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A MULTIFACETED INVESTIGATION ON THE EFFECT OF VACUUM ON THE HEADSPACE SOLID-PHASE MICROEXTRACTION OF EXTRA-VIRGIN OLIVE OIL

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Headspace solid-phase microextraction | Vacuum-assisted headspace solid-phase | microextraction | Extra-virgin olive oil | Central composite design

ABSTRACT

Headspace solid-phase microextraction (HS-SPME) is an easy, effective, and selective technique for the extraction of volatiles and semi-volatiles compounds. For the latter, longer equilibration times are needed, which are typically shortened by applying agitation or heating the sample. A less explored way to improve the extraction kinetics of analytes with a low-affinity for the headspace is to sample under vacuum conditions. The methodology that evolved from this approach was termed "vacuum-assisted HS-SPME" (Vac—HS—SPME) and was mainly used for water- and solid-based samples.

The aim of this work was to investigate the effect of vacuum when dealing with non-aqueous liquid samples. For this purpose, the volatile profile of extra virgin olive oil was analyzed using a divinylbenzene/carboxen/polydimethylsiloxane fiber followed by gas chromatography-mass spectrometry. The effects of extraction temperature and sampling time were investigated using traditional one-variable at a time approach and a two-variable central component design for both Vac—HS—SPME and regular HS-SPME. The results showed an important enhancement in the extraction of semi-volatile compounds when using Vac—HS—SPME, and improved the information gained for the olive oil aroma fingerprint. A theoretical formulation of the underlying process was proposed, providing new insights into the SPME extraction theory. Lowering the sampling pressure effectively reduced gas-sided limitations and accelerated extraction kinetics. However, for viscous samples such as olive oils, the liquid-phase resistance played an important role and delayed extraction. Overall, applying heating (*i.e.* reducing the viscosity of the oily sample and increasing headspace concentrations) next to reducing the total pressure in the headspace is the best analytical HS-SPME strategy for obtaining fast a rich volatile profile from the oily samples.

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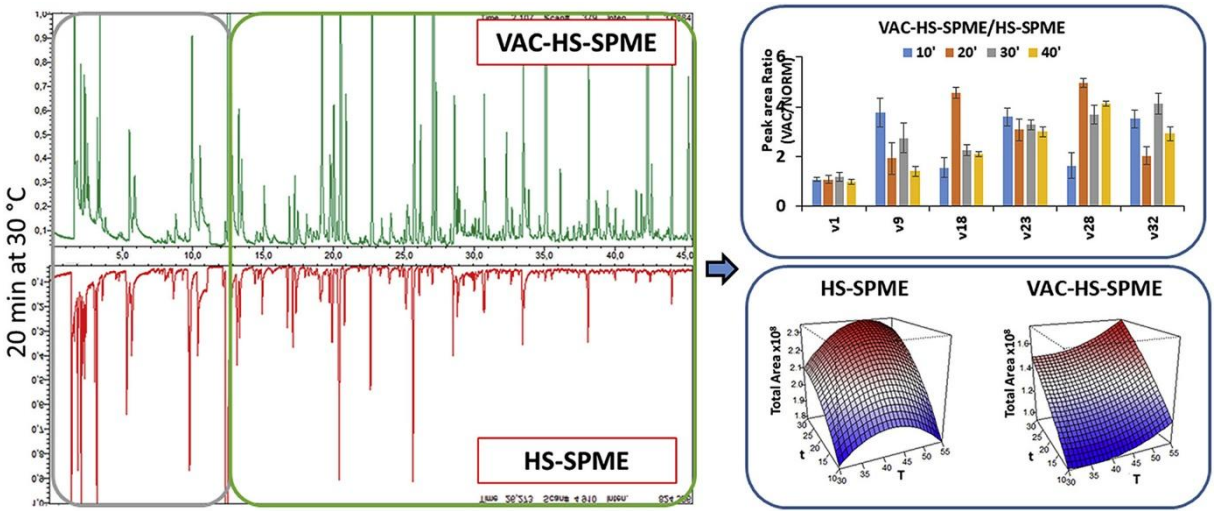
ABSTRACT IMAGE



1. Introduction

Solid-phase microextraction (SPME) is a solvent-free sample preparation technique introduced in 1990 by Arthur and Pawliszyn [1]. Since then, it has known an exponential diffusion in many fields of applications, such as clinical and pharmaceutical [2-4], environmental [5-8], and food [5,9,10]. Despite the many different formats and setups proposed, the initial SPME fiber-format remains the most employed one due to its flexibility and ease of use [11]. Among the many applications, headspace (HS)-SPME has been very successful in the analysis of food volatile and semi-volatiles compounds for quality and authenticity assessment [5,9,10]. The principle behind this extraction is the partition equilibrium among a three-phase system, *i.e.*, sample-headspace-fiber. Equilibration times may vary from a few minutes to several hours, depending mainly on the type of sample and the properties of the target analyte. Typically, a compromise between sensitivity and extraction time is reached when targeting a wide variety of compounds (volatile and semi-volatile), as in the case of fingerprinting food aroma. Different strategies can be applied to improve the kinetics and maximize the number of extracted compounds, such as stirring the sample and increasing the temperature, although the latter may create undesired artifacts, especially when dealing with food samples [12,13].

An alternative and less explored and exploited way to improve extraction kinetics is the application of reduced pressure conditions during sampling. The positive effect of vacuum on HS-SPME was presented for the first time in 2001 by Brunton et al. for the extraction of volatiles from raw turkey meat homogenated with water [14]. In 2005, Darrouzès et al. proposed the use of vacuum to enhance the HS-SPME sampling of organotin compounds from aqueous solutions [15]. The effect of reduced pressure conditions on HS-SPME (method termed vacuum-assisted HS-SPME; Vac—HS—SPME) started to be more rigorously and systematically investigated after the theoretical formulation of

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the underlying processes by Psillakis et al. in 2012 [16-24]. Ever since, Vac—HS—SPME has been successfully applied to aqueous and solid samples, resulting in high extraction efficiencies and excellent sensitivities within shorter sampling times compared to regular HS-SPME (at 1 atm). Vac—HS—SPME also displayed high perfor-mance at milder temperatures, thus preserving the sample volatile profile and avoiding possible decomposition, reactions, or artifacts formation. Few works deal with the application of Vac—HS—SPME on more complex samples. Vakinti et al. Used Vac—HS—SPME for the determination of haloanisoles in wine samples. Although ethanol (acting as a co-solvent) affected the solubilities of target analytes and reduced their headspace abundance, the positive effect of vacuum on HS-SPME sampling remained important. In fact, for 30 min sampling, the performance of Vac—HS—SPME at 25 °C was superior to that with regular HS-SPME sampling at 55 °C [25]. Trujillo-Rodríguez et al. applied Vac—HS—SPME to the analysis of a multi-component system, namely milk and dairy products [22]. The optimization and the comparison with regular HS-SPME were carried out on a water simulant and focused on studying competitive adsorption phenomena taking place on adsorbent-type SPME fibers, rather than investigating the effect of high-fat content in the matrix.

The present work investigates for the first time the use of Vac—HS—SPME to characterize the aroma profiling of an entirely lipidic matrix, namely olive oil. Olive oil, and in particular extra virgin olive oil, is an important ingredient of the Mediterranean diet with well-known health benefits and sensory quality. The latter is correlated to a complex aroma profile, which depends on several parameters (*i.e.*, cultivar, geographical origin, fruit ripeness, processing practices, and storage). Researchers have been dedicating strong efforts to unravel the composition of this informative fraction to understand correlations with quality attributes [26,27]. In this regard, the most widely-applied sampling technique is HS-SPME, and optimum extraction conditions report sampling temperatures ranging from room temperature up to ~80 °C (for volatile characterization) with sampling times generally shortened when higher temperatures were applied [28]. However, olive oil degradation is accelerated when heating the samples, and at the same time, extended sampling times promote competitive displacement on the adsorbent-type SPME fibers [22,29], typically used for aroma profiling [28]. Therefore, HS-SPME sampling under reduced pressure has the potential to overcome these analytical challenges as it can yield higher extraction efficiencies at mild sampling temperatures [23].

The extraction temperature and time profile under reduced and normal pressure conditions were investigated (both using traditional one-variable at a time approach and a two-variable central component design (CCD)). Theoretical considerations on non-equilibrium HS-SPME sampling from olive oil samples are herein reported for the first time. Based on these considerations, we provide some new insights on the HS-SPME mechanism. A divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber was used in this investigation as the most applied one for the analysis of volatile compounds in edible oils [28].

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1.1. THEORETICAL CONSIDERATIONS ON THE EFFECT OF VACUUM ON HS-SPME SAMPLING FROM OLIVE OIL

During HS-SPME sampling, analytes transfer in the three phases involved (oil, headspace and fiber) and across two interfaces (oil/ headspace and headspace/fiber). Mass transfer in the headspace/ SPME polymer interface is considered a relatively fast process [29-31], while, depending on the properties of the analyte, volatilization from the liquid sample can be rate-controlling, *i.e.* a slow equilibration process [31,32]. For this reason, only the pressure dependence of analyte mass transfer from the liquid sample to the headpace has been formulated in the past [30,32]. It is acknowledged however that mass transfer accelerations at the headspace/SPME fiber interface may also occur when sampling under vacuum. Nonetheless, this type of non-equilibrium accelerations are difficult to monitor experimentally taken that the headspace/SPME fiber equilibration times are short anyway. It is noted that the pressure dependence of the process of analyte uptake by high capacity sorbents (stir bar coated with polydimethylsiloxane [33] or a liquid microdrop [34]) was recently formulated and experimentally verified. In these systems, the uptake of analytes from the gasphase is slow and as such, accelerations under vacuum conditions could be experimentally recorded.

In general, the classic two-film theory is used to describe the mass transfer of solutes at the liquid/headspace system. This model assumes that the bulk of each phase is well mixed so that only the two thin layers at the interface are characterized by a concentration gradient. Therefore, the primary resistance to mass transfer lies in these stagnant films, across which solutes transfer by molecular diffusion. The two-film theory has been extensively applied to the problem of volatilization of chemicals from natural waters bodies [35-37], and proved successful in describing the pressure dependence of HS-SPME sampling from water samples under nonequilibrium conditions [23,30]. In the past, the liquid phases considered for the two-film theory were not necessarily aqueous, and the model was also used to simulate the process from nonaqueous phases, *e.g.*, the gas leakage process from transformer oil [38]. According to the two-film approach, the overall mass transfer coefficient, k_O, controlling volatilization of a solute from olive oil can be modeled as follows

$$\frac{1}{k_O} = \frac{1}{k_L} + \frac{1}{K_{GL} k_G} \quad (1)$$

where, k_G and k_L are the mass transfer coefficients for the gas and olive oil boundary layers and K_{GL} is the gas phase-olive oil partition coefficient representing the ratio of the equilibrium concentrations in the gas phase over that in the liquid sample. According to Eq. (1) for a given solute, the overall resistance to transfer from olive oil to the gas phase ($1/k_O$) can be considered as two diffusional resistances in series; namely the sum of the gas-phase resistance ($1/(K_{GL}k_G)$ and the olive oil resistance ($1/k_L$)).

In general, both the liquid-film and gas-film coefficients are assumed directly dependent on the diffusion coefficient in the corresponding phase (*i.e.*, D_L or D_G for the liquid and gas-phases, respectively) raised to some power, which lies between 0.5 and 1 depending on the model used [39-41].

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The estimation of diffusivity in liquids is far more complicated than in gases. Among the different equation proposed, the following Wilke-Chang [42] formula has been used for solvents of high viscosity such as oils [43,44]:

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

with M indicating the molecular weight of the solvent; V the molar volume of the solute; η the viscosity of the solvent; and T the temperature. Eq. (2) shows that in highly viscous solvents like olive oil, diffusion coefficients will be smaller than those in water [43] and should account for additional resistance in the liquid-film compared to an aqueous phase.

The diffusion coefficient in the gas-phase, D_G, can be estimated using different equations, all of which show an inverse proportionality to the total pressure in the system [30]. Therefore, reduction of the total pressure during HS-SPME will increase D_G, and consequently k_G, leading to a reduced gas-phase resistance (expressed as $1/(K_{GL}k_G)$ in Eq. (1)) [30,32]. Accordingly, lowering the total pressure will improve the overall mass transfer coefficient for analytes where gas-phase resistance controls thevolatilization rate; thus resulting in faster HS-SPME extraction kinetics and shorter equilibration times. For the rest, applying a low sampling pressure should not affect the HS-SPME extraction kinetics since the liquid-phase resistance that controls their volatilization rate is independent of the total pressure in the sample container.

According to Eq. (1), acceleration in extraction kinetics will be recorded for those analytes whose K_{GL} is sufficiently small to render the $1/(K_{GL}k_G)$ term comparable or superior to the liquid-phase resistance ($1/k_L$ 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 and solvent-solvent molecular interactions [45]. Data on solute partitioning between olive oil and air are sparse and predictive theoretical models are mostly used [46-48]. For example, linear free energy equation relationships (LFER) exist for certain homologues or families of compounds (*e.g.* ethers, esters, ketones) that correlate partition coefficients in air-olive oil to those in air-octanol system, with octanol representing a solvent that may participate in various combinations of dispersive, dipole-dipole, H-acceptor, and H-donor interactions with solutes of diverse structures [45]. However, olive oil is a mixture of compounds that may vary in composition depending on the origin of the olives. For this reason, reference is made to airolive oil partition coefficients rather than constants [45]. The limited access to air-olive oil partitioning data (*i.e.* K_{GL} values) and the complex interactions of solutes with olive oil, obstructs the establishment of a criterion that can be used for predicting the positive effect of vacuum on any compound present in olive oil. Nonetheless, the theory predicts that sampling under vacuum will accelerate extraction kinetics for those analytes where gas-phase limitations play a major role.

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2. Materials and methods

2.1. CHEMICAL AND REAGENTS

Hexane was HPLC grade (MilliporeSigma®, USA). The mixture of normal alkanes (C_7—C_{30}), used for calculating the linear retention index (LRI) for confirming peak identity, was from Supelco (Bellefonte, PA, USA).

A DVB/CAR/PDMS d_f 50/30 µm/1 cm length fiber was used (kindly offered by Millipore Sigma, Bellefonte, PA, USA).

Extra-virgin olive was purchased in a local supermarket (Gembloux, Belgium).

2.2. VAC—HS—SPME AND REGULAR HS-SPME PROCEDURES

A custom-made closure designed and constructed at the Laboratory of Aquatic Chemistry (School of Environmental Engineering, Technical University of Crete) was used for all experiments [33]. Alternatively, the previously reported modified crimp-top Mininert®valve (Sigma-Aldrich) can be used to ensure gastight conditions inside the sampler during automation [49]. The closure was equipped with a cylindrical Thermogreen®LB-1 septum (Supelco) with half-hole (6 mm diameter × 9 mm length) and could fit a 20 mL screw top vial (Restek, Bellefonte, USA).

For Vac—HS—SPME, the air inside the sampling device was evacuated for 1 min prior to introducing the oil sample, using a MD 4C diaphragm vacuum pump (7 mbar = 0.007 atm ultimate vacuum without gas ballast) manufactured by Vacuubrand GmbH & Co. KZ (Wertheim, Germany). A 5 mL gastight syringe (SGE, Australia) was used to introduce 1.5 g of oil samples in the sample container. The sample was allowed to equilibrate with the headspace for 5 min at the temperature set for extraction. Then, the SPME fiber was exposed to headspace and sampling was performed under agitation (250 rpm) at the selected sampling temperature.

For regular HS-SPME the air-evacuation step was omitted. A 20 mL screw top vials, metallic caps with a hole and polytetrafluoroethylene (PTFE)/silicone septa (Restek, Bellefonte, USA) were used.

Two extraction temperatures were tested, namely 30 °C and 43 °C, at different extraction times (10, 20, 30 and 40 min).

Upon completion of the sampling procedure, the fiber was retracted and transferred for thermal desorption (250 °C for 2 min, split 1:5) and analysis to a GC-MS. All experiments were run in triplicate.

Prior to starting any analytical sequence, the SPME fiber was conditioned for 20 min in the GC injector. Blanks were run periodically to ensure the absence of carryover between runs. All extractions were run in triplicate.

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2.3. SOLID-PHASE MICROEXTRACTION OPTIMIZATION: CENTRAL COMPOSITE DESIGN

A two-variable ($k = 2$) inscribed rotatable ($\alpha = 1/\sqrt[2]{k}$) central composite experimental design (CCD) was used to optimise the sampling conditions, namely extraction temperature and time. These two variables were selected based on previous works [50,51]. The extraction temperature was tested between 30 °C and 55 °C, and the exposition time from 10 to 30 min. Temperatures higher than 55 °C were not tested to avoid the possible formation of artifacts due to oxidation and degradation products. Nine different sampling conditions were included in the design, consisting of a central point, four axial and four factorial points. The experimental runs were randomized to minimize the effect of unexpected variability. The central point was repeated three times to evaluate the repeatability of the method. The extracted-ion peak areas obtained by GC-MS were used to evaluate the extraction efficiency using the response surface plot methodology [8].

All samples were agitated at 250 rpm and incubated for 5 min before fiber exposure at the corresponding extraction temperature. The entire CCD was repeated under normal pressure conditions (regular HS-SPME) and under vacuum (Vac—HS—SPME).

In all the experiments, the fiber was thermally desorbed in the GC injector for 2 min at 250 °C in split mode (1:5).

2.4. GC-MS ANALYSIS

An Agilent 7890B GC coupled to a 5977 MSD was used for all analyses. Helium (5.0 provided by Airliquid, Belgium) was used as carrier gas at 1 mL/min flow rate. Separation was performed on a 30 m × 0.25 mm i.d. × 0.5 mm df SLB-5ms capillary column [silphenylene polymer, practically equivalent in polarity to poly(5% diphenyl/95% methylsiloxane)] kindly obtained from MilliporeSigma (Bellefonte, PA, USA). The GC oven temperature program was as follows: 35 °C for 2 min, programmed to 250 °C at a rate of 3 °C/min and then increased to 300 °C at a rate of 25 °C/min. The MS was operating in EI at 70 eV, the source temperature was 230 °C and the quadrupole temperature was 150 °C. The results were recorded in the full scan mode in the 35—500 m/z range. Data were acquired by MassHunter GC/MS Acquisition software B.07.06.2704 (Agilent, USA), converted into AIA by MSD ChemStation F.001.03.2357 (Agilent) and processed using Shimadzu GCMSolution ver 4.45 (Shimadzu, Japan).

2.5. DATA ELABORATION AND STATISTICAL ANALYSIS

Putative identification was based on the combination of a dual filter, namely: 1) the MS similarity with the NIST17 library and the FFNSC library (Shimadzu) (≥80%) and, 2) the experimental linear retention index (LRI) within a ±10 range. A total of 33 compounds (Table 1) were selected over the entire chromatogram. Several rationales guided the selection: i) differences in physico-chemical properties, such as polarity and volatility; ii) previously reported as important compounds for the extra virgin olive oil aroma characterization [52-55], iii) no or limited coelution. All the

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chemicalphysical properties of the 33 compounds selected (reported in Table 1) were obtained from the ChemSpider website (http://www.chemspider.com/).

All statistical analyses were performed using R v3.3.2 (R Foundation for Statistical Computing, Vienna, Austria) and Minitab 19 (https://www.minitab.com/en-us/).

***Table 1**. List of the selected compounds together with their Chemical Abstracts Service (CAS) number, boiling point (B_p), Henry's constant (K_H, atm m^3 mol^{-1}), octanol-air partition constant (K_{oa}, atm m^3 mol^{-1}), octanol-water partition constant (K_{ow}, atm m^3 mol^{-1}), Vapour pressure (V_p, mmHg at 25 °C), Molecular weight (M_W, g mol^{-1}) and Molecular volume (V_M, cm^3), and linear retention index (I^T) experimentally calculated and reported in the literature.*

#	Compound Name	CAS	M_W (g mol $^{-1}$)	V_M (cm^3)	B_P (°C)	Log K_H (atm m3 mol^{-1})	log K_{oa} (atm m^3 mol^{-1})	log K_{ow} (atm m^3 mol^{-1})	V_p (mmHg at 25 °C)	m/z	I^T_{ex}	I^T_{Lib}
v1	Ethanol	64-17-5	46.1	59.1	72.6	−5.33	3.379	−0.14	82.8	45	601	552
v2	Acetic acid	64-19-7	60.1	56.2	117.1	−5.54	5.218	0.09	13.9	60	634	641
v3	Ethyl Acetate	141-78-6	88.1	98.0	73.9	−3.42	2.991	0.86	111.7	43	648	630
v4	1-Penten-3-ol	616-25-1	86.1	104.0	112.5	−4.64	4.514	1.12	11.2	57	690	685
v5	Penten-3-one	1629-58-9	84.1	103.3	104.3	−3.71	3.748	0.90	31.1	55	691	683
v6	Pentan-3-one	96-22-0	86.1	108.2	101.0	−3.60	3.43	0.75	35.8	57	700	697
v7	2(E)-Pentenal	1576-87-0	84.1	102.0	126.8	−3.86	3.607	1.09	11.5	55	760	751
v8	1-pentanol	71-41-0	88.1	108.6	138,5	4.83	4.785	1.33	2.8	42	772	761
v9	*n*-octane	111-65-9	114.2	160.6	126.4	0.29	3.062	4.27	14.2	43	800	800
v10	Hexanal	66-25-1	100.2	124.9	127.0	−3.45	3.84	1.80	10.9	56	801	801
v11	2(E)-Hexenal	6728-26-3	98.1	118.5	146.5	−3.94	4.279	1.58	4.6	69	852	850
v12	1-Hexanol	111-27-3	102.2	125.0	158.2	−4.76	5.185	1.82	0.9	56	872	867
v13	Pentanoic acid	109-52-4	102.1	105.7	185.3	−5.29	6.105	1.56	0.5	60	881	893
v14	Heptanal	111-71-7	114.2	141.4	150.4	−3.34	4.247	2.29	3.9	70	903	906
v15	2(E)-Heptenal	18829-55-5	112.1	135.0	166.0	−3.81	4.341	2.07	1.8	83	960	956
v16	Benzaldehyde	100-52-7	106.1	101.1	178.7	−4.64	4.442	1.71	1.0	106	965	960
v17	Hexanoic acid	142-62-1	116.1	122.2	204.6	−5.14	6.429	2.05	0.2	60	978	979
v18	6-methylhept-5-en-2-one	110-93-0	126.2	151.1	173.3	−3.75	4.122	2.06	1.3	43	987	986
v19	Octanal	124-13-0	128.2	157.9	163.4	−3.20	4.457	2.78	2.1	84	1004	1006
v20	Hex-(3Z)-enyl acetate	3681-71-8	142.2	157.7	175.2	−3.35	4.195	2.61	1.1	67	1005	1008
v21	Acetic acid, hexyl ester	142-92-7	144.2	164.1	171.5	−3.05	4.494	2.83	1.4	43	1013	1012
v22	ß-Ocimene,(E)	13877-91-3	136.2	175.5	175.2	−0.62	3.398	4.80	1.6	93	1047	1046
v23	Oct-(2E)-enal	2548-87-0	126.2	151.5	190.1	−3.63	5.093	2.57	0.6	70	1060	1059
v24	*n*-octanol	111-87-5	130.2	158.1	194.7	−4.68	5.999	2.81	0.1	56	1074	1076
v25	2-Nonanone	821-55-6	142.2	174.2	193.5	−3.15	4.496	2.71	0.6	58	1092	1093
v26	Nonanal	124.19−6	142.2	174.4	190.8	−3.10	4.793	3.27	0.5	57	1105	1107
v27	Octanoic acid	124-07-2	144.2	155.2	239.3	−4.73	7.488	3.03	0.1	60	1170	1192
v28	Methyl salicylate	119-36-8	152.1	125.8	222.0	−5.24	4.947	2.60	0.1	120	1197	1192
v29	Decanal	112-31-2	156.3	190.9	209.0	−2.95	4.893	3.76	0.2	57	1207	1208
v30	Dec-(2E)-enal	3913-81-3	154.2	184.5	230.0	−3.63	5.451	3.55	0.1	70	1264	1265
v31	Nonanoic acid	112-05-0	158.2	171.7	254.9	−4.67	7.748	3.52	0.0	60	1267	1275
v32	Undec-(8Z)-enal	58296-81-4	168.3	201.0	242.8	−3.35	5.545	4.04	0.0	70	1366	1365
v33	α-Farnesene, (E,E)	502-61-4	204.3	251.5	279.6	−0.19	5.067	7.10	0.0	93	1506	1504

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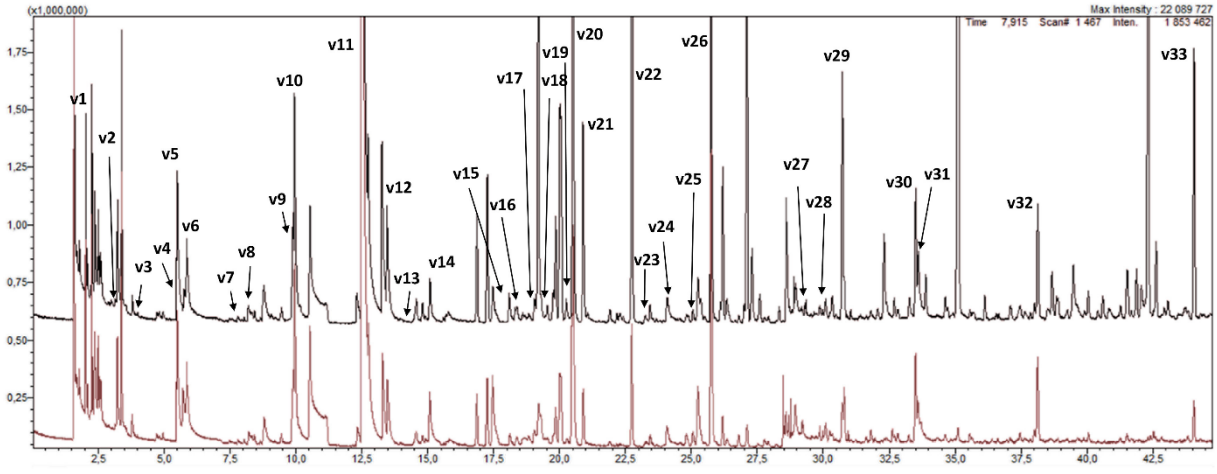
3. Results and discussion

The aroma of extra virgin olive oil is reflected in a complex volatile components profile. Based on previous experience [27], a non-polar column (5% phenyl) was used, along with a rather slow oven temperature program (3 °C min^{-1}) to minimize coelution at this preliminary investigation stage.

Despite a careful selection of the 33 compounds considered, it was not possible to completely avoid the partial coelution of some compounds, especially in the case of the richer profile obtained with Vac—HS—SPME. The partial coelution with other compounds is one of the reasons for some of the rather high relative standard deviations (RSDs %) that were found for some compounds (>15%), as well as some strange behavior in the surface response of the experimental design. In some cases, a low absolute signal was recorded in one of the two sampling conditions affecting repeatability, but a general trend was observed overall. Finally, such higher RSDs compared to previous Vac—HS—SPME experiments can also be explained by the properties and complexity of the matrix, as discussed in more detail in the next section.

Figure 1 reports the chromatograms obtained using regular and Vac—HS—SPME sampling at 30 °C for 20 min, the compounds selected for comparison purposes are highlighted as well.

Figure 1*. Comparison of the total ion chromatogram obtained using regular (brown, bottom chromatogram) and Vac—HS—SPME*/HS-SPME *(black, upper chromatogram) sampling. Compounds identification refers to Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)*



3.1. INSIGHTS ON THE EXPERIMENTAL DATA OBTAINED UNDER VACUUM AND REGULAR PRESSURE CONDITIONS

Figure 2A shows the Vac—HS—SPME/HS-SPME peak area ratios obtained at 30 °C for each sampling time tested. Ratio values sufficiently larger than 1 indicate accelerations in the extraction rates with Vac—HS—SPME compared to regular HS-SPME [23]; while ratio values close to 1 indicate that Vac—

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HS—SPME and HS-SPME perform similarly and that the equilibrium is reached [23]. It is acknowledged that the use of a porous SPME fiber may result in competitive adsorption phenomena, and conferring about reaching equilibrium may not be appropriate [56]. Nonetheless, the word equilibrium is used here and denotes similar performances of Vac—HS—SPME and HS-SPME. Figure 2A shows that compounds characterized by lower molecular weight and higher volatility [ethanol (v1), acetic acid (v2), ethyl acetate (v3), 1-penten-3-ol (v4), penten-3-one (v5), and possibly pentan-3-one (v6)] reached equilibrium, under both pressure conditions, close to 10 min of extraction as the corresponding peak area ratios took values close to 1 at each sampling time tested (Figure 2A). (E)-pentenal (v7), 2(E)-hexenal (v11), and 1-hexanol (v12) reached the equilibrium around 20 min as the Vac—HS—SPME/HS-SPME peak area ratios leveled off after this sampling time. For isopentyl alcohol (v8), octane (v9), and hexanal (v10) a higher uptake under vacuum conditions was observed up to 30 min. For the majority of the rest, the positive effect of vacuum insisted even after 30 min of sampling. For some of these analytes the response of the instrument was low and resulted in some inconsistencies in the sampling time trends recorded.

Figure 2B gives the corresponding Vac—HS—SPME/HS-SPME peak area ratios obtained at 43 °C. The increased temperature impacted the volatilization rates of smaller and more volatile analytes to the extent that the first 12 eluting analytes (ethanol (v1) up to 1-hexanol (v12)) reached the equilibrium faster under regular conditions as well. Note that extraction kinetics were accelerated by the increased temperature, but the final amount of analyte extracted at equilibrium was not affected (Supplementary Figure 1). For the vast majority of the remaining compounds, the effects of higher temperature and low pressure were effectively combined and, compared to 30 °C, resulted in a higher improvement in extraction efficiencies at earlier sampling times. The Vac—HS—SPME/HS-SPME peak area ratios decreased with increasing sampling time, indicating that the equilibrium was approached.

When sampling from water or water-containing solutions, heating the sample under reduced pressure conditions was not always successful [23]. The adverse effect of temperature on Vac—HS—SPME was primarily due to the increased humidity in the headspace, which altered the pressure in the vial. Moreover, it was noticed that the increased humidity affected more the absorbent-type compared to adsorbent-type SPME fibers [32]. Here, the use of olive oil samples excluded the presence of an excessive amount of water molecules in the headspace and allowed studying the synergistic effect of temperature and low-pressure conditions. Nonetheless, the presence of high amounts of water-immiscible hydrocarbons in the headspace and the use of a solid sorbent accelerated swelling of the fiber with a consequently increased presence of siloxane on the GC trace [57].

Cavalli et al. reported the extraction time profiles at 25 °C of some olive oil (Sabine variety) volatile compounds using a DVB/ CAR/PDMS fiber [58]. In their report, the individual curves obtained for some compounds common to the present study, namely octane (v9), β-ocimene (v22), nonanal (v26) and α-farnesene (v33), were far from equilibrium after sampling the headspace for 40 min and the response of the instrument was particularly low for the sesquiterpene α-farnesene (v33). Matich et al. studied a model system consisting of four butanoate esters and α-farnesene dissolved in

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squalane [59]. The HS-SPME extraction time profiles at 20 °C showed that the two lowest molecular weight volatiles equilibrated between the squalane solution, the atmosphere, and the fiber in 5 —10 min, whereas α-farnesene was far from equilibrium even after sampling the headspace for 90 min. Although not directly related to the present studies, the authors also investigated α-farnesene uptake as a function of air movement in the headspace above the sampled fruits. A strong dependency was reported, which pointed to the slow evaporation rate of this analyte as well as the relative importance of the gas-phase resistance during the volatilization process. Here, the extraction of α-farnesene (v33) was largely improved when adopting the Vac—HS—SPME. The present results on α-farnesene are of importance since this compound was often reported to be the most representative terpenic hydrocarbon in extra virgin olive oils from different geographical regions [60,61].

At 30 °C, the results obtained with Vac— and regular HS—SPME showed relatively high variability, especially for analytes not having attained an equilibrium within the sampling times tested, and the effect was more pronounced with Vac—HS—SPME (almost all analytes under non-equilibrium conditions were affected). Heating the sample from 30 °C to 43 °C decreased the error associated with measurements under each sampling pressure tested even for compounds for which an equilibrium was not reached over the tested conditions. The high variability obtained at 30 °C was a rather unexpected finding, especially because Vac—HS—SPME was previously found to improve repeatability when sampling water samples at milder sampling temperatures [22]. A possible explanation may lie in the high viscosity of the olive oil matrix. At 30 °C, a ~49 mPa s viscosity value was measured for the olive oil tested here (Supplementary Table 1), being approximately 60 times larger than that of water at the same temperature. This high viscosity value increased liquid-phase resistance and "delayed" analyte diffusion through the liquid boundary layer of the olive oil matrix. This is particularly important when targeting analytes with a small affinity for the headspace, regardless of the pressure conditions inside the sample vial [31]. For these analytes, HS-SPME is considered a multistage process with analyte molecules being transferred from the liquid sample to the gas phase every time the headspace concentrations fall below equilibrium levels [30,31]. This "replenishment" depends on the resistance in the liquid phase, which is particularly relevant for viscous liquid samples such as olive oil. Although not dependent on pressure conditions, this process is more critical for Vac—HS—SPME due to the intensification of the sampling process under reduced pressure conditions [56,62] and may account for the higher variability at 30 °C. Heating the sample from 30 °C to 43 °C decreased the olive oil viscosity by around 40% (*i.e.*, ~30 mPa s) and improved the liquid-phase diffusivity. At this temperature, the olive oil sample could replenish headspace analyte concentrations faster, and the error associated with the measurements was improved compared to 30 °C.

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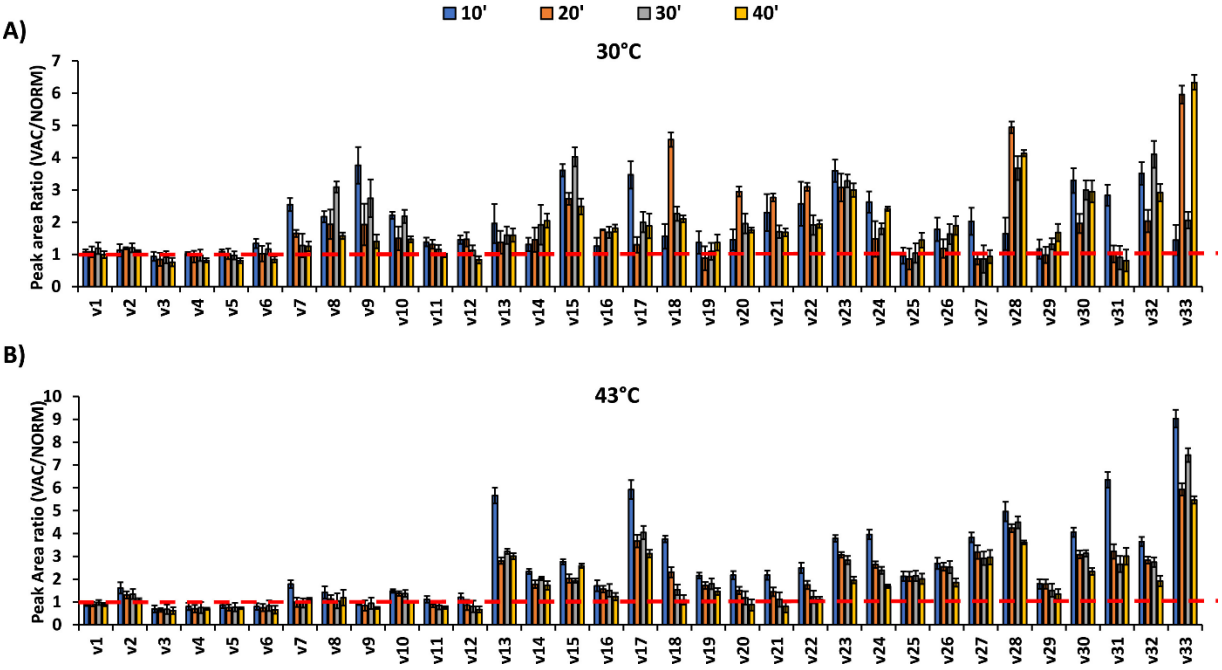
***Figure 2**. Changes in extraction efficiency for each sampling time at A) 30 °C and B) 43 °C upon reducing the total pressure expressed as Vac—HS—SPME/HS-SPME peak area ratios. The red dashed line highlights the threshold 1 above which accelerations in extraction kinetics are recorded with Vac—HS—SPME. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)*



3.2. INSIGHTS ON THE RESULTS OBTAINED USING THE TWO-VARIABLE CCD: A STUDY OF THE RESPONSE SURFACES

Usually, the use of univariate design for SPME optimization might overlook possible variable interaction, limiting the understanding of the phenomena occurring using vacuum conditions compared to classical SPME. In 2008, Pawliszyn et al. pioneered the use of a design-of-experiments (DOE) for HS-SPME optimization in coffee samples investigating five independent parameters: the amount of sample, incubation time, extraction time, incubation/ extraction temperature, and agitation speed [50]. It was shown that extraction time and temperature are the two main variables affecting the performance of HS-SPME. In 2018, Borget et al. confirmed the main significance of these two parameters in extra virgin olive oil samples, after applying a full factorial CCD with three independent factors (time, temperature, and sample quantity) [51].

Based on these previous findings, a two-variables ($k = 2$; temperature and time) CCD, as described in section 2.3, was applied to support the understanding of the vacuum effect on the temperature-time interaction.

The overall effect of the vacuum was evaluated by comparing the total number of peaks and the total peak area. For counting, compounds present in the fiber blank were removed (*e.g.* siloxanes). The total number of peaks did not change much over the different conditions of the CCD; it increased by about 14% using Vac—HS—SPME (~180 peaks, S/N = 50). The total peak area, instead, showed an

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important improvement. As expected from the theory [23], the maximum was reached at milder temperature and shorter time when Vac—HS—SPME sampling were used, namely ~45 °C for ~25 min (Figure 3b); while the extraction yields using regular pressure conditions were still far from a local maximum even at the highest temperature and the longest extraction time tested (Figure 3a). Moreover, the maximum obtained using Vac—HS—SPME showed about a 40% higher intensity compared to the highest uptake observed in regular HS-SPME, denoting that the general equilibrium was still far under regular pressure conditions.

Interestingly comparing the Pareto charts of the standardized effects obtained using regular HS-SPME and Vac—HS—SPME on the total chromatographic area, the statistical significance of each factor and their interaction changed, especially in terms of absolute effect (Supplementary Figure 2). Under regular sampling, both temperature and time had a significant impact on the overall extraction yield, with time playing a more significant role (~3 times higher), as also previously reported in the literature [50]. When Vac—HS—SPME sampling was performed, the standardized effects were largely reduced below the significant level, but time remained the prominent factor. Although the effect of reduced pressure sampling was highly compound-dependent (as aforementioned), the selection of the optimal sampling conditions in complex untargeted applications, like the present one, is usually based on an overall compromise. Further evaluation of every single compound was carried out to support the previous observation on the use of sampling under vacuum and the results are reported in Supplementary Information (Figure S3-S35), while here the general trends are summarized.

For the earlier eluted compounds (v1-v10), the more volatile ones, the surface response recorded under regular condition was generally very similar to the one recorded under Vac—HS—SPME sampling. The higher response was generally obtained at 30 °C for 30 min, although not a maximum, and the response surface showed a descending trend towards higher temperatures. For these compounds, the effect of vacuum was limited, as also previously observed.

The majority of the remaining compounds showed a similar trend under regular HS-SPME extraction, with a local maximum at 55 °C for 30 min of extraction but still not a plateau. For a few compounds, the equilibrium was reached at this point [showing a plateau, as for benzaldehyde (v16), 6-methylhept-5-en-2-one (v18), decanal (v29)]; for these compounds the response surfaces obtained using Vac—HS—SPME extraction showed different behaviors. The appearance of a plateau at the highest/longest condi-tions (55 °C and 30min) or at a shorter time and milder conditions was observed for v13, v14, v16, v17, v18, v23, v24, v25, v26, v28, v30, v33. The response surfaces of oct-(2E)-nal (v23) is reported in Figure 4 as an example of this ideal behaviour.

For all the other cases, the temperature-time interaction was compound dependent and changed in some unexpected way. For instance, for 1-hexanol (v12) the maximum was maintained over the different time tested (10e30 min) when Vac—HS—SPME extraction was performed. Observing the standard effects (Pareto chart reported in Supplementary Information Figure S14) only temperature (and its quadratic relationship) remained significant under vacuum conditions. Indeed, the optimum was obtained at about 35 °C (almost no difference at different extraction times), while

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higher extraction temperature led to a lower uptake independently from the extraction time, probably due to a displacement effect (Figure 5).

A similar behavior but independent from the temperature was observed for octanal (v19), where the optimum extraction time was at 25 min independently of the temperature used. However, the increase of the peak that was partially coeluted with octanal, namely Hex-(3Z)-enyl acetate (v20), was observed, affecting a proper quantification of octanal.

Figure 3. *Response surface for the total chromatographic area for a) regular HS-SPME and b) Vac—HS—SPME sampling.*

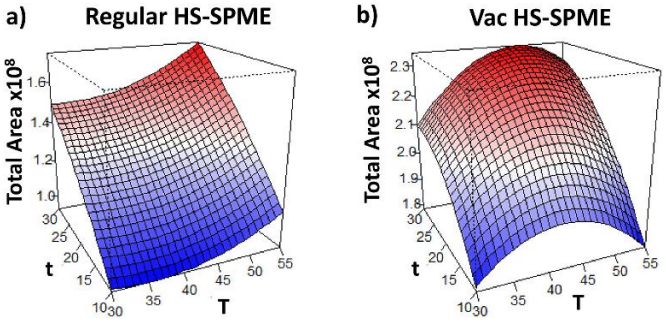


Figure 4. *Response surface for oct-(2E)-nal (v23) under a) regular HS-SPME and b) Vac—HS—SPME conditions.*

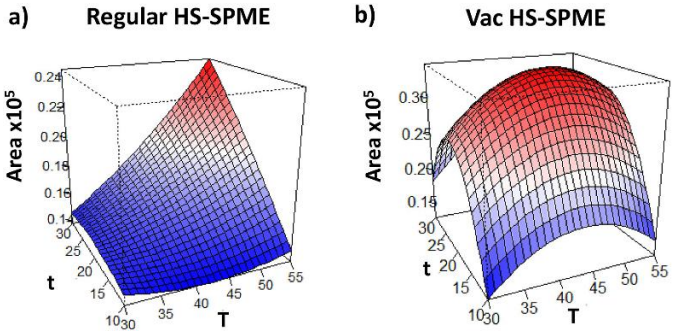
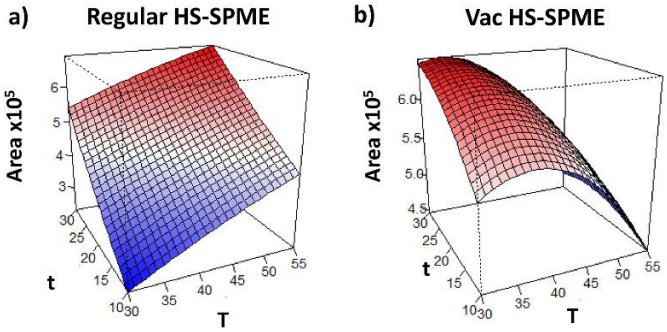


Figure 5. *Response surface for 1-hexanol (v12) under a) regular HS-SPME and b) Vac—HS—SPME conditions.*



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4. Conclusions

This work investigated, for the first time, the application of Vac—HS—SPME to oily samples. The positive effect of vacuum on HS-SPME sampling was shown and discussed thoroughly both using a univariate approach and a CCD. The limited access to air-olive partitioning data and the complex interactions of solutes with olive oil limited the formulation of a definitive criterion for predicting the positive effect of vacuum on HS-SPME. It was observed and postulated that the extraction process can be limited not only by the gas-phase resistance but also by the diffusion coefficient of the analyte in the highly-viscous oily phase. The absence of water in the sample allowed applying heating without a detrimental effect on the Vac—HS—SPME sampling, an effect commonly reported in aqueous samples. It was clearly shown that for highly viscous liquids, the effect of temperature remains important as it increases the diffusivity through the liquid thin film adjacent to the interface and facilitates mass transfer. It was concluded that applying heating next to reducing the total pressure in the headspace is the best analytical HS-SPME strategy for obtaining fast a rich volatile profile from the olive oil samples.

Such a powerful approach can provide a more detailed insight on the volatile fraction of olive oil, supporting the identification of characteristic pattern or specific markers able to discriminate between the different commercial category of olive oil, namely virgin, extra-virgin and lampante oil.

Further investigations are ongoing using a simplify model to reduce possible confounding effects, such as chromatographic coelution and displacement effects on the fiber. Moreover, Vac—HS—SPME will be used to explore the fingerprinting of different oils and evaluate its capability to enhance the extractable information for pattern recognition purposes.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2019.12.053.

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