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A Comparison of 4 GC-MS Extraction Techniques to Determine Comprehensive VOC and Semi-VOC Profiles in Fragrance, Beverage, and Building Products

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Keywords

SPME, SPME Arrow, Twister®, TF-SPME, DHS, GC-MS

Abstract

Thoroughly determining the VOCs and semi-VOCs in various consumer goods using the proper extraction technique for GC-MS is vital for ensuring quality control, batch consistency, regulatory compliance, and successful product development studies. However, conventional sample extraction methods face significant limitations such as the introduction of additional solvents, the inability to handle matrix complexity, and difficulty achieving extremely low detection limits. In this study, solid phase microextraction (SPME), SPME Arrow, thin film solid phase microextraction (TF-SPME), stir bar sorptive extraction (SBSE/GERSTEL Twister®), and dynamic headspace (DHS) were compared and evaluated to determine which extraction technique produced the best comprehensive chromatographic profiles for three different sample types. It will be shown that the DHS extraction technique offers the most efficient extraction, providing the most analyte mass on column, resulting in very comprehensive chromatographic profiles and very low detection limits.

Introduction

The fragrance (or aroma) and flavor of a food, beverage, or fragrance product are crucial contributors to its acceptance and satisfaction among consumers. In reference to material emissions, it is important that compounds released during installation and curing do not have unpleasant odors or harmful properties. Therefore, manufacturers are highly interested in the comprehensive profile of such products to identify key contributors to the consumer's perception of the product. Identifying these compounds enables companies to modify their production processes either to diminish or remove the undesired ones or to identify and amplify the beneficial ones.

Some of the widely used extraction methods for these types of products are SPME, SPE (solid phase extraction), and liquid-liquid extractions (LLE) [1-2]. However, these extraction techniques possess significant disadvantages. SPE and LLE are time-consuming, require additional solvents and large sample amounts, and cannot account for the loss of some polar and semi-VOCs during sample preparation. SPME is not as time-consuming but can produce misleading results. This can be due to the fiber phase not effectively extracting important compounds, the analytes being too soluble in the matrix to partition out effectively, and/or there are competitive sorption effects that lead to calibration inaccuracies. SPME can also have higher detection limits due to a small phase volume and limited capacity. While SPME Arrow has increased phase volume the other disadvantages of traditional SPME still remain. SBSE, TF-SPME, and DHS are newer sample extraction techniques designed to overcome the limitations of traditional methods.

The challenge with producing a comprehensive profile for consumer products involves determining the best extraction tech-

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nique to extract a wide range of analytes from a product's matrix. This must be done without analyte discrimination or additional solvents to maintain the integrity of the sample. In this work, the chromatographic profiles of floor tile, sauvignon blanc wine, and laundered washcloths were obtained to evaluate four different sample extraction techniques.

Experimental

Instrumentation

GERSTEL MPS LabWorks Platform with SPME, SPME Arrow, DHS, on Agilent 8890 GC/5977B Inert Plus.

Analysis Conditions LabWorks Platform SPME

MPS	40 °C incubation/extraction temperature
	3 min incubation time
	60 min extraction time
Fiber	DVB/CAR/PDMS
CIS 4	SPME liner
	Splitless (floor tile)
	20:1 split (wine & washcloths)
	270 °C isothermal

Analysis Conditions LabWorks Platform SPME Arrow

MPS	40 °C incubation/extraction temperature
	3 min incubation time
	60 min extraction time
Fiber	DVB/CAR/PDMS
S/SL	SPME Arrow liner
	Splitless (floor tile)
	20:1 split (wine & washcloths)
	270 °C isothermal

Analysis Conditions LabWorks Platform Twister®/TF-SPME

Twister®	PDMS
TF-SPME	PDMS/HLB
TDU 2	Splitless
	40 °C; 720 °C/min; 250 °C (5 min)
CIS 4	Glass bead-filled liner
	Splitless (floor tile)
	20:1 split (wine & washcloths)
	-120 °C; 12 °C/s; 275 °C (3 min)

Analysis Conditions LabWorks Platform DHS

Trap	Tenax TA®
DHS	25 °C trap temperature
	40 °C incubation temperature
	1250 mL volume
	50 mL/min flow
TDU 2	Splitless
	40 °C; 720 °C/min; 280 °C (5 min)
CIS 4	Glass bead-filled liner
	Splitless (floor tile)
	20:1 split (wine & washcloths)
	-120 °C; 12 °C/s; 275 °C (3 min)

Analysis Conditions Agilent 8890 GC / 5977B MSD

Column	30 m Rxi-5ms (Restek)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics	He, constant flow = 1 mL/min
Oven	40 °C (2 min); 10 °C/min; 280 °C (3 min)
MSD	Scan, 35-350 amu

Samples

To compare the different sample extraction techniques, analysis conditions were optimized with similar extraction temperatures and times to obtain comparative data. Peel-and-stick floor tiles, sauvignon blanc wine, laundry detergent, fabric softener, and washcloths were purchased from a local store.

A 1 cm x 1 cm cutting of the floor tile was made, and the adhesive backing was removed.

A 3 mL aliquot of sauvignon blanc was used for analysis.

The washcloths were washed in the laundry detergent and fabric softener and placed in a dryer using air fluff mode for 20 minutes. Then, a 3 cm x 3 cm cutting of the washcloth was made. The washcloth cuttings were rubbed gently to allow the fragrance capsules to burst and release VOCs. The cuttings were loosely rolled into cylinders to fit into vials.

All samples were placed in individual 20 mL screw-capped vials.

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Results and Discussion

Solid Phase Microextraction

SPME is an extraction method employing a fiber coated with a polymeric phase to absorb or adsorb analytes either from the headspace of a sample or directly from a liquid sample. In headspace SPME, two equilibrium processes take place. The first equilibrium is established between the sample and the headspace, while the second equilibrium occurs between analytes in the headspace and the fiber's sorptive coating. The interaction of analytes with the sorptive phase promotes the release of more volatiles from the sample to re-establish equilibrium. This process enhances concentration while offering analyte selectivity, depending on the polymeric phase.

SPME Arrow

SPME Arrow, much like SPME, employs a fiber coated in a polymeric phase for analyte sorption in an immersive or headspace setting. SPME Arrow comes in various phases and thicknesses (100-250 µm) with the largest phase offering 12 µL of phase volume. Additionally, SPME Arrow has a stainless-steel protective arrow tip that eliminates wear and tear on the fiber and extends the septum lifetime. One caveat to this extraction tool is that it requires a modification to the split/splitless inlet to accommodate the width of the SPME Arrow fiber. Nonetheless, the additional phase volume and surface area enhance extractions compared to SPME.

GERSTEL Twister® and Thin Film Solid Phase Microextraction

TF-SPME and the Twister® follow the same concept as SPME; however, TF-SPME membranes offer different polymeric coatings than SPME fibers, and the combination of TF-SPME membranes and Twister® provides much larger phase volume and surface area. SPME fibers have a 0.6 µL phase volume and 9.4 mm^2 surface area, whereas the combination of TF-SPME membranes and Twister® stir bars have a total of 33 µL phase volume and 344 mm^2 surface area. Additionally, the TF-SPME membranes employ hydrophilic-lipophilic balanced (HLB) particles as well as PDMS. The HLB particles can extract the widest polarity range of compounds. This higher surface area and phase volume of various sorptive materials aids in analyte capacity and offers a more thorough extraction compared to SPME and SPME Arrow. Figure 1 shows the difference in phase volume and surface area between SPME, SPME Arrow, and TF-SPME/Twister extraction devices.

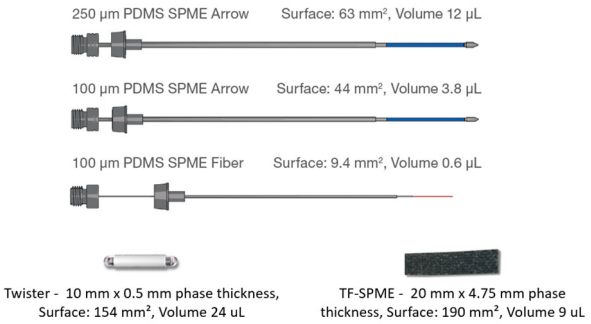

Figure 1: Phase volume and surface area for SPME, SPME Arrow, Twister, and TF-SPME extraction devices.

Dynamic Headspace

DHS is a non-equilibrium-based extraction technique for efficiently extracting volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) from solid or liquid samples. A sample is incubated for a short period of time before inert gas purges the headspace. The analytes are then concentrated onto a sorbent-filled trap for subsequent desorption into a GC system. Figure 2 demonstrates the DHS process. DHS allows for exhaustive extractions due to the continuous sweeping of analytes from the sample matrix onto the sorbent tube. This leads to a much higher extraction efficiency compared to Twister®/ TF-SPME, and especially SPME and SPME Arrow.

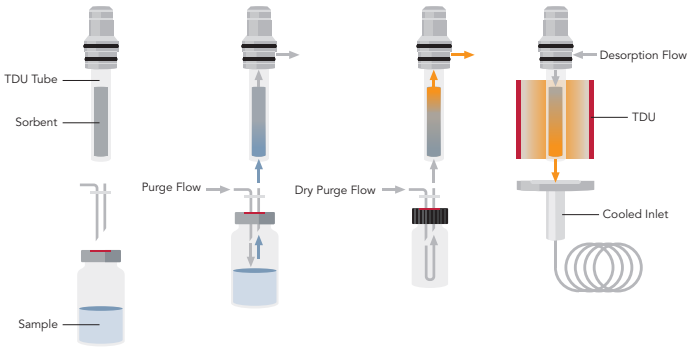

Figure 2: The dynamic headspace workflow from sample insertion to thermal desorption.

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Figure 3 shows the relative peak areas of the floor tile analytes using all four sample extraction techniques. All data was normalized to the DHS results as it was observed that the highest relative peak areas were seen when DHS was the chosen sample extraction technique. The floor tiles off-gassed several compounds, including cyclohexanone, branched and long-chain alkanes, chlorinated alkanes, and phthalates. Additionally, some compounds such as longifolene, diethyl phthalate, and 1-chloro-tetradecane were less distinguished from the baseline using SPME and SPME Arrow. SPME Arrow showed only slight improvements over SPME due to the increased phase volume. DHS substantially increased the signal intensity of these and all other compounds, thus resulting in lower detection limits. This becomes especially important as most of these compounds have a certain degree of toxicity that often needs to be measured to determine potential harm. Phthalates are formulated into indoor building materials for increased durability, and chlorinated alkanes offer flame-retardant properties, which can pose a health risk in significant amounts. DHS successfully identified several compounds with the highest response compared to the other two extraction techniques.

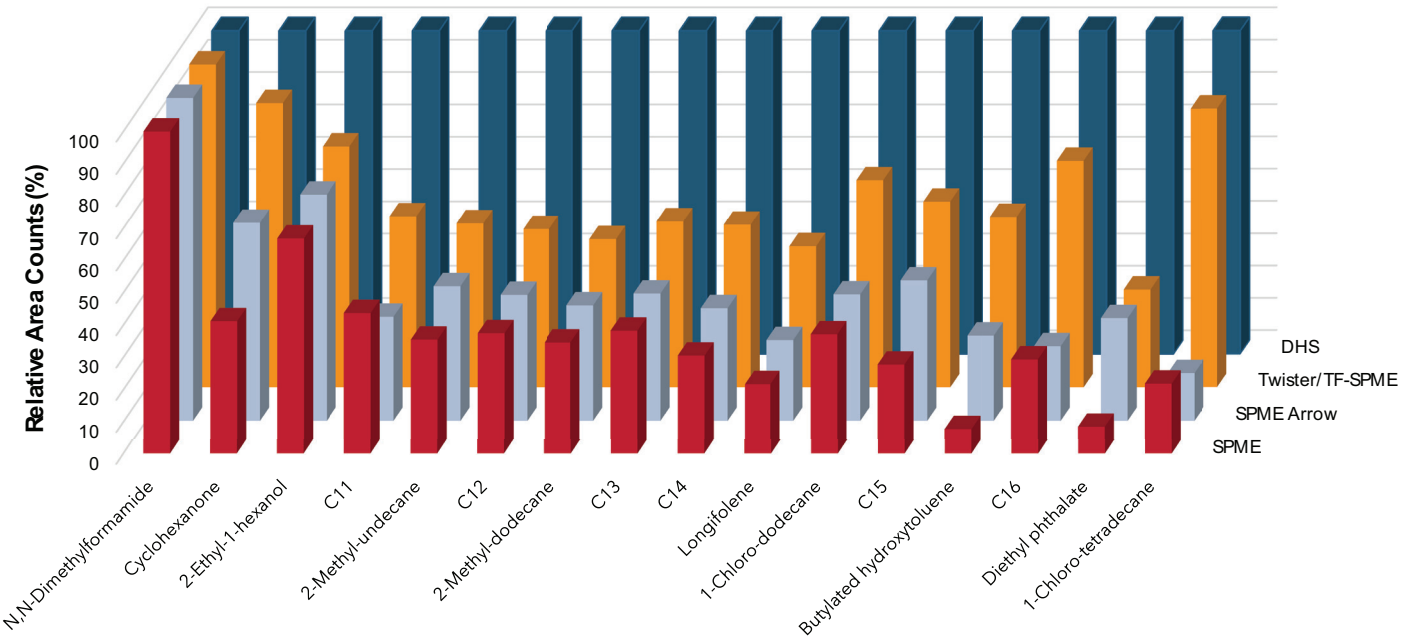

Figure 3: Relative peak areas of the floor tile analytes using all four sample extraction techniques.

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Figure 4 shows the relative peak areas of the sauvignon blanc analytes using all four sample extraction techniques. All the techniques extracted several esters successfully, but the SPME fiber did not preconcentrate the lighter esters in the same magnitude as Twister®/TF-SPME and DHS. Thorough identification of these ethyl esters is imperative in wine analysis as these compounds contribute greatly to the floral and fruity notes that so many consumers enjoy. Since adsorptive SPME fibers have limited capacity, the heavier esters are pre-concentrated on the fiber, creating competition for any remaining sites on the fiber's polymeric phase, preventing the lighter esters from effectively sorbing. SPME Arrow shows the same results, with only slightly elevated area counts for the remaining compounds. On the other hand, the Twister®/TF-SPME and DHS extractions detected all esters with good signal intensity. There were several compounds identified in the Twister®/TF-SPME and DHS extractions that could not be identified with SPME and SPME Arrow. These compounds included ethyl isobutyrate, isobutyl acetate, cis-ethyl crotonate, ethyl 2-methylbutanoate, ethyl isovalerate, ethyl pentanoate, and methyl hexanoate. Since the wine matrix is comprised of mostly water, it is important to choose an extraction technique that can selectively sorb volatile and non-volatile components. Although the DHS extraction achieved greater peak areas for nearly all compounds identified, an immersive extraction with Twister®/TF-SPME may be better suited for this sample type to achieve a more comprehensive profile. Immersive Twister®/TF-SPME extractions have proven beneficial for the determination of compounds in numerous beverages, such as beer, hard seltzers, juice, milk, and tea [3-5]. This combination of extraction devices selectively sorbs both volatile and semi-volatile components from the sample while excluding water and subsequently preventing inlet freezing and reproducibility issues. Headspace extraction, like DHS or HS-Twister®/TF-SPME, would be more appropriate if only the volatile compounds of wine were of interest.

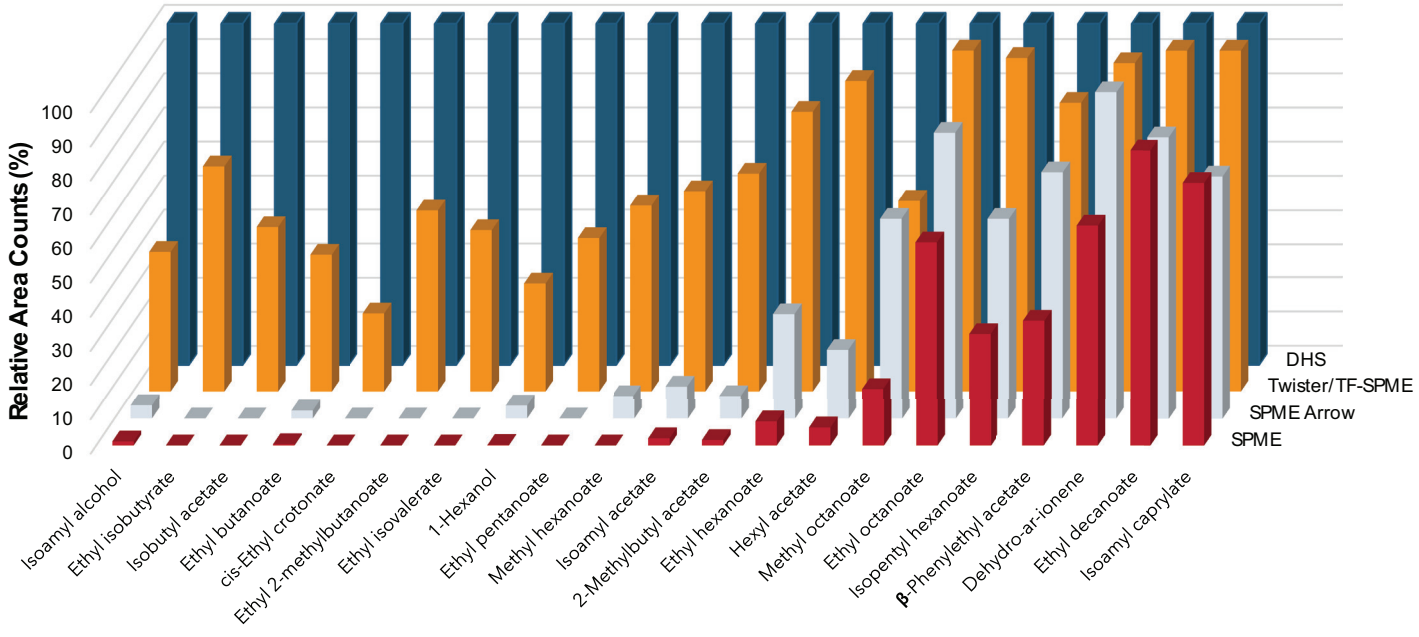

Figure 4: Relative peak areas of the sauvignon blanc analytes using all four sample extraction techniques.

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Laundry detergents and fabric softeners are comprised of many fragrances, solvents, and compounds to promote a longer shelf life, all of which encompass a wide range of volatility and polarity. Choosing a technique that can extract all these compounds from matrices like washcloths, clothing, etc., is beneficial for determining their longevity post-wash and dry cycles. Figure 5 shows the relative peak areas of the laundered washcloth analytes using all four sample extraction techniques. SPME and SPME Arrow could not effectively sorb several of the early eluting terpenes and esters and the Twister®/TF-SPME extraction could not effectively sorb some of the later eluting phthalates and long-chain alkanes. DHS successfully extracted all these analytes with the greatest peak area. Additionally, some of the analytes that DHS was able to extract, at much lower detection limits than the other techniques, are carrier solvents and stabilizers, like diethyl phthalate, alkanes, and butylated hydroxytoluene, some of which need to be identified for potential environmental contamination, regulatory compliance, and consumer safety.

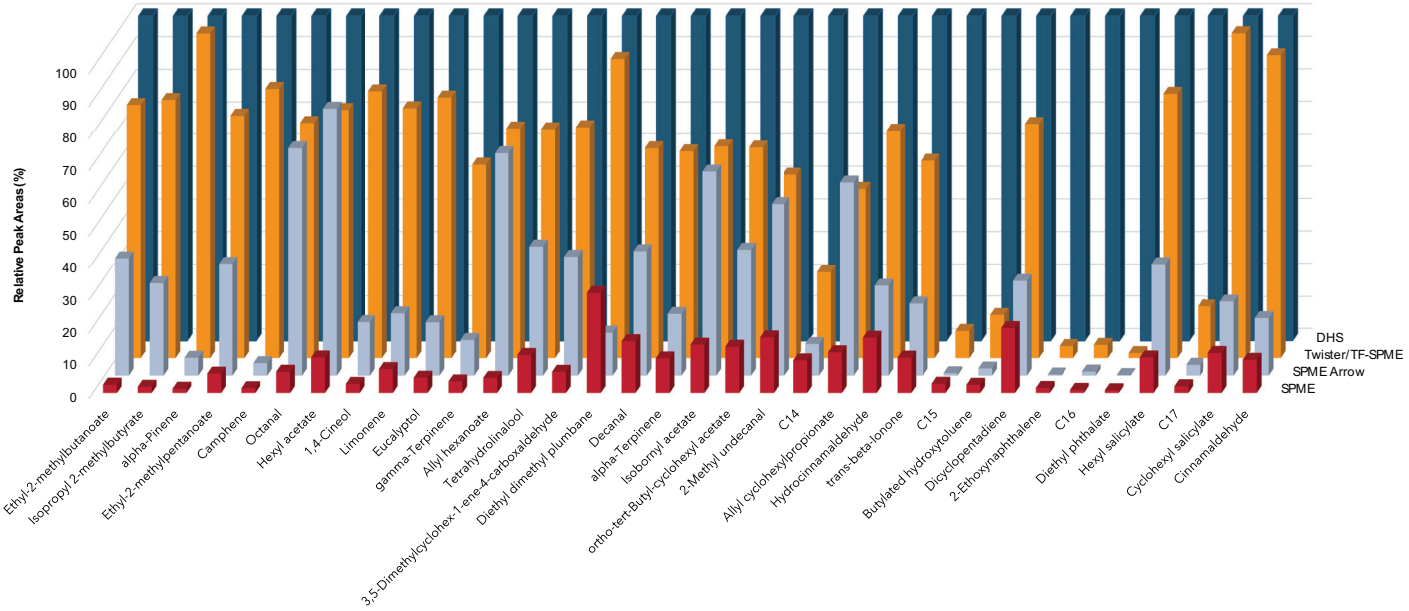

Figure 5: Relative peak areas of the laundered washcloth analytes using all four sample extraction techniques.

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Conclusion

This study provided a comparison of sample extraction techniques for a wide variety of consumer products. Extractions using DHS provided comparatively more analyte mass on column than the other techniques due to the exhaustive nature of the extraction process and sorbent capacity. The most optimal extraction technique must always be determined based on the sample matrix and compounds of interest. DHS provides users with a fully automated approach to sample analysis and produces highly comprehensive chromatograms that cover almost all sample matrices.

References

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[3] AppNote-250 Volatile Organic Compound and Sensory Profiles of Alcoholic versus Non-Alcoholic Beer Using Immersive Twister® and TF-SPME Extraction

[4] AppNote-242 Comparison of Four Immersion Extraction Techniques Using the GERSTEL Twister® and TF-SPME Devices to Determine Analytes Found in Hard Seltzer Flavors

[5] AppNote-219 Comparison of 3 Types of TF SPME for Beverage Extractions