative importance that the user attributes to each of them. The comparison of the RGB results is shown in Figure 4 (available online, along with Figures 5 and 6, by accessing the QR code at the end of the article) and highlights that the analytical performance of the Vac-HS-SPME method is comparable to the conventional method, while strong improvements are obtained in terms of greenness and productivity, indicating that the method is the most reliable for metabolomics characterization of *C. sativa* inflorescences.

As already mentioned, the other parts of the plant are characterized by a different phytocomplex (12). In particular, studies have shown that the aerial parts of hemp (stems and leaves) are mainly characterized by the presence of flavonoids and non-psychotomimetic cannabinoids, which can be simultaneously extracted by ultrasound-assisted methanol solid-liquid extraction (13). The method is reliable, but again, evaluation of the AGREEprep score shows that the method is quite impactful on the environment (Figure 5a).

Deep eutectic solvents (DES) are a more environmentally friendly alternative to conventional solvents thanks to their ease of preparation and low raw material costs. They consist of two or more components that form a hydrogen bonding network, which is key to the formation of the DES. Various natural compounds have been used as hydrogen bond donor (HBD) or acceptor (HBA) to produce both hydrophilic and hydrophobic natural DES (NADES). Hydrophobic natural terpenoids and phenolic compounds (carvacrol, eugenol, linalool, menthol, terpinen-4-ol, and thymol) were used in a dispersive solid-liquid microextraction (DSLME) to isolate non-volatiles from hemp leaves (Figure 6) (19).

The method is certainly faster, more user-friendly, and greener than the conventional method (Figure 5a). Indeed, it only requires 100 mg of the hemp plant, 2 mL of water as co-solvent and 100 µL of eutectic solvent, which is dispersed in the sample by a vortex step, followed by 10 min of ultrasound to help release the target compounds from the plant. The NADES phase is then separated by centrifugation before analysis by HPLC. NADES are very effective in extracting the more hydrophobic cannabinoids (Figure 6b), but are less effective than the conventional method in isolating the more polar flavonoid glycosides. For this reason, a new class of hydrophobic compounds has been developed. The structure of polar choline was used as a model for the development of a new HBA. The hydroxyl functional group of choline was retained to improve the polarity of the new compounds and their ability to form hydrogen bonds, but the length of the alkyl chain substituents appended to the ammonium head group was increased to improve hydrophobicity and broaden the range of application. The developed $[Ch^+][Br^-]$-based salts have been mixed with thymol to form DESs, which showed better extraction of hydrophilic compounds (such as flavonoids) compared to the NADES, while maintaining the same good enrichment for cannabinoids (see Figure 6b) (20). The environmental impact assessment of the method shows a reduction in performance due to the need to synthesize the $[Ch^+][Br^-]$-based salt (Figure 5a). However, the RGB results presented in Figure 5b show better overall performance of this latter method, which is therefore more suitable for reliable metabolomics characterization of the nonvolatile fraction of *C. sativa* aerial parts.

Conclusion

Scientists working in analytical chemistry and, in particular, in the field of sample preparation have made great efforts to improve the environmental performance of their methods, thanks in part to the increasing attention paid to environmental sustainability by government agencies and the public. This improvement is essential as the world is committed to addressing climate and environmental challenges. However, we have shown here that, especially for complex samples, the environmental friendliness of a method should be evaluated along with its productivity and, more importantly, its analytical performance to ensure not only environmental friendliness but also "sustainability" of the results. New metric tools that also take these aspects into account and give appropriate importance to the sample preparation step are therefore desirable for the future.

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This article has additional supplemental information only available online. **Scan code for link.**

Onsite Environmental Extraction Based on Portable and Affordable Stirred Devices

Francisco Antonio Casado-Carmona, Rafael Lucena, and Soledad Cárdenas

Environmental compartments are characterized by their large size and the heterogeneous distribution of the target analytes. Onsite extraction procedures are especially useful in this scenario, allowing the development of ambitious sampling campaigns (including a larger number of locations and periods). This article outlines the relevance of extraction techniques, including exhaustive and non-exhaustive ones, in onsite strategies. However, only stirred units are discussed and described in detail. The discussion of the analytical performance (for example, sensitivity and precision) is intentionally avoided to focus the attention on the devices that can be applied (selecting the sorptive phase) to almost any analytical problem. The impact of open technologies (microprocessors and 3D printing) in the design of these units is also presented.

Onsite environmental analysis is a simplified procedure that measures the target analytes at the sampling point. This strategy reduces errors by eliminating unnecessary steps that add to the total variance of the results (1). Onsite analysis also maintains the sample's representativeness by avoiding storage and transportation, which can alter the sample composition (in ways such as, but not limited to, analyte losses by adsorption in the vessel walls). However, onsite analysis often depends on portable instruments with lower performance than benchtop facilities. The sensitivity and selectivity can be improved by applying an onsite sample preparation step. This combined approach is practical for those problems where the sample matrices are not very complex, and the concentration thresholds are not very strict. If these conditions are not fulfilled, benchtop instruments cannot be avoided. In this case, onsite extraction can be developed in a different way. The analytes are in situ isolated and retained in a sorptive phase, which can be liquid or solid. Once retained, the analytes are less prone to be lost by evaporation or chemical degradation (if the phase is appropriately dried and stored). The sorptive phase is transported to the laboratory, where it can be stored for the final analysis. The portability and affordability of the sample preparation devices are essential in making the last approach practical and useful.

A sample preparation procedure should be as simple and miniaturized as possible to be portable. A closer look at these characteristics reveals some sustainability-related connotations. In fact, simplicity and miniaturization result in procedures with a lower requirement of consumables (solvents, reagents) and energy, thus reducing the environmental impact. It is not surprising that López-Lorente and associates selected portability as the first of the ten principles of green sample preparation (GSP) (2).

The distribution of target analytes in a given environmental compartment is non-uniform, varying both spatially and temporally. Therefore, to have a complete understanding of this distribution, it is necessary to take multiple samples from different locations and at different times. The cost of this multisampling approach dramatically depends on the price of the extraction units. Therefore, affordable devices permit the definition of more ambitious sampling campaigns.

Thanks to their inherent characteristics, microextraction techniques are ideal tools for onsite sample preparation. Solid-phase microextraction (SPME) and related techniques are paradigmatic in this sense. Their miniaturized nature also allows the design of special sampling devices capable of extracting the analytes at difficult-to-access locations. For example, Grandy and co-authors integrated a thin film microextraction device in a floating aerial drone for onsite water extraction at remote locations (3). In the same way, SPME devices have been implemented in aerial drones for environmental air sampling and extraction (4). Readers interested in deepening onsite environmental sample preparation can find further information in recent literature where the topic has been reviewed (5,6). Instead, this article focuses on our experience developing onsite environmental extraction based on stirred devices.

Exhaustive and Non-Exhaustive Extraction Techniques

Green analytical chemistry (GAC) (7) and GSP (2) principles recommend minimizing the sample volume, as this parameter directly influences the resources needed for the analytical procedure. Environmental analysis is particular since the large size of the studied compartments requires a relatively high sample volume to assess its representativeness. Onsite processing of these volumes (typically in the

range of hundreds of mL to a few of L) is challenging since close contact of the sample with the sorptive phase is required to isolate the analytes efficiently. Additionally, the sample volume defines the amount of analyte that is extracted. This effect, which influences the sensitivity of the determination, is typically more marked in exhaustive extractions where the sample volume must be precisely measured. The need to accurately measure the sample volume when applying a non-exhaustive technique depends on the experimental conditions under which the extraction is carried out. In fact, in SPME, when the sample is much larger than the sorptive phase volume, the amount of analyte extracted becomes independent of the sample volume. Rather than being a drawback, this fact allows the development of in situ extraction, where the sorptive phase is directly introduced in the environmental compartment without an apparent (although it is implicit) sampling step. The effect of the sample volume must be understood before designing an onsite extraction.

In solid-phase extraction (SPE), the sample is forced to flow through the sorbent bed, thus increasing the efficiency. In this case, Schulze and associates reported a device capable of onsite processing up to 50 L of sample (8). The device consisted of a customizable SPE cartridge that can be filled with the adequate sorbent, or mixture of sorbents, ad-hoc selected depending on the target analytes. A prefiltration element is incorporated to avoid clogging the cartridge with the suspended particulate matter. A pressurized system is implemented to flow the sample through the cartridge. The device has a power demand of 12 V that can be supplied using a car battery.

In nonexhaustive extraction approaches, like SPME, the extraction significantly depends on the diffusion of the analytes from the bulk sample to the sorptive phase. The sample agitation typically improves this diffusion. In 2018, Piri-Moghadam and associates described a bottle-based apparatus for onsite extraction

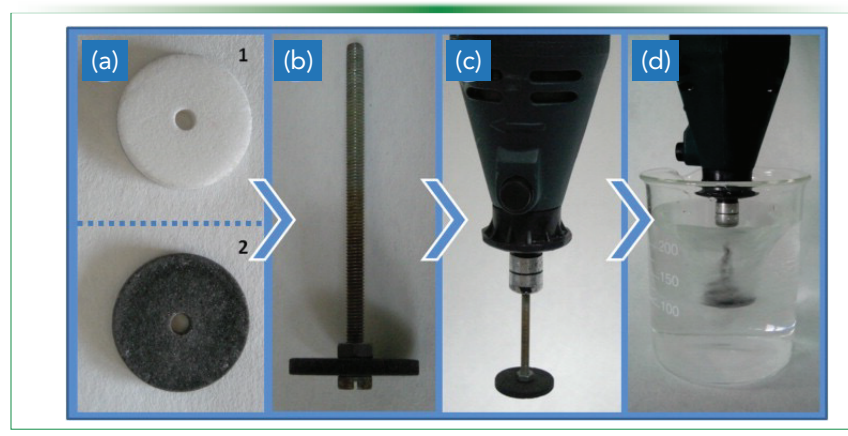

FIGURE 1: (a) Raw borosilicate disk (1) and disk modified with o-SWNHs (oxidized single-wall nanohorns) (2); (b) Attachment of the disk to a metallic axle; (c) Assembly of the disk to the drill; (d) The extraction process. Reproduced with permission of Elsevier from reference (13).

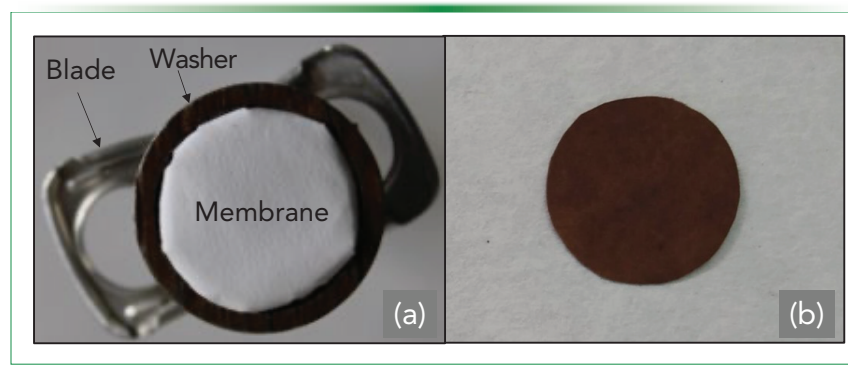

FIGURE 2: (a) Extraction unit designed for polymeric membranes. The membranes are attached to the magnet by a metallic washer; (b) Magnetic membrane synthesized by coating a paper circle into a precursor solution containing a polymeric nanocomposite. Panel (b) reproduced with permission of Elsevier from reference (15).

(9). In this approach, 1 L of the sample is initially taken in a glass bottle and closed with a polytetrafluoroethylene (PTFE) stopper. The thin film microextraction (TFME) phase hangs from the stopper, held by a polymeric thread. A sinker, placed at the end of the thread, guarantees the immersion of the sorptive phase into the sample. An orbital agitator is used to enhance the diffusion of the analytes. Liu and co-authors recently reported an onsite extraction technique consisting of a glass bottle whose inner surface were coated with a polydimethylsiloxane/divinylbenzene film (10). The sample is introduced into the bottle and stirred to retain the analytes (volatile hydrocarbons in this particular example) in the coated walls of the bottle. After the extraction, the sample is discharged, and the vial can be transported to the lab or analyzed in a portable chromatograph.

Onsite Extraction Using Stirred Devices

Drills are cheaper and more portable than orbital shakers and magnetic stirrers and can be operated with batteries. Moreover, they open the possibility of integrating the sorbent phase into the stirring element, which is an additional advantage for the diffusion of the analytes. In 2009, Qin and co-authors proposed using planar sorptive phases coupled to a portable drill as a miniaturized extraction system in environmental analysis (11). Mao and associates have also proposed the combination of stir-bar sorptive extraction (SBSE) with a portable electric drill (12). In this case, the stir-bar is magnetically attached to the drill that is used for sample agitation.

To improve the versatility of the sorptive phases available, our research group described the synthesis of boro-

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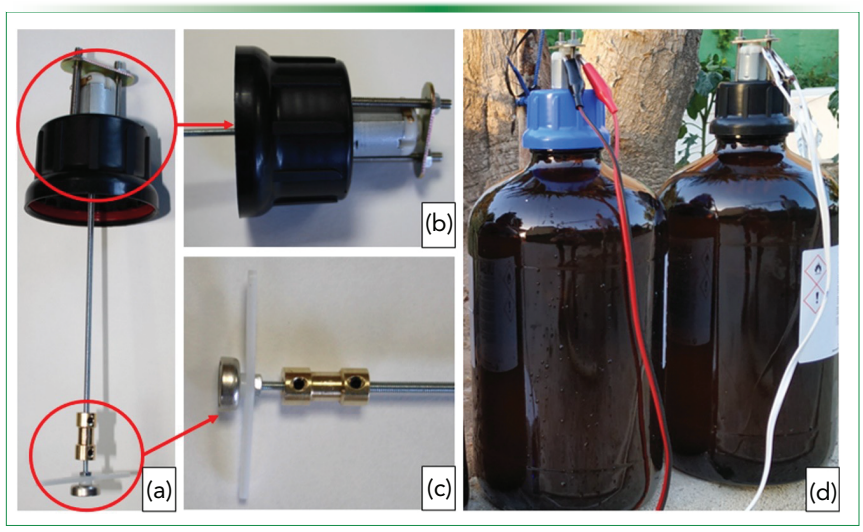

FIGURE 3: (a) Extraction device; (b) Electric motor attached to the plastic stopper; (c) Magnet holder and blades for better agitation; (d) Onsite extraction. Reproduced with permission of Elsevier from reference (16).

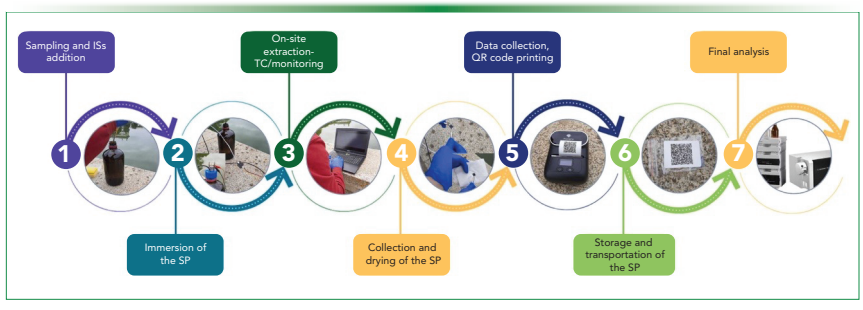

FIGURE 4: Analytical procedure for the Arduino-controlled onsite extraction device. For details, see text. Reproduced with permission of Elsevier from reference (17).

silicate disks modified with carbon nanohorns as a sorbent phase for the extraction of an endocrine disruptor, benzophenone-3, from water samples (13). As shown in Figure 1, the disks were easily attached to a portable drill that allowed them to be agitated inside the sample. This agitation improved the diffusion of the analytes, allowing their quick isolation, thus facilitating sampling at different locations in a single working day.

Carbon disks provided outstanding performance. However, they were not commercially available, thus restricting their potential application in routine analysis. To overcome this limitation, commercial polymeric membranes were proposed as sorbent phases in 2019 (14). The wide diversity of commercial membranes significantly increased the technique's applicability for extracting different contaminants. The robust coupling of these membranes with portable drills posed a challenge. Magnets were proposed as extraction supports to achieve this integration. The polymeric membranes were placed on top of the magnet to which they were attached using a metal washer. Blades were attached to the unit to improve the stirring capability of the devices. The extraction unit is represented in Figure 2a. Although the initial results were promising, the metal washer seemed to reduce the extraction kinetics by creating a reduced diffusion layer over the sorptive phase. To solve the latter limitation, magnetic membranes were proposed as sorptive phases in 2021 (15). The magnetic membranes (Figure 2b), prepared by the control coating of a paper with a polymeric magnetic nanocomposite, could be attached to the magnet directly. Avoiding the metallic washer permits the direct interaction of the sorptive phase with the sample.

Making Stirred Devices Affordable

Simplicity is an added value in onsite extraction techniques as it directly impacts the price of the designed units. In the previous investigations, portable drills were used to agitate the sorbent phases. The price of these drills, around 50 € ($53.00), and the need to recharge their batteries relatively frequently are significant handicaps in designing ambitious sampling campaigns. In 2022, we evaluated the replacement of these drills with electric mini-motors (16). The reduced cost of these motors (about 0.4 € [$0.42] per unit), opens the possibility of manufacturing many sampling devices, thus increasing the number of locations that can be sampled. In addition, these motors operate efficiently with portable 5V batteries, giving them greater autonomy. Figure 3a shows the designed extraction unit. The electric motor is integrated into the stopper of a glass bottle (Figure 3b). The extraction element (a magnet on which the sorbent phase is fixed) is located at the bottom of the unit, where a blade is also placed to improve the diffusion of the analytes (Figure 3c). Both elements, motor and magnet, are connected by a metal rod that transmits the movement. The extraction procedure involves several well-defined sequential steps. Initially, a sample volume in the range of 2.5 L is taken and placed in the glass bottle (Figure 3d). The extraction unit is introduced into the sample by simply closing the stopper, and then 5 V is applied to the motor to agitate the sorptive phase inside the sample. After the extraction, the sorptive phase is recovered and transported to the laboratory for final analysis. A new sorptive phase was designed to boost the extraction of the target analytes. Hydrophilic lipophilic balance particles, which are a common sorbent in environmental analysis, were immobilized using adhesive tape as the binder in a magnetic tape. The microparticles were fixed on the surface of the tape, having a high superficial area to contact with the analytes.

Open technologies can play a fundamental role in lowering the fabrication costs of these devices. Recently, the research group has developed a device based on Arduino technology

that also integrates sensors for online monitoring of various parameters (17). A temperature sensor and conductivity sensor are incorporated into the stopper, allowing the measurement of these parameters during the onsite extraction. The motor is operated by the Arduino microprocessor that controls the extraction time. The onsite extraction procedure is schematically presented in Figure 4, consisting of well-defined steps. Initially, a defined sample volume is taken, and the internal standard is added (Figure 4.1). The extraction is performed while the temperature and conductivity values are monitored (Figure 4.2–3). After the extraction, the sorptive phase is dried (Figure 4.4), and a QR code label containing the information of the sample (GPS coordinates of the sampling point, temperature, conductivity, and other data) is printed in a portable printer (Figure 4.5). The QR label is attached to a plastic bag (Figure 4.6) where the sorptive phase is stored for its transportation to the lab for final analysis (Figure 4.7).

3D printing is a disruptive technology with broad applications in analytical chemistry, and it has been recently used to fabricate stirred extraction devices to be deployed onsite (18). Vargas-Muñoz and associates designed a stirrer whose paddles were 3D printed and coated with a metal-organic framework to extract phenols. After the extraction, the paddles can be removed from the stirrer and chemically eluted before the analysis.

Conclusion

Onsite sample preparation is a useful strategy in environmental analysis with positive effects on the metrological quality (representativeness) and the affordability (easier sampling logistics) of the analytical procedures. Extraction techniques, both exhaustive and non-exhaustive ones, have demonstrated potential in this field. However, due to their miniaturized and simplified character, microextraction technique seems to be a better option. This article outlined the role that stirred-based techniques can play in onsite extraction, presenting our perspective on the topic. The introduction of open technologies (microprocessors and 3D printing) in the design of these devices improves their affordability, which is critical to extending their use. There is room for improvement in this field. Directly coupling these onsite devices with instrumental techniques (spectroscopic and spectrometric ones) can simplify the analytical procedures even more.

Acknowledgments

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Enhance the Performance of Solid-Phase Microextraction by Exploiting Vacuum-Assisted Headspace and Multicumulative Trapping for Olive Oil Characterization

Steven Mascrez, Juan Aspromonte, and Giorgia Purcaro

Headspace-solid-phase microextraction (HS-SPME) is a widely used technique for the analysis of volatile compounds from different kinds of samples and with multiple fields of applications. Despite of its applicability, it can require a long extraction time and it is limited by the volatility of the analytes of interest and the need for equilibrium conditions between the sample and the headspace. Recently, two additional approaches have been proposed to reduce the extraction time and broaden the coverage to less volatile compounds, namely vacuum-assisted HS-SPME and multi-cumulative trapping HS-SPME. This paper illustrates the principle of the two techniques and their potential for extending the applicability of HS-SPME, using them as alternatives or combined to characterize olive oil samples in terms of quality.

Solid-phase microextraction (SPME), was introduced in the 1990s by Pawliszyn and collaborators (1,2), and represents one of the most widely applied techniques for volatile and semi-volatile analysis. When SPME is applied to the headspace (HS), it involves the equilibrium between three phases, and thus, two equilibrium processes—namely, the sample and the HS (characterized by K_{hs}, distribution constant HS-sample) and the HS and the fiber (characterized by K_{fh}). Reaching equilibrium conditions guarantees to maximize the sensitivity. However, when dealing with complex samples and untargeted analysis, the equilibrium condition may not be reached for all the compounds within an acceptable time, and even some analytes may not be properly extracted at equilibrium conditions. Moreover, longer extraction times may promote the occurrence of a competition phenomenon (for example, displacement effect) when solid sorbents are used (3,4). Nevertheless, the direct correlation between the amount extracted (n) and the initial concentration (C_0) is maintained before and at the equilibrium (equation [1]) (5):

$$n = \frac{K_{hs}\ K_{fh}\ V_f\ V_s\ C_0}{K_{hs}\ K_{fh}\ V_f + K_{hs}\ V_h + V_s} \quad [1]$$

where V_s, V_h, and V_f represent the volume of the sample, the HS, and the fiber coating, respectively.

This proportionality can also be expressed as:

$$A = \frac{C_0}{K_{hs} + ß} \quad [2]$$

where A is the chromatographic area, and ß the phase ratio (ß = V_h/V_s). This relationship is valid as long as HS saturation is avoided (6). The HS linearity range depends on the actual concentration in the sample, but also the sampling temperature, time, and ß. The linearity condition of the total sample is a compromise between trace and major components. The same compromise is necessary in terms of extraction time. To accelerate the kinetics of extraction, stirring of the sample and increased temperature are usually applied. A powerful alternative that is gaining attention is the use of vacuum-assisted HS extraction (Vac-HS). It was proposed for the first time in the early 2000s (7,8), but it has gained attention starting from 2012, thanks to the work of Psillakis and associates (9–13). Another alternative to improve the sensitivity of trace compounds using HS-SPME is to perform multiple-cumulative trapping (MCT) extractions from the same samples, thus depleting the HS of the most volatile compounds and facilitate the extraction of the less volatile compounds (14,15).

In this paper, the two aforementioned approaches, namely Vac-HS-SPME and MCT-SPME, are discussed in the context of virgin olive oil profiling.

Vacuum-Assisted HS-SPME in Fatty Samples

The fundamental theory of Vac-HS-SPME in water-based samples was nicely described in a tutorial paper published in 2017 by Psillakis and collaborators (16), and lately extended to oil based samples (17). In both cases, the use of reduced pressure does not impact the thermodynamics of the extraction but only the kinetics. It plays a fundamental role in improving the mass transfer from the sample (liquid or solid) to the HS (16,18).

To explain the limitation of the mass transfer at the interface, the two-film theory is used. This theory assumes a homogenous distribution within the bulk of each phase, while a concentration gradient is present in the stagnant thin layers at the interfaces. This theory successfully explained the behavior of volatile compounds from water-based samples when the pressure is lowered (19–21). According to this theory, the overall mass transfer coefficient, k_O, at the interface can be modeled as follows:

$$\frac{1}{k_O} = \frac{1}{k_L} + \frac{1}{K_{GL} k_G} \quad [3]$$

where; k_G and k_L are the mass transfer coefficients for the gas and liquid boundary layers, and K_{GL} is the gas-liquid phase partition coefficient. Once in the HS, the mass transfer of the analytes to the fiber can be neglected, although it is also improved in Vac-HS-SPME (9,18,22), as shown for other high-capacity sorbents (such as, the stir bar and liquid microdrop) (23,24). Therefore, the overall resistance to transfer from liquid to the gas phase ($1/k_O$) can be considered as two diffusional resistances in series.

The diffusion coefficient in the gas-phase, D_G, has an inverse proportionality to the total pressure in the system (9). On the other hand, the liquid phase resistance is highly dependent from the viscosity of the medium (η) and the temperature (T). The Wilke-Chang (25) formula (Equation [4]) describes the diffusion coefficient in the liquid phase (D_L):

$$D_L = 7.4 \times 10^{-8} \frac{TM^{1/2}}{\eta V^{0.6}} \quad [4]$$

where M is the molecular weight of the solvent, and V is the molar volume of the solute. Therefore, when vacuum is applied to HS-SPME, D_G increases and thus k_G, reducing the gas-phase resistance (see the term $1/(K_{GL}\ k_G)$ in equation 3) (9,16). However, the positive impact in extraction efficiency will be observed for analytes for which K_{GL} is sufficiently small to have the $1/(K_{GL}\ k_G)$ term comparable or superior to the $1/k_L$ term. K_{GL} values for solutes in olive oil as a solvent are substantially different from those with water as a solvent, due to the differences in solute-solvent

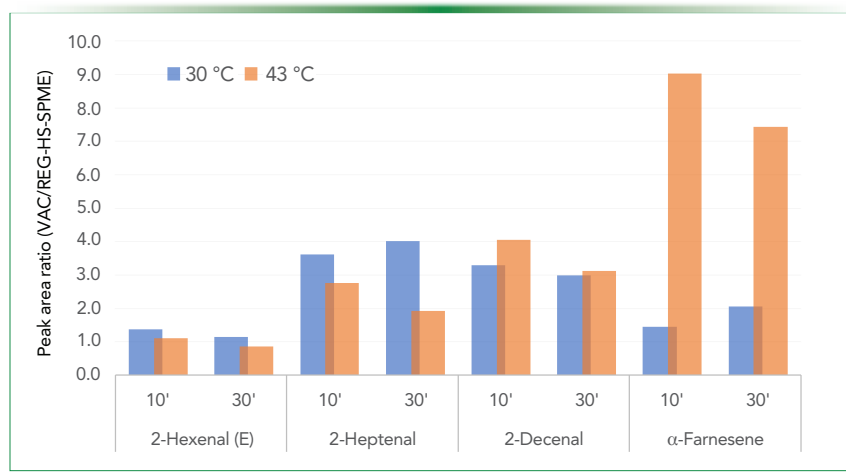

FIGURE 1: Relative increase of the response (peak area) in reduced pressure conditions (VAC) and regular conditions (REG) for the extraction by HS-SPME at two different temperatures, namely (blue) 30 °C, and (orange) 43 °C, from extra virgin olive oil.

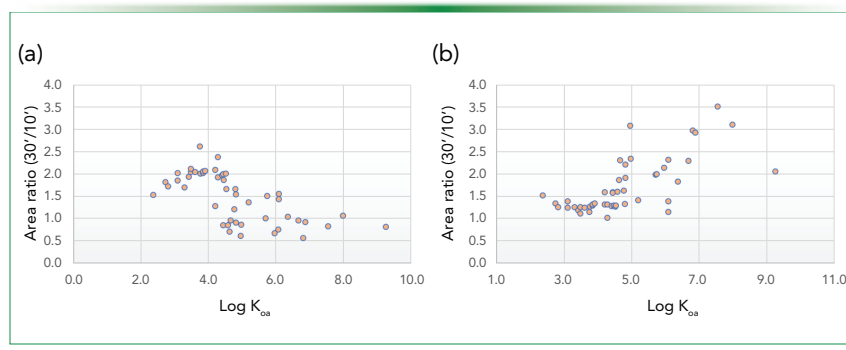

FIGURE 2: Ratio of the chromatographic peak area against the air-octanol coefficient (K_{oa}) of the targeted compounds obtained by HS-SPME-GC extracting, (a) extraction time for 30 and 10 min; and (b) multiple cumulative trapping by 3-times 10 min MCT-HS-SPME and a single 30 min extraction. Adapted from (28).

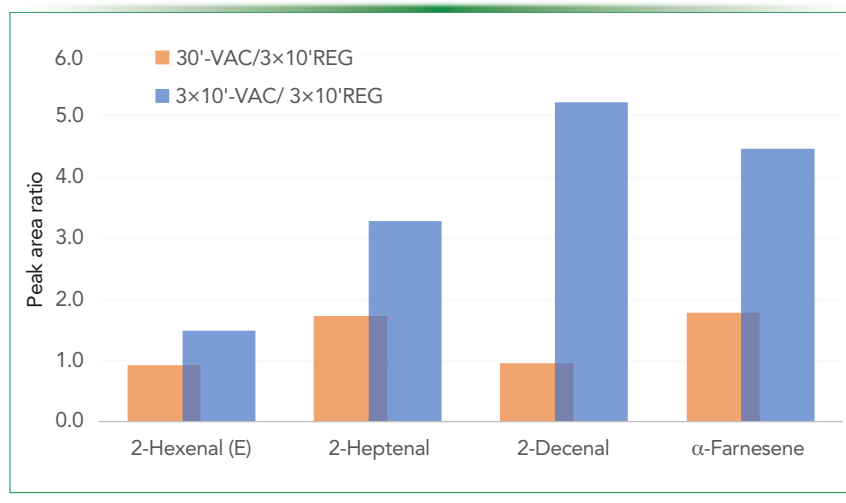

FIGURE 3: Relative increase of the response (peak area) in single 30-minute reduced pressure conditions (VAC) and 3-times 10 minutes MCT regular conditions (REG) and MCT both in regular and Vac conditions for the extraction by HS-SPME from extra virgin olive oil. (Orange) 30'-VAC/3x10'REG, and (blue) 3x10'VAC/3x10'REG.

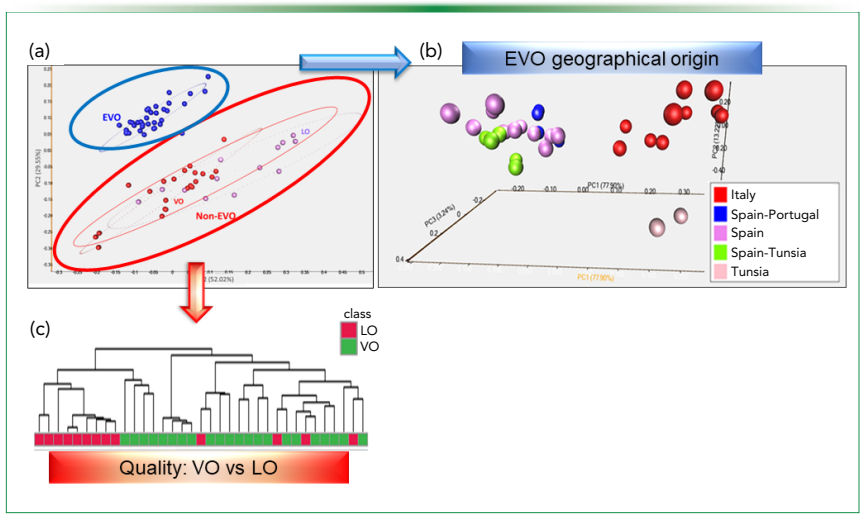

FIGURE 4: (a) Principal component analysis (PCA) obtained using the 20 top discriminatory features obtained with random forest (RF) of 69 samples analyzed by MCT-HS-SPME–GC–MS. Circled in blue the EVO samples (b) exploded according to their geographical origin on the PCA; while circled in red, the (c) non-EVO samples further discriminate using a hierarchical cluster analysis into LO and VO. Adapted from (31).

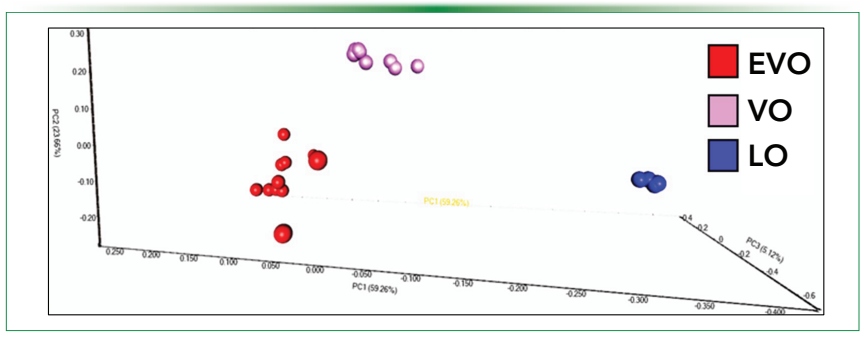

FIGURE 5: Principal component analysis (PCA) obtained using the 20 top discriminatory features obtained with random forest (RF) of 24 samples analyzed by 3×10'MCT-Vac-HS-SPME. EVO, VO, and LO data points are color coded.

and solvent-solvent molecular interactions (26). Therefore, the use of Vac-HS-SPME for water- or oil-based samples mainly differs due to the viscosity of the two media.

Accordingly, lowering the total pressure will improve the overall mass transfer coefficient for analytes where gas-phase resistance controls their volatilization rate. It results in faster HS-SPME extraction kinetics and shorter equilibration times. However, for analytes and samples where the liquid diffusion is the limiting step (as in highly viscous medium, such as oils), the impact of reducing pressure on recoveries is less important. It plays a synergic effect with temperature, which reduces the viscosity, and thus increases D_L. Figure 1 shows an example of the combined impact of reduced pressure and temperature on a series of compounds extracted from the HS of an extra virgin olive oil. In particular, semi-volatile compounds, such as for instance 2-decenal and α-farnesene, benefit significantly from the temperature increase (Figure 1). In fact, at higher temperature the increase in D_L allows the analytes to rapidly reach the liquid-gas interface, and quickly replenish the HS by the facilitated mass transfer due to the reduced pressure.

In the case of water samples, a clear criterion for predicting the effect of vacuum on the extraction of the compounds of interest have been established. However, due to the limited availability of air-olive oil partitioning data (such as K_{GL} values), and the complex interactions of solutes with olive oil, it is not possible to establish a similar criterion for oily samples.

Multiple-Cumulative Trapping HS-SPME in Fatty Samples

As previously mentioned, equilibrium may require a long extraction time to be reached. The longer the extraction time, the higher the risk of displacement effects when using a porous fiber, such as DVB/CAR/PDMS (3,27). Therefore, shorter extraction times are often preferred (also improving the throughput), but this comes at the expense of sensitivity. The payback was calculated for 49 compounds extracted from extra virgin olive oil, comparing the ratio of the responses obtained when extracting for 30 and 10 minutes (28). It was shown that the increment ranged between 0.6 to 2.6 folds, with a clear decreasing trend in uptake gain at 30 min for the less volatile analytes, which showed a ratio of about 1 (Figure 2a).

The use of MCT-HS-SPME was applied to minimize the displacement and enhance the uptake of less volatile compounds. Indeed, as shown in Figure 2b, there is a clear difference on how much better the semi-volatile compounds are extracted when performing MCT-HS-SPME with three extractions of 10 min, compared to a single extraction of 30 min.

Therefore, the use of MCT-HS-SPME proved to be advantageous in further enriching the overall information obtained from HS profiling, while maintaining the key benefit of not affecting sample throughput. This was then extended to the optimization of an additional variable: the number of repeated extractions needed to improve the information extracted (in terms of discrimination capability), but avoiding to increase the noise response, and do not modify the real perceived volatile profile. This is especially important when the intention is to determine the correlation between the volatile profile and aroma, as in the present case of olive oil analysis. It was found that repeating the extraction six times was, in fact, detrimental to differentiating between different olive oil qualities (extra virgin, virgin, and lampante) (28).

Vacuum-Assisted and Multiple-Cumulative Trapping HS-SPME in Fatty Samples

Following the previously discussed advantages of Vac- and MCT-HS-SPME, both should provide similar benefits towards the less volatile compounds. Indeed, when comparing their extraction efficiencies, similar or slightly higher responses can be observed for Vac-HS-SPME (orange bars in Figure 3, a ratio of 1 means equal response). It was decided to evaluate the combination of the two sampling approaches to evaluate the potential of further increasing the responses of the less-volatile compounds in olive oil analysis.

Preliminary tests were carried out to verify that the reduced pressure could be maintained after repeated piercing of the septum, and it proved the MCT-Vac-HS-SPME approach was feasible. Therefore 0.1 g of olive oil was extracted three times for 10 min under regular and reduced pressure conditions. For the four targeted compounds reported in Figure 3, a synergic effect can be easily observed. This is particularly true for the less volatile ones, such as 2-decenal and α-farnesene, where an increment of 4.5-5 times can be observed compared to 3-times 10 min regular pressure MCT-HS-SPME.

Cross-Sample Evaluation Using Enhanced HS-SPME

Physically extracted olive oil is classified into different commercial categories (such as extra virgin oil [EVO], virgin oil [VO], and lampante oil [LO]) based on physicochemical and sensory parameters, according to *European Regulation No 2568/1991* and following modifications (29). Although the sensory evaluation is highly standardized (29,30), it presents a problem due to the inherent low robustness and reproducibility of panel evaluations. Therefore, it is clear the necessity for a robust and objective analytical method to support this classification. Moreover, this application is further complicated by the many variables affecting the aroma profile such as cultivar, geographical origin, fruit ripeness, processing practices, and storage conditions.

Although there is a clear enhanced response of the less volatile compounds by the implementation of reduced pressure conditions (in particular for MCT), this required further evaluation to determine whether it reflects in a gain of overall information obtained from the volatile profile, especially for olive oil. This was preliminary tested in a study consisting of about 70 samples of olive oil of different quality and geographical origins (Italy, Spain-Portugal, Spain, Spain-Tunisia, and Tunisia) using MCT-HS-SPME-GC–MS (31). As it can be observed in Figure 4, the higher quality EVO (blue dots on the left side of Figure 4) were clearly differentiated from the samples that presented some sensory defects (VO and LO, reddish dot on the left side of the top principal component analysis [PCA]). At first glance, it may be seen as the proposed approach does not allow for discrimination between the VO and LO. However, when adding PC3 (here emphasized with a hierarchical cluster analysis) there was a satisfactory discrimination between VO and LO. Although some misclassifications occurred, it has to be kept in mind that the classification into LO can also be related to chemical parameters, such as the acidity or the peroxide value. Thus, the sensory defects may not be the only responsibles of the classification.

Moreover, EVO samples could be further classified based on the geographical origin of the olives. Italian and Spanish oils were very clearly discriminated, as well as Tunisian ones, although only very few samples were available. Unfortunately, no pure Portugal samples were available, and the Tunisian ones were too few to provide enough statistical power to differentiate the mixtures. Nevertheless, their content in the mixtures was far less than 10% of these different origins, thus justifying their clustering with the Spanish EVO.

The implementation of combined MCT-Vac-HS-SPME was also extended to the use of a multidimensional comprehensive GC (GC×GC)–MS separation. The combination of the more powerful separation technique (GC×GC), and the enrichment during sampling, provided a very satisfactory separation of the three groups of olive oil (EVO, VO, and LO). This very good classification obtained with MCT-Vac-HS-SPME is shown in Figure 5.

Conclusions

Vac-HS-SPME and MCT-HS-SPME are two useful alternative techniques that can be used on their own or combined to enhance the profiling of volatile and semi-volatile compounds. The two techniques can be easily implemented and have both shown a significant improvement in the recovery of the semi-volatile compounds. Moreover, if coupled to GC×GC, the enriched extraction profiles can be more comprehensively separated, allowing for a substantial improvement of the discrimination ability among olive oil samples of different quality (i.e., EVO, VO and LO) based on the information rich chromatographic fingerprints obtained.

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Note

The authors declare no competing financial interest.

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Recent Advances and Applications of Passive Sampling Devices

Amir Salemi and Torsten C. Schmidt

Passive samplers have been developed in many different forms and used in different fields of study because of their unique capabilities. One part of recent reports has focused on benefiting from the advantages of passive sampling in areas such as wastewater-based epidemiology and non-targeted analysis. The other part mainly deals with novel approaches to improve the reliability and efficiency of the sampling process. This paper reviews major advances and new applications of this sampling strategy based on recently published scientific publications.

Among the common sampling strategies, that is grab, composite, and passive sampling, the latter has some unique features that have made it a useful tool, especially for environmental studies (1). Passive sampling can provide reliable data on the time-averaged concentration of contaminants. Temporary contamination events, such as provisional discharges and accidental spills which are not normally captured by other sampling strategies, could be recorded (chemically) by the passive sampler. In addition, this approach can enrich the trace contaminants over a rather long exposure and also provide toxicologically relevant data on bioavailable concentrations of the contaminants (2–4). Passive sampling is also possible and useful for the study of atmospheric organic contaminants, in similar approaches (of course taking into account the differences in receiving phases, sampler design, and analytes) (5). Despite its advantages, passive sampling needs a more complicated calibration procedure in order to produce valid quantitative data. This could be done using theoretical estimation of the partition coefficients of the analytes between the sorbents and the sampled media, considering its physicochemical properties (6). Another strategy (considered to be more reliable) is to calibrate the passive sampler in the real environment by comparing its analytical results with those of active sampling (7). In the following section, the most recent applications of various passive sampling devices will be briefly reviewed (Figure 1).

Applications and Developments of Passive Sampling

Since the first reports on quantitative applications of passive sampling for the determination of sulfur dioxide in air in 1973, diverse sorption phases and sampler designs have been reported for studying water and air contamination. Among them, semi-permeable membrane devices (SPMDs) (8), low-density polymer devices (LDPE) (9) providing higher surface areas and reduced consumable costs (10), silicon rubber (SR), Chemcatcher (11), the polar organic chemical integrative sampler (POCIS) (12), and solid-phase microextraction (SPME) (13) have been implemented for water sampling purposes. Regarding atmospheric contamination, SPMDs, similar to what is being used for water sampling, with various sorbing phases (14–16) have been utilized. Furthermore, devices based on porous materials have been developed for different semi-volatile compounds in the atmosphere, using for example polyurethane foam (PUF) (17), naphthylisothiocyanate (XAD) (18), and activated carbon (19) as sorbents.

Wastewater-based epidemiology (WBE) is one of the most recent application fields of passive sampling. In this field of study, untreated wastewater is collected and analyzed for the content and variations of health-related compounds (biomarkers), and the data are compared with the public health situation of the catchment (20). Obviously, grab sampling could only provide a snapshot of the wastewater under study, while the composition of the media is continuously changing due to the population routines as well as the social and climatic conditions, such as working days and holidays, vacation periods, seasonality, and atmospheric precipitations. Composite sampling, as it is conventionally used, could resolve such problems, but its implementation requires higher costs of operation and maintenance and also could produce large volumes of

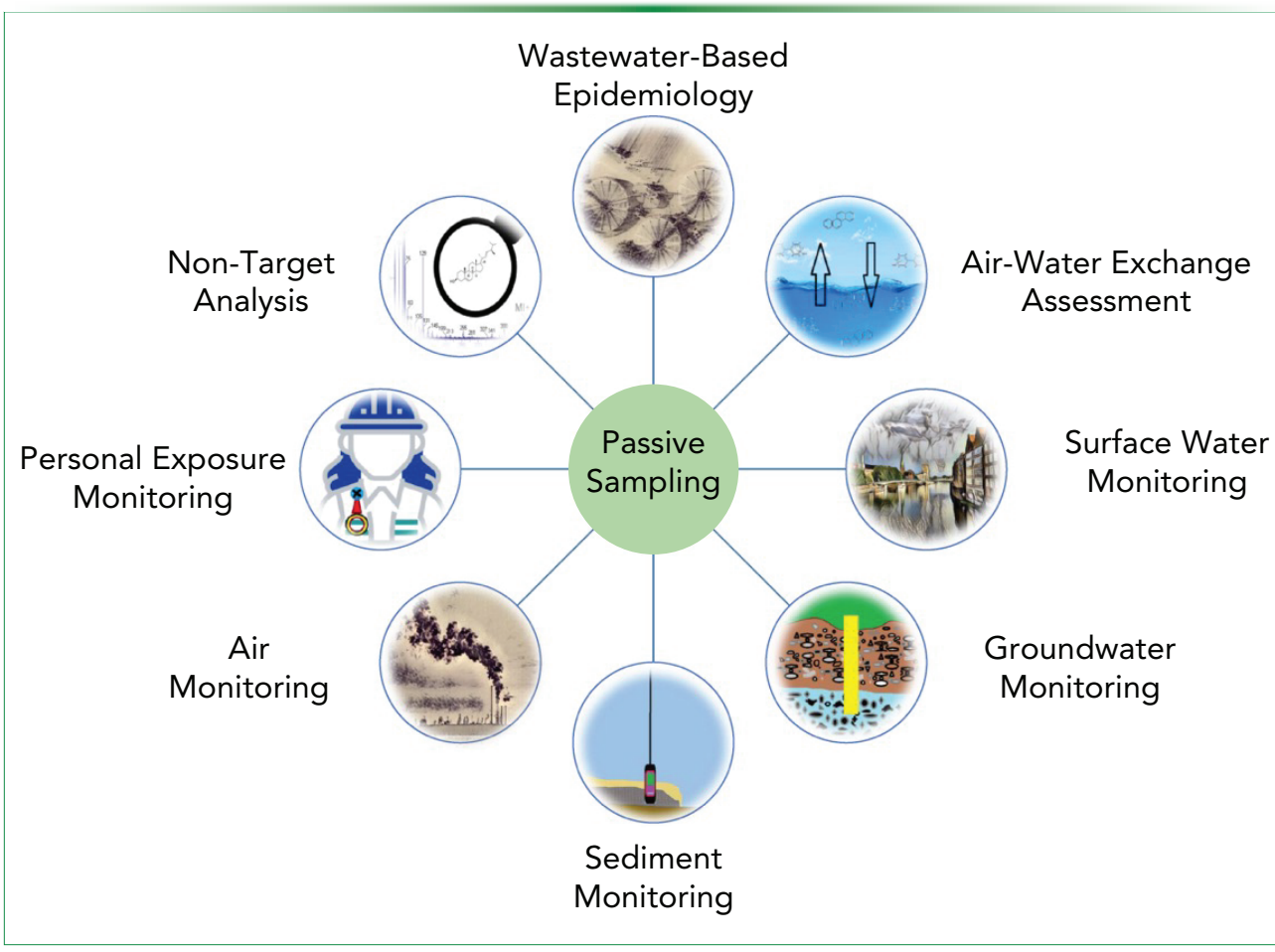

FIGURE 1: Recent application fields of passive sampling.

samples to be handled. Alternatively, passive sampling could significantly reduce cost and labor and at the same time eliminate or simplify many sample pretreatment steps, such as preservation, storage, filtration, extraction, and preconcentration.

One of the most recent applications of passive sampling in WBE studies is the investigation of the spread and dynamics of the SARS-CoV-2 virus (21). In this work, authors deployed polyethylene plastic strips, as simple forms of the sorbing phase, cotton cloth sheets, and unraveled polypropylene plastic ropes to sample the wastewater. The samplers then were transferred to the laboratory to extract and analyze SARS-CoV-2 RNA. The results suggested that considering the enrichment of the target analytes on the sampler, the sensitivity of the passive sampling was better than conventional composite sampling, and it also could provide a better estimation of the infected population rather than the number of incidents. In a similar study, it has been shown that passive sampling using torpedo sampling units (containing a combination of readily available electronegative membranes, cotton buds, and medical gauze) not only makes detection of various viruses in municipal wastewater possible but also could be implemented in much smaller scales, such as an individual building, to produce point-specific data (22).

Another interesting development in the application of passive sampling in WBE is the study of illicit drugs and their metabolites and hence, the assessment of the consumption rates of such chemicals (23). Contrary to the above-mentioned examples, efficient uptake of the chemicals from the complex matrix of untreated wastewater needs strong chemical sorbents and in this case a POCIS consisting of Oasis HLB (a copolymer made from hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene monomers) sandwiched between two polyether sulphone membranes was deployed. The passive sampling method was calibrated in situ for drugs such as cocaine, amphetamine, methamphetamine, and morphine. A few other biomarkers, such as the antihistamine cetirizine and metoprol acid (a metabolite of metoprolol and atenolol), which are more regularly consumed and released into wastewater, were simultaneously analyzed to produce a better estimation of the population, despite its temporal variations.

The highly variable flow of the surface water, especially rivers, could be a serious challenge since it has a dramatic effect on the sampling rate and hence the accuracy and precision of quantitative data. A helpful technique to compensate for the environmental condition changes is to use performance and reference compounds (PRCs). These compounds are selected so that they do not naturally exist in the studied water and are spiked to the sorbent prior to the deployment of the sampler. Then, the dissipation of these compounds during the sampling period is used to estimate and correct the uptake rate of the target analytes. It has been shown that this technique is suitable for hydrophobic (nonpolar) sorbents (24) but the results are not as reliable for hydrophilic samplers. As a solution, a novel approach has been introduced in which a PRC-spiked nonpolar silicon disk has been implemented in parallel with the polar sampler so that the latter was implemented for collecting and quantitating the polar target compounds (of diverse classes) and the former was used to estimate the changes in the sampling rates and to correct the quantitative results (25).

Passive sampling has also been deployed for groundwater monitoring. Regarding the significantly slower movement of the water body, the target analytes could reach an approximate equilibrium between water and the sampler sorbent, a fact that facilitates the calibration of the passive sampler. In addition, spatial (vertical) distribution of the contaminants, as an important feature of groundwater contamination studies, could be determined by deploying so-called diffusive equilibrium high-resolution passive samplers. This type of passive sampler consists of a series of sorbent cells installed inside a stainless steel rod which could be inserted into the groundwater, and the sampling process takes place at different depths. The approach has been reported to be a versatile means for studying groundwater contamination with per- and polyfluoroalkyl substances (PFAS) (26).

Study of sediments is another field in which passive samplers could play an important role. As an example, a passive sampling strategy based on POCIS has been developed for the determination of PFAS in sediments (as well as water) and the results have been used to estimate the bioaccumulation potential of these compounds (27). Beside advantages such as preconcentration of the analytes and time-weighted average concentration values, passive samplers could imitate the uptake behavior of the living organisms and therefore, provide helpful information on the impacts of the contaminants.

Passive samplers have been used in the determination of diverse air contaminants over the past five decades. There are numerous examples in this field, however, studying the transport and exchange of contaminants between different environmental media, using passive samplers, is attracting increasing focus. For example, diffusive exchange flux between the atmospheric gas phase and the freely dissolved water phase of a large set of hydrophobic organic compounds has been studied using the data extracted from passive sampling of water (LPDE and SR) and air (PUF) in high-mountain lakes (28). Such studies could reveal the transport of atmospheric contaminants and also the role of the local anthropogenic pollution sources in the contamination of remote ecosystems.

Regarding the long deployment time of passive samplers which enables collection of both long-term and temporary contamination events in the medium, as well as their preconcentration capability, the number of the collected chemical compounds and also their concentrations could be much higher compared with methods that use grab sampling. Therefore, passive sampling can be of greatest importance in nontargeted analysis, as a recent and growing field of environmental analytical chemistry (29). It has also been shown that when passive sampling is followed by sensitive analytical instrumentation, such as liquid chromatography–high resolution mass spectrometry (LC–HRMS), the number of detected compounds is increased in such a way that implementing advanced data processing methods could become inevitable (30).

Conclusion

It is clear now that despite the difficulty of calibrating passive samplers for quantitative analyses, they benefit from significant advantages such as time-weighted average data, greener analytical methods, and more time, effort, and cost-effective procedures that rationalize their implementation. That is the reason behind the spreading use of this sampling strategy, as can be seen in its progressive novel application fields. Regarding the general modality of this short review, the theoretical aspects and the entire range of the diverse application fields of passive sampling have not been covered and the interested reader is encouraged to refer to more comprehensive and specialized review articles (6).

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Vacuum-Assisted Headspace Solid-Phase Microextraction Sampling Method for the Extraction of Semi-Volatile Compounds: An Overview

Shannon L. Thomas and Kevin A. Schug

Vacuum-assisted headspace solid-phase microextraction (Vac-HS-SPME) is an emerging sampling technique that enhances the extraction of semi-volatile compounds. The one extra step of pulling vacuum from the sampling vial pre-equilibrium increases the concentration of semi-volatiles in the headspace and allows for faster extraction times. This overview highlights the timeline, applications, and fundamentals of Vac-HS-SPME.

Microextraction is an analytical extraction technique where the volume of the extraction phase is substantially smaller than the volume of the sample to be extracted. Because very small amounts of chemical compounds are extracted during sampling, microextraction allows multiple extractions of a sample with minimal change in the sample composition (1). Solid-phase microextraction (SPME) was pioneered by Janusz Pawliszyn in 1990 (2). This widely-used sampling technique was designed for fast and convenient sample preparation with greatly-reduced volumes of solvents applied. It also reduced needed sample volumes, sample handling, and extraction times. Traditional SPME uses a small-diameter fused silica fiber, coated with a small volume of extraction phase for the direct extraction of analytes from a sample. Sampling is typically conducted by direct immersion (DI-SPME) in a liquid sample or by headspace extraction (HS-SPME). In DI-SPME, the fiber is placed directly in the sample and analytes are extracted from the sample matrix. In HS-SPME, the fiber is exposed to the gas phase above a sample, where analytes partition into the fiber phase until equilibrium is reached (3).

The extracted sample components in the fiber are most often sampled using thermal desorption in the injection port of a gas chromatograph (GC). For liquid chromatography (LC), introduction of extracted compounds can be achieved through solvent desorption (4). SPME sampling offers completely automated analysis for increased throughput using commercial autosampler systems and customary analytical instruments.

HS-SPME is used for the extraction of volatile analytes in the headspace. Partitioning equilibration times are dependent on analyte volatility, sample matrix, and the composition of the extraction phase. Due to semi-volatile analytes having a low affinity for the gas phase, equilibration times for semi-volatiles (higher boiling point, lower vapor pressure) are longer than for volatiles (lower boiling point, higher vapor pressure). In order to shorten the equilibration time and enrich the fraction of semi-volatiles available for sampling in the headspace, salt can be added to a liquid sample to disturb analyte hydration (5), and the sample can be heated or agitated (6). Higher temperatures are known to cause sample decomposition or the formation of by-products.

The drawbacks related with long equilibration times and high extraction temperatures to improve HS-SPME sampling of semi-volatile analytes brought about the development of vacuum-assisted HS-SPME. This method consists of an extra step where the pressure in the sample vial is reduced by applying a vacuum prior to equilibration for sampling. Reducing pressure in the sampling vial assists analytes with longer equilibration times under standard atmospheric pressure to increase their concentration in the headspace. For a deep dive into the theory behind vacuum-assisted (Vac) HS-SPME, Psillakis (7) provides an exhaustive tutorial for Vac-HS-SPME sampling with a focus on liquid samples, and Yiantzi and co-authors (5) give a detailed procedure for recovering PAHs from solid matrices. This article gives an overview of the development, applications, and fundamentals of Vac-HS-SPME sampling.

Timeline and Applications

Table I outlines the development and applications of Vac-HS-SPME. In 2001, Brunton and associates (8) reported benefits of reduced pressure HS-SPME sampling of food aroma volatiles from cooked and raw turkey breast. These positive effects were later confirmed by both Darrouzes and coauthors (9) and Groenewold and associates (10). In 2012, Psillakis and coauthors (11) reduced the pressure in the sampling headspace by evacuating the air from a sample container prior to introducing the sample. They presented the theoretical model for pressure dependence and coined the technique as Vac-HS-SPME. Studies using Vac-HS-SPME sampling for liquid samples have included extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples (27), aromatic

amines in water, aromatic compounds in mulberry juice, earthy-musty odor compounds in water, free fatty acids and phenols found in milk (15), haloanisoles in wine (19), and a temperature study with extra virgin olive oil (21). Researchers have also explored Vac-HS-SPME sampling for solid samples, such as PAHs from sand, BTEX from polluted soil, nicotine in hair and tobacco, terpenoids from frankincense resins, butanoic acids in hard cheeses, greener sampling techniques for oil bearing source-rock analysis (24), volatiles from raw fish at subambient temperatures (23), analyzing terpenoids and cannabinoids in hemp inflorescences in one combined method (25), and comparing volatiles among psilocybin and non-psilocybin mushrooms (26).

TABLE I: Vac-HS-SPME timeline of applications, including analytes of interest and sample matrix

Analyte(s) of Interest	Sample Matrix	Year and Author(s)
Aroma-contributing compounds	Cooked and raw turkey breast	2001; Brunton et al. (8)
Ethylated derivatives of butyl- and phenyltin compounds	Sodium ethanoate/ ethanoic acid buffer	2005; Darrouzes et al. (9)
Organophosphorus compounds	Glass surface	2011; Groenewold et al. (10)
Polycyclic aromatic hydrocarbons (PAHs)	Water	2012; Psillakis et al. (11)
Aromatic amines	Water; polyamide spoons	2014; Rubio et al. (12)
PAHs	Sand	2015; Yiantzi et al. (5)
Aromatic compounds	Mulberry juice; tobacco leaf	2015; Lee et al. (13)
Earthy-musty odor compounds	Water	2016; Glykioti et al. (14)
Free fatty acids and phenols	Milk; milk derivatives	2017; Trujillo-Rodriguez et al. (15)
Dimethylhydrazine	Aqueous extracts from soil	2018; Orazbayeva et al. (16)
BTEX	Polluted soil	2018; Ghiasvand et al. (17)
Nicotine	Hair; tobacco	2018; Ghiasvand et al. (18)
Haloanisoles	Wine	2019; Vakinti et al. (19)
Terpenoids	Frankincense resins	2020; Capetti et al. (20)
Aromatic compounds	Extra-virgin olive oil	2020; Mascrez et al. (21)
Butanoic acid	Hard cheeses	2020; Sykora et al. (22)
Fish volatiles	Frozen fish	2021; Delbecque et al. (23)
Steranes and pentacyclic terpanes	Oil-bearing source rock	2022; Pollo et al. (24)
Terpenoids and cannabinoids	Hemp inflorescences	2022; Capetti et al. (25)
Mushroom volatiles	Psilocybin and non-psilocybin mushrooms	2023; Thomas et al. (26)

Vac-HS-SPME Sampling

Vac-HS-SPME sampling involves the evacuation of a sample vial before equilibration for sampling and extraction. There are several things to consider when preparing a sample for extraction, including the type of vessel, how to create a gas-tight seal, the device used to pull vacuum, and the order of vial preparation, which is dependent on sample type.

Sample Containers

Vac-HS-SPME sampling requires a vessel, specifically one which has a gas-tight seal and maintains vacuum for at least 24 h, and, ultimately, a vial that is used for common autosamplers. Psillakis and associates (7) have explored variations of sample containers and seals. Starting with a 1000-mL gas-sampling bulb, this container maintained vacuum up to 150 min, but lacked the ability to be agitated (11). This led to investigating 500-mL and 1000-mL custom-made glass sample vessels (28). These samplers were difficult to heat evenly and awkward to use. Plus, the volume of headspace compared to sample volume reduced the amount of analyte extracted by the fiber. To reduce the headspace volume, a 22-mL container was made from a standard 20-mL headspace vial with the addition of two gas-tight ports capable of accommodating solid samples (5,28). This container still lacked the ability to be automated. Psillakis and coauthors (15,29) explored several versions of seals that would accommodate a standard 20-mL headspace vial. Now, a stainless-steel insert (created by Prof. Elefteria Psillakis, ExtraTech Analytical Solutions SMPC), combined with a Thermogreen LB-1 septum with half-hole (Supelco), can be placed in the vial opening of a 20-mL headspace vial to create a gas-tight seal and be used on a HS-SPME autosampler. This insert has been provided recently to researchers for Vac-HS-SPME studies, including measurements of volatiles and semi-volatiles in hemp (25) and in edible versus psychedelic mushrooms (26).

Evacuation Process

Once a gas-tight seal has been created, one must consider how to evacuate the vial. A gas-tight syringe can be used by hand (10,22). The drawback is the seal could be compromised for the number of times needed to remove the air from the vial. Also, the rate at which one pulls the syringe can be inconsistent and be cause for variability. This method is cost-effective and has the possibility to be automated. A more effective and commonly used approach is to use a vacuum pump. A typical setup, shown in Figure 1, would be a diaphragm vacuum pump (generating ultimate vacuum to approximately 7 mbar) connected via metal tubing to an open/close valve. The metal tubing prevents collapsing, and the open/close valve allows the shut-off pressure from the vacuum pump when desired. A digital pressure gauge can be used to determine the amount of vacuum in the sampling vial, as well as to detect any leaks via pressure decay. A T-joint can be used to connect a digital pressure gauge with tubing on both sides. The other side of the T-joint would connect to tubing with a Luer lock attachment for a Luer lock side-port gas needle.

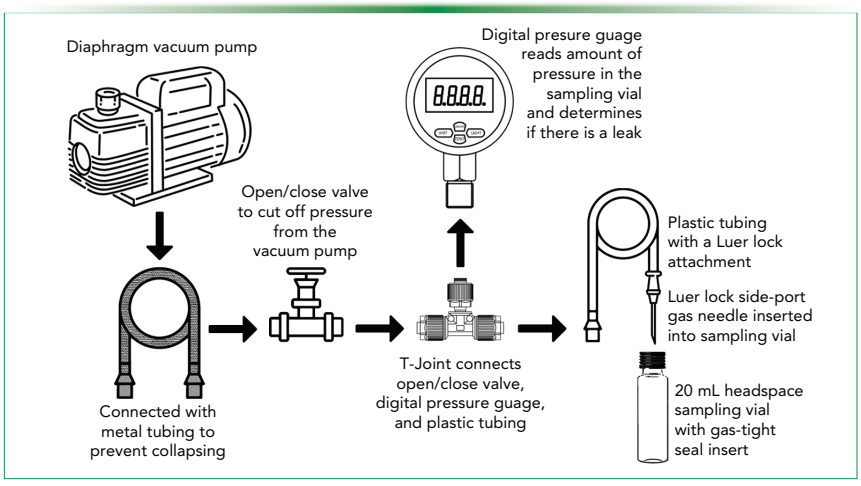

FIGURE 1: Vac-HS-SPME sampling setup.

The steps to evacuate the prepared sampling vial are as follows. Turn on the vacuum pump. Insert the side-port gas needle through the septum of the sealed vial. Vacuum time will be dependent on the type of vacuum pump used and the size of the vial. This can be determined with the use of the attached pressure gauge. Remove the needle while the vacuum pump is still running to ensure maximum vacuum. Only use the open/close valve before sample preparation to check for leaks and to verify vial pressure. The sample vial is now ready for equilibration and HS-SPME extraction.

Vial Preparation

When preparing a liquid sample, the liquid can be introduced before or after the air has been evacuated from the vial (14,27,29). If introduced before pulling vacuum, one needs to consider possible removal of some highly volatile compounds during the evacuation process. One could analyze the highly volatile first by performing traditional HS-SPME before pulling vacuum from the vial, then proceed with Vac-HS-SPME to sample the semi-volatiles, which have lower affinity for the headspace. When vacuum is pulled from the vial first, a syringe is used to introduce the liquid sample. Due to the reduced pressure in the vial, the liquid will be pulled quickly from the syringe and spray on the vial walls. Depending on the properties of the liquid sample, this order of vial preparation could cause variability.

Solid samples need to be placed in the vial prior to air evacuation unless a special device is made, such as those used by Ghiasvand and coauthors (18). Again, this means that highly volatile compounds could possibly be removed during evacuation. Steps can be made to ensure the least amount of volatile loss. A smaller vessel, such as a 20-mL headspace vial, requires less time to evacuate. If using a vacuum pump, one could attach a pressure gauge, as shown in Figure 1, to determine when evacuation is complete to minimize vacuum time and loss of volatiles. One could also freeze the sample immediately after placing it in the vial, as demonstrated by Capetti and associates (20). This would prevent the concentration of volatiles in the headspace and minimize volatile loss during vacuum.

Effects of Temperature and Extraction Time

Temperature is a key parameter used during HS-SPME sampling (3). At room temperature, volatiles will reach headspace equilibrium in a short amount of time. Semi-volatiles will require more time to reach equilibrium and will be at low concentrations in the headspace. Increased temperature speeds up equilibration time and increases the concentration of semi-volatiles. For Vac-HS-SPME, studies have shown that increased extraction temperatures reduced extraction efficiency of semi-volatile analytes (30). One explanation is that increased temperature increases the vapor pressure of analytes, thus increasing the total pressure in the sampling vial and minimizing the effects of Vac-HS-SPME (31). Thus, lower sampling temperatures can be used in Vac-HS-SPME to avoid sample degradation or unwanted by-products, and these conditions can be advantageous for increased extraction yield for many analytes.

Extraction times for semi-volatile analytes under atmospheric pressure take much longer than volatile analytes. It may take only a minute for volatiles to reach equilibrium compared to an hour or more for some semi-volatiles. Reducing the pressure in the sampling vial accelerates equilibration time and increases concentration of semi-volatiles in the headspace. This makes the overall extraction time shorter. Studies have commonly reported shorter extraction times for semi-volatile analytes, as much as half the time, for Vac-HS-SPME compared to traditional HS-SPME (9,15,19,26,27).

Conclusion

Vac-HS-SPME sampling is an advantageous sampling technique for the extraction of semi-volatile compounds. This method can be used for both liquid and solid samples. With the ability to extract at low temperatures, Vac-HS-SPME has the potential for many applications, which involve thermally labile compounds and samples that degrade with increased temperature. The progression of seals designed for standard 20-mL headspace vials, combined with the ability to pull vacuum with a gas-tight syringe, opens the door for this sampling method to be fully automated in the coming future.

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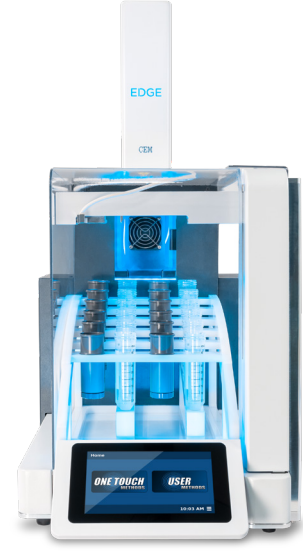

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